Article

In Situ Sequestration of Perfluoroalkyl Substances Using Polymer-Stabilized Powdered Activated Carbon

Chen Liu, James Hatton, William A. Arnold, Matt F. Simcik, and Kurt D. Pennell*

ACCESS | 📊 Metrics & More | 📖 Article Recommendations | 🆘 Supporting Information

ABSTRACT: Remediation of groundwater impacted by per- and polyfluoroalkyl substances (PFAS) is particularly challenging due to the resistance of the molecule to oxidation because of the strength of the carbon−fluorine bond and the need to achieve low nanogram per liter drinking water targets. Previous studies have shown that activated carbon is an effective sorbent for removal of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in conventional water treatment systems. The objective of this study was to evaluate the in situ delivery and sorptive capacity of an aqueous suspension containing powdered activated carbon (PAC) stabilized with polydiallyldimethylammonium chloride (polyDADMAC). Batch reactor studies demonstrated substantial adsorption of PFOA and PFOS by polyDADMAC-stabilized PAC, which yielded Freundlich adsorption coefficients of 156 and 629 L/g^{-n}, respectively. In columns packed with 40−50 mesh Ottawa sand, injection of a PAC (1000 mg/L) + polyDADMAC (5000 mg/L) suspension created a sorptive region that increased subsequent PFOA and PFOS retention by 3 orders of magnitude relative to untreated control columns, consistent with the mass of retained PAC. Experiments conducted in a heterogeneous aquifer cell further demonstrated the potential for stabilized-PAC to be an effective in situ treatment option for PFAS-impacted groundwater.
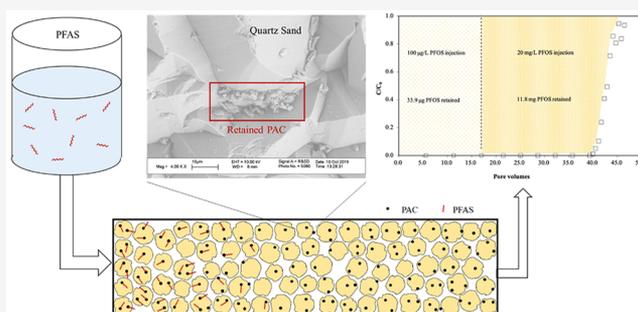
■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) represent a broad class of compounds consisting of a fully or partially fluorinated carbon chain and several types of end or "head" groups including sulfonate, carboxylate, sulfonamide, and alcohol. Due to their unique amphiphilic properties and chemical stability, PFAS have been widely used in products such as firefighting foams, mineral extraction surfactants, floor polishes, photographic film, waterproof clothing, and nonstick coatings for cookware.[1,2] Monitoring studies conducted since the early 2000s have documented the ubiquitous presence of PFAS in the environment and biota.[2−6] Due to concerns over potential human health effects, production of long-chain PFAS was voluntarily phased out by the primary manufacturer (3M) in 2002.[7] The United States Environmental Protection Agency (U.S. EPA) established a health advisory level for total PFOS and PFOA of 70 parts per trillion (ng/L),[8,9] and a number of states have proposed or adopted PFAS regulations with a maximum contaminant level (MCL) as low as 10 ng/L.

Many PFAS, including PFOA and PFOS, are both recalcitrant and mobile in the groundwater as a result of their stability[10−13] and relatively high aqueous solubilities.[14] The covalent carbon−fluorine bond, which has a dissociation energy of 130 kcal/mol,[13] requires extreme conditions (e.g., high temperature)[15−18] to be broken. Chemical oxidation has been effective for PFOA under laboratory-simulated groundwater conditions,[19−21] but has shown minimal applicability for

PFOS,[22] and there is concern over the potential formation of shorter chain byproducts.[23] Biodegradation of PFAS precursors was documented by several research groups,[24,25] and recently, transformation of PFOA and PFOS by *Acidimicrobium* sp. Strain A6 was reported, but the reaction rates are relatively slow.[26] As a result, PFAS-impacted groundwater plumes are typically managed using conventional "pump and treat" remediation approaches that rely on extraction and above-ground treatment with granular activated carbon (GAC) or anion exchange resin.[27−32] While GAC has been shown to exhibit sizable adsorption capacities for longer chain PFAS,[31] effectiveness declines precipitously for shorter chain PFAS species and precursors.[33−36]

An alternative to chemical or biological destruction that could be applied in situ is the injection of particulate materials into the subsurface to create an in situ permeable adsorptive barrier (PAB) that sequesters PFAS, with the intent of concentrating and containing mass from dilute groundwater plumes. The adsorption of PFAS to particulate materials

including ion-exchange resins, minerals, sludge, and activated carbon has also been investigated.[16,31] Activated carbon stands out among these adsorbents due to its high sorption capacity, low cost, and availability from its widespread usage in water treatment applications.[29,37−39] Proprietary formulations containing injectable sorbents, such as PlumeStop[40] and BOS 100, have been marketed by commercial vendors (i.e., Regenesis Bioremediation Products and Remediation Products, Inc., respectively) as a means to create in situ adsorptive or reactive zones that retain and treat dissolved groundwater contaminants. A recent field study[40] demonstrated the ability of injecting colloidal activated carbon (CAC) to reduce measured concentrations of PFOA and PFOS in groundwater to below 30 ng/L. A subsequent modeling study by Carey et al.[41] investigated the longevity of the CAC treatment, but neither study provided information on the carbon adsorption capacity and transport properties of the suspension.

To address these knowledge gaps, the objectives of this work were to develop stable aqueous suspensions of powdered activated carbon (S-PAC), evaluate the delivery and retention of S-PAC, and quantify the ability of S-PAC to sorb PFOA and PFOS under dynamic conditions. Preliminary studies demonstrated that a cationic polymer, polydiallyldimethylammonium (polyDADMAC), which has also been shown enhance PFAS sorption by soils,[37,38] was able to effectively stabilize DARCO 100-mesh PAC in aqueous solutions. Batch reactor experiments were conducted to determine the adsorption capacity of DARCO 100-mesh PAC for PFOS and PFOA. A series of column studies was then performed to evaluate the delivery and retention of PAC in water-saturated Ottawa sand, and subsequently, to assess the sorption of PFOA and PFOS by PAC-treated sand. To further evaluate the performance of S-PAC under more realistic conditions, a heterogeneous laboratory-scale aquifer cell study was completed to assess the S-PAC injection and subsequent retention of PFOS.

■ MATERIALS AND METHODS

Materials. PFOA and PFOS standards (>99% purity) were purchased from Wellington Laboratories (Ontario, Canada) for use as calibration standards. Perfluoro-n-[1,2,3,4-$^{13}C_4$]-octanoic acid and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]-octanesulfonate were also purchased from Wellington Laboratories (>99% purity) to serve as internal standards. PFOS potassium salt (98% purity) and PFOA (96% purity) were purchased from Sigma-Aldrich (St. Louis, MO) for preparation of aqueous solutions. PolyDADMAC (40% active ingredient, molecular weight ∼240 000 Da) was purchased from Accepta (Manchester, U.K.). DARCO 100 mesh (<149 μm) PAC was purchased from Sigma-Aldrich (St. Louis, MO). Ottawa sand (40−50 mesh) was selected as a solid phase for this study to represent a high permeability, low adsorption capacity aquifer material. The 40−50 mesh size fraction (300−420 μm) was obtained by sieving F-50 Ottawa sand (U.S. Silica, Berkeley Springs, WV) for 10 min cycles with a Model RX-29 Ro-Tap sieve shaker (W.S. Tayler, Inc., Mentor, OH). The 40−50 mesh size fraction was then used in column studies without further treatment (e.g., acid washing). Aqueous solutions were prepared with deionized (DI) water (18.2 MΩ cm^{-1}, total OC < 5 μg/L) that had passed through a Milli-Q Reference Water Purification System (EMD Millipore).

Batch Adsorption Studies. For batch adsorption tests, 2 or 10 mL of S-PAC (2 or 10 mg as PAC) was combined with either PFOA or PFOS in 10 mM NaCl (to minimize dispersion of fines) in 35 mL Corex glass centrifuge tubes (Kimble Chase, Vineland, NJ) to achieve concentrations ranging from 0 to 400 mg/L. Tubes were prepared in triplicate with controls at the same PFAS concentration without PAC and blanks containing only PAC and 10 mM NaCl. The contents of tubes were then mixed for 96 h on a rotary shaker. The mixing time was selected based on previous studies that have evaluated PFAS adsorption on activated carbon.[16,29,31,33,42−44] After mixing, the tubes were allowed to settle for 1 h, and the supernatant was transferred to a polypropylene centrifuge tube and separated at 4000 rpm for 30 min. A 1 mL aliquot was then filtered through 0.45 μm GE Healthcare Whatman GD/X Glass Micro Fiber (GMF) syringe filters and diluted prior to analysis.

Column Studies. On the basis of a series of preliminary stability tests, 1000 mg/L PAC + 5000 mg/L polyDADMAC were combined and sonicated in a Fisherbrand CPX3800 ultrasonic bath at power level high for 24 h to prepare stable aqueous suspensions (S-PAC). Sonication served to reduce the size of the PAC and promote the formation of a stable suspension. Column experiments were performed to assess the delivery and retention of PAC within the column, and to quantify the sorption of PFOA or PFOS under dynamic conditions following the S-PAC treatment. The columns consisted of borosilicate glass with dimensions of 2.5 cm (i.d.) × 10 cm (length). After packing with air-dried 40−50 mesh Ottawa sand, the columns were flushed with CO_2 gas for 1 h, and then saturated with 10 pore volumes (PV, where 1 PV ≈ 30 mL) of electrolyte solution (10 mM NaCl) at a flow rate of 1.0 mL/min. Nonreactive tracer tests were performed by injecting 3.5 PV of 10 mM NaBr followed by 3.5 PV 10 mM NaCl using a Chrome Tech P-010 isocratic pump (Apple Valley, MN). Effluent samples were collected continuously, and bromide concentrations were measured using a bromide probe (Cole Parmer, Vernon Hills, IL). A schematic diagram of the column apparatus is shown in Figure S1 of the Supporting Information (SI).

To assess in situ delivery and retention of S-PAC, a pulse (3.5 PV) of S-PAC suspension (1000 mg/L PAC + 5000 mg/L polyDADMAC) was introduced into a column containing water-saturated 40−50 mesh Ottawa sand at a flow rate of 0.12 mL/min using a Chemyx Nexus 3000 syringe pump (Stafford, TX), which was followed by flushing with 10 mM NaCl at the same flow rate to remove unretained PAC and polyDADMAC. Transport and retention of PAC was observed visually, and solid samples were collected at the conclusion of each experiment to measure the amount of retained PAC by carbon analysis. Baseline transport behavior of PFOA and PFOS in untreated 40−50 mesh Ottawa sand (negative control) was evaluated in a set of preliminary column studies by introducing a pulse (3.5 PV) of the PFOA or PFOS (100 μg/L) in 10 mM NaCl at a flow rate of 0.12 mL/min (pore-water velocity ≈ 1 m/day), followed by a pulse (3.5 PV) of 10 mM NaCl. Aqueous solutions containing either PFOS (100 μg/L) or PFOA (100 μg/L) and a background electrolyte (10 mM NaCl) were then injected into separate columns that had been treated with S-PAC at a flow rate of 0.12 mL/min. After approximately 20 PV, the influent concentration of PFOA or PFOS was increased from 100 μg/L to 20 mg/L to determine to maximum retention capacity of the treated sand. Effluent samples were collected continuously to monitor for PFOA and PFOS breakthrough. At the completion of each column experiment, sand was removed in 5 sections of approximately
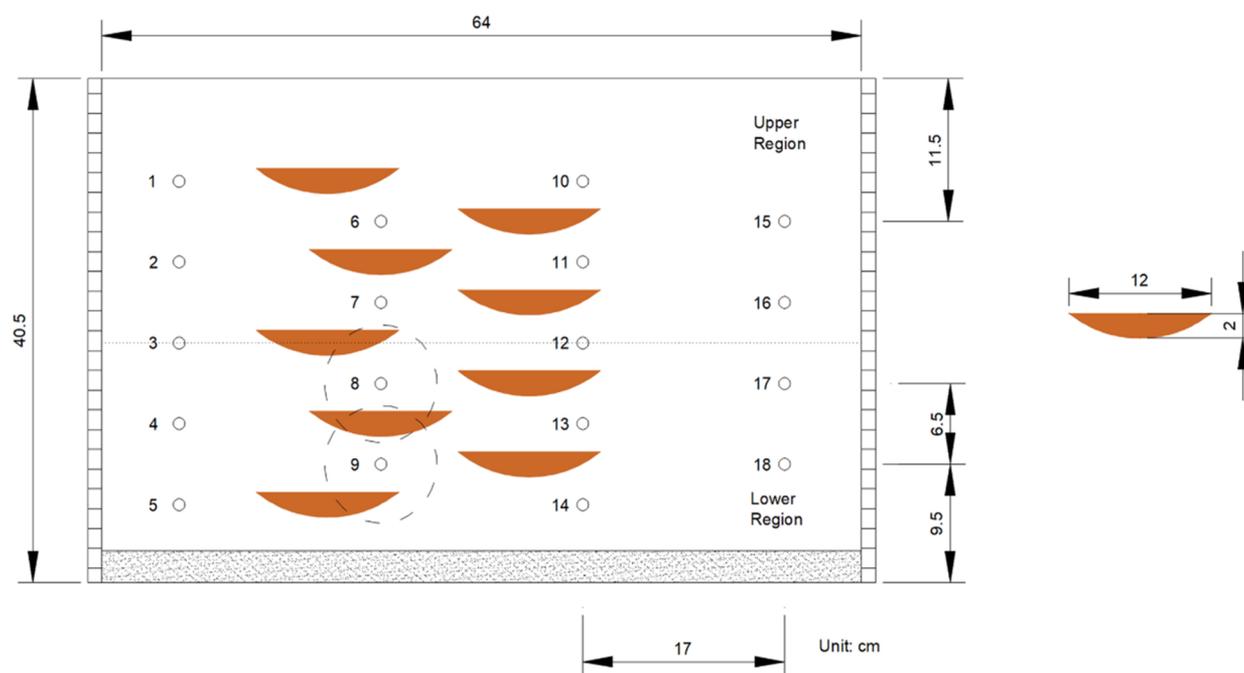
Figure 1. Schematic diagram of the aquifer cell showing the overall dimensions, location of injection and side ports, and size and location of lower-permeability lenses.

20 g each and analyzed for total carbon to obtain a PAC retention profile.

Aquifer Cell Experiment. An aquifer cell (64 cm length × 40.5 cm height × 1.4 cm internal thickness) was constructed using two pieces of glass separated by a stainless-steel frame. The interface between the frame and glass was sealed with rubber O-ring embedded in the notch on the frame. Stainless-steel screws along the two end plates and bottom boundary of the frame were used to secure the glass within the frame. The flow cell was packed under water-saturated conditions with 40−50 mesh Ottawa sand as the background porous medium. A layer of F-90 Federal fine sand, approximately 5 cm thick, was packed at the bottom of the aquifer cell to serve as a lower confining layer. Soil was collected from a Department of Defense facility located in the south-central United States within the Central Redbed Plains of the Central Lowland Physiographic Province.[38] The soil is classified as a silty sand derived from the Hennessey group and has a distinct red color due to the presence of ferric anhydride. The field soil was oven-dried at 105 °C, gently ground with a motar and pestle, sieved (ASTM 20-mesh, <850 μm) and then packed within the 40−50 mesh Ottawa sand as 9 separate arc-shape lenses, approximately 2 cm height ×12 cm length to create the heterogeneous domain. Open chambers (1.27 × 1.27 cm^2) located at each end of the aquifer cell were screened over the entire height of the flow cell. The influent and effluent wells were constructed from 0.64 cm outer diameter stainless steel tubing that was inserted into the screened end chambers. A schematic diagram of the packed flow cell, which had a PV of approximately 1.45 L, is shown in Figure 1. The front-side glass panel was fitted with 18, 2 mm diameter holes using a water jet milling machine. Small-bore borosilicate glass tubes were glued into each hole using silicone glue (Dow Corning Corporation, Auburn, MI). The side-ports were then capped with Grace ThermoRed Septa (Columbia, MD). A constant head reservoir was used to deliver the background electrolyte solution (10

mM NaCl) at a pore-water velocity of approximately 1.52 m/day. The influent solution flowed through stainless steel screens that were placed inside the influent chamber to promote uniform flow into the aquifer cell.

The aquifer cell was initially saturated with an aqueous solution containing 10 mM NaCl. After the flow rate stabilized, a nonreactive tracer test was carried out by injecting a 0.5 PV pulse of aqueous solution containing 10 mM NaBr and 20 mg/L fluorescein at flow rate of 2.4 mL/min (pore-water velocity of 1.52 m/day), followed by the background solution (10 mM NaCl). Images were collected every 20 min using an EOS Rebel T2 digital camera (Canon; Melville, NY). Effluent samples were collected in 50 mL polypropylene centrifuge tubes using a fraction collector. To create a permeable adsorption region within the aquifer cell, the S-PAC suspension (1000 mg/L PAC + 5000 mg/L polyDADMAC) was injected through side-ports 8 and 9 of the aquifer cell (Figure 1). Approximately 80 mL of S-PAC was injected into each side port at a flow rate of 0.08 mL/min to create treatment zone with a radius of approximately 5 cm. After the S-PAC injection, the background flow was resumed at a flow rate of 2.4 mL/min. The S-PAC suspension was not injected into the upper portion of the aquifer cell (ports 6 and 7), which served as an untreated control region. Solutions containing 50 μg/L PFOS, 50 μg/L PFOA, and 10 mM NaBr were then injected using a peristatic pump through side-ports 2 (upper region) and 4 (lower region) at a flow rate of 0.23 mL/min for 24 h (ca. 330 mL total injected volume). During the PFOA and PFOS injection, the background solution (10 mM NaCl) continued to flow through the aquifer cell at a flow rate of 2.4 mL/min to simulate a realistic injection scenario. Aqueous samples were collected from the effluent continuously and from down-gradient side-ports every 3 h.

Analytical Methods. Analysis of PFOA and PFOS, along with their corresponding ^{13}C-labeled internal standards, was
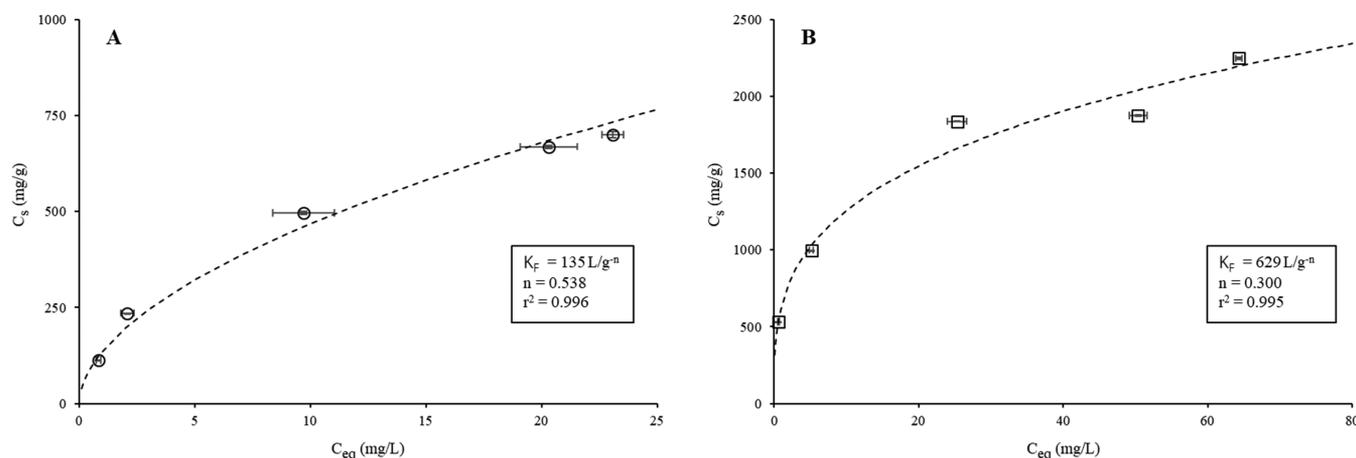
Figure 2. Adsorption of PFOA (A) and PFOS (B) on 100-mesh PAC and corresponding fits to the Freundlich adsorption model. Error bars represent standard deviation of mean for three replicates.

performed following the method of McCord et al.[45] Detection was achieved using a Waters ACQUITY ultra performance liquid chromatograph coupled with a Waters Xevo triple quadrupole mass spectrometer (UPLC−MS) (Waters Corporation, Milford, MA). The injection volume was 10 μL. Analyte separation was achieved on a Waters BEH C-18 column (1.7 μm dia., 2.1 × 50 mm^2) operated at a flow rate of 0.4 mL/min with an eluent gradient consisting of 2 mM ammonium acetate in water or methanol. Mobile phases were prepared using LC−MS grade water, methanol, and ammonium acetate purchased from Honeywell Burdick & Jackson (Muskegon, MI). The mass spectrometer was operated in negative electrospray ionization (ESI-) and multiple reaction monitoring (MRM) modes. Quantification was achieved using a 7-point calibration curve and ^{13}C labeled standards were used to verify compounds identity. Method detection limits for PFOA and PFOS were 5.16 and 33.2 ng/L, respectively. Additional instrument parameters are provided in the SI.

The carbon content of dried sand collected at the conclusion of each column study was measured using a Shimadzu total organic carbon analyzer equipped with a solid sample module (TOC-SSM, Columbia, MD). Bromide concentrations in aqueous samples collected from column and aquifer cell studies were quantified using a bromide specific probe (Cole Parmer, Vernon Hills, IL) using a 5-point standard curve. The hydrodynamic diameter of stabilized PAC was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS Analyzer (Malvern Instruments Ltd., Southborough, MA) operated in backscattering mode at an angle of 173°. To obtain scanning electron microscopy (SEM) images of Ottawa sand before and after S-PAC treatment, grains of sand were dried at 80 for 24 h and mounted on carbon adhesive tabs and attached to aluminum mounts (Electron Microscopy Sciences, Hatfield, PA). The mounted samples were sputtered with gold for 5 min and imaged on a Zeiss Leo 1530 VP SEM coupled with an Oxford Instruments 7426 Energy Dispersive Spectrometer (EDS) system.

■ RESULTS AND DISCUSSION

Batch Adsorption Studies. The results of batch adsorption tests conducted with PAC (DARCO, 100 mesh, < 149 μm) and either PFOA or PFOS are shown in Figure 2. Using a nonlinear least-squares regression procedure, the adsorption data were fit to the Freundlich adsorption model;

$$C_s = K_F C_w^n$$

where C_s is the solid-phase concentration, K_F is the Freundlich distribution coefficient, C_w is the concentration in water, and n is the Freundlich exponent. The Freundlich model is based on the premise that a range of adsorption sites exist with varying free energies, resulting nonlinear behavior.[46] The fitted values of K_F (135 and 629 L/g^{-n}) and n (0.54 and 0.30) obtained for PFOA and PFOS are similar to those reported in the literature for PAC.[31,47]

Column Studies. After each column was packed with 40−50 mesh Ottawa sand and completely saturated with water, a nonreactive tracer test was performed to assess hydrodynamic dispersion and confirm the pore volume, which was approximately 20 mL. A representative effluent breakthrough curve (BTC) for the tracer test is shown in Figure S2. Preliminary column experiments were undertaken to evaluate the injection of S-PAC (3.5 PV of 1000 mg/L PAC + 5000 mg/L polyDADMAC) and subsequent distribution of retained PAC after flushing with 3.5 PV of background solution (10 mM NaCl) at a flow rate of 0.12 mL/min (pore-water velocity ≈ 1 m/day). Representative photographs of the S-PAC injection sequence are shown in Figure S3, while the resulting PAC retention profile after flushing with the background solution are shown in Figure S4. Dynamic light scattering indicated that the particle size of the PAC ranged from approximately 70 nm to greater than 1 μm, with an average diameter of 225 nm (Figure S5). The total amount of PAC measured in each column ranged from 17.6 to 23.5 mg, equivalent to 24 to 32% of the injected PAC was retained. On the basis of the measured PAC carbon content of 85%, these values correspond to an average solid phase carbon content of 0.19 to 0.25 mg C/g dry sand. To further evaluate PAC retention by the solid phase, grains of quartz sand were collected from S-PAC treated and untreated (control) columns for SEM-EDS analysis. As shown in Figure S6, PAC was deposited in localized regions on the mineral surface, leading to a nonuniform or "patchy" coverage.

Following the establishment of retained PAC within each column, an aqueous solution containing either PFOA or PFOS was introduced at a flow rate 0.12 mL/min, which corresponds to a residence time of approximately 2.75 h. The resulting PFOA and PFOS effluent breakthrough curves (BTCs) are shown in Figure 3. Initially, the injected solution contained
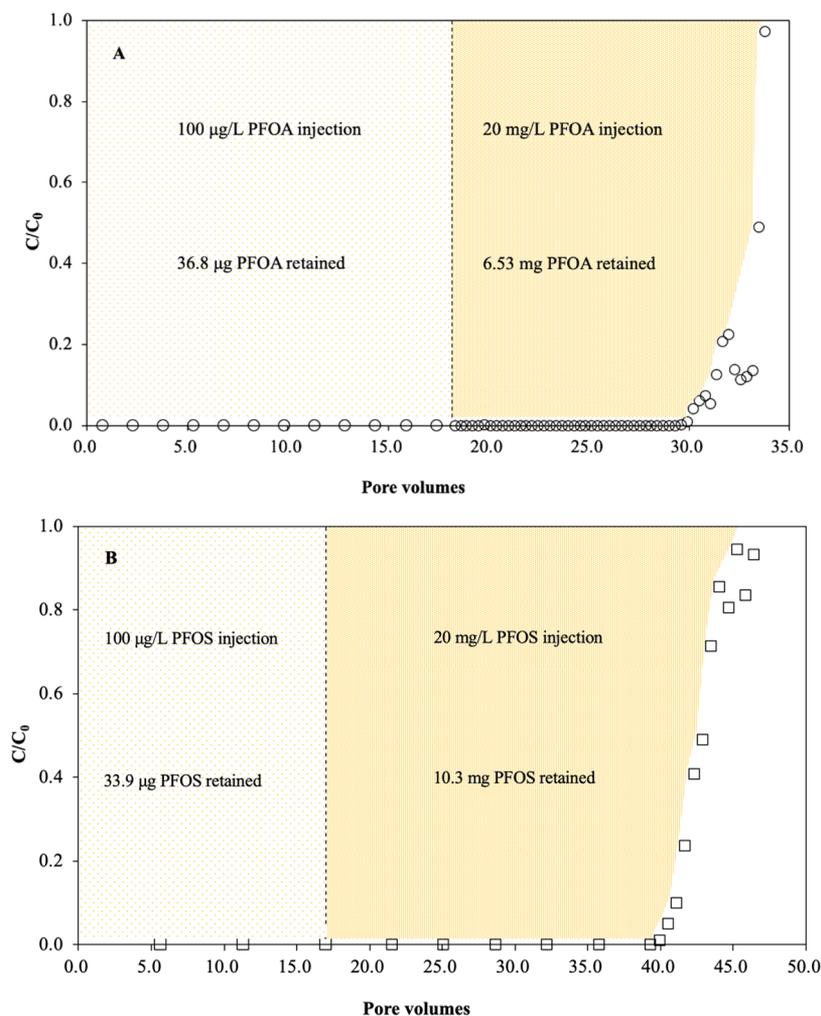
Figure 3. Effluent breakthrough curves obtained for the injection of either (A) PFOA or (B) PFOS (100 μg/L then 20 mg/L) in water-saturated columns containing S-PAC treated 40−50 mesh Ottawa sand. Shaded areas show the amount of PFOA or PFOS retained in the columns. The pore volume of each column was approximately 20 mL and the flow rate was 0.12 mL/min, yielding a residence time of 2.75 h.

100 μg/L of PFOA or PFOS in 10 mM NaCl, but no breakthrough was observed after approximately 15 PVs. Therefore, the influent concentration was increased to 20 mg/L PFOA or PFOS to evaluate the overall adsorptive capacity of S-PAC treated columns. For PFOA, breakthrough occurred at approximately 30 PVs, while PFOS breakthrough occurred after approximately 40 PVs. In contrast, breakthrough of PFOA or PFOS occurred after only 1 and 3 PVs, respectively, in columns packed with untreated 40−50 mesh Ottawa sand (negative control) at a similar flow rate (0.12 mL/min) and influent concentration (100 μg/L) (Figure S7). Upon the basis of the difference between the mass of PFOA or PFOS injected and the amount measured in the column effluent, a total of 6.57 mg of PFOA and 10.30 mg of PFOS were retained within the S-PAC treated columns (Figure 3). Thus, the addition of PAC with polyDADMAC increased PFOA and PFOS retention by 3 orders of magnitude compared to the untreated 40−50 mesh Ottawa sand. In these columns, 17.3 to 20.8 mg of PAC were retained, yielding overall adsorption capacities for PFOA and PFOS of 379.8 mg/g and 495.2 mg/g, respectively. In prior work, Aly et al.[37,38] reported that treating of 40−50 mesh Ottawa sand with a 5000 mg/L polyDADMAC solution increased the retention of PFOA or PFOS by 6 to 10 times, while treating a natural

soil with a 5000 mg/L polyDADMAC solution increased the retention of PFOA or PFOS by 4 to 6 times, respectively. On the basis of the results shown in Figure 3, injection of a solution containing 100 μg/L PFOA or PFOS into an S-PAC treated column would not be expected to result in break-through until 4060 and 6360 PVs, respectively, representing more than a 3 order of magnitude increase in retention capacity compared to untreated Ottawa sand (Figure S7) or a polyDADMAC treatment alone.[37]

Aquifer Cell Studies. The aquifer cell was configured to represent a heterogeneous formation with regions of high- and low-permeability porous media. In this scenario, the S-PAC suspension was injected into the lower high-permeability zone (ports 8 and 9) with the goal of reducing PFOA and PFOS mass flux from the cell, while causing minimal alteration to the local permeability field (Figures S8 and S9). A solution containing 50 μg/L PFOS, 50 μg/L PFOA, and 10 mM NaBr was introduced immediately upgradient of the upper control region (port 2) and the lower S-PAC treated region (port 4), and down-gradient side-port and effluent well samples were collected over a period of 70 h or approximately 7 total PVs. In the untreated upper region of the aquifer cell, both PFOA and PFOS appeared in the down-gradient side ports (6 and 7) within 5 and 10 h after injection (Figure 4A, C), respectively,
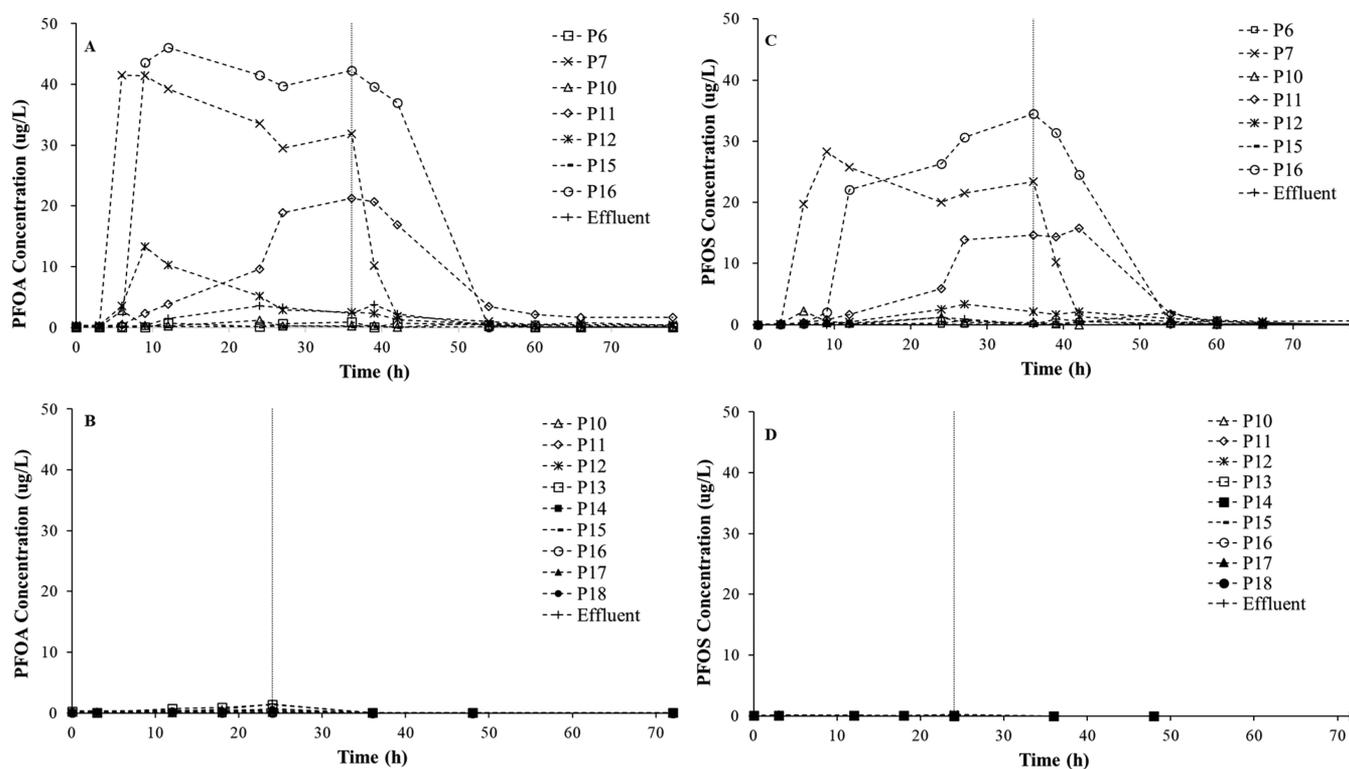
Figure 4. Aquifer cell side-port and effluent samples for PFOA in (A) upper untreated control region and (B) lower S-PAC treated region, and for PFOS in (C) upper untreated control region and (D) lower S-PAC treated region. A 260 mL pulse of solution containing 50 μg/L PFOS, 50 μg/L PFOA, and 10 mM NaBr (tracer) was injected through ports 2 and 4 immediately up-gradient from the control and S-PAC treated regions of the aquifer cell, respectively. The legend indicates the port number from which aqueous samples were collected.

and approached the injection concentration of 50 μg/L, consistent with appearance the nonreactive tracer in ports 6 and 7, which was injected simultaneously (Figure S10). Immediately down gradient of the S-PAC treated region of the aquifer cell, PFOA and PFOS concentrations were greatly reduced, with a maximum of 0.23 μg/L PFOS detected in side-port 12 at 24 h. Maximum PFOA concentrations of 1.36 μg/L and 0.63 μg/L were detected in ports 13 and 18 at 24 h, respectively (Figure 4C). On the basis of the effluent data collected over time, 85.5% and 99.2% of the injected PFOA and PFOS were retained, respectively. Despite the appearance of low concentrations of PFOA and PFOS in the effluent, the aquifer cell experiment demonstrated the ability of the S-PAC to create an in situ adsorptive zone in the higher permeability regions of a heterogeneous domain with minimal bypassing.

The results of this study provide promising proof-of-concept data to support the potential development and use of polymer-stabilized activated carbon for in situ treatment of PFAS-impacted groundwater. There are several important limitations of this work, however, that require further study, including assessments of long-term performance of injected activated carbon, effects of cocontaminants (e.g., PFAS mixtures, natural organic matter) on the adsorption capacity and desorption/release of PFAS from activated carbons, effects of solution conditions including pH and ionic species, and delivery and retention of activated carbon in lower permeability and heterogeneous porous media.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c00155.

Description of mass spectrometer parameters, schematic diagram of the column apparatus, nonreactive tracer BTC, photographs of S-PAC injection and retention 40−40 mesh Ottawa sand, S-PAC particle size distribution determined by DLS, SEM-EDS images of retained S-PAC, PFOA, and PFOS BTCs in control (untreated) columns, photographs of S-PAC injection in the aquifer cell, fluorescein aquifer cell tracer test, and aquifer cell nonreactive tracer side-port and effluent data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Kurt D. Pennell − *School of Engineering, Brown University, Providence, Rhode Island 02912, United States;* ⓞ orcid.org/0000-0002-5788-6397; Email: kurt_pennell@brown.edu

Authors

Chen Liu − *School of Engineering, Brown University, Providence, Rhode Island 02912, United States*

James Hatton − *Jacobs Engineering Group, Incorporated, Englewood, Colorado 80112, United States*

William A. Arnold − *Department of Civil, Environmental and Geo-Engineering, University of Minnesota, Minneapolis, Minnesota 55455, United States;* ⓞ orcid.org/0000-0003-0814-5469

Matt F. Simcik − *School of Public Health, University of Minnesota, Minneapolis, Minnesota 55455, United States;* orcid.org/0000-0001-9421-4023

■ REFERENCES

(1) Kissa, E. *Fluorinated Surfactants and Repellents*; CRC Press: Boca Raton, FL, 2001; Vol. 97.

(2) Moody, C. A.; Field, J. A. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environ. Sci. Technol.* 2000, 34 (18), 3864−3870.

(3) Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* 2001, 35 (7), 1339−1342.

(4) Lanza, H. A.; Cochran, R. S.; Mudge, J. F.; Olson, A. D.; Blackwell, B. R.; Maul, J. D.; Salice, C. J.; Anderson, T. A. Temporal monitoring of perfluorooctane sulfonate accumulation in aquatic biota downstream of historical aqueous film forming foam use areas. *Environ. Toxicol. Chem.* 2017, 36 (8), 2022−2029.

(5) de Vries, P.; Slijkerman, D. M. E.; Kwadijk, C. J. A. F.; Kotterman, M. J. J.; Posthuma, L.; de Zwart, D.; Murk, A. J.; Foekema, E. M. The toxic exposure of flamingos to per- and Polyfluoroalkyl substances (PFAS) from firefighting foam applications in Bonaire. *Mar. Pollut. Bull.* 2017, 124 (1), 102−111.

(6) Navarro, I.; de la Torre, A.; Sanz, P.; Porcel, M. A.; Pro, J.; Carbonell, G.; Martinez, M. d. l. A. Uptake of perfluoroalkyl substances and halogenated flame retardants by crop plants grown in biosolids-amended soils. *Environ. Res.* 2017, 152, 199−206.

(7) 3M. Phase-out Plan for POSF-Based Products. *Filtr. Sep.* 2000, AR-226−060, 37, 4.

(8) USEPA. *Office of the Federal Register*; Washington DC, 2012, 77, 26071−26101.

(9) USEPA. *Office of the Federal Register*; Washington DC, 2016, 81, 33250−33251.

(10) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* 2013, 47 (15), 8187−8195.

(11) Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* 2016, 3 (10), 344−350.

(12) Anderson, R. H.; Long, G. C.; Porter, R. C.; Anderson, J. K. Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties. *Chemosphere* 2016, 150, 678−685.

(13) Banks, R. E.; Smart, B. E.; Tatlow, J. C. *Organofluorine Chemistry: Principles and Commercial Applications*; Springer Science & Business Media, 2013.

(14) Giesy, J. P.; Kannan, K. Peer Reviewed: Perfluorochemical Surfactants in the Environment. *Environ. Sci. Technol.* 2002, 36 (7), 146A−152A.

(15) Liu, C. S.; Higgins, C. P.; Wang, F.; Shih, K. Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by persulfate activation in water. *Sep. Purif. Technol.* 2012, 91, 46−51.

(16) Ochoa-Herrera, V.; Sierra-Alvarez, R. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. *Chemosphere* 2008, 72 (10), 1588−1593.

(17) Cheng, J.; Vecitis, C. D.; Park, H.; Mader, B. T.; Hoffmann, M. R. Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in groundwater: Kinetic effects of matrix inorganics. *Environ. Sci. Technol.* 2010, 44 (1), 445−450.

(18) da Silva-Rackov, C. K. O.; Lawal, W. A.; Nfodzo, P. A.; Vianna, M. M. G. R.; do Nascimento, C. A. O.; Choi, H. Degradation of PFOA by hydrogen peroxide and persulfate activated by iron-modified diatomite. *Appl. Catal., B* 2016, 192, 253−259.

(19) Mitchell, S. M.; Ahmad, M.; Teel, A. L.; Watts, R. J. Degradation of Perfluorooctanoic Acid by Reactive Species Generated through Catalyzed H2O2 Propagation Reactions. *Environ. Sci. Technol. Lett.* 2014, 1 (1), 117−121.

(20) Park, S.; Lee, L. S.; Medina, V. F.; Zull, A.; Waisner, S. Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation. *Chemosphere* 2016, 145, 376−383.

(21) Bruton, T. A.; Sedlak, D. L. Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate under Conditions Representative of in Situ Chemical Oxidation. *Environ. Sci. Technol.* 2017, 51 (23), 13878−13885.

(22) Park, S.; Zenobio, J. E.; Lee, L. S. Perfluorooctane sulfonate (PFOS) removal with Pd0/nFe0 nanoparticles: Adsorption or aqueous Fe-complexation, not transformation? *J. Hazard. Mater.* 2018, 342, 20−28.

(23) Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Thelakkat Kochunarayanan, P.; Kalve, E.; Hurst, J. S.; Dasgupta, S. S.; Burdick, J. A review of emerging technologies for remediation of PFASs. *Remediation* 2018, 28 (2), 101−126.

(24) Liu, J.; Wang, N.; Szostek, B.; Buck, R. C.; Panciroli, P. K.; Folsom, P. W.; Sulecki, L. M.; Bellin, C. A. 6−2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. *Chemosphere* 2010, 78 (4), 437−444.

(25) Royer, L. A.; Lee, L. S.; Russell, M. H.; Nies, L. F.; Turco, R. F. Microbial transformation of 8:2 fluorotelomer acrylate and methacrylate in aerobic soils. *Chemosphere* 2015, 129, 54−61.

(26) Huang, S.; Jaffé, P. R. Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by Acidimicrobium sp. Strain A6. *Environ. Sci. Technol.* 2019, 53, 11410−11419.

(27) Espana, V. A. A.; Mallavarapu, M.; Naidu, R. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing. *Environ. Technol. Innov.* 2015, 4, 168−181.

(28) Bartell, S. M.; Calafat, A. M.; Lyu, C.; Kato, K.; Ryan, P. B.; Steenland, K. Rate of decline in serum PFOA concentrations after granular activated carbon filtration at two public water systems in

Ohio and West Virginia. *Environ. Health Perspect.* **2010**, *118* (2), 222−228.

(29) McNamara, J. D.; Franco, R.; Mimna, R.; Zappa, L. Comparison of activated carbons for removal of perfluorinated compounds from drinking water. *J. - Am. Water Works Assoc.* **2018**, *110* (1), E2−E14.

(30) Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C.; Dickenson, E. R. V. Treatment of poly-and perfluoroalkyl substances in US full-scale water treatment systems. *Water Res.* **2014**, *51*, 246−255.

(31) Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. *Water Res.* **2009**, *43* (4), 1150−1158.

(32) Carter, K. E.; Farrell, J. Removal of perfluorooctane and perfluorobutane sulfonate from water via carbon adsorption and ion exchange. *Sep. Sci. Technol.* **2010**, *45* (6), 762−767.

(33) Xiao, X.; Ulrich, B. A.; Chen, B.; Higgins, C. P. Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon. *Environ. Sci. Technol.* **2017**, *51* (11), 6342−6351.

(34) Higgins, C. P.; Luthy, R. G. Sorption of Perfluorinated Surfactants on Sediments†. *Environ. Sci. Technol.* **2006**, *40* (23), 7251−7256.

(35) Pan, G.; Jia, C.; Zhao, D.; You, C.; Chen, H.; Jiang, G. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. *Environ. Pollut.* **2009**, *157* (1), 325−330.

(36) Xiao, F.; Simcik, M. F.; Gulliver, J. S. Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. *Water Res.* **2013**, *47* (1), 49−56.

(37) Aly, Y. H.; Liu, C.; McInnis, D. P.; Lyon, B. A.; Hatton, J.; McCarty, M.; Arnold, W. A.; Pennell, K. D.; Simcik, M. F. In Situ Remediation Method for Enhanced Sorption of Perfluoro-Alkyl Substances onto Ottawa Sand. *J. Environ. Eng.* **2018**, *144* (9), 4018086.

(38) Aly, Y. H.; McInnis, D. P.; Lombardo, S. M.; Arnold, W. A.; Pennell, K. D.; Hatton, J.; Simcik, M. F. Enhanced adsorption of perfluoro alkyl substances for: In situ remediation. *Environ. Sci. Water Res. Technol.* **2019**, *5* (11), 1867−1875.

(39) Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *J. Hazard. Mater.* **2014**, *274*, 443−454.

(40) McGregor, R. In Situ treatment of PFAS-impacted groundwater using colloidal activated Carbon. *Remediation* **2018**, *28* (3), 33−41.

(41) Carey, G. R.; McGregor, R.; Pham, A. L. T.; Sleep, B.; Hakimabadi, S. G. Evaluating the longevity of a PFAS in situ colloidal activated carbon remedy. *Remediation* **2019**, *29* (2), 17−31.

(42) Senevirathna, S. T.; Tanaka, S.; Fujii, S.; Kunacheva, C.; Harada, H.; Shivakoti, B. R.; Okamoto, R. A comparative study of adsorption of perfluorooctane sulfonate (PFOS) onto granular activated carbon, ion-exchange polymers and non-ion-exchange polymers. *Chemosphere* **2010**, *80* (6), 647−651.

(43) McCleaf, P.; Englund, S.; Östlund, A.; Lindegren, K.; Wiberg, K.; Ahrens, L. Removal efficiency of multiple poly- and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. *Water Res.* **2017**, *120*, 77−87.

(44) Zhang, D.; Luo, Q.; Gao, B.; Chiang, S. Y.; Woodward, D.; Huang, Q. Sorption of perfluorooctanoic acid, perfluorooctane sulfonate and perfluoroheptanoic acid on granular activated carbon. *Chemosphere* **2016**, *144*, 2336−2342.

(45) McCord, J.; Newton, S.; Strynar, M. Validation of quantitative measurements and semi-quantitative estimates of emerging perfluoroethercarboxylic acids (PFECAs) and hexafluoroprolyene oxide acids (HFPOAs). *J. Chromatogr. A* **2018**, *1551*, 52−58.

(46) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2ⁿᵈ ed.; Wiley Interscience, 2003.

(47) Hansen, M. C.; Børresen, M. H.; Schlabach, M.; Cornelissen, G. Sorption of perfluorinated compounds from contaminated water to activated carbon. *J. Soils Sediments* **2010**, *10* (2), 179−185.