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Low-pressure reverse osmosis membrane separation of non-fluorinated and perfluorinated organic compounds in water

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ABSTRACT

The purpose of this study is to compare retention characteristics of perfluorinated organic compounds (PFCs) and similar-structured non-fluorinated organic compounds (NFCs) by new generation low-pressure reverse osmosis (LPRO) membranes based on physicochemical properties of the compounds and the results of bench-scale membrane efficiency batch tests as the first-step screening. Molecular weight (MW), molecular size, and hydrophobicity of the compounds greatly influence their retentions by loose and low-desalting membranes than those by tight and high-desalting membranes. The retentions in general increased with increasing MW and molecular length (ML). The retentions are explained more reliably by using both MW and molecular width/height parameters. The roles of MW and ML on the retentions could not be differentiated, since MW increases almost linearly with ML. The NFCs are more easily rejected than the PFCs by the membranes most probably due to hydrophobic adsorption of the PFCs to membranes leading to their slippage through membrane pores owing to their slender molecular structures. Though retentions of NFCs and PFCs in their undissociated states are governed by steric/size exclusion mechanism, hydrophobic adsorption to membrane is a major event for PFCs while it is not for NFCs. Unlike NFCs, retentions of PFCs in their dissociated states are greatly enhanced due to overwhelmingly greater efficacy of electrostatic exclusion. This is the first study comparing retentions of NFCs and PFCs by LPRO membranes and is expected to serve as an important reference for further works.

Keywords: Electrostatic exclusion; Hydrophobicity; Molecular length; Molecular size; Molecular weight cutoff; Steric exclusion

1. Introduction

Membrane separation is an outstanding method for eliminating a wide range of organic and inorganic constituents in water and wastewater treatments [1–7]. Reverse osmosis (RO) membrane separation is the best among all the available membrane separation methods attributed to its ability to remove all kinds of solutes in water [1,8–10]. But the process requires considerably high pressures resulting in high operational costs. Nanofiltration (NF) is an alternative to RO process,

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but permeate quality has to be compromised with NF. During the past decade, low pressure reverse osmosis (LPRO) membranes have emerged as a very promising alternative to RO membrane filtration [11–14]. As LPRO membrane concept is relatively new, people often face difficulty in recognizing its place in categorization of membrane filtration process. In general, all NF membranes are considered as LPRO membranes, but not all LPRO membranes are NF membranes. The LPRO membranes with big pore sizes and less than 90% NaCl rejection efficiencies are considered as NF membranes. In fact, operating pressure is a very important parameter in distinguishing LPRO membranes. These membranes can be used under very low pressures (<1.0 MPa), while their solute retention efficiencies are comparable with those of RO membranes.

Separation of organic/inorganic pollutants in water by membrane filtration is indeed a very complex process with respect to retention mechanisms. Solute and membrane characteristics and feed water composition play vivid roles in solute retention efficiency and mechanism [4]. Size/steric exclusion, electrostatic repulsion, hydrophobic adsorption, and diffusion are pointed out as some of the important solute retention mechanisms with RO membranes [9,15], LPRO membranes [11–14] and NF membranes [8,16–17]. However, the first screening of solute retention in membrane filtration is normally carried out with respect to physicochemical characteristics of solutes and membranes [18–19] due to its simplicity and cost consideration. Molecular weight (MW), molecular size, molecular weight cutoff (MWCO), acid dissociation constant (pK_a), hydrophobicity ($\log K_{ow}$) and membrane pore size are some of the important parameters employed in the screening.

Perfluorinated organic compounds (PFCs) as micropollutants in water environment have a very short history and are recently classified as emerging organic contaminants. Occurrence of PFCs in water environment [20–24] and their negative impacts to living organisms [25] are well documented despite the short history of their recognition as micropollutants. Very little is known about membrane retention characteristics of these compounds as only few investigations have been devoted to the subject until now [11]. The non-fluorinated organic compounds (NFCs) like sugars, polyethylene glycols (PEGs), and carbohydrates are to some extent similar to PFCs with respect to their molecular lengths. The most apparent characteristic feature of their molecules is the absence of fluorine atoms. Although sugars and glycols have a very long history as industrial substrates/products, there are not apparently many published articles on their membrane separation behaviors [1,26–28]. Nevertheless, it is interesting and important to compare membrane separation characteristics of NFCs (well-known industrial substrates/products) and PFCs (emerging perfluorinated organic contaminants) in the light of similarity in carbon chain length and dissimilarity in fluorine content.

The aim of this study is to compare retention behaviors of PFCs and NFCs (particularly sugars and glycols) during LPRO membrane filtration based on laboratory bench-scale membrane efficiency test results and physicochemical characteristics of the solutes and membranes as the first-stage screening. Six commonly used PFCs (four perfluoroalkyl carboxylates (PFACs) and two perfluoroalkyl sulfonates (PFASs)), seven sugar compounds, six glycols, and five new generations commercial LPRO membranes were used for this purpose in the tests as described in the following sections.

2. Materials and methods

2.1. Chemicals and standards

The NFCs and PFCs tested in this investigation are listed in Tables 1–3. The standards of PFCs were obtained from Wako Pure Chemical Industries Ltd., Osaka. Internal standards of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), and purified mixed standards of the PFCs used for calibration curves were obtained from Wellington Laboratories, Canada. The standards of NFCs and other necessary reagents were obtained from Wako Pure Chemical Industries Ltd., Osaka. Stock solutions

Table 1
Physicochemical properties of investigated PFCs

Compound	Abbreviation	Molecular formula	MW	pK_a
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	264.04	–
Perfluorobutanesulfonic acid	PFBS	$C_4HF_9O_3S$	300.09	–
Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	314.05	–
Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	364.06	–
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	414.07	2.50
Perfluorooctanesulfonic acid	PFOS	$C_8HF_{17}O_3S$	500.13	3.27

Table 2
Physicochemical properties of investigated sugar compounds

Compound	Abbreviation	Molecular formula	MW	pK_a
Glycerol	GR	$C_3H_8O_3$	92.09	14.20
Glucose	GC	$C_6H_{12}O_6$	180.16	12.28
Sucrose	SC	$C_{12}H_{22}O_{11}$	342.30	12.62
Raffinose	RF	$C_{18}H_{32}O_{16}$	504.42	12.81
Maltotetraose	MT	$C_{24}H_{42}O_{21}$	666.58	11.90
Maltopentaose	MP	$C_{30}H_{52}O_{26}$	828.73	11.80
Maltoheptaose	MH	$C_{42}H_{72}O_{36}$	1153.00	12.00

Table 3
Physicochemical properties of investigated PEGs

Compound	Abbreviation	Molecular formula	MW	pK_a
Ethylene glycol	EG	$C_2H_6O_2$	62.07	14.2
Diethylene glycol	DEG	$C_4H_{10}O_3$	106.12	–
Polyethylene glycol (200)	PEG200	$HO(CH_2CH_2O)_nH$	200.00	–
Polyethylene glycol (400)	PEG400	$HO(CH_2CH_2O)_nH$	400.00	–
Polyethylene glycol (600)	PEG600	$HO(CH_2CH_2O)_nH$	600.00	–
Polyethylene glycol (1,000)	PEG1,000	$HO(CH_2CH_2O)_nH$	1000.00	–

of each PFC (1.0 g/L) in pure water were prepared separately and stored in refrigerator (4–10℃) for further use. Diluted solutions of the PFCs (1.0 mg/L for each compound) in pure water were used for membrane efficiency tests. Freshly prepared solutions of sugars (50 mg/L for each compound) and glycols (0.5% by weight for each compound) in pure water were used for membrane efficiency tests.

2.2. Membranes

Three types of five LPRO membranes from two different manufacturers were employed in this investigation. The basic characteristics of the membranes as provided by the manufactures are listed in Table 4. These characteristics are discussed a little later in this study.

2.3. Laboratory test procedures

New membranes (as received from manufacturers) were first washed with pure water for 30 min followed by NaCl (1.0×10^{-3} M) rejection efficiency evaluation tests ($pH = 7.0 \pm 0.1$). They were washed again with pure water for 30 min before being used in retention efficiency tests with the selected NFCs and

Table 4
Properties of tested membranes

Membrane	ES-20	NTR-759HR	NTR-729HF	NTR-7450	UTC-60
Manufacturer	Nitto Denko	Nitto Denko	Nitto Denko	Nitto Denko	Toray
Material	APA	PA	PVA	SPS	APA
NaCl rejection (%)	99.5	99.0	90.0	50.0	55.0
Working pH	2–10	2–10	2–8	2–11	–10
MWCO (Da)	150	150	150–200	600–800	150
PZC	2.66	3.40	3.74	3.27	2.79
MOP (MPa)	4.12	2.94	2.94	4.90	NA
MOT (℃)	40.0	40.0	40.0	60.0	NA
PWF (kg/m^2.h)	18.67	13.61	12.55	29.63	41.16

Notes: MWCO: molecular weight cutoff; APA: aromatic polyamide; PA: polyamide; PVA: polyvinyl alcohol; SPS: sulfonated polysulfone; PZC: point of zero charge; MOP: maximum operating pressure; MOT: maximum operating temperature; NA: not available; PWF: pure water flux at 0.30 MPa pressure.

PFCs. Bench-scale batch tests were conducted to evaluate retention efficiencies of the compounds in laboratory (20–23℃). A schematic diagram of the test setup is shown in Fig. 1. A stainless steel pressure-resistant cell (model: C-70B, volume: 350 ml and effective membrane area: 32.0 cm^2 from Nitto Denko Corporation, Japan) was used for all the tests. The reaction solution (300 ml) inside the cell was continuously mixed (500 rpm) using a magnetic bar and stirrer to avoid concentration polarization. The tests were conducted under nitrogen atmosphere with an operating pressure of 0.30 MPa. The retention tests for PFCs were carried out at four different solution pH values (3, 5, 7, and 9) while those for sugars and glycols were conducted at pH = 3.0. Solution pH was adjusted using HCl (0.01 N) and NaOH (0.01 N) solutions. Solute retention ratio for each case was calculated using the following equation:

$$R = \left(1 - \frac{2C_P}{C_{F0} + C_F}\right) \times 100 \qquad (1)$$

where R: retention ratio (%), C_P: solute concentration in permeate solution, C_{F0}: solute concentration in feed solution just before the experiment begins (i.e. $t = 0$), and C_F: solute concentration in feed solution after the experiment starts. Permeate samples were taken at 10 min, and then at every 20 min interval until 170 min period for NTR-729HF, NTR-759HR, and ES-20 membranes, and the samples with steady solute concentrations (110 min onward) were used for retention efficiency evaluation. These values for NTR-7450 and UTC-60 membranes were 10, 20, 110, and 70 min; and 5, 20, 85, and 45 min, respectively. After the tests were over, the membranes were washed with pure water followed by NaCl rejection efficiency evaluation tests as mentioned earlier. The membranes were reused without any treatment if the NaCl retention efficiencies did not decrease significantly. Otherwise, they were washed with 0.01 N HCl (ES-20, NTR-759HR, NTR-729HF, and UTC-60) and 0.01 N NaOH (NTR-7450) before being used in further tests.

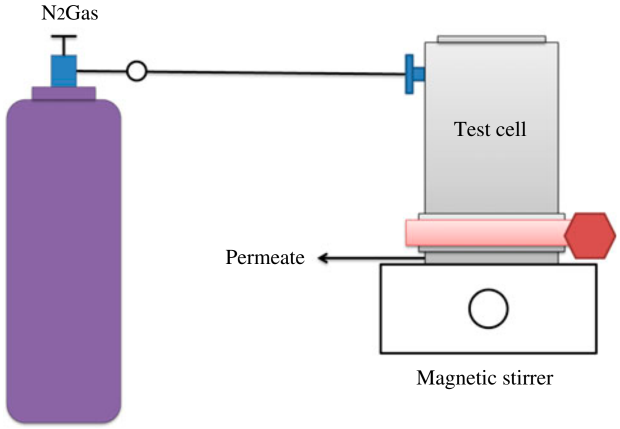

Fig. 1. A schematic diagram of experimental setup.

2.4. Sample analysis

Concentrations of the PFCs in permeate samples were measured using waters acquity ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS). The UPLC system was equipped with a binary pump and ACQUITY UPLC BEH HILIC column (50 mm × 2.1 mm, 1.7 μm). Mobile phases for LC separation consisted of 10 mM ammonium acetate in pure water and acetonitrile in gradient elution (200 μL/min). Electrospray ionization in negative mode was used as ion source, and mass detection was carried out in multiple reactions monitoring mode. The sugars and glycerol in permeate samples were measured using UPLC-MS system (Waters Corporation) and ACQUITY UPLC BEH Amind column (100 × 2.1 mm, 1.7 μm). A mixture of 80% acetonitrile (v/v) in pure water with 0.2% triethylamine (v/v) and another mixture of 30% acetonitrile (v/v) in pure water with 0.2% triethylamine (v/v) in gradient elution (120 μL/min) were used as mobile phases. The concentrations of glycols in samples were measured using high-performance liquid chromatography (HPLC, D-7000, Hitachi High-Tech, Japan) with Refractive Index detector (L-7490) and OHpak SB-803 HQ column (300 × 8.0 mm, 6.0 μm; Showa Denko K.K., Japan). Pure water at 800 μL/min flow rate in isocratic elution was used as mobile phase in HPLC separation of glycols.

3. Results and discussion

Each of the efficiency tests involving the selected compounds and membranes was conducted in triplicate, and averages of the corresponding values are presented in the figures in this section. However, error bars in the figures are omitted for clarity as most of the data points are very close to each other.

3.1. Characterization of tested compounds

The molecular length (ML), width, and height values of the investigated compounds were calculated using ChemOffice Pro 2004 ver8.0 software (CambridgeSoft Corporation) while the log K_{ow} values were calculated using ACD/Labs software (version 2012). The very small pK_a values for PFOA and PFOS (slightly less than 3.0, Table 1) show that the compounds in solution remain in dissociated states under wider pH range. The large positive log K_{ow} values for PFCs (2.65–5.14) shows highly hydrophobic character of the compounds. The ML of the PFCs (0.9–1.5 nm) increases with increasing carbon chain length while molecular widths (0.40–0.50 nm) and heights (0.40–0.50 nm) are almost the same for all of them. Unlike PFCs, the sugar compounds have very large pK_{a} values (11.8–14.2, Table 2) indicating their undissociated states in solution under very wide pH range. Unlike PFCs, the sugars are highly hydrophilic (log $K_{\text{ow}} = -1.73$ to -9.54) and the hydophilicity increases with MW. Similar to PFCs, ML of these compounds (0.66–2.25 nm) increases with MW. However, increasing molecular width (0.28–1.42 nm) and height (0.35–1.52 nm) with increasing ML due to ring structures in molecules is a distinct feature of sugar compounds among the three groups of compounds. Therefore, the sugar compounds unlike PFCs grow in overall molecular size with increasing ML. Though pK_{a} values for all the tested glycols could not be known, the very high value (14.2) for ethylene glycol indicates that glycols like the sugar compounds do not get dissociated under very wide pH range. The negative log K_{ow} values for glycols (-1.09 to -1.95) once again show that the compounds are hydrophilic. But the glycols appear being less hydrophilic than the sugar compounds based on their log K_{ow} values. Like PFCs and sugar compounds, ML of glycols (0.50–8.54 nm) increases with increasing MW. But the molecular width (0.25–0.26 nm) and height (0.29–0.31 nm) are almost the same with increasing MW like in PFCs.

3.2. Characterization of tested membranes

Some important characteristics of the tested membranes are shown in Table 4. The membrane materials consist of aromatic polyamide (APA), polyamide (PA), polyvinyl alcohol (PVA), and sulfonated polysulfone (SPS). PA membranes are considered to be less polar than cellulose acetate membranes [4]. Salt rejection ratio is an important parameter in evaluating micropollutant retention efficiency of a membrane. The NaCl rejection values for ES-20, NTR-759HR, and NTR-729HF are more than 90%, while those for NTR-7450 and UTC-60 are close to 50%. MWCO is another important parameter that is commonly employed for estimating membrane capability to retain dissolved uncharged compounds [4]. A MWCO value is an indirect indication of membrane pore size. The ES-20, NTR-759HR, NTR-729HF, and UTC-60 have low MWCO values (150–200 Da) exhibiting their small pore sizes. On the other hand, NTR-7450 has large MWCO value (600–800 Da) indicating its large pore size. In this respect, the first four are called as tight membranes, while NTR-7450 is called as a loose membrane. Despite very similar MWCO value of UTC-60 to those of the three other tight membranes, the permeate flux value for UTC-60 is almost 2-fold larger than those for the three. This characteristic may be attributed to membrane materials and desalting efficiencies. Membrane surface charge is another important parameter influencing retention efficiency. A point of zero charge (PZC) is the solution pH at which a membrane surface has net zero charge. The PZC values for all the five membranes are very close to 3.0.

3.3. Retention of NFCs

Fig. 2 shows retention ratios of EG, PEGs, and sugars at solution pH = 3.0 by a tight membrane (NTR-729HF) and a loose (NTR-7450) membrane against (a) MW, (b) ML, and (c) hydrophobicity of the compounds. The retention ratios increased for larger MW compounds with the both membranes. However, the retention with tight membrane is very distinct from those with loose membrane. First of all, MWCO value for NTR-729HF (150–200 Da) appears to have played a critical role in retaining both PEGs and sugars. The retention ratio increased drastically with increasing MW for MW values less than or equal to MWCO. Then, the increase in retention with increasing MW is minimal. The retentions with NTR-7450 are very small than those with NTR-729HF, which is obvious. It is important to note that retention of sugars by NTR-7450 (MWCO = 600–800 Da) followed similar pattern to that by NTR-729HF despite smaller retentions with the loose membrane pointing toward the role of MWCO. But the same is not evident for PEGs with NTR-7450. The different retention behaviors of sugars and PEGs with NTR-7450 despite their very similar molecular weights may be attributed to the difference in molecular size.

The plots between retention ratios and ML (Fig. 2 (b)) are very similar to those between retention ratios and MW (Fig. 2(a)). Therefore, ML alone apparently is not sufficient to describe the different retention behavior of PEGs with NTR-7450. If we look to overall molecular dimensions (length, width, and height) of the compounds, sugars are characterized by increasing ML, width, and height with increasing MW, while PEGs exhibit increasing ML only (widths and heights being almost the same for all PEGs) with increasing MW as mentioned earlier. The overall

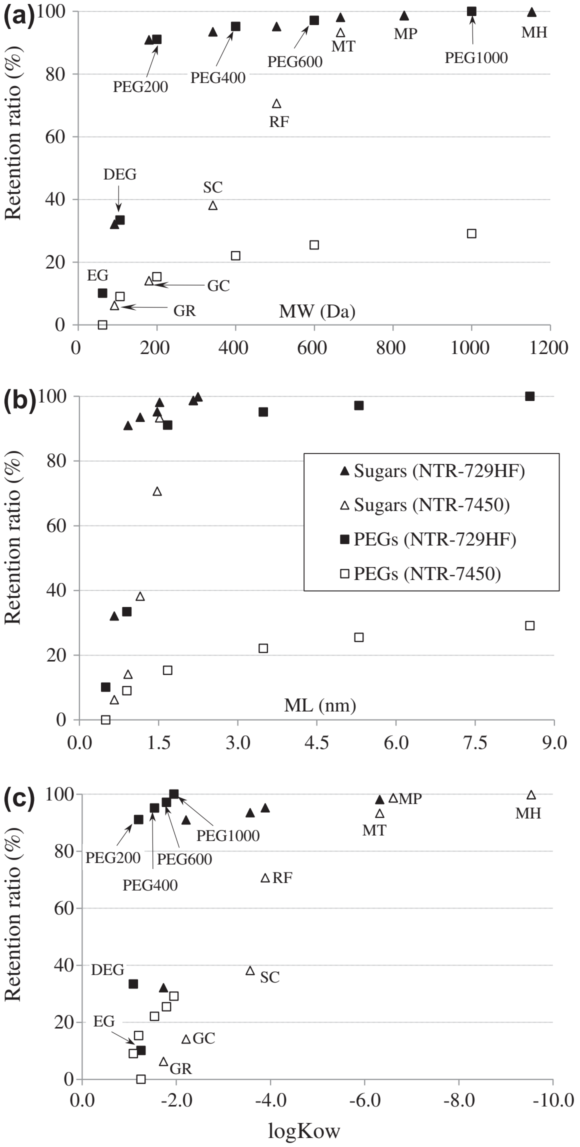

Fig. 2. Plots of MW, ML and log K_{ow} against the corresponding retention ratios for sugars and glycols (pH = 3.0).

molecular size appears being not very important for the retention of sugars and PEGs by tight membranes (e.g. NTR-729HF). But overall molecular size is apparently very important for their retention by loose membranes (e.g. NTR-7450). Sugar molecules may be expected to be retained very easily by NTR-7450 due to increasing overall molecular size with MW while PEGs could easily be slipped through the membrane pores despite their increasing ML with MW. Therefore, overall molecular size rather than ML should be a more suitable parameter for describing retention of long carbon-chain molecules by loose membranes.

Hydrophobicity/hydrophilicity of micropollutants is an important parameter in membrane filtration. Though both glycols and sugars are nonpolar and neutral compounds, the membrane efficiency tests were conducted at pH = 3.0 to confirm almost neutral charge on membrane surface so that any effect of membrane surface charge on solute retention is negligible. Retentions of these compounds by NTR-729HF and NTR-7450 are plotted against log K_{ow} values of the compounds (Fig. 2(c)) and the plots for these two groups of compounds are very distinct from each other, which is attributed to log K_{ow} values. Unlike PFCs, sugars, and glycols are hydrophilic compounds, and sugars (log $K_{ow} = -1.73$ to -9.54) are more hydrophilic than glycols (log $K_{ow} = -1.09$ to -1.95) despite their very similar MW values. In contrast to hydrophobic compounds, hydrophilic compounds tend to remain in water phase resulting in their very small or no adsorption to membranes. Thus, adsorption apparently does not play a significant role in retention of sugars and glycols. Although the retention in general shows direct correlation with hydrophilicity of the compounds, it is more evident in case of sugar compounds (Fig. 2(c)) owing to their very small (almost 5-fold) log K_{ow} values.

MW has been widely used to describe retention of various micropollutants due to size exclusion [1,12,14,28]. But the correlations of solute retention against MW and ML particularly for long carbon-chain slender molecules (e.g. glycols) and long carbon-chain fat molecules (e.g. sugars) with a loose membrane (NTR-7450) varied considerably in this investigation. Agenson et al. [18] found molecular width rather than MW better describing retention of volatile organic molecules by NF membranes. In the present case, retentions of sugars and glycols by NTR-7450 are described more reasonably using overall molecular size due to the fact that glycol molecules (long carbon-chain slender structure) are more likely to easily slip through membrane pores than sugar molecules (long carbon-chain fat structure). Direct correlations between hydrophilicity of the compounds (sugars and glycols) and their retentions by LPRO membranes are evident in this research. However, the correlations are more apparent in case of sugars due to their almost 5-fold larger hydrophilicity than those of glycols. Direct correlations between solute hydrophobicity and their retention during membrane filtration are also reported [4,12]. But a unique characteristic difference between retention mechanisms of hydrophobic and hydrophilic compounds is whether or not solute adsorption to membranes is a major event.

3.4. Retention of PFCs

Retention of four PFACs and two PFASs (Table 1) with five LPRO membranes (Table 4) was tested. Unlike PEGs and sugars, PFCs are hydrophobic with very small pK_a values (≈3.0), and hence, solution pH is expected to influence their retention. Figs. 3 and 4 illustrate retention ratio profiles of the compounds against solution pH (3–9) with the membranes. Retentions of the compounds by ES-20 and NTR-759HR (Fig. 3) are more than 98% irrespective of solution pH. On the other hand, solution pH showed big impact on the retentions by other three membranes (Fig. 4). The retentions at pH = 3.0 exhibited minimum values with big differences among the PFCs. But, retentions at pH = 5.0 increased very drastically (>95% with NTR-729HF/NTR-7450 and >65% with UTC-60). Though this trend continued further at higher pH, the rate of increase in retention is very slow. Moreover, NTR-729HF, NTR-7450, and UTC-60 are in the order of decreasing retention ratio at all the tested pH.

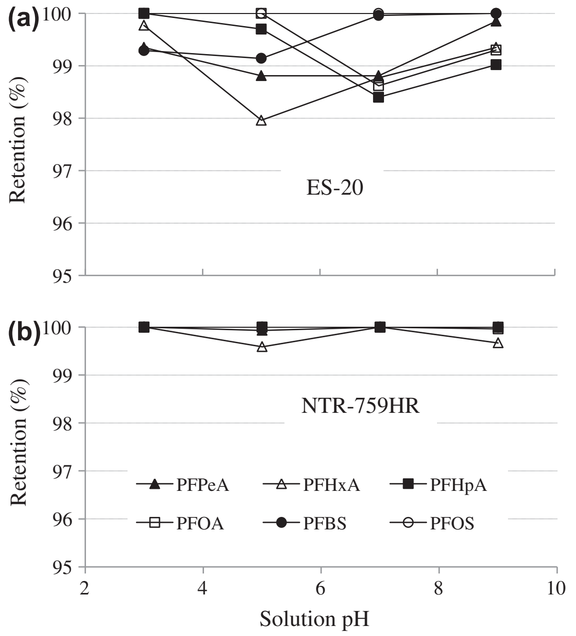

Fig. 3. Influence of solution pH on retention of PFCs by (a) ES-20 and (b) NTR-759HR membranes.

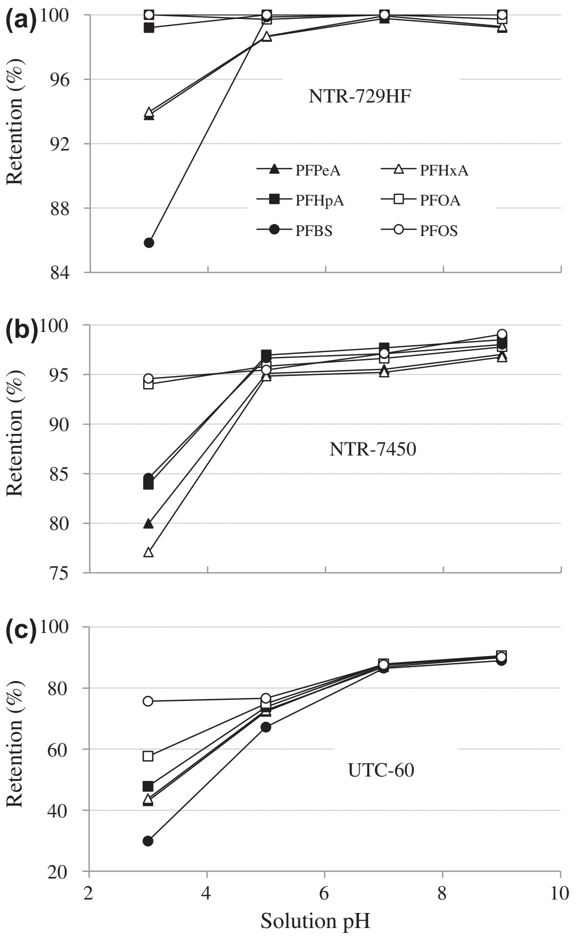

Fig. 4. Influence of solution pH on retention of PFCs by (a) NTR-729HF, (b) NTR-7450, and (c) UTC-60 membranes.

The PFCs at pH = 3.0 have minimum dissociation (p$K_a \leqslant 3.0$) within the tested pH range (3–9). Their dissociation increases at higher pH. It is evident that retention of PFCs by tight membranes with more than 99% salt rejection (Fig. 3) is overwhelmingly governed by steric mechanisms, and it is unimportant whether the compounds are in dissociated or undissociated states. But electrostatic mechanisms seemingly have a bigger role to play on retention by less tight and loose membranes particularly with very low desalting efficiencies (e.g. NTR-7450) if the PFCs are more and more in their dissociated states (Fig. 4). In contrast to an earlier result on endocrine disruptors and pharmaceuticals [9], desalting efficiency rather than MWCO possibly played a major role on retention of PFCs by UTC-60 in this investigation. Retention of PFCs at pH = 3.0 by the membranes (Fig. 4) is governed by steric mechanisms. For example, MW of the compounds and their retention ratios in general showed positive correlations. On the other hand, pH = 5.0 is seemingly a critical point with respect to PFCs retention due to electrostatic mechanisms. The similar characteristics have been observed earlier in case of pharmaceuticals and pesticides also [12]. Solution pH influences membrane properties in two ways: surface negative charges and membrane pore size increase at higher solution pH [4,12]. The increased PFCs retention at higher pH demonstrates dominant role of electrostatic mechanisms on the retention. The pH = 3.0 is the most suitable condition for tests to examine steric retention characteristics of PFCs with the selected LPRO membranes from the viewpoints of working pH range and PZC values of the membranes and pK_a values of the PFCs. The characteristics are discussed in the following paragraphs.

The plots of retention ratios ($pH = 3.0$) against MW, ML and $\log K_{ow}$ values of PFCs are shown in Fig. 5. Irrespective of MW, the compounds are removed almost completely (>99%) by ES-20 and NTR-759HR (Fig. 5(a)). This behavior is understandable as both the membranes are tight ($MWCO = 150$ Da) with high desalting efficiencies (≈99%) and MW of the PFCs are well above the MWCO values. Despite very big differences in desalting efficiencies and MWCO values, NTR-729HF and NTR-7450 showed similar retention patterns, for example, more than 80% retention ratios and positive correlations between retention and MW. On the other hand, retentions by UTC-60 are very small than that with other membranes despite the same MWCO value (150 Da) to those of ES-20 and NTR-759HF and similar desalting efficiency (55%) to that of NTR-7450 (50%), but still a positive correlation between retention and MW is maintained in case of UTC-60.

The plots between retention ratio and ML (Fig. 5(b)) appear very similar to those between retention ratio and MW (Fig. 5(a)) presumably due to ML and MW increase in the same/similar ratio with increasing carbon chain length in PFCs. Laboratory test data of our earlier investigation [11] indicated better correlation of PFCs diffusion through membranes with MW rather than carbon chain length (i.e. ML). Nevertheless, it is hard to differentiate at this stage the contributions of MW and ML on retention of PFCs by LPRO membrane filtration. Furthermore, unlike sugar molecules, PFCs are characterized by almost the same molecular widths (0.40–0.50 nm) and heights (0.40–0.50 nm) as mentioned in earlier section. As a result, any steric resistance experienced by PFCs at membrane surface and/or in membrane pores due to molecular width and height should be very similar irrespective of carbon-chain length of PFCs. Therefore, molecular width and height seemingly do not have any impact on retention among the PFCs.

The plots between retention ratio and $\log K_{ow}$ (Fig. 5(c)) are slightly different than those between retention and MW, and retention and ML due to $\log K_{ow}$ values for all the tested PFCs not increasing proportionately with their MW and ML values. The two sulfonate compounds (i.e. PFBS and PFOS) have smaller $\log K_{ow}$ values than those of similar MW carboxylate compounds. Unlike sugars and glycols, PFCs are highly hydrophobic in nature resulting in their greater affinity for adsorption to membranes.

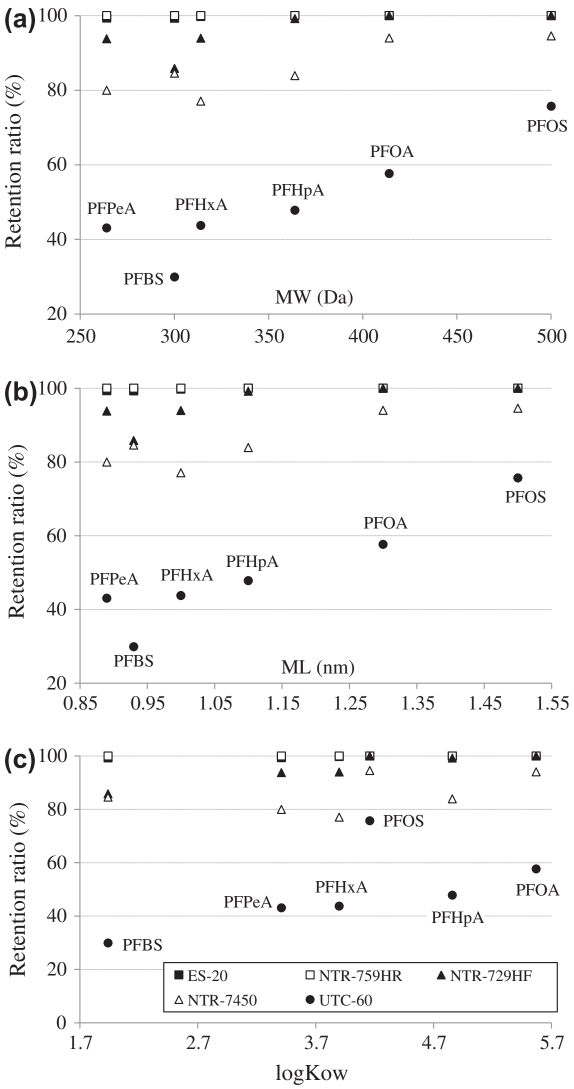

Fig. 5. Plots of MW, ML and $\log K_{ow}$ against the corresponding retention ratios for PFCs ($pH = 3.0$).

Although retention ratios and $\log K_{ow}$ values in general show positive correlations for NTR-729HF, NTR-7450, and UTC-60, any impact of hydrophobicity on retention appears to be insignificant for tight membranes with high desalting efficiencies. That is to say, MW rather than hydrophobicity may be a more useful parameter in describing PFCs retention by these types of membranes. However, hydrophobicity is a useful parameter in case of loose membranes and membranes with low desalting efficiencies. It should be noted that retention mechanisms for PFCs are different than those for sugars and glycols. Being hydrophobic in nature, PFCs are expected to get adsorbed to membranes as the first step in retention [7,12]. Then, steric forces [4,14,18] and/or diffusion forces [11] should be responsible for their further fate. As the membrane surfaces have PZC very close to 3.0 (Table 4) and the PFCs are in minimum dissociated states at pH = 3.0 (Table 1), any role of electrostatic forces/mechanisms on their retention can be expected to be insignificant.

3.5. Parallels and differences

MW is the most easily accessible and a useful parameter for describing retention of micropollutants in membrane filtration. The retention of sugars, glycols, and PFCs by LPRO membranes in this investigation is positively correlated to MW of the compounds. But MWCO value marked a borderline for a change in retention behavior. For example, the increase in retention with larger MW is very fast up to MWCO value, and it is extremely slow afterwards. One characteristic feature of these compounds is their carbon chain length. Although, ML showed good positive correlations with retention ratios, the roles of MW and ML could not be differentiated due to the fact that ML increases almost linearly with MW of the compounds. Therefore, the role of carbon chain length on retention is not very clear. However, molecular size (i.e. width and/or height) is found to highly influence retention of the compounds by loose membranes. The molecular width and height of PFCs and glycols do not change significantly with increasing ML whereas the molecular widths/heights do increase in case of sugars. Thus, PFC and glycol molecules have similar retention behaviors due to size exclusion, while sugar molecules behave differently as their lateral molecular sizes (widths/heights) increase with increasing ML (Figs. 2(a), 5(a), [18]). It is therefore, apparent that retention behaviors of PFCs, glycols, and sugars can be better understood by using both MW and molecular size than by using MW or molecular size alone.

Hydrophobicity/hydrophilicity and dissociation properties of the compounds play a crucial role on their retention mechanisms. Being highly hydrophilic in nature (log K_{ow} varying between −1.09 and −9.54) and in undissociated state in a wide pH range ($pK_a > 11.0$), adsorption presumably does not have a significant role on retention of sugars and glycols. Thus, sugar and glycol molecules are retained solely due to size exclusion mechanism [1] and their adsorption to membranes being insignificant. On the other hand, hydrophobic adsorption is a key step in the retention of hydrophobic compounds by LPRO and NF membranes [7,12]. Being hydrophobic in nature (log $K_{ow} = 1.94–5.57$), adsorption of PFCs to membrane surface can be expected to be a major step in their retention by LPRO membranes. Therefore, hydrophobic adsorption is a key point in distinguishing retentions of NFCs (e.g. sugars and glycols) and PFCs by LPRO membranes. With very small acid dissociation constant values ($pK_a \approx 3.0$), PFCs remain in dissociated state in a wide pH range and hence charge exclusion mechanism also comes into picture in addition to size exclusion mechanism in their retention particularly at pH larger than their pK_a values. Though fluorine atom in molecules is another distinguishing character among the investigated compounds, its significance in retention is not understood at this stage.

4. Conclusions

Retention behaviors of PFCs and similar-structured NFCs by new generation LPRO membranes with the focus on their (solutes and membranes) physicochemical properties are compared as the first-step screening. The conclusions are as follows:

1. The influences of MW, molecular size, and hydrophobicity/hydrophilicity of the tested compounds (PFCs and NFCs) on their retention by loose and low-desalting membranes are very distinct than those by tight and high-desalting membranes.
2. In general, retention of both PFCs and NFCs by the membranes increases with increasing MW and molecular size of the compounds.
3. Although MW is an easily accessible and widely used parameter for explaining retention of micropollutants in membrane filtration, retention of NFCs, and PFCs by the membranes can be explained more reliably by using MW as well as molecular size (particularly width/height) parameters.
4. Despite ML being a characteristic feature of the investigated compounds, the roles of MW and ML on their retention could not be distinguished due to the fact that MW increases almost linearly with ML.
5. The NFCs (hydrophilic) are more easily rejected than the PFCs (hydrophobic) by the membranes most probably due to hydrophobic adsorption of PFCs to membranes leading to their slippage through membrane pores owing to their slender molecular structures.
6. Retentions of NFCs as well as PFCs in undissociated states are governed by steric/size exclusion mechanism. However, hydrophobic adsorption of solutes to membrane is a major step in case of PFCs, but it is not so with NFCs.

(7) In contrast to NFCs, retentions of PFCs in their dissociated states are greatly enhanced than those in their undissociated states, which are attributed to overwhelmingly greater efficacy of electrostatic exclusion mechanism in the latter case.

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