



Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids

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HIGHLIGHTS

- Removal of perfluoroalkyl acids by GAC and NF was evaluated.
- Virgin and fouled NF270 membranes were tested using artificial groundwater.
- Multiple carbons tested using rapid small scale column tests with and without DOM.
- NF270 had >93% removal of all PFAAs during all experiments.
- Carbon performance varied based on type, water chemistry, and sorbate.

ARTICLE INFO

Article history:

Received 28 February 2013

Received in revised form 27 May 2013

Accepted 15 June 2013

Available online 21 June 2013

Keywords:

Perfluoroalkyl acids

Nanofiltration

Granular activated carbon adsorption

ABSTRACT

Perfluoroalkyl acids (PFAAs) are of concern because of their persistence in the environment and the potential toxicological effects on humans exposed to PFAAs through a variety of possible exposure routes, including contaminated drinking water. This study evaluated the efficacy of nanofiltration (NF) and granular activated carbon (GAC) adsorption in removing a suite of PFAAs from water. Virgin flat-sheet NF membranes (NF270, Dow/Filmtec) were tested at permeate fluxes of 17–75 L m⁻² h⁻¹ using deionized (DI) water and artificial groundwater. The effects of membrane fouling by humic acid on PFAA rejection were also tested under constant permeate flux conditions. Both virgin and fouled NF270 membranes demonstrated >93% removal for all PFAAs under all conditions tested. GAC efficacy was tested using rapid small-scale columns packed with Calgon Filtrasorb® 300 (F300) carbon and DI water with and without dissolved organic matter (DOM). DOM effects were also evaluated with F600 and Siemens AquaCarb® 1240C. The F300 GAC had <20% breakthrough of all PFAAs in DI water for up to 125,000 bed volumes (BVs). When DOM was present, >20% breakthrough of all PFAAs by 10,000 BVs was observed for all carbons.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are a growing concern because of their persistence in the natural environment, and tendency to accumulate in water resources. PFASs are frequently added to a variety of industrial and consumer products for their water and oil-repelling abilities [1], used in or during the

manufacturing of a variety of products, including ScotchGard™ and Teflon™, and are also used in food packaging products [2]. The chemicals are also found as an ingredient in aqueous firefighting foams (AFFF), and utilized in specialized industries including semiconductor and metal plating [3]. According to Prevedouros et al. [4], chemical releases (both in air and industrial waste) from fluoropolymer manufacturing are responsible for more than 60% of the total emissions of perfluorocarboxylates. Other sources include landfill leachate from discarded products and packaging, wear from the textile and carpet industry, use and disposal of AFFFs, and emissions from reapplication to carpets or textiles [5]. These sources can emit PFASs into the air, water, and soil. The chemicals, especially the end product PFASs, do not generally remain in the gaseous state [6], and adsorption to soil, sediments and sludge is expected to be

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limited based on their physicochemical properties, so they are most likely going to accumulate and travel in water resources [1,4,7].

A subset of PFASs is the perfluoroalkyl acids (PFAAs) family. The basic structure of a PFAA is a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain. The two most commonly studied PFAAs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). These two chemicals have proven to be recalcitrant both in the environment and in conventional water and wastewater treatment utilities [8,9]. Conventional treatment processes, including coagulation followed by sedimentation and/or filtration and oxidation/disinfection, were found to be mostly ineffective for PFOS and PFOA removal [8,10]. Therefore, there is a need to examine the efficiency of advanced physical separation processes, such as high pressure membranes and adsorption processes. Bench-scale work examining the removal of PFASs using high pressure membranes and adsorption is limited. One study evaluating nanofiltration (NF) [11] measured the rejection of a suite of 15 PFASs by four NF membranes (NF270, NF200, DK, and DL). The flat sheet membranes were tested originally as virgin membranes, and then fouled with an alginate solution to evaluate the impact of the fouling layer on PFAS rejection. For the PFASs, average rejections were 99.3% for the virgin membranes, and 95.3% for the fouled membranes. For perfluorooctane sulfonamide (FOSA), rejection decreased from about 93% to 43% as a result of fouling. Unfortunately, this study only examined the effect of fouling on the perfluoroalkyl sulfonic acids (PFSAs) and FOSA, but not the perfluoroalkyl carboxylic acids (PFCAs). While removal was generally good (93% or greater), the trans-membrane pressure was not increased to maintain an identical permeate flux during the fouled and virgin membrane experiments. Maintaining constant operational conditions (e.g., flux, cross-flow velocity, and recovery) is important for comparing contaminant rejection by fouled and unfouled membrane specimens due to their impact on the observed rejection values. While it has been shown [12] that fouling, specifically cake enhanced concentration polarization, can cause an increase in solute transport across the membrane surface, findings from the previous study may be explained by the fouled membranes being operated at a significantly lower flux than the virgin membranes.

To date, multiple batch test studies on PFAA removal have been performed with GAC, although they have been limited to mostly PFOS and PFOA [3,13–15], with the exception of one study that also examined perfluorobutane sulfonic acid (PFBS) [16]. These studies revealed that GAC can be effective at removing PFAAs under certain conditions. Studies on the effects of potentially limiting factors for GAC performance with these chemicals, such as the presence of dissolved organic matter (DOM), have not yet been explored. Rapid small-scale column tests (RSSCTs) are the most commonly used tool for GAC evaluation (i.e., carbon types), though issues arise when attempting to scale treatment performance for trace organic compounds, since RSSCTs are not representative of full scale systems with trace organic compounds in the presence of DOM [17].

The objective of this study was to evaluate two advanced treatment technologies, GAC and NF, for the removal of a suite of PFAAs of varying sizes, including both PFCAs and PFSAs, from water. NF

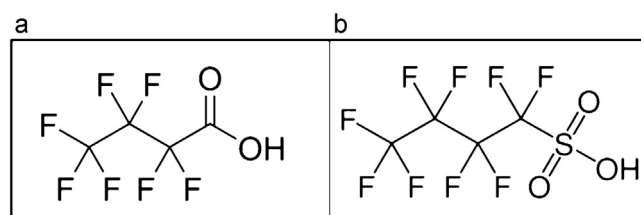


Fig. 1. (a) Left and (b) right: chemical structures of PFBA and PFBS.

experiments were conducted to evaluate the rejection behavior of unfouled and fouled NF270 membrane specimens at constant permeate flux. For GAC, RSSCTs were performed to: (1) compare three carbons of varying composition, two bituminous coal and one coconut shell carbon, in their removal efficacy; and (2) assess the effect of DOM on GAC removal efficiency using a natural water source spiked with PFAAs.

2. Materials and methods

2.1. Materials

The NF270 (Dow/FilmTec, Minneapolis, MN), a polyamide thin-film composite flat-sheet membrane, was used for all NF experiments. Three different types of GAC, whose properties are listed in Table 1, were evaluated for the RSSCT experiments, including Filtrasorb®300 (F300) and F600 (Calgon Carbon Corporation, Pittsburg, PA) and AquaCarb® 1240C (Siemens Water Technologies, Munich, Germany). Raw PFAA materials for the spiking solution were obtained from Sigma–Aldrich, and included perfluorobutyric acid (PFBA) (214 g/mol), perfluoropentanoic acid (PFPeA) (264 g/mol), perfluorohexanoic acid (PFHxA) (314 g/mol), PFOA (414 g/mol), perfluorononanoic acid (PFNA) (464 g/mol), perfluorodecanoic acid (PFDA) (514 g/mol) PFBS (300 g/mol), perfluorohexane sulfonic acid (PFHxS) (400 g/mol), and PFOS (500 g/mol). Fig. 1a and b displays the chemical structures of two representative PFAAs, PFBA and PFBS.

2.2. Membrane experiments

The set-up for the membrane experiments was the same as previously described [12], with a few modifications. The modifications included a larger feed volume (200 L barrel) which enabled the system to be operated in flow through mode as opposed to recycling the permeate and concentrate back into the feed tank (as had been done in previous studies [11]), and the operation of two SEPA cells (Osmonics) in series with the concentrate from the first as the feed to the second to provide results from two representative flat-sheet membranes. Three filtration experiments were performed. The first was performed with spiked DI water and virgin membrane specimens. This was followed by an experiment with new membrane specimens and spiked artificial ground water (AGW), whose recipe is described elsewhere [18] and summarized in Table S5 in the Appendix A. These membrane specimens were then fouled with a solution containing Aldrich Humic Acid (AHA) with DOM levels at 2.5 mg/L (method described below), and the third experiment with the spiked AGW matrix was performed again with a fouled layer present.

For all three experiments, feed solutions were spiked with approximately 1 µg/L of each PFAA and feed flow was kept constant at 1 L/min with a temperature of approximately 18 °C, and a pH of 6.7. For the two virgin membrane experiments, the apparatus was operated for 2.5 h starting at 25 psi, and the pressure was increased in increments of 25 psi every 30 min with samples of feed, concentrate, and permeates for PFAAs taken at 15 and 30 min. A prior

Table 1
Properties of the three activated carbons evaluated.

Name	F300	F600	1240C
Manufacturer	Calgon	Calgon	Siemens
Carbon type	Bituminous coal	Bituminous coal	Coconut shell
Mesh size, U.S. Sieve	12 × 40	12 × 40	12 × 40
Iodine no., mg I ₂ /g	900	850	1100
Abrasion no., wt. %	78	80	85
Apparent density, g/cc	0.48	0.62–0.65	0.46–0.52

study [11] looked at steady state rejections (defined as the drop in rejection over a 24 h period being less than 1%) of PFAAs and observed that they reach steady-state rejection with the NF270 after a few minutes, therefore a 30 min experimental duration for each pressure was deemed sufficient. Samples of the feed, concentrate, and permeate were also taken every 30 min for inorganic anions, metals, and TOC analysis. Permeate flow was measured using a differential flowmeter (Cole Parmer, Model #32908-43), and verified with a graduated cylinder and stopwatch. For the second AGW experiment with the fouled membrane, 30 min intervals were used again, but pressures were increased to match permeate flux conditions in the first AGW experiment.

The same membrane specimens were used for both AGW experiments. To sufficiently foul the membrane specimens, a 200 L solution was created based on previous research [19] with 1 mmol Ca^{2+} , 10 mmol total ionic strength, and AHA added to raise the TOC level to approximately 2.5 mg/L. During the fouling process, the system was operated with the permeate and concentrate being recycled back into the feed tank. Prior to the addition of AHA, the system was operated for 24 h to equilibrate the membranes with the background electrolytes with the pressure held constant at 125 psi and permeate flow monitored for stabilization. Once permeate flow stabilized, AHA was added to the feed, and a constant permeate flow of 20 mL/min was maintained by increasing pressure until the flux declined by 35%, which occurred after 200 min of operation. A visible fouling layer was present upon inspection of the membranes after the experiments. Figure S1, in the Appendix A, displays the normalized specific permeate flux decline during the fouling stage. Samples were taken for inorganic anions, metals and TOC analysis before and after the addition of AHA, as well as in the final minutes. For the fouling solution, pH was approximately 6.5 and temperature was 18 °C.

2.3. GAC experiments

Two sets of RSSCT experiments were performed during this study. The first set employed triplicate columns loaded with F300 carbon, and the second employed duplicate columns of the F300, F600, and 1240C carbons (six columns in total). All columns were made of glass and prepared the same way: the carbon was ground up until the diameter was approximately 0.21 mm (60 × 80 mesh size, US sieves), and then decanted with DI to remove fines. The diameter of the column was 0.7 cm, over 33 times the diameter of the particles to minimize column channeling effects. Once the carbon was wet, it remained as a slurry solution for the remainder of the experiments. To degas the carbon, the carbon slurry was boiled for 5 min in DI water, then poured into a 50 mL falcon tube and placed on a shaker table for 24 h. Next, a dropper was used to transfer carbon to a depth of 1 cm in the column, which already contained a layer of glass beads and glass wool. Additional glass wool was then inserted on top to hold the carbon in place. A three-way stopcock was placed on both sides of the column with a sample line running from it on both the influent and effluent lines. All columns were run in up-flow mode at a rate of 1.0 mL/min using a low speed Ismatec® HPLC pump yielding an empty bed contact time (EBCT) of 0.38 min.

For the triplicate F300 columns, the feed solution was DI water nominally spiked with 1 µg/L of each PFAA. The feed for the second experiment was surface water collected from Clear Creek (Golden, CO) that was filtered through a 1 micron filter, and then nominally spiked with 1 µg/L of each PFAA. Column effluent samples were collected every 3–4 days, and influent samples were taken once per week. A summary of parameters can be found in Table S2 in the Appendix A.

Table 2
NF270 PFAA rejection results. Rejection measurements arising from permeate samples with PFAAs measured above the LOQ are in bold and italicized. Molecular weights (g/mol) are listed next to chemical names.

Membrane/water	Pressure (psi)	Permeate flow (mL/min)	Permeate flux (LMH)	J/J_0^a	PFBA (214)	PFPeA (264)	PfHxA (314)	PFOA (414)	PFNA (464)	PFDA (514)	PFBS (300)	PFHxS (400)	PFOS (500)
LOQ (ng/L)					20	20	20	20	20	20	10	10	10
Avg. Influent Conc. (ng/L)					330	679	414	664	817	721	937	973	866
Influent st. dev.					26	40	17	34	39	75	74	52	75
AGW-virgin	25	4.5	17	1	>94%	>97%	>95%	>97%	>98%	>97%	>99%	>99%	>99%
	50	9	33	1	>94%	>97%	>95%	>97%	>97%	>97%	>99%	>99%	>99%
	75	13.5	50	1	>94%	>97%	>95%	>97%	>98%	>97%	>99%	>99%	>99%
	100	16	59	1	>95%	>97%	>95%	>97%	>98%	>97%	99%	>99%	>99%
	125	20.5	75	1	>94%	>97%	>95%	>97%	>98%	>97%	98%	>99%	>99%
AGW-fouled	40	4.5	17	0.63	>95%	>97%	>95%	>97%	>98%	>97%	>99%	>99%	>99%
	70	9	33	0.71	>94%	>97%	>95%	>97%	>97%	>97%	>99%	>99%	>99%
	96	13.5	50	0.78	>94%	>97%	>95%	>97%	>97%	>96%	>99%	>99%	>99%
	110	16	59	0.91	>94%	>97%	>95%	>97%	>98%	>97%	>99%	>99%	>99%
	140	20.5	75	0.89	>94%	>97%	>95%	>97%	>98%	>97%	>99%	>99%	>99%
DI-virgin	25	5.5	20	1	>93%	>97%	>95%	>97%	>98%	>97%	>97%	>97%	>97%
	50	7.5	28	1	>93%	>97%	>95%	>97%	>98%	>98%	98%	98%	>99%
	75	12	44	1	>93%	>97%	>95%	>97%	>98%	>98%	96%	97%	>99%
	100	16	59	1	>94%	>97%	>95%	>97%	>98%	>98%	96%	96%	>99%
	125	19	70	1	>93%	>97%	>95%	>97%	>97%	>98%	95%	96%	>99%

^a Normalized specific flux change where J_0 is the specific permeate flux at time 0 (i.e., constant flux normalized to net driving pressure, J/J_0).

2.4. Sample preparation and analysis

All samples were collected in 20 mL plastic scintillation vials. Aqueous samples were prepared and analyzed by isotope dilution using direct injection with liquid chromatography (LC)/tandem mass spectrometry (MS/MS) on an ABSciex 3200, a method detailed in a previous study [18]. Table S6 in the Appendix A displays the analytes and stable isotopes used in this study. Limits of quantification (LOQs) were 20 ng/L for all of the PFCA, and 10 ng/L for all of the PFSA.

TOC samples were analyzed using a Sievers 900 total organic carbon analyzer. The method used was Method 5310C (persulfate oxidation/UV irradiation) from “Standard Methods for the Examination of Water and Wastewater” [20]. Inorganic anions, specifically sulfate and chloride, were measured using a Dionex ICS-90 ion chromatography system using EPA method 300.1 [21]. Metals, specifically calcium, magnesium, and sodium, were analyzed using a Perkin-Elmer Optima 3000 with EPA method 200.7.

2.5. Quality assurance and quality control

For the LC/MS/MS runs, a double blank was placed in between sets of six samples. For all batches analyzed in this study, at least three blanks containing only the stable isotope surrogate standards were analyzed throughout the batch to enable evaluation of possible sample carryover. For the GAC column experiments, triplicates were run for the initial experiment, followed by duplicates for each carbon type for the latter experiments. During the NF experiment, the system was operated in flow-through mode and the feed solution was well mixed, so all influent samples were considered replicates. The analytical variation for these replicates is displayed in Table S1 in the Appendix A. Samples of the permeates and influent were analyzed for inorganic anions, metals, and TOC to ensure that the integrity of the membranes was maintained throughout the experiment, and the results can be found in Tables S3 in the Appendix A.

Prior to the GAC experiments, the systems were operated with no media present to test for PFAA leaching by running DI water through the system and sampling all ports. A similar process was performed for the membrane system. All samples analyzed had concentrations below the LOQs for all PFAAs. Sorption tests were also performed on the GAC and membrane systems using DI water spiked with PFAAs with no GAC present and membrane present in the experimental setups. The materials used in the experiments were selected in order to reduce PFAA sorption. Concentrations in the influent and effluent were within analytical variability; therefore any sorption that may have been occurring was minimal.

3. Results and discussion

3.1. Membrane experiments

Samples for the analysis of salts, metals, and TOC were taken to evaluate the integrity of the membrane throughout the experiments. TOC data were limited to the samples of the fouling solution with AHA in it because levels of TOC in the AGW feeds were measured to be about 0.5 mg/L, which is also the analytical variability (± 0.5 mg/L) of the method used. Approximately 82% TOC rejection was observed by the two membranes during the fouling process. According to the manufacturer's website, the NF270 is expected to have rejection rates for sodium chloride and magnesium sulfate of 50% and >98%, respectively. As can be seen in Table S3 in the Appendix A, the rejection for sulfate surpassed the manufacturer's specifications for all samples at >99%. Magnesium rejection was >97% for nearly all samples with the exception of two which were

81% and 93%. Chloride and sodium were rejected >50% throughout the duration of the experiment, and calcium rejection was >80% in all but the two lowest permeate flux samples for the fouled membranes (further details can be found in the Appendix A). Based on these data, the integrity of the membranes was maintained throughout the duration of the experiments.

Table 2 shows the average percent rejection ($n=4$) of the two membranes for each PFAA in the three experiments at different flux conditions. Permeate concentrations for PFOS and all of the PFCA were below their LOQs. PFBS and PFHxS, however, were detected in the permeate above their LOQs (10 ng/L and 20 ng/L, respectively), in the virgin membrane experiments. In fact, for the spiked DI water, PFBS and PFHxS were detected at all permeate fluxes with the exception at 17 LMH for PFHxS, and with concentration ranges of 12–41 ng/L and 30–40 ng/L, respectively. While past research has demonstrated that NF membranes achieve high rejection of negatively charged organic compounds through electrostatic exclusion [22,23], the detection of the two smaller molecular weight PFSA, but not PFOS, suggests that size exclusion is also an important mechanism for PFAA rejection. For the AGW virgin-membrane experiment, PFBS was detected at the higher permeate fluxes (50, 59, and 75 LMH) at concentrations of 13–20 ng/L. Although these two chemicals were detected in the permeate, rejection for all PFAAs was >93%. Excluding PFBA, the shortest chain PFCA which had a lower feed concentration (350 ng/L) than the other chemicals, rejections were all >95%. Interestingly, the shortest chain PFCA in the Steinle-Darling and Reinhard [11] study was PFPeA, and it only had a rejection of 72% by the virgin membrane using spiked DI water. The study herein examined a shorter chain PFCA (i.e., PFBA) and, both PFBA and PFPeA exhibited rejection at >93% and >97% rejection, respectively.

The permeate samples from the AGW experiment with the fouled membrane did not have any PFAA concentrations above respective LOQs. Therefore it was observed that the fouling layer on the NF270 did not have a negative effect on PFAA rejection. In fact, the two chemicals that were detected in the permeate of the virgin membranes, PFBS and PFHxS, were not detected in the permeates of the fouled membranes, suggesting that the fouling layer increased rejection. An increase in rejection has been shown for some organic chemicals resulting from changes in the membrane surface characteristics due to organic matter fouling such as contact angle (an index of hydrophobicity), zeta-potential, functionality, and surface morphology [24].

Enhanced rejection due to membrane fouling has been observed in past studies, particularly for organic compounds with molecular weights greater than the molecular weight cut-off of the membrane [25,26]. Such an effect has been attributed to increased steric hindrance caused by foulants on or within the membrane structure, but could also be due to enhanced electrostatic exclusion and solute–foulant interactions [27]. Better performance from the fouled membrane contradicts findings presented by Steinle-Darling and Reinhard [11] in which the authors observed that organic matter fouling decreased rejection of several PFAAs. The authors explained this decrease as the result of cake enhanced concentration polarization in which solutes accumulate within the fouling layer due to hindered back-diffusion. This effect has been shown in other past studies [12] to increase the mass transport of certain trace organic compounds. However, it appears that rejection experiments with the virgin and fouled membrane specimens were not operated at the same flux during the Steinle-Darling and Reinhard [11] study. Operating the virgin and fouled membrane at the same pressure would have resulted in a significantly lower flux for the fouled membrane specimen and consequently, lower rejection. Regardless of the reason, membrane fouling did not appear to impact the rejection of PFAAs during this study. It is worth noting that during experiments evaluating rejection with the fouled

membrane, the fouling layer, which originally resulted in a flux decline of 35%, was apparently partially removed, and at the final two fluxes the membrane was functioning at a normalized flux of approximately 90% (Table 2). Rejection was not compromised while the fouling layer was being reduced.

The NF270 membrane exhibited high rejection for all PFAAs examined during this study, including the shorter chain PFCAs. These bench scale results are promising as NF is a less energy intensive process compared to reverse osmosis. Further experiments are warranted using either the NF270 or even a looser NF membrane at the pilot- and/or full-scale operated for a continuous and longer period (i.e., months).

3.2. GAC experiments

Breakthrough curves for the average triplicate F300 columns from the RSSCT experiment with spiked DI water are displayed in Fig. 2. Initial breakthrough occurred at approximately 30,000 bed volumes (BVs), or 8 days of operation, for all of the chemicals except for PFNA, PFDA, and PFHxS in which breakthrough started at 45,000 BVs, and PFOS whose effluent values never measured more than 2% (at 98,000 BVs) of influent concentration. For the 125,000 BVs (~33 days) for which this experiment was conducted, only the two smallest PFAAs, PFBA and PFPeA, had >10% breakthrough (at approximately 72,000 and 83,000 BVs, respectively). Other PFAAs that reached >5% breakthrough, in order of breakthrough, included PFOA (~56,000 BVs), PFHxA (~72,000 BVs), PFBS (~83,000 BVs), and PFHxS (~83,000 BVs). PFOA and PFHxA did not exhibit a chain length dependent breakthrough. The overlapping error bars of these two chemicals in Fig. 2 indicate that this may have been due to experimental variability. The two largest chain PFCAs, PFNA and PFDA, as well as the largest chain PFSA,

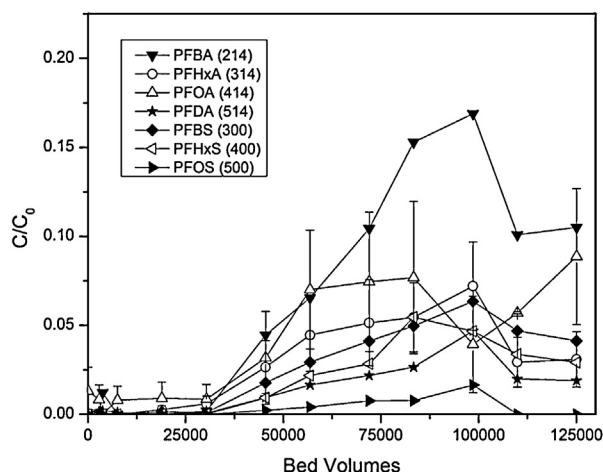


Fig. 2. Average PFAA breakthrough for three F300 columns with spiked DI water. For clarity, PFPeA and PFNA were omitted, and only the standard error was included for PFOA and PFHxA. The number in parenthesis next to each chemical is the molecular weight (g/mol) of the protonated form.

PFOS, never reached >5% breakthrough. The two smallest chain PFCAs had the fastest breakthrough, and the two largest PFCAs had the slowest breakthrough, so in general, a chain length dependent pattern was observed, but not for all of the PFCAs. The sorption of PFAAs is likely due to both specific and nonspecific interactions between the sorbate and sorbent. Previous work deduced that PFOS sorption to a coal-based activated carbon involved electrostatic and hydrophobic interactions [12].

Breakthrough results of all PFAAs from the next set of columns, using filtered Clear Creek water with a DOC of 1.7 mg/L, can be

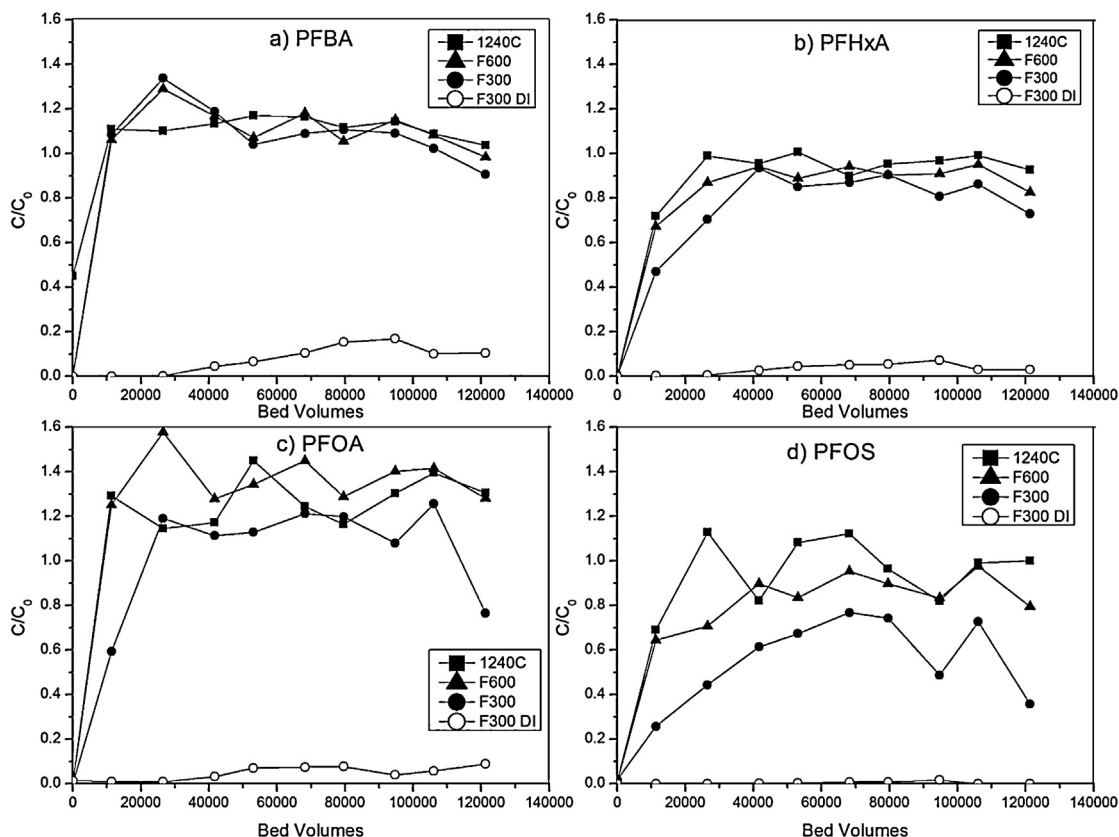


Fig. 3. (a)–(d) Comparison of breakthrough times for PFBA, PFHxA, PFOA and PFOS with three different carbons (1240C, F300, and F600) and two different water matrices (spiked Clear Creek and spiked DI water).

found in Figures S2–S4 in the Appendix A. All PFAAs had a breakthrough of >20% within the first 3 days (~11,000 BVs) of operation for all three carbons—levels that had not been reached for any chemicals within the 125,000 BVs of the DOM-free experiments. PFBA and PFPeA, the two shortest chain PFCAs, were the fastest to breakthrough for all three carbons, exceeding full (100%) breakthrough by 11,000 BVs. When the effluent concentration exceeds the influent, this is believed to be due to competitive effects with other sorbing species (perhaps longer chain PFAAs and/or organic matter) leading to desorption and release of sorbed PFBA and PFPeA over time. For the F600 and 1240C carbons, PFOA also achieved full breakthrough within 11,000 BVs, and for the F300 carbon it took approximately 26,000 BVs. The rapid breakthrough makes it clear that the presence of DOM has a large effect on carbon performance in the removal of PFAAs. This effect is likely attributed to the organic matter occupying pore space or sorption sites in the GAC rendering it unable to sorb other compounds. Although other studies have not been performed on the competitive effects of DOM with PFAAs, similar results have been seen in batch and pilot column studies with other organic compounds, i.e., pesticides and pharmaceuticals, where both powdered activated carbon (PAC) [28,29] and GAC [30] removal efficacy was significantly reduced as a result of competition for adsorption sites with DOM.

Fig. 3a–d compares the performance of the three types of carbon by examining the breakthrough of PFBA, PFHxA, PFOA, and PFOS. Figures S5–S10 in the Appendix A display comparisons of the other PFAAs. As a result of the initial breakthrough of all PFAAs for the three carbons occurring by the second sampling (~11,000 BVs), the extent of breakthrough here is addressed to compare carbon performance. PFBA and PFPeA reached full breakthrough by 11,000 BVs for all three carbons. By this time, PFOA had also achieved full breakthrough for the 1240C and the F600, but only reached 59% breakthrough for the F300. The most notable differences in performance between the three carbons were observed for the larger chemicals PFNA, PFDA, and PFOS. These three chemicals had breakthroughs of 75%, 78%, and 69%, respectively, with the 1240C and had similar breakthroughs of 63%, 83%, and 64% with the F600. The F300 carbon clearly outperformed these carbons with breakthroughs of 32%, 31%, and 26% for PFNA, PFDA, and PFOS, respectively. The difference between the F600 and the 1240C is more apparent when looking at breakthrough over the entire duration of the experiment where all PFAAs reached full breakthrough for the 1240C, but PFHxA, PFNA, PFDA, and PFOS never achieved full breakthrough for the F600. For carbon comparison, these results make it apparent with DOM present, the F300 was the most effective of the three, followed by the F600, then the 1240C. One possible explanation is that the coconut-based carbons, like 1240C, have a more microporous structure, than the coal-based carbons, like F300 and F600 [31]. It is possible that the tighter structure of 1240C resulted in a kinetic limitation, causing this carbon to be less effective than the other two. The slightly better performance in the F300 versus the F600 could be due to its physical structure. The F300 has a higher iodine no. of 900 mg I₂/g than F600 (850 mg I₂/g), which indicates F300 has a higher microporosity and Brunauer–Emmett–Teller (BET) surface area [32] and possibly makes it more favorable for the sorption of the PFAAs.

4. Conclusions

This study looked at the efficacy of NF and GAC for the removal of PFAAs using bench-scale experiments. The NF270 membrane was observed to reject almost all of these chemicals to below LOQs at various permeate fluxes and with two different water matrices. When a fouling layer was present on the membrane, rejection was maintained and, for certain PFAAs, greater with the fouled

membrane specimen compared to the virgin membrane specimens. These findings are promising in that NF treatment could be an effective barrier for PFAAs with a range of molecular weights, but this needs to be validated at the pilot- or full-scale. An appropriate disposal or treatment of the membrane concentrate stream needs to be considered, especially the application of high-pressure membranes for inland communities.

GAC was assessed using RSSCTs in an attempt to observe the kinetic effects of a flow through system and compare different types of carbon. The effect of the presence of DOM was also evaluated, where results indicate that GAC is more effective at removing PFAAs in low DOC water than when DOC is present, which stresses the importance of understanding the type and quantity of DOM that could have impact on the degree of PFAA removal. Of the three carbons, the F300 performed the best, but it was less effective with the shorter chain PFCAs, PFBA and PFPeA, which were well removed by NF. Industry is currently moving toward the use of shorter chain PFAAs, therefore future studies should be performed looking at adsorbents capable of targeting these smaller PFCAs.

Acknowledgements

The authors thank the Water Research Foundation (Alice Fulmer and project advisory committee) for financial support for this project (WaterRF 4322). In addition, the authors thank Dr. Jörg Drewes at the Colorado School of Mines for his advisement and guidance of the project, and Dr. Dean Heil and Jennifer Sepulvado for their help with sample analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.06.033>.

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