Nanofiltration of Perfluorohexanoic Acid in Industrial Wastewater: Membrane Selection and Impact of pH and Salts on Membrane Rejection Performance

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic compounds, which have been widely used in industries due to their unique physicochemical properties, including surface activity, thermal and chemical stability, etc. Typically, they consist of a fluorocarbon chain ($CF_3(CF_2)_n$–) and a head group (carboxylic or sulfonate group). In the past decades, they have attracted attentions from both academic and industrial scientists as they were found to be toxic, persistent and bioaccumulative. Recently, one kind of six carbon chain PFASs – perfluorohexanoic acid (PFHxA, $CF_3(CF_2)_4COOH$) – has been detected in the water environment with a high concentration, which supposed to be caused by industrial discharge [1, 2]. This suggested that some industries have shifted to use PFHxA as the alternative of the long-chain PFASs. As PFHxA was found to be persistent in the environment and potentially toxic, technique for the recovery of PFHxA from industrial wastewater should be developed so that PFHxA pollution in the environment could be reduced. In a study conducted by Soriano Á *et al*, a commercially available nanofiltration (NF) membrane (NF 270) made from polyamide (PA) was found to be able to reject PFHxA in industrial wastewater efficiently (>96%) [3]. However, the rejection mechanism of PFHxA by NF membranes was still not fully investigated in their study.

The objective of this study was to examine the possibility of applying NF membranes for the recovery of PFHxA in industrial wastewater. Two types of NF membranes have been tested. One is NF 270, which is made from PA. Another one is NTR-7450, which is made from sulfonated polyethersulfone (SPES). According to the data reported by Mänttäri M. *et al*, NF membranes made from PA and SPES showed different rejection properties [4]. Thus, a comparison between these two NF membranes can provide some useful guides for membrane selection in practical engineering. Meanwhile, impact of pH and salt on the rejection performance of PFHxA by NF 270 was examined.

2. Materials and methods

Industrial wastewater: Industrial wastewater was sampled in a fluorochemical industry. The characteristics of the wastewater were shown in **Table 1**. The total organic carbon (TOC) in the wastewater was 50.18 mg/L and it was much higher than the TOC contributed by the PFHxA. Therefore, the industrial wastewater contained organic matter with unknown nature. Additionally, a large amount of inorganic salts also existed in the wastewater, including SO_4^{2-}, Cl^-, Ca^{2+} and Na^+, etc.

Table 1 Wastewater characteristics

Parameter		Unit	Value
PFHxA		mg/L	63.12
Anion	SO_4^{2-}	mg/L	274.56
	NO_3^-	mg/L	26.66
	Cl^-	mg/L	186.02
Cation	Ca^{2+}	mg/L	182.12
	Mg^{2+}	mg/L	13.30
	Na^+	mg/L	54.34
pH		–	7.0
Conductivity		mS/cm	1.21
Total organic carbon		mg/L	50.18

Chemicals and membranes: All the chemicals used in this study were HPLC/MS/MS grade. Chemicals including acetonitrile, PFHxA (98%), NaCl, $CaCl_2$, Na_2SO_4 and $CaSO_4$ were purchased from Wako Pure Chemical (Osaka, Japan). Two NF membranes were tested in this study and their basic information was shown in **Table 2**, including molecular weight cut-off (MWCO), ζ-potential and NaCl rejection rate, etc.

Membrane filtration test: Membrane filtration test was carried out with a crossflow test cell, which was schematically described in **Fig. 1**. The feed water was pumped into the membrane cell by a diaphragm pump. Transmembrane pressure and crossflow rate in the membrane cell were kept at 0.7 MPa and 1.0 L/min, respectively, by adjusting the valve 1 and 2 throughout the whole filtration test manually. For each test, a new membrane coupon (60 cm^2) was used. Prior to the filtration test, the new membrane was pretreated by filtration with pure water at 0.7 MPa. The temperature of feed water was controlled at 29 – 30 ^oC.

Table 2 Characteristics of membranes used in this research

Membrane	NF 270	NTR-7450
MWCO (Da)[5]	200	600 - 800
ζ-potential at pH 7.0 (mV)[5]	-21.6	-16.6
Pure water permeability ($m^3/(m^2 \cdot MPa \cdot d)$)	3.92	2.62
NaCl rejection rate (%)	58	55
Manufacturer	FilmTech, USA	Nitto Denko, Japan

For filtration test with industrial wastewater, 20 L industrial wastewater was added into the feed tank. The filtration test was conducted in concentration mode. Permeate from membrane cell was discharged to the permeate tank, while the retentate was recycled to the feed tank. Throughout the filtration test, PFHxA in feed water was concentrated and the volume of feed water kept decreasing. The filtration test was stopped once it became difficult to continue the filtration test. Samples were collected continuously throughout the filtration test. The concentration of PFHxA in collected water samples were analyzed by HPLC/MS/MS (Agilent Technologies, USA) after dilution by 40% acetonitrile solution. The instrument detection limit of PFHxA was 0.02 ng/mL. Additionally, the membrane flux and permeate volume were also monitored throughout the filtration test. The rejection rate of PFHxA was calculated by equation (1):

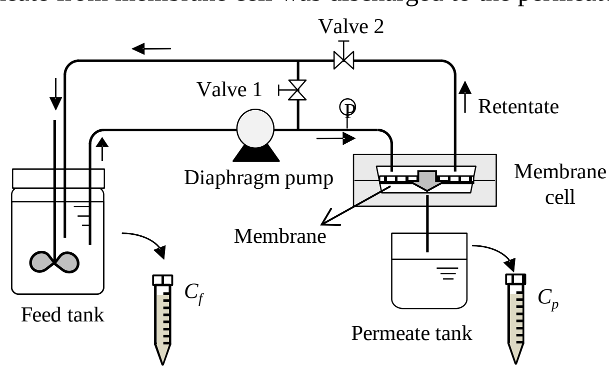

Figure 1 Experimental set-up

$$Rejection\ rate\ (\%) = (1 - C_p/C_f) \times 100 \quad (1)$$

C_p: PFHxA concentration in permeate sample (mg/L);
C_f: PFHxA concentration in feed sample (mg/L).

As shown in **Table 1**, industrial wastewater contains various kinds of inorganic cations and anions, such as Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-} and Cl^-, etc. The pH of industrial wastewater may also vary in practice. To know the impact of pH and salt on the rejection of PFHxA, filtration test was also conducted with synthetic wastewater at different pH in total recirculation mode, in which both retentate and permeate were recycled back to the feed tank. pH of the feed water was adjusted by NaOH and HCl solution. Five kinds of feed water have been tested: 100 mg/L PFHxA, 100 mg/L PFHxA + 200 mg/L NaCl, 100 mg/L PFHxA + 200 mg/L $CaCl_2$, 100 mg/L PFHxA + 200 mg/L Na_2SO_4;

100 mg/L PFHxA + 200 mg/L $CaSO_4$. At each pH value tested, water samples were collected after filtration for at least 1 hour. The rejection rate of PFHxA was also calculated by equation (1).

3. Results and discussions

PFHxA rejection rates and flux of NF membranes: The PFHxA rejection rates by two NF membranes throughout the filtration test were shown in **Fig. 2**. NF 270 showed a much higher rejection rate to PFHxA in industrial wastewater than NTR-7450 (especially at the beginning of filtration), even though these two NF membranes had similar NaCl rejection rate. This result was quite different from the PFOS ($CF_3(CF_2)_7S(O)_2OH$) rejection properties by reverse osmosis (RO) and NF membrane, whose rejection was highly correlated to the salt rejection [6, 7]. This might be caused by the different carbon chain length between PFOS (C8) and PFHxA (C6) as well as different functional head groups among them ($-SO_3^-$ for PFOS and $-COO^-$ for PFHxA). Additionally, the initial PFHxA rejection rates for NF 270 and NTR-7450 were 98.1% and 86.5%, respectively. After starting the filtration, both two membranes showed an increase of PFHxA rejection rate. Such kind of increase might be due to the entrapment of PFHxA or other foulants into the selective layer of NF membranes, which can hinder the further passage of PFHxA as well as the water. At longer duration of filtration test, decline of PFHxA rejection rate was obtained with both two membranes. Two reasons might account for such kind of decline: concentration polarization and membrane fouling. The precipitation of foulants on membranes' surface was also observed directly in this experiment.

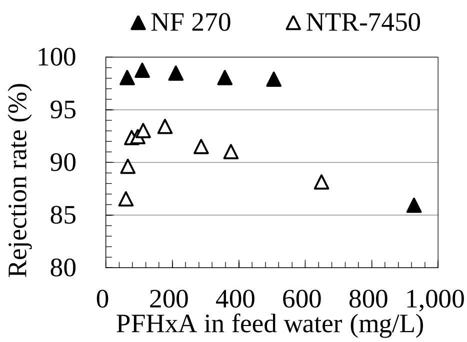

Figure 2 PFHxA rejection rate of NF 270 and NTR-7450 throughout the filtration test

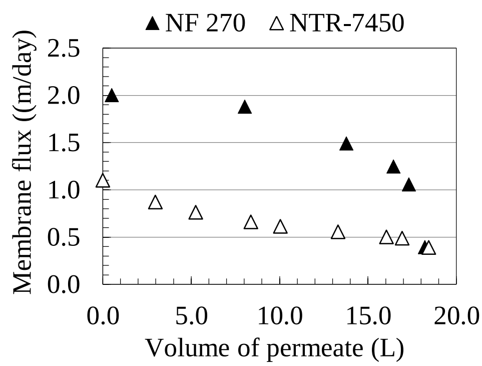

Figure 3 Membrane flux over the volume of permeate passed through the membrane

Fig. 3 showed the membrane flux of NF 270 and NTR-7450 at different volume of permeate passed through the membrane. Overall, NF 270 showed a better flux performance than NTR-7450. From an operational point of view, NF 270 was a better option for the recovery of PFHxA from industrial wastewater because it showed a higher PFHxA rejection rate and membrane flux. However, more severe membrane fouling was also observed with NF 270. It is well known that higher membrane flux could lead to more severe membrane fouling as a result of increased permeate drag force in addition to the enhanced concentration polarization [8]. Additionally, in the filtration with NF 270, the concentration of solutes in feed water increased more rapidly than that in filtration with NTR-7450. Thus, the concentration polarization happened with NF 270 was enhanced further. In summary, PFHxA in industrial wastewater could be concentrated by NF 270 efficiently.

Impact of salt and pH on PFHxA rejection rate by NF 270: As discussed before, NF 270 was a better option for the recovery of PFHxA from industrial wastewater. Thus, it was selected for further experiment to investigate the impact of salt and pH on the rejection of PFHxA. The results were shown in **Fig. 4**. It can be found that increasing the feed water pH can enhance the rejection of PFHxA in synthetic wastewater. This could be explained by the electrical repulsion between membrane surface charge and PFHxA ion. NF 270 has the iso-electric point at 4<pH<5 [4]. Increasing the pH can make the membrane surface charge become more negative. Meanwhile, PFHxA is a kind of weak acid with pKa of –0.16 [9]. Thus, increasing the pH can promote the dissociation of PFHxA and increase the portion of PFHxA ion ($CF_3(CF_2)_4COO^-$) in feed water. Overall, the electrical repulsion between PFHxA ion and membrane surface charge was enhanced when increasing pH and resulted in a higher rejection rate.

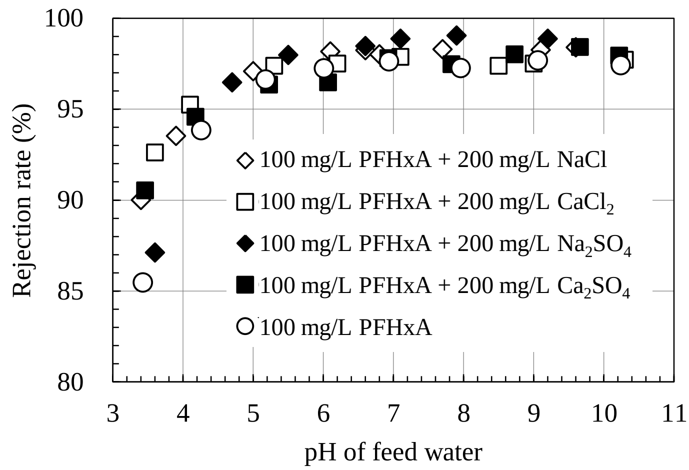

Figure 4 Impact of pH and salt on the rejection rate of PFHxA by NF 270

However, the impact of salt on the rejection of PFHxA in synthetic wastewater was not significant, which was quite different from the rejection of PFOS by NF 270. According to the result reported by Changwei Z. *et al*, addition of $CaCl_2$ could enhance the rejection of PFOS by NF 270 through the co-ions competition effect (the ion with less charge and higher mobility are prone to penetrate through the membrane) as well as the potential bridging between Ca^{2+} and sulfonate functional groups of PFOS [10]. This suggested that PFASs with different carbon chain length and functional groups may be rejected by NF membranes through different mechanisms.

Reference

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