

Removal of PFOA by hybrid membrane filtration using PAC and hydrotalcite

Romchat Rattanaoudom, Chettiyapan Visvanathan*

*School of Environment, Resources and Development, Asian Institute of Technology,
P.O. Box 4, Klong Luang, Pathumthani, 12120, Thailand
Tel. +662 524 5640; Fax +662 524 5625; email: visu@ait.ac.th*

Received 1 September 2010; Accepted in revised form 12 January 2011

ABSTRACT

Perfluorooctanoic acid (PFOA) is one of the major perfluorinated compounds (PFCs) contaminating global water sources. Considering the difficulty faced in current treatment for removal of concentrated PFOA in industrial wastewater, there is a need to develop an effective treatment system. This study focused on the development of an adsorption-based hybrid membrane technology to remove high concentration of PFOA from industrial sources. The most effective process was the combination of hydrotalcite and nanofiltration (NF), which showed a 95% removal, without adverse effect on flux reduction as compared to direct membrane filtration. NF alone removed varying PFOA concentrations in the range of only 60–85% and severe flux reduction was observed at high PFOA concentrations. Due to the dense layer of hydrotalcite which formed on the membrane's surface, membrane rejection was increased by 30% in the hydrotalcite hybrid NF system. Moreover, significant increase in permeate flux was observed in powder activated carbon (PAC) hybrid membrane process, although removal efficiency was decreased as compared to direct membrane filtration. In conclusion, the hydrotalcite-PAC hybrid membrane process showed effective removal of high concentrations of PFOA bringing about: a) effective adsorption with adsorbent; b) enhanced membrane rejection by adsorbent layer; and c) enhanced permeate flux by adsorbent.

Keywords: PFOA; Hybrid process; Nanofiltration; Ultrafiltration; Hydrotalcite; Powdered activated carbon

1. Introduction

At present, perfluorinated compounds (PFCs) are reported to be a synthetic organic compound of concern in the global environment. Perfluorooctanoic acid (PFOA), PFC, is an anthropogenic compound, mainly used in the industrial sector. Various industries use PFOA in their processes such as fluoropolymer/fluorotelomer relating processes, material surface coating, metal plating, etc. Thus, high concentrations of PFOA are reported in industrial wastewater. For example, in a semiconduc-

tor industry, wastewater from the photolitho process was estimated to have 1,000 mg/L of PFOA [1]. While conventional wastewater treatments such as activated sludge processes do not treat PFOA, it enhances PFOA concentration in effluent through degradation of PFOA's precursor.

PFOA is also reported to be found in seawater sources [2,3]. As compared to other PFCs, PFOA dissolves and disperses quickly in water. Due to this property, PFOA is found in many water sources far from the source of pollution. For example, in the Pacific Ocean, PFOA concentration was found to be around 50 ng/L [3], whereas the concentration increased to 19.2 µg/L in Tokyo Bay

* Corresponding author.

where municipalities and various industries of Japan are located [2].

Moreover, another important issue is contamination of tap water and drinking water with trace concentrations of PFOA. For example, 45.9 ng/L of PFOA was found in tap water in Shenzhen, an urban city of China [4]. Higher concentrations ranging up to 560 ng/L were reported in the drinking waters of Hochsauerland, a district of Germany (Cited in [5]). Similar values were found in nearby surface waters which were water sources of local treatment plants. The conventional water treatment units are not designed to remove even low concentrations of PFOA reported in surface water sources.

While the adverse effects of PFOA on humans (that is, its toxicity levels) have not been well characterized, a correlation between the death of workers in PFOA/PFOS industries and the number of bladder and prostate cancers were observed (cited in [6]). In addition, its effect on aquatic organisms should be given much attention as they are the first victims of pollution discharge. Expression of estrogenicity (female characteristics) after exposure to water contaminated with lower than 5 mg/L of PFOA and PFOS has been reported in male aquatic organisms, namely, the rare minnow and tilapia [7,8]. Finally, PFOA was also found to have bioaccumulation and biomagnifications in living species through food chain. Thus, the current situation of treated concentrations of PFOA in industrial wastewater indicates the need for research in the development of an effective treatment system.

Oxidation, photolysis/photocatalysis, sonochemical and sorption processes are the most common treatment technology for removal of low PFOA concentration. Moreover, application of these technologies to treat large volumes of diluted PFOA wastewater, which contains various impurities, is not a technically and economically viable option. For example, granular activated carbon (GAC) was used in 3M® (US) industries to treat secondary effluent from wastewater treatment plants before discharging the water into the Mississippi river. Due to the presence of other dissolved organic substances in the secondary effluent, a rapid breakthrough of GAC filtration was observed. Similar observations were also reported with trial ion-exchange resin, even though it removed >99% of concentrated PFOA prepared in pure water [1]. Furthermore, low adsorption capacity of powder activated carbon (PAC) and GAC with concentrated PFOA was reported by many researches [9,10].

In order to avoid the above technical issues on treatment of PFOA at the end of pipe system, one possible alternative would be to develop an in-line treatment system. Here, PFOA containing waste is segregated at the industrial process level, thus one obtains a highly concentrated wastewater with limited additional contaminants.

Membrane filtration is a promising technology for compound removal/separation at high concentrations. Reverse osmosis (RO) was reported to be very effective for

PFOS removal, which provided greater than 99% removal [11]. But severe reduction of permeate flux was observed at high PFOS concentrations (≥ 1000 mg/L). Moreover, membrane pre-treatment, such as adsorption process, coagulation, membrane filtration, etc., was indicated as a need to remove impurities contained in actual wastewater to enhance RO efficiency. In the case of PFOA, however, current literature does not discuss membrane treatment.

A number of researchers have developed hybrid membrane processes (that is, the combination of sorption process and membrane filtration) to improve the drawbacks of individual methods. The adsorbent applied in previous studies include activated carbon, resin, poly-aluminum chloride, oxide particles, etc. Higher removal efficiency in the hybrid membrane process was observed as compared to membrane treatment alone [12–14]. In addition, permeate flux decreased [13,15]. Similar compound removal of hybrid membrane processes and direct membrane filtration were also reported [16].

This study is designed to develop a hybrid membrane filtration with the application of an effective adsorbent for the removal of high PFOA concentrations. The membranes used in this study were both of nanofiltration (NF) and ultrafiltration (UF).

2. Materials and methods

2.1. Chemical and materials

PFOA [$\text{CF}_3(\text{CF}_2)_6\text{COO}^-$, 414 g/mol] was purchased from Wako Pure Chemical Industry, Ltd., Japan. The required concentration of PFOA was prepared using Milli-Q water of high purity. Commercial adsorbents were purchased and used, including: a) hydrotalcite [$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$] from SIGMA-ALDRICH, Inc., St. Louis, USA; and b) PAC (Fluka: 72343) from SIGMA-ALDRICH, Netherland. Hydrotalcite was pre-treated in an oven at 500°C for 2 h to remove impurities. PAC was heated at 105°C for 48 h to remove humidity then kept in desiccators until it was used.

2.2. Membrane and membrane filtration unit

XN45 (NF type) and UE10 (UF type) flat sheet membranes were purchased from Trisep Corporation. Molecular weight cut-offs (MWCOs), reported by the manufacturer, were 200 Da and 10 kDa for XN45 and UE10, respectively. Membrane properties are presented in Table 1.

The bench-scale membrane filtration unit with cross flow module is illustrated in Fig. 1. Ten liters of feed tank (double wall) was connected to a cooling system to keep the feed solution at a constant temperature, $25\pm 1^\circ\text{C}$. Hydra-Cell Industrial Pump (Model G-20), which is connected with an inverter (VS mini J7 Series), delivered feed solution from the feed tank to the membrane filtration unit. A dampener was installed immediately after the

Table 1
Membrane properties

Type	Membrane	MWCO ^a (Da)	Pure water flux (m ³ m ⁻² d ⁻¹ b ⁻¹)	Material of mem- brane surface	Z _p (mV) at pH 6	Contact angle (°)	Salt rejection (%) ^b	
							NaCl	Mg ₂ SO ₄
UF	UE10	10,000	0.86 ± 0.11	Polyethersulfone	-92 [17]	49.3 ± 3.5 [17]	-	-
NF	XN45	< 200	0.26 ± 0.02	Polyamide	-15 [18]	57 ± 1 [19]	42.25	61.97

^aData from the Manufacturer.

^bInitial concentrations were 1,000 mg/L for NaCl and 2,000 mg/L for MgSO₄.

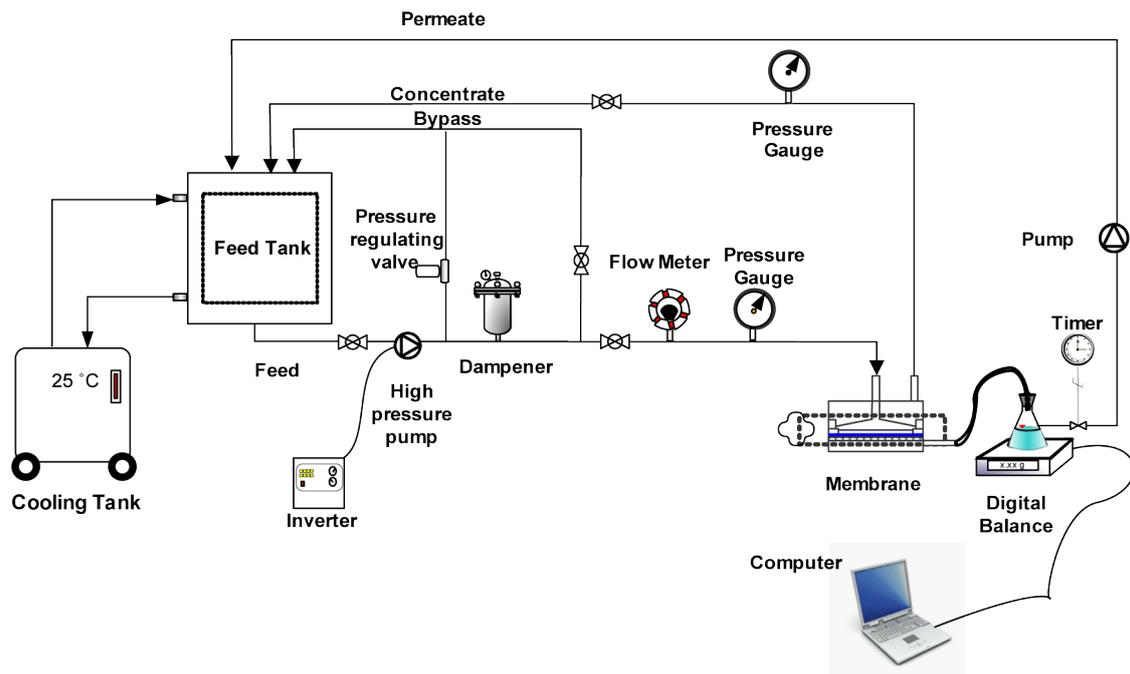


Fig. 1. Schematic diagram of the membrane experimental unit.

pump to stabilize the flow before reaching other instruments. The circular membrane module with an effective membrane area of 32 cm² was used. Flow rate of feed solution was fixed at 2,060 mL/min to provide average cross flow velocity of 15 cm/s over the membrane. This membrane filtration unit was constructed from two types of material, including: a) 316 stainless steel was used at high pressure levels; and b) polymer material was used at low pressure levels. Adsorptions of PFOA in these two materials were reported to be negligible. Permeate flux was measured automatically by an electronic balance which was connected to a computer. The pressure levels applied in the membrane system were 3 and 15 bar for UF and NF, respectively.

A new membrane was soaked in Milli-Q water at least for 5 days prior to use. During this period, Milli-Q water was replaced every day with a new volume of Milli-Q water. Prior to starting the experiment, the new membrane was inserted in the membrane module and pre-

compacted with Milli-Q water for 10 hours at operating pressures to stabilize the permeate flux. In order to maintain constant feed concentration, the membrane system was operated in a recycling mode in which concentrates and permeates were recycled back to the feed tank.

Permeate flux (J) could be calculated by Eq. (1):

$$J(\text{m}^3/\text{m}^2\text{d}) = \frac{V}{A \times t} \quad (1)$$

where V is volume of permeate, A is effective membrane area and t is time.

Rejection or removal (R) of PFOA by membranes was determined using Eq. (2):

$$R(\%) = \left(\frac{1 - C_p}{C_f} \right) \times 100 \quad (2)$$

where R is percent rejection/removal of tested membrane, C_p is the concentration of PFOA in permeate, and C_f is the concentration of PFOA in feed.

2.3. Experimental procedure

To study the efficiency of hybrid membrane treatment, two sets of experimental runs were conducted. The first included membrane filtration with varying PFOA concentrations tested. The run used both UF and NF membranes aimed to investigate the efficiency of the membrane alone as well as to compare it with hybrid processes. In the second experimental run, that is, using the hybrid membrane filtration mode, a combination of adsorption and membrane filtration was conducted. Initially, laboratory scale adsorption studies were conducted with various adsorbents. Based on this study, the suitable adsorbent amount was estimated for PAC and hydrotalcite to give 70% PFOA removal. Based on this lab-scale data, bench-scale adsorption runs were conducted, and the supernatant was collected and used as the feed solution.

2.3.1. Membrane filtration

Each membrane was initially run with PFOA concentration of 0.1 mg/L, followed by 10 mg/L, then 1,000 mg/L. The membrane was operated for 12 h with each concentration. Permeate samples were collected every 4 h for PFOA measurement. The permeate volumes were measured every two hours in direct filtration and hourly in hybrid experiment.

2.3.2. Hybrid membrane filtration

Based on the preliminary adsorption test, 0.62 g/L of hydrotalcite and 3.12 g/L of PAC were applied to achieve around 70% PFOA removal. A sample containing 1,000 mg/L of initial PFOA was shaken with PAC and hydrotalcite at 140 rpm and 25°C for 4 h. After shaking, the sample was allowed to settle for 1 h. A supernatant was used as the feed solution for the hybrid membrane experimental solution.

2.4. Analyses

For PFOA measurement, samples of membrane feed and sorption were filtered with a 0.22 μm PVDF filter. This filtrate was further diluted by acetonitrile in an ultrapure water (40/60, v/v) mixture to the required range for measurement with liquid chromatography-mass spectrometry (LC-MS). Whereas, the membrane permeate sample was directly diluted for its measurement.

PFOA concentration was determined by LCMS (Agilent 6400 Series) using a column (Eclipse Plus C18, 2.1X100 mm 0.18 μm) from Agilent Technologies, USA. The mixture of acetonitrile/10 mM $\text{CH}_3\text{COONH}_4$ in ultrapure water (40/60, v/v) was used for the mobile phase at a flow rate of 0.25 mL/min. Membrane and adsorbent characteristics were analyzed using a scanning electron microscope (SEM).

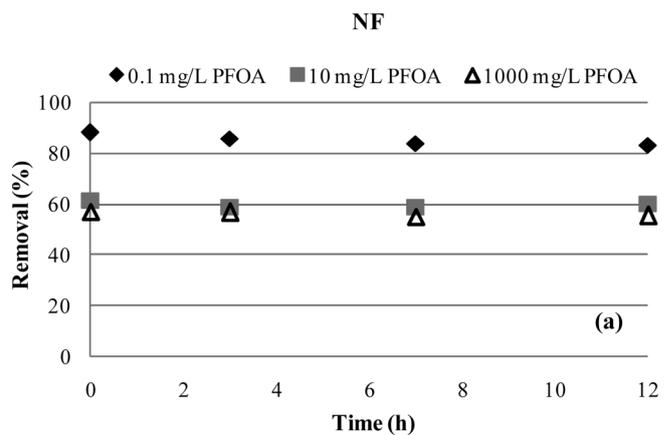
3. Results and discussion

3.1. Membrane filtration

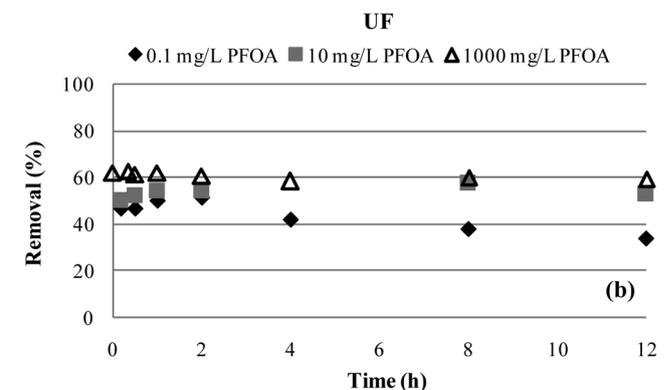
Fig. 2 presents the PFOA removal as a function of feed concentration for both NF and UF direct filtration. In general, the rejection rate is higher in NF than it is in UF.

To understand the mechanisms of rejection, PFOA properties are summarized as: molecular weight (MW) of 414 g mol⁻¹, solubility of 3.4 g/L, and pKa of 2.5 [6]. Moreover, log Kow, which indicates the hydrophobicity of the compound, was reported to be 6.28 [20]. The pHs of the feed solution in all experiments were found to vary in ranges of 3–5.5 in which the functional group of PFOA showed a negative charge (COO⁻).

As the MWCO of NF was less than 200 Da, one expects the complete removal of PFOA. However, this relatively higher passage of PFOA through the membrane is linked to the low salt rejection (60–70% NaCl rejection) as reported in Table 1. In addition, the linear molecular structure of PFOA under high operating conditions could have assisted the passage through the membrane. The higher rejection (85%) at a low concentration of 0.1 mg/L



(a) PFOA removal for NF filtration



(b) PFOA removal for UF filtration

Fig. 2. PFOA removal as a function of feed concentration: (a) NF; and (b) UF.

indicates that adsorption of PFOA on the membrane surface plays a predominant role.

In contrast to the NF operation, UF resulted in the lowest PFOA removal at 0.1 mg/L. The removal was enhanced with increasing concentrations (Fig. 2b). Hence, the UF membrane pores are relatively large, thus one expects all the PFOA to penetrate through its pores. However, at higher concentrations, more PFOA were proportionally adsorbed by both the internal and surface areas of the membrane pores which led to progressive pore reduction. This phenomenon is accelerated at higher feed concentrations. The progressive pore plugging phenomena improved PFOA removal. For example, a maximum of 60% removal was observed at 1,000 mg/L.

PFOA has a $\log K_{ow} > 2$ that show its hydrophobicity. Due to its hydrophobicity nature, PFOA tends to adsorb on the hydrophobic NF and UF membrane. However, PFOA rejection-based mechanism of XN45 might be slightly different from UE10. Adsorption of PFOA on the membrane surface might be a major initial rejection by XN45; thus, the highest removal appeared at the lowest feed concentration. When the membrane surface was saturated with PFOA, lower removal was demonstrated. It corresponded to a slow reduction of permeate flux in NF filtration. Easier sorption of PFOA on the surface of XN45 as opposed to UE10 might be supported by membrane surface properties including more hydrophobicity (more contact angle) and less negative surface charges repelling PFOA (Table 1).

The pH values of the feed solutions in all experiments were found to vary in ranges between 3 and 5.5 as a function of feed concentration. Normally, the pH of a solution affects the charge of a compound and the membrane which directly relates to rejection due to their electrostatic interaction. However, the pH affects the membrane removal mainly at the period before membrane saturation. Moreover, average removals with both membranes at 10 mg/L, with pH levels of 5.5, were not much different from removals at 1,000 mg/L, with a pH of 3, in both membranes. This indicates that in PFOA removal, the feed solution pH within the range tested does not play a significant role in removal efficiency.

Fig. 3 presents the permeate flux reduction as function filtration time for both direct and hybrid membrane filtration operations. Here, both UF and NF operations for direct filtration, showed that as the feed PFOA concentration increases, the flux decreases. This demonstrates the effect of the concentration polarization on the membrane surface. During filtration of low concentrations of PFOA (0.1 and 10 mg/L PFOA), the initial flux reduction was relatively small, that is $<20\%$. When the feed concentration was increased to 1,000 mg/L, around 40% flux reduction was measured in both UF and NF membranes. This observation reveals the possible adsorption of PFOA on the membrane surface. Furthermore, the flux reduction is more significant in UF than in NF, which could be

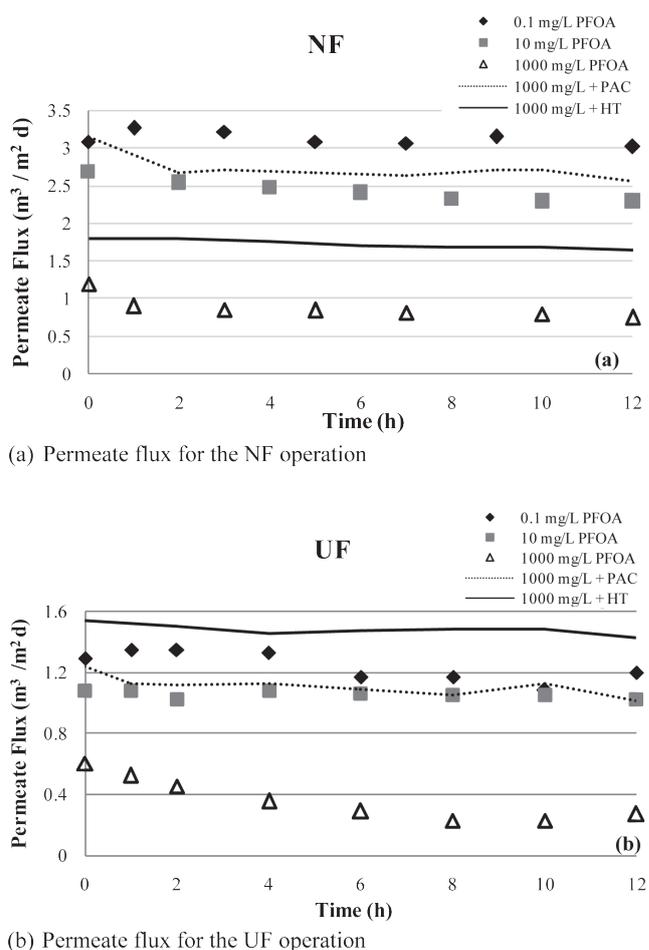


Fig. 3. Permeate flux of direct and hybrid membrane processes: (a) NF; and (b) UF.

linked to the adsorption of PFOA molecules within UF membrane pores, thus forming addition internal fouling resistance.

In conclusion, both of UF and NF observations have shown 60% removal at >10 mg/L of PFOA and severe permeate flux reduction of $>40\%$ at 1,000 mg/L.

3.2. Hybrid membrane process

3.2.1. Adsorption

Detailed laboratory scale adsorption studies were conducted to identify the best adsorbent to remove PFOA. Based on these experimental results, for an initial feed concentration of 1,000 mg/L, 0.62 g/L of hydrotalcite and 3.12 g/L of PAC resulted in 72% and 69% removal of PFOA. The initial pH of the feed solution was 3, which, by the end of the adsorption process, increased to 6–7 in both cases. Normally, hydrotalcite has large positive charges on the surface due to composed metals (Al^{3+} and

Mg²⁺). The positive zeta potential values of 35–50 mV observed at that pH range in the preliminary test indicate the presences of positive charges on the surface. CO₃²⁻ ion, originally intercalated between layers of hydrotalcite, could have been exchanged with other existing anions in the solution. Then the electrostatic bond, classified as a strong bond, was formed between the metal and functional group of PFOA (COO⁻). For PAC, it showed the range of zeta potential values of +17 to –13 mV at a pH variation of 3–7. Moreover, hydrophobicity of PAC was reported to play a role on PFOA adsorption [10]. Based on those mentioned properties, PAC adsorbs PFOA through hydrophobic and possibly electrostatic bonds.

3.2.2. Hybrid membrane process

The different efficiency of hybrid membrane processes is related with properties of its membrane, compounds, adsorbent bonding, impurities, etc. However, this study found that the hybrid membrane process showed higher compound removal and permeate flux than membrane treatment alone. The details are described below.

Fig. 4 presents the PFOA removal by the hybrid process for both UF and NF membrane systems. The overall removal in the case of the UF process was not much different from both adsorbents, which was around 80%. However, the NF system revealed higher PFOA removal with 95% in hydrotalcite application. The main PFOA removal in all membrane hybrid processes was taken at part of sorption as demonstrated in Section 3.2.1 above.

The permeate flux in hybrid membrane processes is illustrated in Fig. 3. At the same initial PFOA concentration of 1,000 mg/L, the permeate flux of hybrid membrane processes were larger than that of the membrane treatment alone. One reason for the flux increase might be the reduction of PFOA concentration from 1,000 mg/L to 300 mg/L due to sorption (around 70% removal). However,

interestingly enough, the permeate flux of some hybrid processes were even higher than that of the membrane filtration alone with 10 mg/L initial concentration. Hence, the presence of adsorbent in the feed might decrease the PFOA fouling on membrane surface.

The permeate flux of hybrid PAC processes fluctuated as compared to other cases, especially in NF. It indicates unstable sorption among PFOA, PAC and the membrane. PFOA has a hydrophobic-fluorinated chain that could adsorb on membrane surface and PAC while its functional group (COO⁻) could dissolve back into water. Yet, in the case of hydrotalcite, it attached the functional group of PFOA strongly by electrostatic interaction while the membrane surface was adsorbed with hydrophobic-fluorinated chain of PFOA. Thus, a more stable flux reduction of the hydrotalcite hybrid process than that of the PAC was observed. Moreover, the layer of hydrotalcite formed on the membrane was very dense as compared to PAC as shown in Figs. 5c and 5d. Thus, lower permeate flux of hydrotalcite over that of PAC application was shown in the hybrid NF process.

In contrast to NF, hydrotalcite provided larger permeate flux than PAC in hybrid UF processes. There are many possible reasons to explain this observation, one of which is that the particle of hydrotalcite could pass through UF pores and decrease pore fouling. This was true even while agglomerated hydrotalcites were bigger than UF pores as shown in Figs. 5c and 5b, respectively. Hydrotalcite formed the denser layer on the membrane surface, while original hydrotalcite of lateral dimension was around a few hundred nanometers of hexagonal platelets and a few ten nanometers of thickness [21]. Moreover, low pressure in the UF might assist to form a loose and movable layer of hydrotalcite that was supported with fluctuation of permeate (Fig. 3b). PAC was reported to have an original size of 10–50 μm (data from the manufacturer). As shown in Figs. 5b and 5d, some PAC particles might block the top of the UF pores. Thus, a more permeate flux in hydrotalcite application than PAC was found in UF, as opposed to NF.

The permeate flux reduction in all cases of hybrid processes were less than 20% of its initial value. However, for membrane treatment alone at the same 1,000 mg/L initial PFOA concentration, flux reduction was 40–50%, which is much higher as compared to the hybrid processes (Fig. 3). The highest improvement of permeate was found in the hybrid hydrotalcite UF process. The most stable permeate flux was observed in the hybrid hydrotalcite NF process.

Moreover, the removal efficiency of the hybrid hydrotalcite NF process (95%) was higher than that of adsorption (70%), NF alone (~60% at ≥ 10 mg/L PFOA) or the removal efficiency of combined adsorption and NF processes (88%: from calculation). Therefore, it is interesting to compare membrane rejection between the hybrid membrane process and the membrane treatment alone. For the membrane hybrid process, the solution

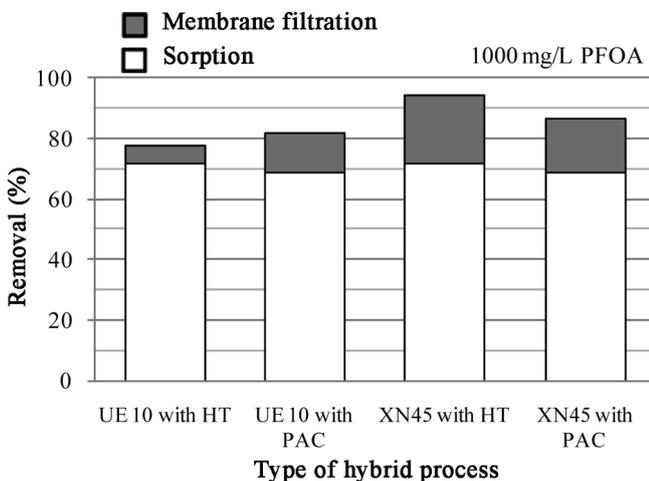


Fig. 4. PFOA removal by the hybrid membrane process.

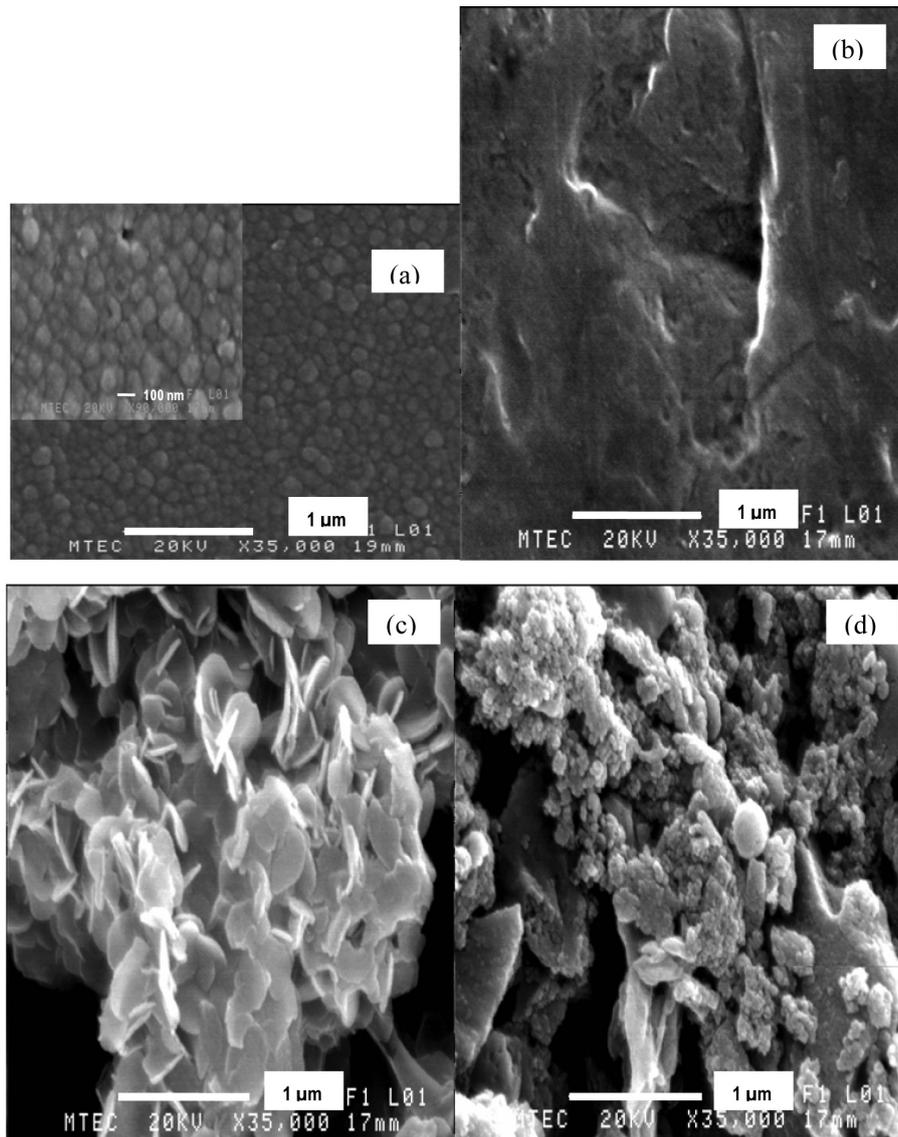


Fig. 5. Scanning electron microscope (SEM) images (X 35,000) of virgin membranes and appearance of adsorbents after the hybrid experiment: (a) NF (XN45); (b) UF (UE10); (c) hydrotalcite; and (d) PAC.

containing PFOA (~300 mg/L) and non-settleable (within 1 h) adsorbent were fed to the membrane system. The comparison of averaged membrane rejection between the membrane treatment alone and the hybrid membrane is shown in Fig. 6.

The efficiency of the membrane treatment increased for only the hydrotalcite pretreated PFOA with NF. In membrane filtration alone, XN45 showed less than 60% of removal with an applied PFOA concentration of ≥ 10 mg/L. But it showed around 86% removal in the presence of hydrotalcite in the hybrid membrane system at applied initial PFOA concentrations of 300 mg/L. The enhanced removal efficiency of hybrid hydrotalcite NF could be due to adsorption by hydrotalcite and denser layer forming

which acts as a barrier on the surface of membrane as shown in Figs. 6b and 6c.

In the case of PAC, the efficiency of XN45 with PAC application decreased while its permeate flux increased as discussed in the previous section. Considering the pore size, PAC could not pass through NF pores, however it formed a movable layer filtration as shown in Fig. 5d. Thus, decreased efficiency of XN45, as compared to membrane treatment alone, might result from unstable sorption or movement of PAC on the membrane surface, followed by the minimized PFOA sorption on the membrane. Further, the movable PAC layer could have resulted in the fluctuating permeate flow as shown in Fig. 3a.

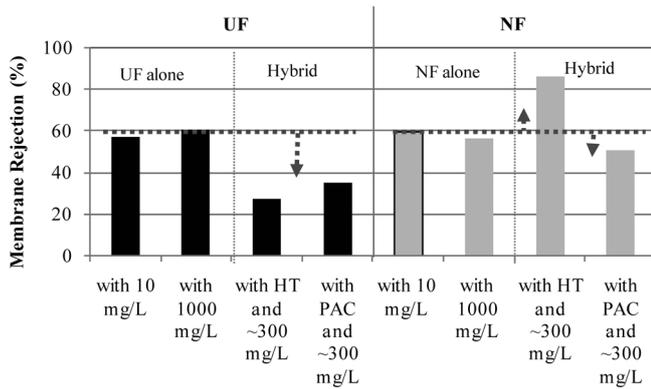


Fig. 6. Comparison of PFOA rejection by membrane in direct filtration and in hybrid filtration (HT is hydrotalcite).

The efficiency of membrane rejection in the hybrid UF process was around half of that in UF alone (Fig. 6). In Section 3.1, it was described that adsorption on membrane surface and sieving size by fouled pores are involved in PFOA rejection of UF. Thus, decreasing PFOA rejection in the hybrid UF process might have resulted from the lower adsorption and fouling on the membrane. This corresponded with improved permeate flux in the UF hybrid process. Furthermore, the movable PAC layer retained on the membrane surface could decrease membrane rejection. But in the case of hydrotalcite, it was possible for some particles to pass through UF pores and then decrease pore fouling. This may have been another cause of it having the lowest PFOA removal and the highest permeate flux among all UF processes.

Even though the PAC membrane hybrid process has shown low membrane rejection as compared to membrane alone, UF application is interesting to be coupled for PFOA removal by PAC adsorption. This is because low fouling occurred and long membrane filtration cycle could be operated.

In addition, less amount of adsorbent applied in the hybrid membrane process is another important aspect of this technique. A preliminary test demonstrated that sorption alone required around 2 g/L of hydrotalcite for complete removal (for 1,000 mg/L of initial concentration), whereas when hybrid hydrotalcite NF was used, 0.62 g/L of hydrotalcite was needed to achieve a high comparable removal (~95%: as presented in Fig. 4). For PAC, around half of adsorbent amount required in sorption alone was used in membrane hybrid process to achieve similar removal.

Earlier reported RO and resin sorption technologies [1 and 11] revealed higher removal efficiency in comparison with this hybrid NF and UF processes. However, the filtration flux obtained in this hybrid study was higher than the RO system. It is also important to note that the RO membrane has higher permeate flux reduction, thus

making hybrid systems to be more attractive in long term practical applications. However, there is a need to further investigate to improve the PFOA removal efficiency by adopting membrane in series (UF-NF or NF-RO) combination with sorption processes.

4. Conclusions

Hybrid membrane filtration was found to be effective for the removal of high PFOA concentrations as compared to the adsorption process or UF/NF alone. High removal has been observed in the case of the combination of NF with adsorbents, specifically with hydrotalcite. The hybrid hydrotalcite NF process enhanced membrane rejection without adverse effects on the permeate flux as compared to NF alone. The amount of adsorbents required in the NF hybrid membrane process were less than 1/2 of one applied in sorption alone to achieve a highly comparable removal. Moreover, it is interesting to note that the presence of PAC in the membrane feed enhanced the permeate flux as compared to UF and NF alone even though the removal efficiency of the membrane was decreased. Thus, hybrid NF process was effective for PFOA removal with regards to removal efficiency, amount of treated water produced and the amount of adsorbent used. Further, UF application is the viable option to be coupled with adsorbent sorption for PFOA removal due to long membrane operation cycle.

Symbols

A	— Effective surface area of membrane, m^2
C_f	— Concentration of compound in membrane feed, mg/L
C_p	— Concentration of compound in permeate, mg/L
J	— Membrane permeate flux, $m^3/m^2 d$
$\log K_{ow}$	— Logarithm of octanol-water partitioning coefficient
PFOA	— Perfluorooctanoic acid
PAC	— Powdered activated carbon
pK_a	— Acid dissociation constant
R	— Rejection/removal of compound, %
t	— Time, h
V	— Volume of membrane permeate, m^3

Acknowledgement

This study was funded by New Energy and Industrial Technology Development Organization (NEDO). The authors would like to express their gratitude to Dr. Narin Boontanon, Department of Environmental Engineering, Mahidol University for his support during the research.

References

- [1] D.J. Lampert, M.A. Frisch and G.E. Speitel, Jr., Removal of perfluorooctanoic acid and perfluorooctane sulfonate from wastewater by ion exchange, *Pract. Periodical Hazard. Toxic Radioactive Waste Mgmt.*, 11 (2007) 60–68.
- [2] N. Yamashimota, K. Kannan, S. Taniyasu, Y. Horii, G. Petrick and T. Gamo, A global survey of perfluorinated acids in oceans, *Mar. Pollut. Bull.*, 51 (2005) 658–668.
- [3] S. Wei, L.Q. Chen, S. Taniyasu, M.K. So, M.B. Murphy, N. Yamashita, L.W.Y. Yeung and P.K.S. Lam, Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica, *Mar. Pollut. Bull.*, 54 (2007) 1813–1838.
- [4] Y.H. Jin, W. Liu, I. Sato, S.F. Nakayama, K. Sasaki, N. Saito and S. Tsuda, PFOS and PFOA in environmental and tap water in China, *Chemosphere*, 77 (2009) 605–611.
- [5] DW. Provisional evaluation of PFT in drinking water with the guide substances perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) as examples. Statement by the Drinking Water Commission (Trinkwasserkommission) of the German Ministry of Health at the Federal Environment Agency, 2006.
- [6] S. Fujii, C. Polprasert, S. Tanaka, N. P. H. Lien and Y. Qiu, New POPs in the water: distribution, bioaccumulation and treatment of perfluorinated compounds – a review paper, *J. Water Supply Res. Technol.–Aqua*, 56(5) (2007) 313–326.
- [7] Y. Wei, J. Dai, M. Liu, J. Wang, M. Xu, J. Zha and Z. Wang, Estrogen-like properties of perfluorooctanoic acid as revealed by expressing hepatic estrogen-responsive genes in rare minnows (*Gobiocypris rarus*), *Environ. Toxicol. Chem.*, 26 (2007) 2440–2447.
- [8] C. Liu, Y. Du and B. Zhou, Evaluation of estrogenic activities and mechanism of action of perfluorinated chemicals determined by vitellogenin induction in primary cultured tilapia hepatocytes, *Aquat. Toxicol.*, 85 (2007) 267–277.
- [9] S. Tanaka, S. Fujii, K. Kimura, M. Nozoe and Y. Qiu, Removal characteristics of PFOS and PFOA by granular and powder activated carbons in composite samples, *Organohalo. Comp.*, 69 (2007) 2820–2824.
- [10] Q. Yu, R. Zhang, S. Deng, J. Huang and G. Yu, Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study, *Wat. Res.*, 43 (2009) 1150–1158.
- [11] C. Y. Tang, Q. S. Fu, C. S. Criddle and J. O. Leckie, Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse Osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater, *Environ. Sci. Technol.*, 41 (2007) 2008–2014.
- [12] J. Meier, T. Melin and L.H. Eilers, Nanofiltration and adsorption on powder adsorbent as process combination for the treatment of severely contaminated wastewater, *Desalination*, 146 (2002) 361–366.
- [13] Y. Wang, L. Shu, V. Jegatheesan and B. Gao, Coagulation and nanofiltration: A hybrid system for the removal of lower molecular weight organic compounds (LMWCO), *Desal. Wat. Treat.*, 11(2009) 1–9.
- [14] C.A. Basar, A. Karagunduz, A. Cakici and B. Keskinler, Removal of surfactants by powdered activated carbon and microfiltration, *Wat. Res.*, 38 (2004) 2117–2124.
- [15] S.-J. Lee, K.-H. Choo and C.-H. Lee, Conjunctive use of ultrafiltration with powdered activated carbon adsorption for removal of synthetic and natural organic matter, *J. Ind. Eng. Chem.*, 6 (2000) 357–364.
- [16] K. Benrachedi, K. Bensouali and H. Houchati, Coupling ultrafiltration with adsorption on activated coffee for use as reverse osmosis pretreatment, *Desalination*, 239(2009) 122–129.
- [17] A.M. Comerton, R.C. Andrews, D.M. Bagley and P. Yang, Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds, *J. Membr. Sci.*, 303 (2007) 267–277.
- [18] S. Mandale and M. Jones, Interaction of electrolytes and non-electrolytes in nanofiltration, *Desalination*, 219 (2008) 262–271.
- [19] R.H. Peiris, C. Halle, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck and R.L. Legge, Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices, *Wat. Res.*, 44 (2010) 185–194.
- [20] H. Sanderson, T.M. Boudreau, S.A. Mabury and K.R. Solomon, Impact of perfluorooctanoic acid on the structure of the zooplankton community in indoor microcosms, *Aquat. Toxicol.*, 62 (2003) 227–234.
- [21] S. Chen, Z.P. Xu, Q. Zhang, G.Q. Max Lu, Z.P. Hao and S. Liu, Studies on adsorption of phenol and 4-nitrophenol on MgAl mixed oxide derived from MgAl-layered double, *Separ. Purif. Technol.*, 67 (2009) 194–200.