Nanofiltration of perfluoroctanoic acid and perfluoroctane sulfonic acid as a function of water matrix properties

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ABSTRACT

Nanofiltration (NF) is a promising technology to remove the perfluoroalkyl acids, perfluoroctanoic acid (PFOA) and perfluoroctane sulfonic acid (PFOS) from water; however, little information is available as to how the natural water matrices impact PFOA and PFOS rejection when using NF. This study investigated the removal of PFOA and PFOS in laboratory-prepared water, surface water, and groundwater via NF to determine the effect of water matrix properties on PFOA and PFOS rejection by NF. PFOA and PFOS rejections were up to approximately 38% higher in the natural water matrices when compared to the laboratory-prepared water. The rejection of PFOA did not vary in the tested river water and groundwater; however, an increasing trend in PFOS rejection was observed and attributed to enhanced size exclusion of PFOS-cation complexes via the sulfonate (—SO3) ‘head’ of the PFOS ions and cation-induced membrane fouling by natural organic matter. Compound rejection increased with declining flux that was consistent with the dissolved organic matter (DOM) content of the respective water matrices. This study confirmed that DOM and cations indigenous to natural water matrices can lead to improved rejection of PFOA and PFOS when using NF.

Key words | cations, dissolved organic carbon, nanofiltration, perfluoroctane sulfonic acid, perfluoroctanoic acid, water matrix

INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of compounds that have been commercially produced and used in many consumer and industrial products for many decades (Rahman et al. 2014). Perfluoroalkyl acids (PFAAs) are widely used PFASs consisting of a carbon-fluorine base structure linked to a functional group. The rigid polar covalent bond in the molecular structure of PFAAs contributes to their persistence in the environment, which raises a major environmental concern. Perfluoroctanoic acid (PFOA) and perfluoroctane sulfonic acid (PFOS) are the most commonly investigated PFAAs that have bioaccumulative properties and a strong persistence in the environment. PFOA and PFOS have been reported at a range of concentrations in surface waters and wastewater treatment plant effluent (Quiñones & Snyder 2009), drinking water (Hu et al. 2016), and groundwaters in several US states and multiple cities in Western Europe (Xiao et al. 2015).

The occurrence and persistence of PFOS and PFOA in the environment is due to the carbon-fluorine bonds in their structure, which makes their decomposition and removal challenging. The hydrophobic fluorinated chain in common PFASs is usually linked to a hydrophilic carboxylic or sulfonic group that enhances high water-solubility. Additionally, PFOA and PFOS exhibit non-biodegradable, high polarity and stability characteristics. Over the last
decade, PFOS and PFOA have risen environmental and health concerns due to their toxicity and bioaccumulation properties, leading to the discontinuity of the production of PFOS in the US in 2002 (Thompson et al. 2014). PFOA and PFOA-related compounds that possess foaming and coating properties are still being produced by a limited number of industries. Nonetheless, concerns for the potential health effects of PFOA and PFOS have prompted the establishment of health advisory levels at 70 parts per trillion by the EPA (USEPA 2016).

PFOS, PFOA and many other PFASs are persistent against oxidation-reduction, volatilization, as well as photolytic, microbial, and metabolic degradations and, hence, conventional treatment processes are not efficient in eliminating PFAS from water (Takagi et al. 2014; Eschauzier et al. 2015). Membrane processes, particularly nanofiltration (NF) and reverse osmosis have demonstrated high (>90%) rejection of PFOS and PFOA (Appleman et al. 2014; Hang et al. 2015), likely via charge and size exclusion, or due to sorption onto the membrane (Saleh et al. 2019). NF efficiency of many contaminants of emerging concern is compound-specific and may significantly be influenced by the water matrix components (Sadmani et al. 2014c). The effects of cations on the rejection of PFOS and PFOA in laboratory-prepared waters have been investigated only very recently and these studies have suggested that specific divalent cations might improve their rejection by NF as a result of complex formation between the compounds and the cations (Zhao et al. 2016, 2018). Nevertheless, little information is available on the impacts of natural water matrices so as to derive practical conclusions when treating real waters. The objective of this study is to compare the rejection of PFOA and PFOS in laboratory-prepared, groundwater, and surface waters and determine PFOS/A rejection as a function of water matrix properties when using NF.

MATERIALS AND METHODS

PFOA and PFOS characteristics

PFOA (Sigma Aldrich, Saint Louis, MO, USA) and PFOS salts (Dr. Ehrenstorfer GmbH, Augsburg, Germany) with 96% and 98.5% purities, respectively, were used to prepare the stock solutions. The physicochemical properties of the PFOA and PFOS solutions are presented in Table 1.

Membrane selection and characteristics

The thin-film composite polyamide NF membrane, NE70 (NE-4040-70, TCK Membrane America, Inc.) selected for this study is classified as a loose membrane and suited for surface and groundwater applications. Zeta potential (ZP) and contact angle (CA) measurements suggest that NE70 is a negatively charged (ZP @ pH 8 = –36 mV) and hydrophobic (CA = 54.1°) membrane (Sadmani et al. 2014d). NE70 has a molecular weight cut-off (MWCO = 350 Da) less than the molecular weights of PFOA and PFOS (Table 1). Previous studies (Appleman et al. 2014; Hang et al. 2015) showing high rejection of PFOS/A used tighter membranes with MWCO = 200–300 Da, whereas the application of a looser membrane allows for the assessment of the effects of the interaction of water matrix components on PFOS/A rejection.

Table 1 | Physicochemical properties of PFOA and PFOS

<table>
<thead>
<tr>
<th>Perfluorinated compounds [CAS registry #] Structure</th>
<th>Molecular weight (g/mol)</th>
<th>Log $K_{ow}$</th>
<th>Solubility (g/L)</th>
<th>$pK_a$</th>
<th>Vapor pressure (Pa)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctanoic acid (PFOA) [335-67-1]</td>
<td>414.1</td>
<td>6.4</td>
<td>13.6</td>
<td>0.5</td>
<td>4.17 (25 °C)</td>
</tr>
<tr>
<td>Perfluorooctane sulfonate (PFOS) [1763-23-1]</td>
<td>500.1</td>
<td>4.5</td>
<td>7.5</td>
<td>–3.3</td>
<td>3.31 x 10^{-4} (25 °C)</td>
</tr>
</tbody>
</table>

$^a$Log $K_{ow}$ = Log of octanol–water partition coefficient.

$^b$Rodea-Palomares et al. (2012).

$^c$Rahman et al. (2014).
Water matrices

Three water matrices were investigated in this study: a surface water, a groundwater, and a laboratory-prepared water. The surface water was collected from the Ocmulgee River from the intake of Emerson L. Burford water treatment plant (WTP), Jackson, GA, USA. The groundwater was collected from the intake of the Town of Jupiter WTP, Jupiter, FL, USA. The laboratory-prepared deionized (DI) water served as a ‘control’ (see Table 2).

NF filtration set-up and experimental protocol

A CF042 crossflow cell assembly (Sterlitech Corp., Kent, WA, USA) was used for bench-scale membrane filtration experiments. The flat sheet membranes were precut and stored at room temperature in DI for at least 24 h before testing and the coupons were compacted with DI water for 2 h. Then, the system was drained out, filled with the mixture of PFOA and PFOS at a target dosage of 1 μg/L of each of the compounds. The feed water temperature was maintained at 25 °C using a chiller unit. The permeate and concentrate were recycled back to the feed tank during the experiment. The feed and permeate samples were collected in 250 mL polypropylene bottles after 20 h and placed in a 4 °C refrigerator, or extracted directly. Transmembrane pressures, flux decline, and permeate recoveries, when filtering the three different water matrices over the experimental duration, are shown in Table S1 in the online Supplementary Materials.

Analytical methods

Dissolved organic carbon (DOC) (method detection limit, MDL = 0.25 mg/L) was analyzed using a Fusion Total Carbon Analyzer (Teledyne Tekmar Inc., Mason, OH, USA), following the method as outlined in Standard Method 5310 D (APHA 2014). UVA at 254 nm was measured using a DR5000 spectrophotometer (Hach, Loveland, CO, USA). The cation concentration measurements were carried out using an inductively coupled plasma (ICP) spectrometer (Perkin Elmer Optima, MA) according to standard methods 3120 B. pH, alkalinity, conductivity, turbidity, and total dissolved solids (TDS) of the feedwaters were measured in the University of Central Florida (UCF) drinking water research laboratory based on standard methods (APHA 2014). PFOA and PFOS were analyzed using a solid phase extraction and liquid chromatography–tandem mass spectrometry (LC-MS/MS) method based on the EPA Method 537 Rev. 1.1 (USEPA 2009) using a Thermo Scientific Accela High Speed LC/TSQ Quantum Access MAX mass spectrometer system, equipped with an Accucore C18 LC column (2.1 mm ID × 100 mm, 2.6-μm particle size) preceded by a Hypersil GOLDTM C18 reversed phase analytical column (2.1 mm ID × 50 mm, 3-μm particle size) (Thermo Fisher Scientific, CA, USA). More details on the analytical methods can be found in the online Supplementary Materials.

RESULTS AND DISCUSSION

Water matrix characteristics

The surface and groundwaters selected for this study distinctly varied in matrix composition (Table 2). The Jupiter groundwater contained only approximately 3.8 times DOC when compared to that of the Ocmulgee River water; however, the groundwater exhibited approximately 159 times UVA_{254} and 44 times specific UV absorbance (SUVA_{254}) of the surface matrix.

Table 2 | Water matrix characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Deionized water</th>
<th>Ocmulgee river</th>
<th>Jupiter groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5</td>
<td>7.13</td>
<td>6.96</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>ND</td>
<td>34.5</td>
<td>300</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>3</td>
<td>0.187</td>
<td></td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>126</td>
<td>801</td>
<td></td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>64</td>
<td>555</td>
<td></td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>0.1</td>
<td>8</td>
<td>122</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>0.06</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>&lt;0.250</td>
<td>2.8</td>
<td>10.5</td>
</tr>
<tr>
<td>UVA_{254} (m⁻¹)</td>
<td>0</td>
<td>0.26</td>
<td>41.3</td>
</tr>
<tr>
<td>SUVA_{254} (L/mg-m)</td>
<td>ND</td>
<td>0.09</td>
<td>3.93</td>
</tr>
</tbody>
</table>

ND, not determined or not detected.
water, indicating the dominance of hydrophobic fraction of natural organic matter (such as humic substances) in the groundwater (Leenheer & Croué 2003). While both the waters contained low concentrations of Mg$^{2+}$, the Ca$^{2+}$ concentration (122 mg/L) in the groundwater was about 15 times higher than that in the surface water (8 mg/L). The groundwater had markedly higher alkalinity, TDS, and conductivity than the surface water (Table 2). The background PFOA and PFOS concentrations in the water matrices were found to be below the method detection limits. Previous studies (Sadmani et al. 2014a, 2014b) have demonstrated that the dissolved organic matter (DOM) and cations in natural water matrices may significantly influence the rejection of specific organic micropollutants when using NF. The impacts of DOC and cations (Ca$^{2+}$ and Mg$^{2+}$) will be discussed in the following sections.

**PFOS/A rejections from different water matrices**

The average rejection of compounds varied between 71% and 80% for PFOA and 42% and 80% for PFOS by the NE70 membrane tested (Figure 1). Past studies have reported greater than 90% removal for PFOA and PFOS using NF270 membrane (Hang et al. 2015; Pramanik et al. 2017), which is a tighter membrane (MWCO = 200 Da) compared to NE70 (MWCO = 350 Da). Despite having a higher molecular weight (PFOS molecular weight = 500.1 g/mol) compared to PFOA (414.1 g/mol), PFOS exhibited lower rejection (by up to 28.4%) in the three water matrices. Membrane adsorption may have played a dominant role in the rejection of PFOA, which is more hydrophobic (Log $K_{OW} = 6.4$) than PFOS (Log $K_{OW} = 4.5$). While the rejection of PFOA was approximately 10% higher in natural waters than in the DI water, the rejection did not vary in the natural waters (surface water vs. groundwater), indicating that PFOA’s interactions with water matrix components were not as pronounced as in the case of PFOS. Up to approximately 38% higher rejection of the compounds was observed in the natural water matrices when compared to the laboratory-prepared water (‘control’), implying that water matrix components play an important role in the NF of PFOS and PFOA due to compound interactions with water constituents (e.g. DOM and cations) and the membrane. Both PFOA and PFOS exhibited higher rejection (>80%) in the groundwater than in the surface water (approximately 66% to 79%) and DI water (around 42% to 71% rejection). Hence, higher rejections were observed in the water containing markedly higher cations (122 mg/L Ca$^{2+}$, 5 mg/L Mg$^{2+}$) and organic matter (10 mg/L as DOC) when compared to the surface water (8 mg/L Ca$^{2+}$, 2 mg/L Mg$^{2+}$, 2.8 mg/L as DOC) and DI water (0.1 mg/L Ca$^{2+}$, 0.06 mg/L Mg$^{2+}$, <0.25 mg/L as DOC).

**Effect of cations on PFOA and PFOS rejection**

An increasing trend in PFOS rejection was observed as the Ca$^{2+}$ and Mg$^{2+}$ concentrations increased in the respective water matrices (Figure 2(a) and 2(b)). This trend was, however, less noticeable in the case of PFOA rejection. The increasing trend in PFOS rejection as a function of cation concentration (and valence) was recently reported by Zhao et al. (2016, 2018), who attributed this phenomenon to the bridging between cations and PFOS molecules. They demonstrated that multivalent cations could combine with multiple PFOS ions resulting in larger molecules (Zhao et al. 2016). However, these studies were conducted in PFOS-spiked synthetic waters using a tight NF membrane (MWCO = 200 Da) and hence the impact of natural water matrices on rejection was not investigated. Our study conducted a relative comparison of PFOS and PFOA (not investigated in the above-mentioned studies) and confirmed the effect of cations in real water matrices when using a looser NF membrane (MWCO = 350 Da). The cations present in the river and groundwater may form

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**Figure 1** PFOA and PFOS rejection from DI water, surface water, and groundwater matrices by the NF membrane.
macromolecular complexes with the PFOS ions by attaching to the polar, hydrophilic sulfonate (–SO3) ‘head’, leading to enhanced size exclusion by the NF membrane. As indicated by the pKa values (Table 1), PFOS is more negatively charged (pK_a = 3.3) compared to PFOA (pK_a = 0.5), which contains a carboxylic acid functional group (–COOH). Hence, the cations probably exhibited less interactions with PFOA (vs. PFOS), which explains why PFOA rejection did not vary in the natural waters. It is interesting to note that the impact of interactions with Mg^{2+} on PFOS rejection was more pronounced when compared to that with Ca^{2+}. Our future study will investigate the potential mechanisms of preferential interactions with specific ions present in various water matrices. The specific and synergistic impacts of other water constituents will be investigated in the future study as well.

**Effect of DOM and fouling on rejection**

The higher rejection of PFOA and PFOS in the natural water matrices, when compared to the DI water, can be associated with the higher concentration of DOC in the surface and groundwater (2.8 mg/L and 10.5 mg/L, respectively) (Figure 2(c)), in addition to the cation content of the waters as discussed in the previous section. This can be attributed to the synergistic effect of PFOS/A-cation complexation and the DOM fouling of the membrane. Among the three water matrices, the highest rejection (>80%) was observed in the groundwater, which contained the highest concentrations of both DOC and cations (Table 2). The presence of cations caused more compact layer(s) of foulant that resulted from membrane and DOM charge screening and ‘coiled’ conformation of DOM due to its reduced intramolecular electrostatic repulsion (Zhao et al. 2016). A less compact foulant layer was formed on the NF membrane when filtering the lower cation-containing river water, leading to less compound rejection when compared to the groundwater.

One reason of the flux decline (28% and 56% for the river and groundwater, respectively, compared to 12% for the control) that was observed during NF of the natural waters might be the deposition of calcium ions, leading to membrane pore blockage and subsequent increase in compound rejection (Wang et al. 2015). While flux decline may result from foulant enhanced concentration polarization (Steinle-Darling & Reinhard 2008), consequently decreasing

![Figure 2](http://iwa.silverchair.com/ws/article-pdf/19/8/2199/661831/ws019082199.pdf)
PFOS rejection, the opposite trend was observed in the present study. As shown in Figure 2(d), PFOA and PFOS rejection increased with declining fluxes, with the highest rejection of approximately 80% observed at the maximum flux decline (~56%). While investigating PFOS rejection by NF in DI water spiked with 10 mg/L of humic acid (HA), Zhao et al. (2016) reported a 50% decline in permeate flux that further declined to 70% when the feed solution was spiked with both HA and Mg²⁺. The current study demonstrated that DOM and cations indigenous to natural water matrices can play a vital role in facilitating rejection of PFOA and PFOS due to the compounds’ association with cations and increased resistance due to membrane fouling.

CONCLUSIONS

NF rejection of PFOA and PFOS was higher (by up to approximately 58%) in the natural water matrices when compared to the laboratory-prepared water. Both PFOA and PFOS exhibited higher rejections (>80%) in the groundwater that contained higher cations and organic matter than in the surface water and DI water. While the rejection of PFOA did not vary in the natural waters, an increasing trend in PFOS rejection was observed as the cation concentrations increased in the respective water matrices. This was likely due to the synergistic effect of enhanced size exclusion of PFOS/A-cation complexes and cation-induced compact membrane fouling upon filtration over a longer duration (20 h) when compared to the past studies. The preferential interaction of PFOS (vs. PFOA) with cations may be because of the polar, hydrophilic sulfonate (-SO₃⁻) ‘head’ of the PFOS ions at the experimental pH. PFOA and PFOS rejection increased with declining fluxes that were consistent with the DOC content of the respective water matrices, with the highest rejection (approximately 80%) observed at the maximum flux decline (~56%) when filtering groundwater (DOC = 10.5 mg/L). This study confirmed that DOM and cations indigenous to natural water matrices can lead to improved rejection of PFOA and PFOS when using NF. Hence, the NF membrane as well as the pre-treatment method, when targeting PFOA and PFOS, should be selected and optimized based on the composition of the source water to be treated.

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SUPPLEMENTARY DATA

The Supplementary Data for this paper are available online at http://dx.doi.org/10.2166/ws.2019.099.

REFERENCES

APHA 2017 Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, WEF, Washington, DC.


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