Ion Exchange Treatment of Perfluorinated Carboxylic Acids in Water: Comparison of Polystyrenic and Polyacrylic Resin Structure and Impact of Sulfate on their Performance

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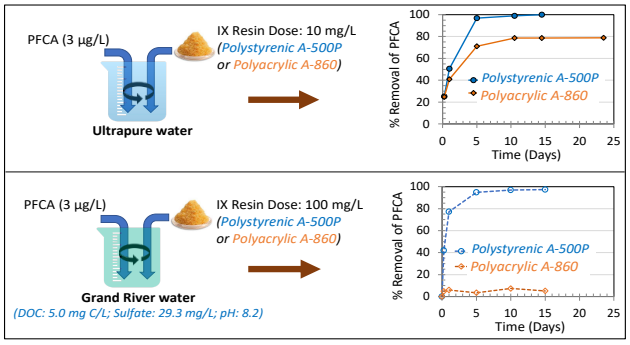
ABSTRACT: The removal of three perfluorinated carboxylic acids (PFCA) - PFHpA, PFOA, and PFNA in ultrapure and river water was evaluated using two anion exchange resins- previously unreported macroporous polystyrenic A-500P and a more widely studied macroporous polyacrylic A-860. Both resins had similar properties, allowing direct comparison of PFCA removal performance between the two resin structures/matrices. This study also presents a new gas chromatography-mass spectrometry (GC/MS) method developed for PFCA analysis in water. In ultrapure water, A-500P exhibited higher removal capacity and faster removals compared to A-860, suggesting greater effectiveness of the polystyrenic structure compared to the polyacrylic structure. In Grand River water, the target PFCA were well removed by A-500P but not A-860. However, both resins achieved similar high overall reductions of dissolved organic carbon (~75%) suggesting, later confirmed in ultrapure water experiments, that inorganic anions (sulfate particularly) were the dominant competitors for the A-860 resin. The uncharged styrenic and acrylic beads (base materials) of the two tested resins were unable to remove PFOA, implying that the dominant removal mechanism involves charge interactions between the negatively charged PFCA and the positively charged anion exchange functional groups.

KEYWORDS: *Drinking water, Ion exchange, Natural organic matter, Perfluorinated Carboxylic Acids (PFCA) removal, Per- and polyfluoroalkyl substances (PFAS) removal, sulfate.*

SYNOPSIS: PFCA removal in ultrapure- and river water using IX resins demonstrated superior performance of the tested polystyrenic resin than the polyacrylic resin, and presence of sulfate more severely affected performance of the latter.

TOC graphic



1.0 INTRODUCTION

Per- and Polyfluoroalkyl substances (PFAS) are an emerging class of drinking water contaminants that have been detected globally at trace concentrations in drinking water.[1-4] Due to their widespread occurrence, long half-life in human tissue, and potential human health impacts,[5-7] several PFAS-related regulations or guidelines for drinking water are currently in force or are being considered in various jurisdictions.[5] For example, Heath Canada guidelines for maximum acceptable concentrations (MACs) for perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) in drinking water are 0.2 µg/L and 0.6 µg/L, based on exposure solely to PFOA and PFOS, respectively.[8,9] On the other hand, the USEPA made final determinations to regulate PFOA and PFOS, confirming that it will move forward with the process to propose and promulgate a national primary drinking water regulation for the two contaminants under the Safe Drinking Water Act of 1996.[10]

PFAS have been reported to be not amenable to a variety of drinking water treatment processes including conventional coagulation-flocculation, biofiltration, ozonation, and even advanced oxidation processes.[2,3,11,12] On the other hand, advanced treatment processes such as tight membrane filtration and activated carbon adsorption have been reported to be effective in removing PFAS from drinking water.[3,13,14] In addition to these processes, ion exchange (IX) resin treatment is being considered as a potential alternative for the removal of PFAS. Available bench-scale studies corroborate the promise of anion exchange resins for the removal of PFAS from drinking water.[15-23]

Recent studies also reported simultaneous removal of PFAS, natural organic matter (NOM) and inorganic anions from natural water using anion IX resins. However, both NOM and inorganic anions, especially owing to their higher concentration in water (~mg/L) as opposed to PFAS (ng/L to µg/L) would exert competition for removal sites.[19,20] A recent review paper[24] on PFAS removal by IX treatment concluded that "any demonstration of IX treatment efficacy for PFAS must examine the role of NOM and inorganic ions on the efficacy of PFAS uptake in natural waters. With the exception of few studies, most of the available data focuses on the PFAS removal in deionized waters or synthetic waters with standard isolated NOM fractions." In addition, investigation is also needed to understand the effect of the resin matrix on PFAS removal and elucidate the effect of electrostatic interaction as opposed to hydrophobic interaction during PFAS removal using ion exchange resins.

This study was undertaken to provide new insights on the use of IX resins for removal of the target PFCAs while experiencing competition from NOM. In doing so, the primary objective of the study was to elucidate the effectiveness of two ion exchange resins for the removal of three PFAS – perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) - from ultrapure and natural water at environmentally relevant concentrations. All three target compounds are perfluorinated carboxylic acids (PFCA), a sub-group of PFAS and have been reported widely in natural water and finished drinking water.[3]

The study was designed to use two IX resins which have similar properties (Table 1) but differ in the resin backbone/matrix, thereby enabling a direct comparison of the impact of the IX resin structure (polyacrylic vs polystyrenic) on PFCA removal. Moreover, the study investigated the currently underreported direct competitive effect from background water quality parameters (namely NOM and inorganic anions) on PFCA removal using IX treatment. The dominant removal mechanisms for the selected PFCAs by

IX resins were also studied, i.e. the role of electrostatic vs hydrophobic interactions was elucidated by comparing performance of resins with and without ion exchange sites (i.e. uncharged resin beads/ resin base material). Apart from these, two additional novel aspects of the study are: i) PFCA removal performance of A-500P resin which has not been reported to-date in the literature compared to the well-studied A860; and ii) a new method for PFCA analysis involving more widely accessible but less commonly adopted gas chromatography-mass spectrometry (GC/MS) instrumentation (as opposed to liquid chromatography-mass spectrometry (LC/MS).

2.0 MATERIALS AND METHODS

2.1 Target Compounds

PFHpA (99%), PFOA (96%), and PFNA (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Molecular structures and the physicochemical properties for each of the selected target compounds are provided in the Supporting Information (SI) (Table SI-1). Except for the mass labelled internal standard ($^{13}C_8$-PFOA), all target PFCA were obtained as solids, and stock solutions of individual PFCA were prepared at a concentration of 1,000 mg/L in methanol and stored at 4°C. Working standards of PFCA mixtures or individual PFCA were prepared by diluting stock solutions appropriately to either 10 mg/L or 1 mg/L and were also kept refrigerated at 4°C. Prepared solutions (both stock solutions and working standards) were stored for no longer than 9 months in the refrigerator. Note that stock solutions for spiking in the resin experiments were prepared in ultrapure water (see 2.3).

2.2 Resins and uncharged resin beads

Two organic scavenging strong-base anion exchange resins from Purolite: macroporous polystyrenic A-500P® and macroporous acrylic A-860® (Purolite, Bala Cynwyd, PA) were selected for the study. Both ion exchange resins were used as received without further treatment. Base materials of the two resins, the uncharged resin beads (polyacrylic and polystyrenic resin beads), were donated by Purolite Canada. These uncharged beads were washed with 200 bed volumes of ultrapure water (UPW) to remove fines and organics in which they were stored or produced. Typically, styrenic resins and styrenic beads are more hydrophobic while acrylic resins and acrylic beads are more hydrophilic in nature. The resin beads are uncharged while both ion exchange resins have quaternary ammonium groups as their anion exchange functional groups. The exact compositions of these functional groups are proprietary.

PFAS removal efficacy of A-500P has not yet been reported in the published literature, while A-860 has been studied previously.[18-20,25] Except for the resin matrix, both anion exchange resins have similar properties (Table 1) which facilitated direct comparison of PFCA removal effectiveness between polyacrylic and polystyrenic IX resins. Del Moral et al.[25] previously compared polystyrenic A-520E and polyacrylic A-860 both of which possess strong-base quaternary ammonium functional groups and macroporous struc

ture. However, the resins differ in the nature of the quaternary ammonium groups as A520E has triethyl ammonium functional groups (total capacity, 0.9 eq/L) whereas A860 has trimethyl ammonium functional groups (total capacity, 0.8 eq/L). They[25] noted: "although polymer composition was the focus of resin properties in this research, the differing functional groups between A520E and A860 does present a confounding factor." The choice of resins used for the current study though was able to overcome this confounding factor as both resins possess trimethyl-ammonium functional groups, have the same capacity and other similar properties. Both resins were from the same manufacturer and were also used in practice as organic scavengers.

It is noteworthy to mention that A-500P has been discontinued and replaced with A-500Plus which has the same chemical composition but a different bead size (information obtained through email communication with Mr. Don Downey from Purolite®, Canada). Hence, even though A-500P is discontinued, findings of the current study are still relevant.

Table 1. Properties of the anion exchange resins and resin beads

Resin/ bead	Matrix	Capacity (Cl- form)* (eq/L)	Functional group*	Moisture content (%)**	Particle size range (mm)*	SBET (m^2/g)+	Pore volume (cm^3/g)
A-860	Macroporous polyacrylic	0.8	Quaternary ammonium (trimethyl ammonium) (Type-I)	67.7	0.3—1.2	< 1	could not be measured
A-500P	Macroporous polystyrenic	0.8	Quaternary ammonium (trimethyl ammonium) (Type-I)	68.0	0.425—1.2	4.06	0.021
Acrylic beads	Macroporous polyacrylic	N/A	none	48.3	N/A	9	0.044
Styrenic beads	Macroporous polystyrenic	N/A	none	36.7	N/A	< 1	could not be measured

*Data from manufacturer; N/A- not available; ** determined by drying resin beads in oven at 105°C for 24 h; moisture content of the beads was determined on bead samples that were washed with 200 bed volumes of UPW; + SBET- Brunauer–Emmett–Teller (BET) Specific Surface area; SBET analysis of the resins and resin beads were conducted at a certified commercial laboratory (Quantachrome Laboratory, Florida, US).

2.3 Waters

UPW (18.2 MΩ) generated from a Millipore Milli-Q UV Plus® system (Mississauga, ON) was used throughout the study. Dissolved organic carbon (DOC) levels in the UPW were always below 0.3 mg C/L and pH values ranged between 4.9—6.1.

Raw (untreated) Grand River water (GRW) (Southern Ontario, Canada) was collected from the intake of a drinking water treatment plant located on this river. Two batches of GRW were collected for the study and none of the target PFCA were detected in these batches. The 1st batch was collected on February 3, 2014, spiked, and then used to conduct the experiments with the selected adsorbents (Set 1 experiments). The 2nd batch was collected on May 9, 2014, and a second set of experiments (Set 2 experiments) was conducted to confirm the trends observed. Properties of the two batches of GRW are listed in Table SI-2. The river water had al-

ready gone through initial screening. No further alterations were made to the collected raw waters except that they were stored overnight in the lab at 4°C (thus allowing precipitation of some of the particulate matter) before being spiked with the target PFCA. Prior to the experiments the spiked water was carefully poured off to exclude the settled particulates.

No pH adjustments were done during this study. Untreated Grand River water pH values were 8.2 and 8.5, respectively, for set 1 and set 2 (reported in Table SI-2). Ultrapure water pH ranged from 5.4 to 5.9. The pH of the water did not change during the experiments. The target PFCA are strongly acidic (estimated pKa<1) and are expected to be in anionic form in the pH ranges of ultrapure and surface water.[5,26] Stock solutions of the target PFCA used for resin experiments were prepared in UPW at a concentration of 10 mg/L without any organic solvent and stored for a maximum of 9 months at 4°C. Throughout the study, UPW and GRW were spiked as required using the stock prepared in UPW. Following spiking with the target PFCA, the water was allowed to equilibrate overnight prior to starting kinetic experiments. The individual nominal compound target spike concentration was 3.0 µg/L in all tests. The actual spiked concentrations were measured at the beginning of each experiment.

2.4 Experimental approach

To illustrate and compare PFCA removal performance of the two selected resins, kinetic and isotherm experiments were conducted as described below. The test protocols/experimental conditions such as resin doses and initial PFCA concentrations used in the current study are comparable to previously published studies (See Table SI-3). Three types of controls, namely: pure blanks (no PFCA, no resin), spiked blanks (negative control i.e. spiked PFCA, no resin) and treatment blanks (no PFCA, resin added) were used for both UPW and GRW experiments.

2.4.1 Kinetic experiments

Bottle point adsorption kinetic experiments with the selected resins and resin beads were conducted in 1 L polypropylene opaque bottles (VWR, West Chester, PA) at 150 rpm on an orbital shaker (Barnstead/Thermolyne, Dubuque, IA). For kinetics experiments in UPW, wet resins equivalent to 10 mg dry weight of resin were added to 1 L of spiked water solution containing PFCA. For GRW kinetics experiments, 1 L of spiked surface water was poured into each sample bottle and wet resins equivalent to 100 mg dry weight of resin were added. The higher dosage of IX resins in GRW as opposed to UPW was used anticipating direct competition from the natural water matrix.

Both UPW and GRW were spiked with a mixture of PFCA and with only PFOA in some selected experiments (termed PFOA only). Spiked raw water blanks were also monitored for potential PFCA degradation and contamination. Sample bottles were then taken off the shaker at different time intervals and processed to monitor the time dependent removal of the spiked contaminants. All experiments were conducted at room temperature (~ 20°C) to minimize the effect of temperature change on adsorption. To differen-

tiate the effect of sorption of PFAS onto particulate matter, spiked blanks (negative control – PFCA added, no resin) were used for UPW water and the GRW experiments. No reduction in PFCA concentration was observed in the spiked blanks.

A pseudo-second order model developed by Ho[27] has been widely used to quantitatively describe adsorption kinetics.[28,29] The rate law for the pseudo-second-order model can be described as follows (Eq. 1):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{…… (1)}$$

where k_2 ($mg.ng^{-1}.d^{-1}$) is the rate constant for adsorption, q_e ($ng.mg^{-1}$) is the total amount adsorbed at equilibrium and q_t ($ng.mg^{-1}$) is the amount adsorbed at time t (d).

Integrating Eq. (1) for the range within the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ provides the expression for sorption kinetics as follows (Eq. 2):

$$q_t = \frac{q_e^2 k_2 t}{(1+q_e k_2 t)} \qquad \text{……..…. (2)}$$

Eq. (2) can be rearranged to obtain Eq. (3):

$$q_t = \frac{t}{\left({}^{1}/_{k_2 q_e^2} + {}^{t}/_{q_e}\right)} \qquad \text{…… (3)}$$

The pseudo-second-order model can be expressed in a linearized form as in Eq. (4). The initial sorption rate ϑ ($ng.mg^{-1}d^{-1}$) reflects kinetic performance and is expressed in Eq. (5). The last two equations will be used to describe PFAS removal kinetics in UPW and GRW using the tested resins.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad \text{…….…… (4)}$$

$$\vartheta = k_2 q_e^2 \qquad \text{…….. (5)}$$

2.4.2 Isotherm experiments

For isotherm experiments (to determine the adsorptive capacity of the resins), different amounts (dry weights ranging from 0.5 mg to 12 mg) of the tested resins were added to 1 L of UPW solution. All isotherm experiments were conducted with single solutes at a target nominal concentration of 3 µg/L. Samples were then stirred for the time to reach removal equilibrium as was determined during the UPW kinetic experiments (10 days).

Various models are used to describe isotherms. However, the Freundlich isotherm model is most frequently used in water treatment practice[30] and as such was used in the current study as well. The linear form of the Freundlich model is expressed as below (Eq.6):

$$log\ q_e = log\ K_F + \frac{1}{n} \log C_e \qquad \text{…….. (6)}$$

where q_e is the equilibrium solid phase concentration (ng/mg), C_e is the equilibrium liquid phase concentration, and K_F and 1/n are Freundlich parameters. Experimental data were fitted to the model using Microsoft Excel®.

2.5 Analysis

Analyses of the target compounds in water samples were performed using gas chromatography with mass spectrometry (GC/MS) preceded by solid phase extraction (SPE) and derivatization. The target PFCA were derivatized using butanol in the presence of sulfuric acid and heat. By employing a central composite factorial design, the optimum derivatization reaction conditions were established. The method detection limits (MDLs) were 11-30 ng/L in UPW and 16-49 ng/L in GRW water depending on the target compound. In order to achieve these low detection limits the entire 1L volume of a sample bottle from the isotherm/kinetic experiments was required for the solid phase extraction (SPE). This also made it necessary to have one bottle for each data point. GC/MS method performance parameters are listed in Table SI-4. Brief details of the GC/MS analytical method can be found in the supporting information (SI-C) and the detailed analytical method development has been described by Rahman.[31]

It should be noted that PFAS are typically analyzed using LC/MS as opposed to GC/MS. A new GC/MS method was developed for the purpose of this study as we did not have access to an LC/MS at the time of this study. The developed GC/MS method remains a novel aspect of this study. While it can be argued that LC/MS is the technology of choice, the existence of a GC/MS method can open the world of PFAS testing and research to analytical lab users who cannot afford to purchase an LC/MS or have sufficient funds to support off-site PFAS analyses. Having said that, using the GC/MS-based method imposed several limitations, for example: perfluoroalkyl sulfonates (PFSA) including PFOS were not amenable to the developed GC/MS method. Also, the performance of the method for small chain PFCA (<C6) was poor. Hence, the target compounds of the study were limited to three long-chain PFCA (PFHpA, PFOA and PFNA), which at that point in time (2013-2015) were being considered under USEPA's 3rd unregulated contaminant monitoring rule UCMR3. Furthermore, sample preparation for the method owing to the SPE and derivatization process took much longer compared to sample preparation for LC-MS which does not require these steps. This also limited the number of samples that could be analyzed during each batch of experiments. The study therefore, instead of using replicates, repeated experiments in both UPW and GRW to confirm the PFCA removal trends using the tested IX resins.

The DOC content of the UPW was measured using a wet oxidation OI Analytical Model 1010 TIC-TOC analyzer (College Station, TX). The oxidizing agent was 100 g/L $Na_2S_2O_8$. The samples were initially preserved by lowering the pH to 2-3 using 1N H_3PO_4. The instrument was calibrated using standard solutions of potassium biphthalate ($C_8H_5KO_4$) at appropriate concentrations to measure low DOC levels in UPW.

The injection volume was 5 mL and 3 replicates of each sample were processed. NOM fractions (humic substances, biopolymers, and building blocks) were measured by liquid chromatography with organic carbon detection (LC-OCD) (DOC Labor Dr. Huber, Karlsruhe, Germany).[32] UV_{254} absorbance was measured with UV-vis spectrometer (Cary 100, Agilent Technologies, Mississauga, ON), and SUVA was calculated as follows:

$$\text{SUVA (L/mg-M)} = (\text{UVA (cm}^{-1}) / \text{DOC (mg C/L)}) * 100 \text{ cm/M}$$

Sample pH was measured using an ORION 720A pH meter (Boston, MA) and conductivity was measured with a Mandel conductivity meter (Weilheim, Germany). Inorganic anions were analyzed with a Dionex AS-DV ion chromatography system (Thermo Scientific) using standard ASTM test methods for anions in water (ASTM Designation D4327-11).

3.0 RESULTS AND DISCUSSION

3.1 Kinetics of PFCA removal

The removal kinetics of the target PFCA in both UPW and GRW are presented in Figure 1. In UPW at a resin dose of 10 mg/L, the polystyrenic anion exchange resin A-500P exhibited higher removal and faster kinetics for all three target PFCA (Figure 1A-C) compared to the polyacrylic A-860 resin. In GRW at a resin dose of 100 mg/L, A-500P was able to achieve greater than 93% removal of the target PFCA, while A-860 exhibited less than 15% removal (Set 1 experiments in Figure 1D-F). Higher removal of PFCA by polystyrenic resins as opposed to polyacrylic resins in both waters is also in line with other studies.[15,18,24,25,33] Experiments in natural water were repeated using a different batch of water (Set 2 experiments in Figure 1D-F), which confirmed the reproducibility of the removal trends for both resins.

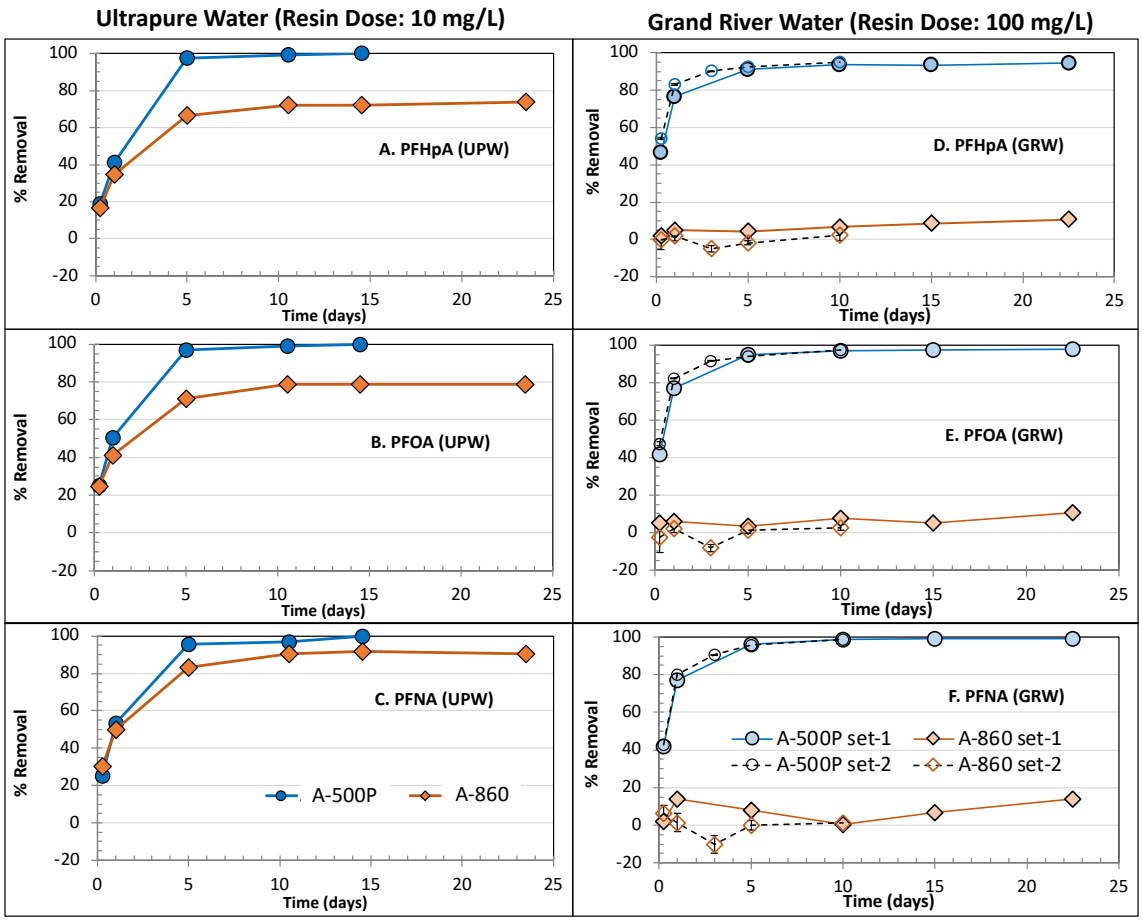


Figure 1. Removal of target PFCA as a function of time in UPW (panels A-C) and GRW (panels D-F). Experimental conditions: target nominal spiked PFAS concentration was 3 µg/L and all three target PFAS were spiked simultaneously; pH not adjusted in UPW or GRW.

Resin dose was 10 mg/L in UPW and 100 mg/L in GRW; in GRW, Set-1 experiments were conducted using water collected on February 3, 2014 (DOC: 5 mg C/L; pH: 8.2; sulfate: 29.3 mg/L) and Set 2 experiments used water collected on May 9, 2014 (DOC: 4.7 mg C/L; pH: 8.5; sulfate: 16.6 mg/L). Error bars in Set-2 experiments indicate the maximum and minimum removals of two replicate analysis (i.e. two sample bottles per data point for the Set-2 experiments). Removal of PFCA by IX resins in GRW illustrated the reproducibility of removal trends.

The fitted pseudo-second-order model parameters (expressed in mass-base units), including the corresponding correlation coefficients along with the experimentally derived equilibrium adsorption amounts, are presented in Table 2 (model parameter values are expressed in molar base units and 95% confidence interval values of the parameters are presented in Table SI-5 and Table SI-6, respectively). As seen from the pseudo-second-order rate constants listed, A-500P exhibited superior kinetics in both UPW and GRW, suggesting better performance of the polystyrenic structure compared the polyacrylic structure. While the removal rates in UPW were comparable between the two tested resins, in GRW the removal rate was considerably higher for A-500P. The poor removal of PFCA by A-860 resin in GRW explains the poor fit of the pseudo-second-order model, in particular for PFNA.

It is noteworthy to mention that the parameters of the pseudo-second order model are dependent on resin/contaminant ratio.[18,34] This study did not attempt to establish a resin dose for actual treatment conditions, but rather intended to understand and compare the performance of the two ion-exchange resins. Given the experimental conditions used herein (the relatively low resin doses and the PFAS level higher than expected in natural waters), the kinetic parameters reported here should be interpreted with this in mind in considering full-scale/actual treatment conditions.

Although the polyacrylic anion exchange resin A-860 achieved 73-95% removal of the target PFCA in UPW at a resin dose of 10 mg/L, it failed to achieve any substantial removals of the target PFCA in GRW even though the resin dose was 100 mg/L. Dixit et al.[19] reported over 70% of reduction in PFOA (500 ng/L) by A-860 at a 50 mg/L resin dose in the presence of both NOM and inorganic anions in Eagle Lake water (DOC: 3 mg C/L; sulfate 5 mg/L; bicarbonate 4.5 mg/L). When the resin dose was increased to 1000 mg/L, A-860 resin was able to achieve complete removal of PFOA simultaneously with NOM and inorganic anions in Eagle Lake water. At a resin dose of 50 mg/L, A-860, however exhibited lower removal of PFOA in Eagle Lake water containing both NOM and inorganic anions, compared to water containing only NOM (Suwannee River NOM 5 mg/L) indicating detrimental impact of inorganic anions on PFCA removal by IX resins.[19] GRW contained inorganic anions (in addition to DOC at 4.7-5.0 mg C/L) and the sulfate concentration (Table SI-2) was higher than reported for Eagle Lake water. The collective competition exerted for A-860 resin sites likely explains the loss of PFCA removal capacity in natural water observed during the current study. However, Del Moral et al.[35], while observing a loss in PFAS capacity of A-860 in their study with synthetic water having groundwater as background matrix, did not observe as drastic a loss of PFAS removal capacity of A-860. Their study at DOC: 9.3 mg/L, sulfate: 94 mg/L and initial PFOA concentration of concentration of 298 μg/L resulted in about 40% removal of PFOA after 24 h (See Table SI-7). Liu[35] using a different set of IX resins also reported loss of removal capacity for PFAS in GRW owing to competition from

inorganic anions and NOM. Impact of inorganic anions on PFCA removal by both A-860 and A-500P is discussed in detail in Section 3.4.

Table 2. Pseudo-second order kinetics model parameters in UPW and GRW for the target PFCA for mixed-solute experiments

Resins	q_e (ng/mg)	Exp. q_e (ng/mg)	q_e (ng/mg)	Exp. q_e (ng/mg)	q_e (ng/mg)	Exp. q_e (ng/mg)	k_2 (mg.ng^{-1}.d^{-1})			ϑ (ng.mg^{-1}.d^{-1})			R^2		
	PFHpA		PFOA		PFNA		PFHpA	PFOA	PFNA	PFHpA	PFOA	PFNA	PFHpA	PFOA	PFNA
UPW (resin dose: 10 mg/L; individual nominal target PFCA concentration: 3000 ng/L)															
A-500P	418	371	397	362	403	371	0.0020	0.0028	0.0031	357	435	500	0.99	0.99	0.99
A-860	288	276	303	290	357	347	0.0037	0.0047	0.0046	303	435	588	0.99	0.99	0.99
GRW (resin dose: 100 mg/L; individual nominal target PFCA concentration: 3000 ng/L)															
A-500P	39	38	35	35	36	35	0.096	0.093	0.095	143	116	120	0.99	1.00	1.00
A-860	5	4	3	4	2	5	0.057	0.085	0.027	1.2	1.0	0.1	0.89	0.71	0.02

Exp. q_e : experimental q_e

3.2 Isotherms

Single solute Freundlich adsorption isotherms for A-860, and A-500P in UPW for the three target PFCA are presented in Figure 2. As with the kinetic experiments, A-500P resin exhibited a higher removal capacity for all three target PFCA compared to A-860. It is also evident that for A-500P and A-860, adsorption data at equilibrium during kinetics experiments are similar to that for the obtained isotherms (except for the PFOA data for A-860), indicating that adsorption trends at equilibrium obtained from both types of experiments are similar, as would be expected. The deviation of the PFOA data for A-860 (Figure 2) may have been due to the removal behaviour reflected in the high 1/n value as well as the narrow equilibrium liquid phase concentration range observed with this specific isotherm (see Table SI-8).

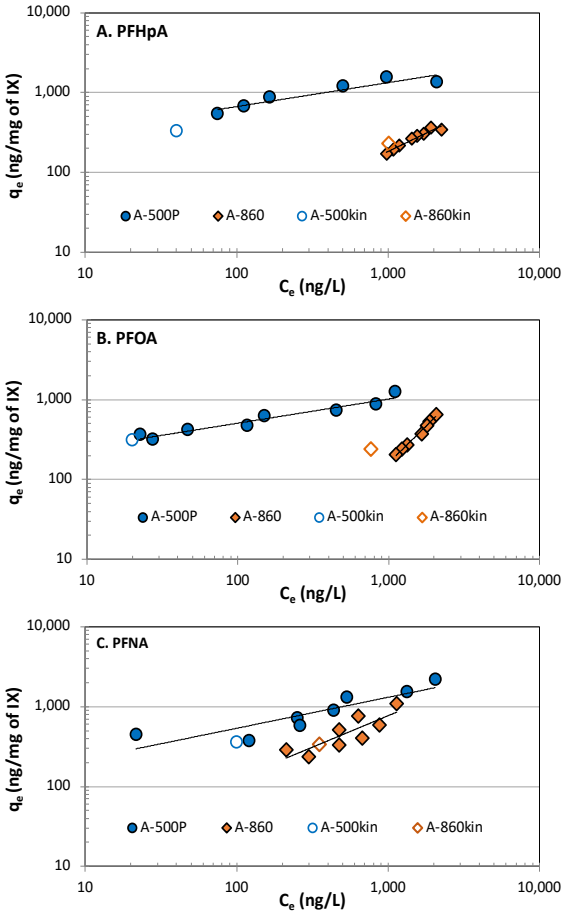


Figure 2. Single solute adsorption isotherms in UPW on two IX resins for the three target PFCA: A) PFHpA, B) PFOA, C) PFNA. kin= kinetic experiments data points at equilibrium.

3.3 Removal of NOM and NOM fractions

The selected anion exchange resins are marketed as organic scavengers and can achieve high DOC removals (Purolite, 2006). LC-OCD analysis of the PFCA spiked raw and treated GRW (Set 1 experiments) revealed that at a resin dose of 100 mg/L, both anion exchange resins achieved nearly 75% removal of the DOC present in GRW within 10 days of contact time and the removals did not improve substantially even after an additional 12 days of contact (Figure 3A). As can be seen in Figure 3, polyacrylic A-860, being hydrophilic, removed DOC faster than polystyrenic A-500P. Reproducibility of DOC and DOC fractions removal trends using the two resins were confirmed during Set 2 experiments which used a different batch of GRW (Figure SI-1). Removal of DOC observed during this study was comparable to previous studies[18,25] that used A-860 resin (See Table SI-7). Dixit et al.[18] reported that at a resin dose of 1,000 mg/L or above, A-860 resin was able to achieve ~90% removal of NOM.

NOM removal during ion exchange is primarily based on electrostatic interactions between negatively charged functional groups in the NOM and ion exchange sites, rather than physical adsorption.[36,37] Cornelissen et al.[36] commented that during ion exchange treatment, physical adsorption may incidentally occur but is "neither an effective nor controllable mechanism compared to the pri-

mary mechanism." It has also been reported that inorganic anions, in particular sulfate, may be an important determinant of DOC removal in natural water compared to other inorganic anions such as bicarbonate, nitrate and bromide.[38]

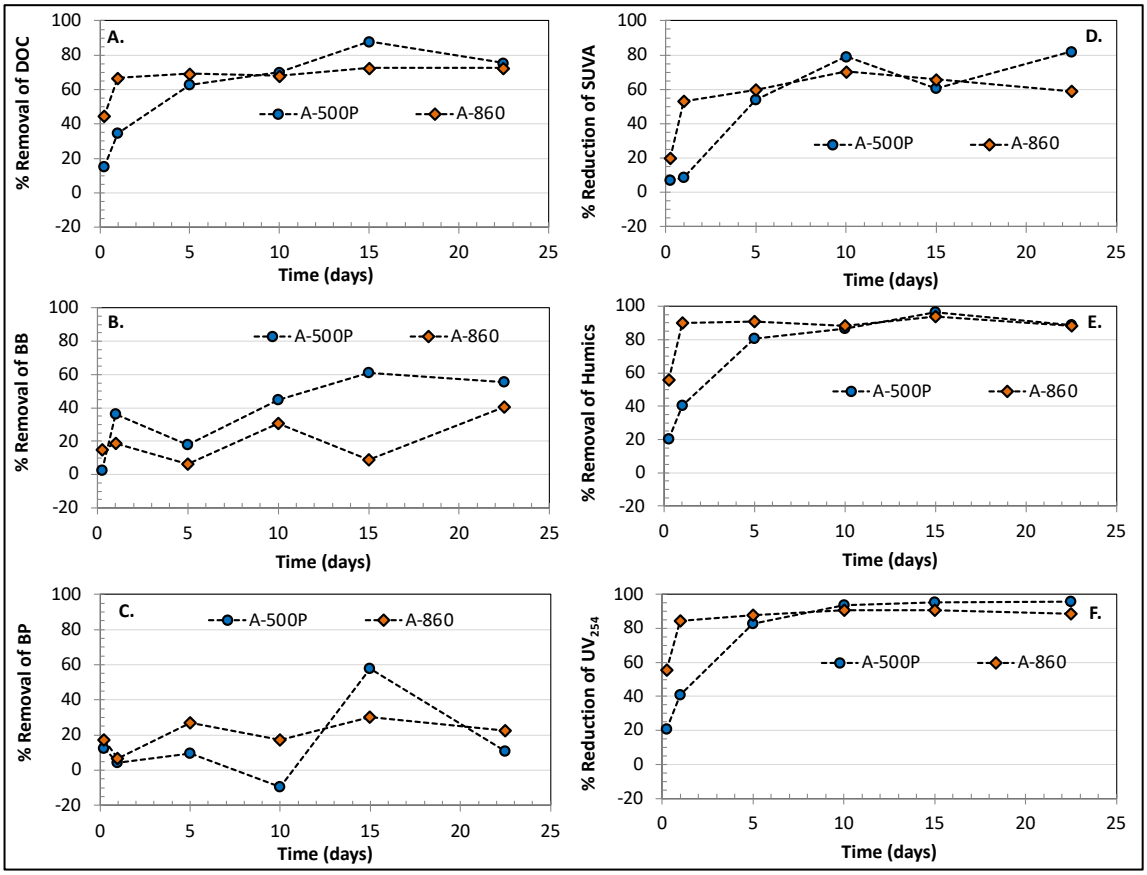


Figure 3. Removal of DOC and select DOC fractions in GRW (Set 1 experiments) over time; A) DOC, B) biopolymers (BP), C) building blocks (BB), D) SUVA, E) humics, F) UV254; DOC- 5.0 mg C/L, humics- 3.6 mg C/L, BP- 0.25 mg C/L, BB- 0.65 mg C/L; IX resin dose 100 mg/L.

The removal of various DOC fractions of GRW by the selected IX resins is illustrated in Figure 3 B-F. The anion exchange resins preferentially removed humics compared to other measured LC-OCD fractions, as illustrated by over 90% removal of this dominant DOC fraction in GRW (Figure 3E). Similar preferential removals of humics have been observed by others as well.[36,39] Of the two resins, polyacrylic A-860 resin, perhaps owing to its hydrophilic structure, more rapidly removed humics compared to the poly-styrenic A-500P resin. Of the two resins, A-500P appeared to remove higher concentrations of building blocks (BB) compared to A-860 (Figure 3B), while the latter resin generally achieved higher removal of biopolymers (BP) (Figure 3C). However, the overall removal of BP was low (< 35%). The scatter in biopolymer percentage reduction is likely due to their generally low initial concen-trations. Others have reported low effectiveness of anion exchange resins in removing biopolymers from water as well.[36]

Specific UV absorbance at 254 nm (SUVA), which is used as a surrogate parameter for the aromatic content of NOM, was also substantially (~60%) decreased following anion exchange resin treatment (Figure 3B). Such decreases in SUVA in GRW indicate that the DOC composition of GRW is considerably altered, i.e. more hydrophilic, following treatment with the two selected anion

exchange resins. Preferential removal of aromatic fractions of DOC by IX resins has been observed by other previous studies as well.[16,40]

A-500P has a high equilibrium PFCA removal capacity (Figure 1B) while the DOC removal kinetics with A-860 are substantially faster compared to A-500P (Figure 3A). Such trends indicate that A-860 could potentially be used as a pre-treatment step for an A-500P type resin (since A-500P is no longer manufactured) or in a mixture with an A-500P type resin in natural water and thereby reduce direct competition from inorganic anions and NOM for anion exchange sites on A-500P type resin, leading to improved removal efficiency for the PFCA. Future studies could thus investigate whether combining the anion exchange resins with activated carbon treatment or even combining the two types of resins can enhance overall PFCA removal in natural water.

3.4 Effect of Inorganic Anions on PFAS Removal

As discussed previously, PFCA removal capacities of both resins, in particular A-860, were substantially decreased in GRW, indicating the negative impact of the natural water matrix during treatment with IX resins. Studies by Dixit and colleagues[18-20] reported that background water matrix, more specifically the charge density and molecular weight distribution of source water NOM, and inorganic anions, affected PFAS uptake during IX treatment. Arevalo Perez[21] and Del Moral et al.[25] noted that DOC has relatively less of an adverse impact on PFAS removal by ion exchange compared to the ionic strength of a water (i.e. the concentration of ions present). Substantial differences in PFCA removals and similar DOC removals by the two tested resins (both having similar capacity) in natural water observed during the current study also indicate that for the tested experimental conditions inorganic anions may have been the dominant competitors for the target PFCA removal.

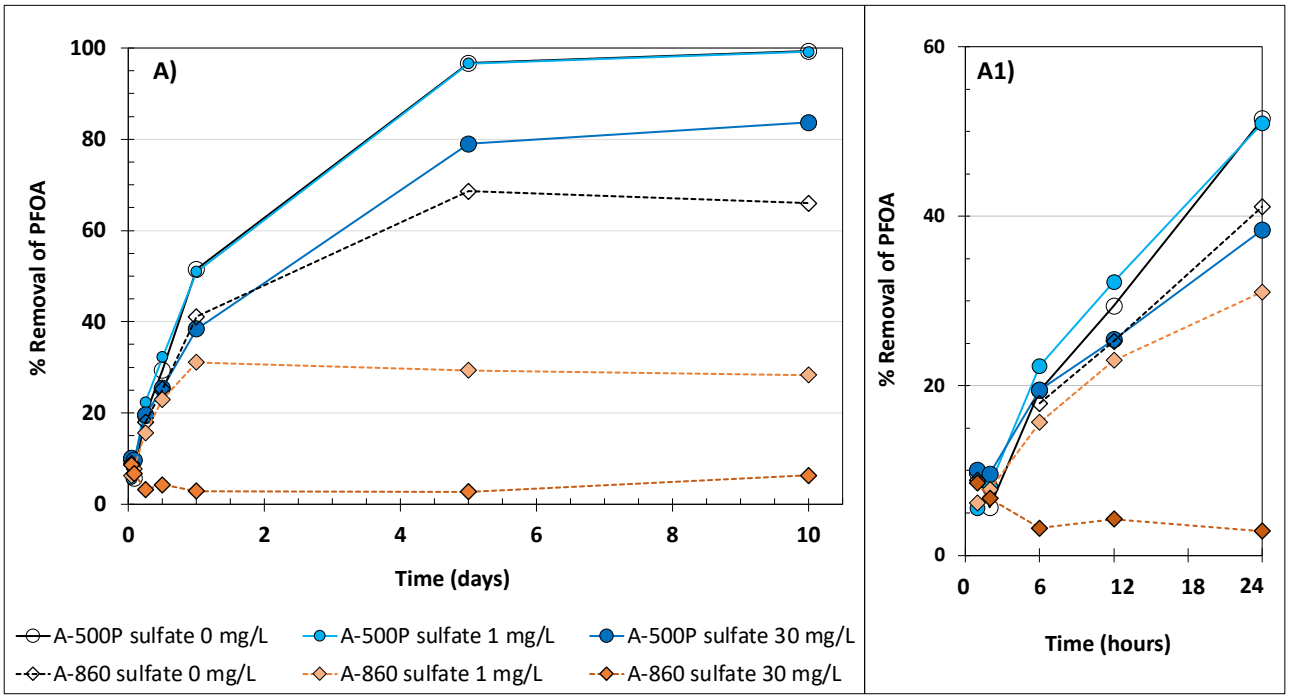


Figure 4. Effect of sulfate on PFOA removal kinetics in UPW; resin dose= 10 mg/L; plot A1 provides enhanced resolution of the initial data points shown in plot A; only PFOA was spiked in UPW; pH not adjusted.

In GRW, A-860 resin achieved somewhat higher removal of sulfate compared to A-500P, while A-500P achieved better nitrate removal (Figure SI-2). Thus, it can be postulated that the loss of PFCA removal capacity of A-860 probably resulted from the competition exerted by the high concentration of sulfate present in GRW.

Subsequent experiments in UPW spiked with 1 mg/L and 30 mg/L sulfate confirmed that increasing sulfate concentration more severely affected PFAS removal capacities for A-860 than for A-500P (Figure 4). The higher sulfate dose 30 mg/L was chosen as the GRW sample used during Set-1 experiments contained 29.3 mg/L of sulfate. The study intended to confirm if the removal trends in ultrapure water match those in GRW in the presence of a similar level of sulfate. Dixit et al. (2020) also conducted their experiments in synthetic and natural water that contained similar levels of sulfate. The lower sulfate dose 1 mg/L was chosen to see the impact of a relatively small amount of sulfate on removal performance of the two resins in ultrapure water.

In UPW in the presence of 30 mg/L of sulfate and at a resin dose of 10 mg/L, A-860 nearly completely lost its PFOA removal capacity, while for A-500P PFOA removals decreased only by about 20% compared to UPW without sulfate. This confirmed the higher sulfate selectivity of A-860 over A-500P. Liu[35] using a different set of IX resins also concluded that sulfate as opposed to nitrate had a more detrimental impact on PFAS removal in GRW.

Since natural water matrices will vary depending on their location and source, the PFCA removal trends observed during the current study will not universally apply to other natural water matrices. Dixit et al.[19] reported that A-860 at a resin dose of 1,000 mg/L was able to achieve complete removal of a suite of PFAS (concentration 500 ng/L) from Eagle Lake water while the removals were

less than 30% in the same water when the resin dose was lowered to 50 mg/L. Nonetheless, if sulfate is present, particularly at elevated concentrations, utilities considering treatment of PFAS should consider this effect carefully with respect to using A-860 type IX resins.

3.5 Removal Mechanism Using Ion Exchange Resin

PFCA can be removed by two possible mechanisms during IX treatment: a) ion exchange (electrostatic interaction between the anionic functional group of the PFCA and the cationic functional group on the anion exchange resin) and b) adsorption (hydrophobic interactions between the polymer backbone of the IX resin and the hydrophobic PFAS chain).[23] To investigate the contributions of hydrophobic interactions, PFOA removal experiments evaluated the two base resins beads used for the production of A500P and A-860. The beads were donated by the manufacturer. It was assumed that since the beads were uncharged any removal of PFOA by the resin beads should result from the hydrophobic interaction of PFOA molecules and the resin beads. This would then indicate the contribution of hydrophobic/hydrophilic interaction towards the overall uptake of PFOA. Figure 5 demonstrates that the uncharged styrenic and acrylic beads (base materials) of the two tested resins were unable to remove PFOA. Indeed, the very low BET surface area (< 10 m^2/g) and pore volume (< 0.044 cm^3/g) of the uncharged resin beads (Table 1) also support the observation of negligible adsorption potential of PFCA via hydrophobic interactions. Hence, it can be inferred that the dominant removal mechanism involves charge interactions between the negatively charged PFCA and the positively charged anion exchange functional group.

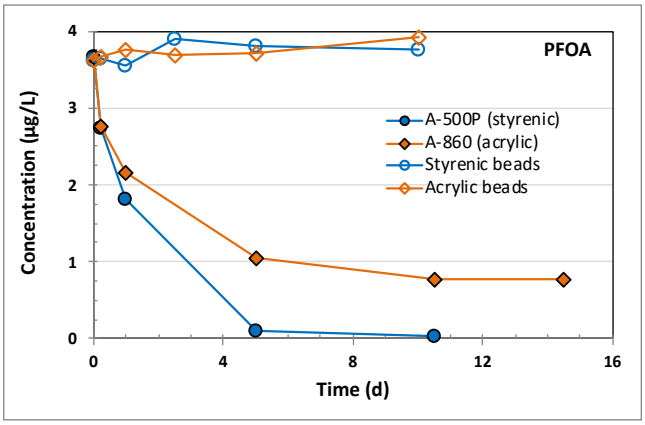


Figure 5. PFOA removal in UPW as a function of time using ion exchange resins and uncharged resin base materials termed as resin beads (e.g styrenic beads are the base material for A-500P while acrylic beads are for A-860). Experimental conditions: resin/beads dose: 10 mg/L; target nominal spiked PFAS concentration was 3 µg/L and all three target PFAS were spiked simultaneously; pH not adjusted in UPW or GRW.

Yu et al.[23] observed a higher adsorption of PFOA onto the anion exchange resins at pH 3 compared to pH 7. Thus, they indicated that the increased adsorption at the lower pH may have been due to the hydrophobic interaction of the uncharged species of PFOA and the resin. However, the pKa of PFOA has been reported[25] to be <1 and thus, PFOA is expected to be in its anionic form at pH

3. Hence, the increased adsorption of PFOA at pH 3 observed by Yu et al.[23] may not necessarily have been due to hydrophobic interaction between the neutral species of PFOA and the anion exchange resin surface. Other previous studies have also suggested a minor role for hydrophobic adsorption during the removal of PFAS via IX processes.[20,41]

As discussed in Section 3.1, the current study along with several previous studies observed better performance of polystyrenic resin structure as opposed to polyacrylic resin structure during PFCA removal, which suggest that hydrophobic (polystyrenic) composition of resins is more effective for PFCA removal. However, experiments with un-functionalised beads reveal negligible removal of PFCA through hydrophobic interaction. This apparent contradiction could not be clarified as details of the functional groups on the IX resins are proprietary. Furthermore, it is unclear if the resin surface is altered once functional groups are attached to the resin base materials when manufacturing the IX resins.

4.0 CONCLUSIONS

The current study assessed the removal potentials of three selected PFCAs in Ultrapure water (UPW) and Grand River water (GRW) by ion exchange. In addition, it investigated the impact of the ion exchange resin matrix (polyacrylic vs polystyrenic) on PFCA removal. To do so, the investigation was designed using two organic scavenger strong-base anionic resins, namely: macroporous polystyrenic A-500P and microporous polyacrylic A-860. Both resins, with the exception of their base structure/matrix, had very similar properties, which enabled direct comparison between the removals achieved by the two resins. Two specific novel aspects of the current study are: i) PFCA removal performance of previously unreported A500P resin and its comparison with well-studied A860; and ii) the new GC-MS method that was developed for PFCA analysis in water. Under the conditions tested, the following conclusions can be drawn from the study:

- Depending on resin dose, resin properties, and natural water matrix, IX can be used to achieve simultaneous removal of NOM, inorganic anions, and PFCA.
- NOM and inorganic anions substantially impacted PFCA removal in GRW, particularly in the case of the A-860 resin, which failed to achieve removal of PFCA despite having a higher resin dose compared to UPW experiments.
- Similar removals of DOC achieved by the two resins in GRW suggested that inorganic anions (sulfate in particular) were the dominant competitors for the anion exchange resin A-860. Experiments in UPW confirmed that the presence of sulfate more severely affected PFCA removals for A-860 than for A-500P. Thus, if sulfate is present, particularly at elevated concentrations, utilities assessing treatment of perfluorinated compounds should consider this competition carefully when considering A-860 type ion exchange resins for PFCA removal.
- The uncharged styrenic and acrylic beads (base materials) of the two tested resins were unable to remove PFOA, implying that the dominant removal mechanism involves charge interactions between the negatively charged PFCA and the positively charged anion exchange functional groups.

389

390 • Polystyrenic A500-P anion exchange resin compared to polyacrylic A-860 exhibited higher adsorptive capacity and faster

391 overall kinetics for the target PFCA in UPW.

392

393 Future studies could explore whether combining the tested anion exchange resins in series with granular activated carbon treatment

394 or even combining the two types of resins could enhance overall PFCA removal in natural water.

395

396 **ASSOCIATED CONTENT**

397 **Supporting Information**

398 The Supporting Information is available free of charge on the ACS Publications website.

399 SI-A: List of supporting information tables; Properties of the target Perfluoroalkyl carboxylic acids (PFCA) (Table SI-1); Properties of

400 Grand River Water (Table SI-2); GC/MS analysis and method performance parameters (Table SI-3); Freundlich isotherm parameters for

401 selected adsorbents in ultrapure water (Table SI-4).

402 SI-B: List of supporting information figures; Removal of target PFAS from Grand River water as a function of time illustrating reproduci-

403 bility of removal trends (Figure SI-1); Removal of selected inorganic anions from Grand River water as a function of time (Figure SI-2)

404 (file type: PDF)

405 SI-C: Description of the GC/MS analytical method.

406

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411 **Author Contributions**

412 The manuscript was written through contributions of all authors.

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417

418 **Notes**

419 The authors declare no competing financial interest. The mention of the commercial products and/or chemicals, labs in this article does not
420 constitute endorsement or recommendation for their application.

421

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