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Removal and recovery of perfluorooctanoate from wastewater by nanofiltration

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ABSTRACT

Perfluorooctanoate (PFOA) is a persistent chemical that has been detected globally in the natural aquatic environment, while the waste discharge of fluoropolymer industry is one of the major sources of PFOA pollution. In this study, the removal and recovery of PFOA by nanofiltration (NF) were investigated with ammonium perfluorooctanoate model solutions under a wide range of PFOA concentrations. Performances of two commercially available NF membranes, namely NF270, NF90, were evaluated. The results show that the NF90 membrane offered a higher PFOA rejection (almost 100% at a PFOA concentration below 800 mg L^{-1}). Using NF90 membrane, a model solution with a higher initial PFOA concentration of 1000 mg L^{-1} was used to further test the membrane performance. Both stable osmotic pressure at membrane surface and high PFOA rejection (99.3%) were obtained when the PFOA concentration was larger than a certain value due to the formation of micelles. Furthermore, membrane operation parameters (i.e. stirring speed, pH, temperature, and permeate flux) on the TMP and the PFOA concentration in permeate were investigated under a much higher initial PFOA concentration (10,000 mg L^{-1}). The experimental results clearly confirm that recovery of highly concentrated PFOA of more than 117073.7 mg L^{-1} could be achieved by one-step NF treatment, while the permeate could be further treated by multi-stage NF to fully recover the PFOA. It was also found that the permeability of membrane could be recovered completely by simple water rinse, suggesting that NF is highly applicable for recovery of PFOA from wastewater in fluoropolymer production.

1. Introduction

Perfluorooctanoate (PFOA), as one of the most important perfluorocarboxylates (PFCAs), has been widely used in the production of fluoropolymers, lubricants, fire-fighting foams, water- and oil-resistant surface coatings [1–3]. Due to its strong carbon–fluorine bonds and high water solubility, it is very difficult to degrade PFOA with physical or chemical methods, and thus PFOA has been detected in various natural aquatic as well in the blood of humans and animals [4–6]. Animal toxicology and human epidemiology studies show that PFOA has a potential hazard on animals and humans [7]. Drinking water intake was found to be an important contributor to the total human exposure of PFOA [3,7]. As reported by Prevedouros et al. [8], the waste discharge of the fluoropolymer manufacturing is one of the major sources of PFOA pollution. A lot of effort was undertaken to limit the use and emission of PFOA in the U.S. and elsewhere [2]. However, in China, the wastewater containing PFOA was even discharged directly into water with the rapid development of fluoropolymer industry [9]. Therefore, there is an urgent need for technology development for PFOA removal and recovery from wastewater.

Some physicochemical technologies were used to remove PFOA from wastewater, such as sorption [10–12], coagulation [13,14], and membrane filtration [15–23]. Additionally, some advanced treatments including sonochemistry [24–26], photocatalysis [27], and electrochemical decomposition [28] have been developed to decompose PFOA. However, the decomposition of PFOA requires special conditions and is an energy-intensive process, while the sorption and coagulation processes will produce extra solid wastes. Membrane technology is emerging as one of the leading contenders in the removal of PFOA from polluted water. Thompson et al. [15] found that almost all perfluorinated alkyl compounds (PFCS) (including 16 ng L^{-1} PFOA) can be removed from the finished water by reverse osmosis (RO) in a water reclamation plants. Similar results were also reported by Flores et al. [16] and they found that the removal of PFOA (<15–26 ng L^{-1}) in a drinking water treatment plant (DWTP) by RO membrane was ⩾99%.

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Baudequin et al. [17] investigated the application of RO to remove fluorinated surfactants from firefighting waters, and the rejection of 99.4–99.9% was high enough to ensure that the fluorinated surfactant concentration in permeate matched the aimed concentration of <0.1 mg L^{-1}, but RO membrane suffered from low permeability (0.5 L m^{-2} h^{-1} bar^{-1}) and severe flux decline (75–80%) in the treatment process. Nanofiltration (NF) was also promising in the removal of PFOA, owing to its higher water flux and lower cost compared to RO. Steinle-Darling and Reinhard [19] found that four NF membranes (i.e. NF270, NF200, DK, and DL) could effectively remove ionic perfluorinated surfactants (>95%). Appleman et al. [20] reported that the removal rate of PFOA (664 ± 34 ng L^{-1}) by NF270 membrane was more than 95%, and the rejection of some PFAAs even increased with membrane fouling.

Accordingly, the membrane based processes are attractive to the treatment of the wastewater containing perfluorochemicals. However, the above-mentioned investigations mainly focused on the removal of trace perfluorochemicals from treated water by NF/RO. Furthermore, the inherent limitation of these processes is the disposal of the PFOA-enriched concentrate [18]. More importantly, much attention should be paid to the efficient recovery of these perfluorochemicals from wastewater, which can greatly decrease its discharge from effluents. For instance, one major industrial application of PFOA is used as a surfactant in the emulsion polymerization of fluoropolymers, and wastewater produced in fluoropolymers production normally contains 50–200 mg L^{-1} PFOA, which exists as ammonium perfluorooctanoate. If such a diluted PFOA solution can be concentrated, then, it can be directly reused in the emulsion polymerization process or recovered by a simple precipitation (i.e. by acidification). This will not only eliminate pollution sources, but also bring out a good economic benefit for the fluoropolymer producers. Since NF offers higher flux than RO and significantly better retention than ultrafiltration (UF) for low molecular weight solutes, NF may be a desirable alternative for the recovery of PFOA from wastewater.

To the best of our knowledge, the recovery of PFOA from wastewater by NF has not been reported yet, and there has few available data regarding NF performance with highly concentrated surfactant solution (PFOA is a synthetic fluorosurfactant). This study focused on the recovery of PFOA from the diluted ammonium perfluorooctanoate model solution by concentration with NF. Since as high as possible PFOA concentration would be preferred for the efficient recovery of PFOA, while PFOA concentration in wastewater could be less than 100 mg L^{-1}, therefore, concentration of PFOA by NF was carried out under a wide range of PFOA concentrations. All experiments were performed under constant flux mode, and therefore the effects of osmotic pressure, concentration polarization (CP) and fouling could be observed in terms of the increase in transmembrane pressure (TMP). The effect of the membrane type on PFOA rejection was investigated. In order to alleviate the CP and fouling during the treatment of highly concentrated PFOA by NF, the operating conditions were also optimized. The outcome of the present work can not only clarify the NF performance in highly concentrated surfactant solution, but also provide guide for process design in industrial application.

2. Materials and methods

2.1. Chemical and materials

Ammonium perfluorooctanoate was purchased from Tokyo Chemical Industry CO., Ltd., Japan. The main physical–chemical properties of perfluorooctanoate acid and ammonium perfluorooctanoate are presented in Table 1 [29–31]. To maintain consistency with other literature, the term PFOA is used when referring to the anion form of ammonium perfluorooctanoate. Based on solubility data in Table 1, highly concentrated PFOA can be recovered easily by lowering the pH of ammonium perfluorooctanoate solution, where perfluorooctanoate acid will precipitate due to saturated crystallization. In this work, ammonium perfluorooctanoate was slowly dissolved in deionized water to prepare model solution with the PFOA concentrations of 100, 1000, and 10,000 mg L^{-1}, respectively. All solutions were prepared using ultrapure water. The pH was adjusted by 0.1 M sodium hydroxide (NaOH) or hydrochloric acid (HCl). The model solutions were further filtered and degassed using 0.22 μm filters (MEMBRANA, Germany) under vacuum. All other chemicals and materials were either reagent grade or the highest quality commercially available.

Table 1
Main physical–chemical properties of perfluorooctanoate acid and ammonium perfluorooctanoate.

Property	Perfluorooctanoate acid	Ammonium perfluorooctanoate
Formula	$C_8HF_{15}O_2$	$C_8HF_{15}O_2{\cdot}H_3N$
Molecular weight (g mol^{-1})	414	431
CAS number	335-67-1	3825-26-1
Dissociation constant [29]	3.8 ± 0.1 infinite dilution solution ~2.3 at higher concentrations	
Krafft point [30]	20 °C	2.5 °C
Solubility in water at 25 °C (g L^{-1}) [30,31]	4.4	>500
Critical micelle concentration (mmol L^{-1}) at 25 °C	9.1 [30]	26.2[a]

[a] Measured in the present work.

2.2. Analytical methods

The PFOA concentration in both feed and permeate were determined by using a HPLC/MS system. Chromatographic separation was performed using an Agilent 1100 HPLC (Agilent Technologies, Santa Clara, United States) equipped with a Zorbax SB C18 column (2.1 mm × 150 mm, 5 μm) (Agilent Technologies, Santa Clara, United States). The mobile phase was a binary mixture of solvent A (0.1% TFA in water) and B (0.1% TFA in 100% methanol). The gradient expressed as changes in solvent B was as follows: 0–13 min, a linear increase from 30% to 90% B, 13–20 min, hold at 90% B, 20–25 min, a linear decrease from 90% to 30% B, 25–30 min, hold at 30% B. The flow rate of mobile phase was 0.2 mL min^{-1}. The sample volume injected was 50 μL. Mass spectrometric measurements were carried out on an electrospray ionization mass spectrometry (LCD DecaXP, Thermo Electron, San Jose, CA, USA) equipped with an electrospray ionization operating in negative ion mode. The spray voltage was set to 4.5 kV, and the heat capillary was kept at 300 °C. The scan range of the mass spectra ranged from 412 to 414.

The critical micelle concentration (CMC) of PFOA was determined by conductivity measurements using FG3-ELK (Mettler-Toledo Instruments, Shanghai, China) as a function of PFOA concentration, and the value was obtained from the intersection of two linear segments on a plot of conductivity versus PFOA concentration. The total osmolality of the PFOA solutions were measured with a Gonotec OSMOMAT Model 030 Cryoscopic Osmometer (Gonotec GmbH, Berlin, Germany). The pH values of the solutions were measured by FG2-ELK pH meter (Mettler-Toledo Instruments, Shanghai, China).

Zeta potential measurements were performed using the SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Graz,