Sorption of Perfluorochemicals to Granular Activated Carbon in the Presence of Ultrasound

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Supporting Information

ABSTRACT: Perfluorochemicals (PFCs) are emerging pollutants of increasing public health and environmental concern due to their worldwide distribution, environmental persistence, and bioaccumulation potential. Activated carbon adsorption is an effective method to remove PFCs from water. Herein, we report on the sorption of four PFCs: perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), perfluorobutane sulfonate (PFBS), and perfluorobutanoate (PFBA), from deionized water (MQ) and landfill groundwater (GW) by granular activated carbon (GAC) in the absence and presence of 20 kHz ultrasound. In all cases, the adsorption kinetics were found to be well-represented by a pseudosecond-order model, with maximum monolayer sorption capacity and initial sorption rate values following the orders $q_e$ (PFOS) > $q_e$ (PFOA) > $q_e$ (PFBS) > $q_e$ (PFBA) and $v_0$ (PFOS) > $v_0$ (PFOA) > $v_0$ (PFBS) > $v_0$ (PFBA), respectively. The equilibrium adsorption was quantified by the BET multilayer adsorption isotherm, and the monolayer sorption capacity increased with increasing PFC chain length: $q_m$ (PFOS) > $q_m$ (PFOA) > $q_m$ (PFBA). The equilibrium PFC sorption constants, $q_e$ and $q_{mo}$ and the sorption kinetic constants, $v_0$ and $k_2$, were greater in Milli-Q water than in landfill groundwater with or without pretreatment, indicating competition for sorption sites by natural and cocontaminant groundwater organics. Ultrasonic irradiation significantly increased the PFC–GAC sorption kinetics, 250–900%, and slightly increased the extent of PFC equilibrium adsorption, 5–50%. The ultrasonic PFC–GAC sorption kinetics enhancement increased with increasing PFC chain length, suggesting ultrasound acts to increase the PFC diffusion rate into GAC nanoparticles.

INTRODUCTION

Perfluorochemicals (PFCs) have been widely used for over 50 years for commercial applications as stain repellents in textiles, leather, carpet, specialty paper, and cardboard and have also found industrial applications as cleaning agents, floor polishes, fire-fighting foams, photographic products, and semiconductor etching.1–3 An increase in PFC levels in humans and wildlife was observed up to the late 1990s.4,5 Long chained perfluorooctane sulfonate (PFOS, C$_{8}$F$_{17}$SO$_{3}^{-}$) and perfluorooctanoate (PFOA, C$_{8}$F$_{15}$COO$^{-}$) are the most widely detected anionic PFC surfactants in the biosphere because of their relatively large bioaccumulation factors.6,7 PFOS and PFOA were phased out of production in 2000 by 3M8 and have been replaced with the less bioaccumulative, shorter-chain compounds perfluorobutanoate (PFBA) and perfluorobutane sulfonate (PFBS).9 PFBA has been detected in arctic wildlife,10 but is generally below detectable levels.11,12

Because of PFCs’ strong carbon–fluorine (C–F) covalent bonds, most conventional chemical and microbiological degradation technologies are ineffective.13–16 Possible advanced PFC treatment technologies for aquatic PFCs include persulfate photolysis,17,18 reduction,19–25 ultrasonic irradiation,23,24 indirect photolysis,25–27 and membrane-based removal processes.28,29 However, the energy demand of these processes limits their use for the remediation of dilute (<ppm) PFC-containing waters such as those detected in wastewater treatment plant effluent.3,13,15

Adsorptive removal by granular activated carbon (GAC) offers a viable alternative for the removal of dilute anionic PFC surfactants from aqueous streams. GAC adsorption is widely applied in the removal of organic contaminants in wastewaters due to its efficacy, robustness, and low-cost.3M used a GAC column for PFOA sorption and determined that 6 mg of PFOA per 1 g of GAC was removed in their flowing system.30 Long-term batch experiments of PFC sorption by GAC yielded larger adsorption coefficients for PFOA and PFOS in the range of 100–200 mg of PFC per 1 g of GAC.31,32 However, the equilibration times of at least 1 week are not practical for capture and removal in a continuous-flow system. Another study evaluating the application of GAC to remove dilute PFCs from a
Ultrasound. Ultrasound irradiation has been observed to increase PFC sorption and desorption kinetics\(^\text{37,39}\) by enhancing mass transfer processes such as diffusion into micropores (\(d = 1\text{–}3\) nm). Ultrasonically mediated GAC adsorption kinetics for phenolic compounds have been reported to be increased 2\text{–}4 times with concomitant decreases in equilibrium adsorption by 10\text{–}30\%.\(^\text{38,40}\) Extent of ultrasonic mediated sorption is dependent upon both ultrasonic frequency and power.\(^\text{7,37}\) Ultrasonic irradiation has negligible effects on GAC structure in terms of pore size and surface area,\(^\text{38,41}\) indicating that the increased adsorption kinetics are primarily due to mass transfer enhancements.

Herein, we report on adsorptive removal of PFOS, PFBA, PFBS, and PFBA from Milli-Q water and from a landfill groundwater by granular activated carbon in the absence and presence of ultrasound. Our objectives are to determine the GAC adsorption kinetics and isotherms as (1) a function of the aqueous-phase constituents, (2) a function of PFC chain length, and (3) a function of ultrasonic irradiation.

**ExPERIMENTAL METHODS**

**Chemical Reagents.** Perfluorooctane sulfonate (PFOS-K\(^+\)), perfluorooctanoate (PFOS-\(\text{NH}_4^+\)) were provided by 3M. Perfluorobutryrate (PFBA-Na\(^+\)) and perfluorobutane sulfonate (PFBS-K\(^+\)) were purchased from Sigma Aldrich. Calgon F-600 granular activated carbon (GAC) was used as the adsorbent. Calgon Filtrasorb 600 granular activated carbon was selected from Calgon’s many activated carbon products for this study as it was designed to maximize the density of high-energy sorption sites for aqueous organic contaminants (www.calgoncarbon.com). Calgon F-600 was also utilized in previous GAC column experiments for the removal of PFCs from wastewater.\(^\text{30}\) BET surface area measurement was carried out using N\(_2\) as the adsorptive gas (Micromeritics Gemini 2360 VS). The Calgon F-600 had a measured surface area of 670 nm\(^2\) g\(^{-1}\). Ammonium acetate (>99%) and methanol (HR-GC, >99.99%) were obtained from EMD Chemicals Inc. Purified water (18.2 M\(\Omega\) cm\(^{-1}\) resistivity) was generated from a Millipore Milli-Q Gradient water purification system. The groundwater used in this study was sampled from beneath a landfill located within the city of Oakdale, MN. The groundwater characterization was described elsewhere,\(^\text{42}\) and a table of the components can be found in the Supporting Information, Table S1.

GAC Adsorption of PFCs. Sorption isotherm experiments were conducted in 50 mL polystyrene tubes that were loaded with the sorbent GAC and 50 mL of Milli-Q water (MQ) or landfill groundwater (GW) spiked with the PFCs to a concentration of 50 mg L\(^{-1}\). The PFC concentration of 50 mg L\(^{-1}\) was selected as a worst-case scenario, to allow for more chemically relevant experiments (e.g., this is the first study to observe multilayer formation) and for experimental design purposes. For example, in Figure 1, 20 mg of GAC was added to 50 mL of water for each experiment. If the PFC concentration were decreased to 50 \(\mu\)g L\(^{-1}\), then only 20 \(\mu\)g of GAC would be necessary to maintain the same sorbate-to-sorbent ratio, and we did not have the ability to accurately measure such a minute weight. The content of the polystyrene tubes was continuously agitated using a rotating mixer (RKVSD, ATR, Laurel, MD) at 30 rpm at ambient temperature (\(\sim\)293 K). At set time points, sample aliquots were withdrawn from the solution and diluted with methanol to a proper concentration range for analysis (ca. 50 ppb). The methanol-diluted sample was then filtered through a 0.22 \(\mu\)m syringe filter to remove any particulate. Methanol was utilized as a diluent to eliminate stratification, reduce matrix effects, and ensure complete PFC dissolution. Any remaining matrix effects are significantly reduced by the sample, and thus matrix, dilution factor that was generally in the range of 100\text{–}1000. The volume change due to withdrawal of sample was negligible, and we assume sorption to the container surface will also be negligible due to the relatively small total container surface area as compared to total GAC surface area.

The sorption kinetics experiments were completed by first adding 50 mL of a water sample, 2.5 mg of PFC, and 20 mg of GAC to a 50 mL centrifuge tube. The centrifuge tube was then attached to a rotating mixer at 30 rpm. For GAC sorption kinetics in the absence of ultrasound, aqueous PFC samples were taken once every 4\text{–}8 h for the first 24 h, then every 12 h for the next 24 h, and then once every 24 h for the remainder of the experiment that totaled 9\text{–}10 days. For GAC sorption kinetics in the presence of ultrasound, aqueous PFC samples were taken once every 15\text{–}30 min for 24 h. The shorter time-scale for the ultrasound experiments was utilized because the probe sonicator required frequent (~hourly) maintenance for optimal performance and was a noise hazard. Twenty-four hours was chosen for the ultrasound experiments because that was the time necessary for a similar extent of adsorption in the absence of ultrasound. All experiments were completed in at least duplicate under identical conditions. The sorption kinetic data were modeled using a pseudo second-order model as detailed in the text.

The sorption isotherm experiments were completed by first adding 50 mL of a water sample, 2.5 mg of PFC, and 1\text{–}100 mg of GAC to a 50 mL centrifuge tube. Each data point for an individual PFC represents a different mass of GAC. The centrifuge tube was then attached to a rotating mixer at 30 rpm. For GAC sorption isotherms in the absence of ultrasound, 240 h was allowed for sorption, and then the aqueous PFC concentration was quantified. For GAC sorption isotherms in the presence of ultrasound, 24 h was allowed for sorption, and then the aqueous PFC concentration was quantified. All data points were collected in at least duplicate under identical conditions. The PFC>GAC sorption isotherm data were modeled using a multilayer isotherm as detailed in the text.

GAC Adsorption of PFCs in the Presence of Ultrasound. Ultrasound-mediated GAC adsorption experiments of PFCs were performed in a 250 mL jacketed glass reactor at a frequency of 20 kHz using a Branson Sonifier Cell Disruptor 200. The ultrasonic transducer tip was immersed 2\text{–}3 cm below the
liquid surface. The solution was constantly mixed by a magnetic stirrer at the bottom of the reactor. The applied power density was 150 W L\(^{-1}\) with an average energy transfer efficiency of 30\%, as measured by calorimetry. The solutions were maintained at 293 K by water cooling during the course of the experiment. The ultrasonicator probe tip was frequently (∼hourly) sanded to smoothness to ensure optimal operation of the system. Because of this necessary maintenance and the ambient sonicator noise, shorter sorption times were utilized for the ultrasound experiments. In all experiments, the initial concentrations of PFOS, PFOA, PFBA, and PFBS were 50 mg L\(^{-1}\). To evaluate the effects of ultrasonication on the GAC structure, BET surface area measurements and adsorption isotherms were determined before and after extended (2 h) ultrasonication of GAC particles. The observed changes were negligible, consistent with previous studies.\(^{38,41}\) The volume change due to withdrawal of sample was negligible, and we assume sorption to the container surface will also be negligible due to the relatively small total container surface area as compared to total GAC surface area.

**Pretreatment of Landfill Groundwater.** Pretreatment of landfill groundwater containing PFCs by ultrasound and hydrogen peroxide, H\(_2\)O\(_2\), was performed in a 250 mL jacketed glass reactor. The H\(_2\)O\(_2\) was added to a concentration of 6 mM, and the solution was ultrasonically irradiated for 6 h at a calorimetric power density of 45 W L\(^{-1}\). The reaction temperature was maintained by jacket-cooling at 293 K. The pretreatment was completed to evaluate whether the PFC sorption could be increased by oxidation of the natural organic matter and organic cocontaminants. Initial experiments showed the effect of pretreatment on the removal efficacy to be relatively minor, so no further oxidative pretreatment experiments were completed.

![Figure 1. Time-dependent sorption of PFCs (a) PFOS; (b) PFOA; (c) PFBS; (d) PFBA) to GAC over a range of solution and ultrasonic conditions. [PFC]\(_i\) = 50 mg L\(^{-1}\); GAC = 0.4 g L\(^{-1}\). Open symbols are experiments in the absence 20 kHz ultrasound, closed symbols are in the presence 20 kHz ultrasound, and the line without symbols is ultrasound alone.](image)

<table>
<thead>
<tr>
<th></th>
<th>PFOS</th>
<th>PFOA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_2 \times 10^{-3}) (g mg(^{-1}) h(^{-1}))</td>
<td>(q_e) (mg g(^{-1}))</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td>Y 3.67 112.1 45.1</td>
<td>3.97 102.7 41.9</td>
</tr>
<tr>
<td>landfill groundwater</td>
<td>Y 3.45 105.4 38.3</td>
<td>3.78 98.8 36.9</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td>N 0.42 110.0 5.06</td>
<td>0.73 93.9 6.42</td>
</tr>
<tr>
<td>pretreated landfill groundwater</td>
<td>N 0.41 106.8 4.73</td>
<td>0.72 87.1 5.42</td>
</tr>
<tr>
<td>landfill groundwater</td>
<td>N 0.40 106.4 4.49</td>
<td>0.71 84.7 5.11</td>
</tr>
</tbody>
</table>

\(^{a}R^2 > 0.99\) for all regressions.
The sorption kinetics of the PFCs, PFOS, PFOA, PFBA, and PFBS, respectively. Ultrasound alone (no GAC) is represented by a line. GAC alone is represented by open symbols. GAC in the presence of ultrasound is represented by closed symbols. \( [\text{PFCs}]_0 \) represents the initial concentration of PFCs.

**RESULTS AND DISCUSSION**

**PFC–GAC Sorption Kinetics.** The sorption kinetics of the PFCs, PFOS, PFOA, PFBS, and PFBA, by GAC were studied.

<table>
<thead>
<tr>
<th>Aqueous Medium</th>
<th>Ultrasonic Irradiation</th>
<th>( k_2 \times 10^{-3} ) (g mg(^{-1}) h(^{-1}))</th>
<th>( q_e ) (mg g(^{-1}))</th>
<th>( v_0 ) (mg g(^{-1}) h(^{-1}))</th>
<th>( k_3 \times 10^3 ) (g mg(^{-1}) h(^{-1}))</th>
<th>( q_e ) (mg g(^{-1}))</th>
<th>( v_0 ) (mg g(^{-1}) h(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>Milli-Q water</td>
<td>Y</td>
<td>6.62</td>
<td>82.1</td>
<td>44.6</td>
<td>7.05</td>
<td>44.6</td>
<td>14.0</td>
</tr>
<tr>
<td>Landfill groundwater</td>
<td>Y</td>
<td>6.02</td>
<td>79.2</td>
<td>37.8</td>
<td>6.84</td>
<td>36.8</td>
<td>9.24</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td>N</td>
<td>1.38</td>
<td>78.6</td>
<td>8.52</td>
<td>2.65</td>
<td>46.4</td>
<td>5.72</td>
</tr>
<tr>
<td>Pretreated landfill groundwater</td>
<td>N</td>
<td>1.05</td>
<td>76.0</td>
<td>6.07</td>
<td>2.57</td>
<td>32.4</td>
<td>2.70</td>
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<tr>
<td>Landfill groundwater</td>
<td>N</td>
<td>0.92</td>
<td>75.1</td>
<td>5.19</td>
<td>2.49</td>
<td>28.9</td>
<td>2.09</td>
</tr>
</tbody>
</table>

* \( R^2 > 0.99 \) for all regressions.

**LC/MS Analyses of PFCs.** PFOS, PFOA, PFBA, and PFBS were analyzed using HPLC-MSD-Ion Trap (Agilent). The samples were placed into 750 \( \mu \)L polypropylene autosampler vials and sealed with a silicone septum crimp cap, and 20 \( \mu \)L of the methanol diluted sample was injected onto an Agilent 1100 LC for separation on Thermo-Electron Betalis C18 column (100 \( \times \) 2.1 mm, 5 \( \mu \)m particle size). An identical guard column was placed between the eluent pump and the sample injector. The flow rate was maintained at 0.3 mL min\(^{-1}\) with a mobile phase of 2 mM ammonium acetate in water (A) and methanol (B). The eluent gradient began at 5% B for the first minute, was ramped to 90% B over the next 10 min, and held at 90% B for 2.5 min, then ramped back to 5% B over 0.5 min and held for 3 min, and the run finished with a 3 min post-time. Chromatographically separated samples were analyzed by an Agilent Ion Trap in negative mode monitoring for the perfluorooctanesulfonate molecular ion (\( m/z = 499 \)), decarboxylated perfluorooctanoate (\( m/z = 369 \)), decarboxylated perfluorobutanoate molecular ion (\( m/z = 169 \)), and perfluorobutanesulfonate molecular ion (\( m/z = 299 \)). The nebulizer gas pressure was 40 PSI, while the drying gas flow rate and temperature were 9 L min\(^{-1}\) and 325 \( ^\circ \)C, respectively. The capillary voltage was set at +3500 V, and the skimmer voltage was −15 V. Quantification was completed by first producing a calibration curve using eight concentrations between 1 and 200 ppb fitted to a quadratic with \( X^2 \) weighting. Blanks and quality controls were utilized to ensure analytical robustness. A typical run sequence consisted of two blanks (always one methanol and one water), the calibration curve, two blanks, five samples, two blanks, five samples, two blanks, two quality controls (repeats of a calibration point), two blanks, and the sample-blank-sample-blank-QC-blank sequence was repeated until all sample runs were complete. If the PFC samples had peaks lower than the blank peaks, the samples were reanalyzed. If the quality controls deviated by >15% as compared to the initial calibration point, all samples afterward were reanalyzed.

**TOC Analyses of Landfill Groundwater.** Total organic carbon was determined (TOC, OI Analytical Aurora model 1030) with an autosampler (OI Analytical model 1096). A heated course catalyst bed was heated to 680 \( ^\circ \)C. Samples were acidified with HCl and purged for 1 min prior to injection with instrument grade air to remove any dissolved carbonate or bicarbonate. Samples were measured in triplicate. The as-received landfill groundwater contained between 10 and 20 mg L\(^{-1}\) TOC, which was mostly semivolatile organics such as acetone and ethers.

**Figure 2.** Pseudo second-order GAC sorption kinetic rate constants from eq 1 for PFOS, PFOA, PFBS, and PFBA under various solution and ultrasonic conditions. (a) \( v_0 \) (mg g\(^{-1}\) h\(^{-1}\)) and (b) \( k_2 \) (g mg\(^{-1}\) h\(^{-1}\) × 10\(^3\)).
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The sorption kinetic model, eq 1, fits the experimental data very well, $R^2 > 0.99$ in all cases. The fitted values for $q_e$, $k_2$, and $v_0$ can be found in Tables 1 (PFOS and PFOA) and 2 (PFBS and PFBA). The kinetic parameters, $k_2$ and $v_0$, are also plotted in Figure 2 for visual comparison. In all cases, 20 kHz ultrasound significantly increases the sorption kinetic coefficients by a factor of 2.5–9. This is similar to previous reports on ultrasound increasing sorption kinetics for phenolic species by factors of 2–7.38–40 However, ultrasound only has minor effects on the amount of PFC sorbed at equilibrium, $q_e$ which increase by a factor of 1.05–1.5, Tables 1,2 and Figures 3,4. This indicates that ultrasonic irradiation is primarily acting to increase PFC diffusion rates into GAC sorption sites, consistent with previous reports.39,40 The slight increases in equilibrium adsorption are consistent with negligible changes in GAC BET surface area after 6 h of 20 kHz ultrasound.

**PFC–GAC Equilibrium Sorption.** In Figure 3a,b, $q_e$ versus $C_e$ is plotted for PFOS (■), PFOA (△), PFBS (left-pointing △), and PFBA (○) sorption to GAC during mechanical mixing (30 rpm) and ultrasonic mixing (20 kHz, 45 W L$^{-1}$), respectively. Experiments were conducted in either Milli-Q water (open symbols) or landfill groundwater (closed symbols). Each data point is representative of an experiment completed under identical conditions in at least duplicate. The concentration is strongly dependent on the specie, $C_i$.

\[ q_i = \frac{k_2 q_e^2}{k_2} \]

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\[ q_e = k_2 q_e^2 + \frac{1}{k_2} \frac{1}{q_e} \]
pretreated groundwater was not evaluated because there was not a significant improvement due to pretreatment observed during the kinetic experiments. In all cases, isotherm data were obtained using an initial PFC concentration (C<sub>i</sub>) of 50 mg L<sup>-1</sup>.

The PFC–GAC equilibrium sorption data were fit using the Brunauer–Emmett–Teller (BET) isotherm, eq 3. The BET multilayer isotherm is an extension of the Langmuir monolayer isotherm.\(^{48}\)

\[
\frac{C_e}{(C_e - C_i)q_e} = \frac{1}{Bq_m} + \frac{(B - 1) C_e}{Bq_m} C_i
\]

\(q_e\) is the amount of pollutant sorbed per unit weight of sorbent at equilibrium (mg g<sup>-1</sup>), \(C_e\) is the equilibrium concentration of the solute in solution (mg L<sup>-1</sup>), \(q_m\) is the maximum monolayer sorption capacity (mg g<sup>-1</sup>), \(B\) is a constant, and \(C_i\) is the saturation concentration of the solute in solution (mg g<sup>-1</sup>). The BET isotherm parameters obtained by linear regression of the data can be found in Table 3. The experimental data were well fit by the BET model, and in all cases \(R^2 > 0.99\).

\(q_e\) values from eq 1 and the \(q_m\) values from eq 3 are plotted in Figure 4a and b, respectively. In all cases, the equilibrium PFC sorption, \(q_e\) values from the kinetic model are greater than monolayer PFC sorption values, \(q_m\), from the BET model. The kinetic sorption model, eq 1, did not take into account the multilayer PFC–GAC sorption.

The \(q_e\) and \(q_m\) values calculated in the present study for PFOS and PFOA sorption of 60–110 mg g<sup>-1</sup> are similar to values calculated in previous studies that range from 20 to 200 mg g<sup>-1</sup>.\(^{33,32}\) We did not observe a significant decrease in equilibrium sorption in the groundwater as previously reported,\(^{33}\) which may be due to the higher PFC concentrations used in this study, 50 mg L<sup>-1</sup> versus 10–100 ng L<sup>-1</sup>. All previous PFC sorption studies have utilized monolayer isotherms such as Langmuir\(^{48}\) or Freundlich to model the equilibrium adsorption. However, it is obvious from the experimental data in Figure 3 and the fits to eq 3 that the data presented here correspond to a BET multilayer adsorption isotherm. The possibility of a PFC multilayer sorption was suggested in a previous study to occur through hemi-micelle or micelle formation at the GAC surface.\(^{32}\) This is not unexpected because all the PFCs utilized in this study except PFBA may be considered surfactants.\(^{49,50}\) For example, attempts at measuring an octanol–water partitioning coefficient for PFOS were hindered by the formation of the third “fluoro” phase.\(^{23,25}\) A similar third “fluoro” phase may be responsible for the PFC multilayer sorption observed here.

The equilibrium monolayer PFC sorption obtained in the presence of ultrasound is greater than that obtained under mechanical mixing, even though the sorption time during ultrasonic irradiation (24 h) was only 10% of that under mechanical mixing (240 h). The equilibrium maximum monolayer adsorption capacity of PFOS, PFOA, PFBS, and PFBA in Milli-Q water increases by 36%, 27%, 20%, and 8% under ultrasonic irradiation, respectively. The equilibrium maximum monolayer adsorption capacity of PFOS, PFOA, PFBS, and PFBA in landfill groundwater increases by 28%, 11%, 39%, and 40% under ultrasonic irradiation, respectively. This is consistent with previous reports showing ultrasonic irradiation resulted in increases or minor decreases in equilibrium GAC sorption of species such as Cu<sup>2+</sup>/Pb<sup>2+</sup> (50%),\(^{52}\) phenol (30%),\(^{36}\) and chlorophenol (−10%).\(^{40}\) The increases in sorption capacity are relatively small as compared to increases in sorption kinetics (250–900%). The significantly greater effect of ultrasound on sorption kinetics versus sorption equilibrium supports the conclusion that ultrasound primarily acts to increase PFC diffusion into the GAC nanopores.

Ultrasonic GAC irradiation increases in sorption capacities may be due to increases in the number of GAC adsorption sites or due to the GAC adsorption sites present becoming more kinetically accessible. Here, we will argue for the latter. To determine if ultrasound increases the number of GAC adsorption sites, the BET surface area was measured before and after ultrasonic treatment of GAC in Milli-Q water with no PFCs present. The effect of ultrasound on the GAC BET surface area was negligible (i.e., before and after US irradiation the GAC BET surface area was measured to be 670 m<sup>2</sup> g<sup>-1</sup>), in agreement with previous reports.\(^{38,44}\) Thus, the influence ultrasound on the GAC surface area or pore structure is negligible. This result indicates that ultrasound makes the GAC adsorption sites more kinetically accessible. The ultrasonic enhancement of the sorption capacity is likely related to acoustically driven hydrodynamic (e.g., microstreaming and microjets) and thermal processes (e.g., surface cavitation increasing temperatures) resulting in faster diffusion into the GAC nanopores.\(^{39,40,53,54}\) These ultrasonic processes result in an improvement of both PFC sorption equilibrium and kinetics.

**PFC Sorption: Chain Length Effects.** From a visual inspection of Figures 2 and 4, it is obvious that PFC chain length effects both sorption kinetics and equilibrium. The compounds are listed in increasing order in the figures with their number of tail carbons for easy comparison (e.g., PFBA-C<sub>3</sub>). Equilibrium sorption constants increase with increasing number of tail carbons for both kinetic, eq 1, and BET isotherm, eq 3, calculations under all aqueous and mixing conditions. This is in agreement with studies of PFC sorption to various solids\(^{31,44}\) and was an expected result because the addition of a −CF<sub>2</sub>− unit results in the increase of PFC hydrophobicity thus increasing partitioning out of bulk water\(^{23,44,50}\) into the GAC.

### Table 3. BET Adsorption Isotherm Constants for PFC Adsorption onto Granular Activated Carbon (GAC) in the Presence and Absence of 20 kHz Ultrasound<sup>a</sup>

<table>
<thead>
<tr>
<th>Aqueous medium</th>
<th>Ultrasonic irradiation</th>
<th>PFOS (q_m) (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>B</th>
<th>PFOA (q_m) (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>B</th>
<th>PFBS (q_m) (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>B</th>
<th>PFBA (q_m) (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milli-Q water</td>
<td>Y</td>
<td>110.5</td>
<td>31.4</td>
<td>96.3</td>
<td>21.5</td>
<td>48.0</td>
<td>68.7</td>
<td>16.5</td>
<td>113.0</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td>N</td>
<td>81.3</td>
<td>42.9</td>
<td>76.1</td>
<td>21.1</td>
<td>40.0</td>
<td>134.2</td>
<td>15.3</td>
<td>340.1</td>
</tr>
<tr>
<td>Landfill groundwater</td>
<td>Y</td>
<td>85.3</td>
<td>31.7</td>
<td>70.6</td>
<td>63.4</td>
<td>45.0</td>
<td>66.2</td>
<td>9.3</td>
<td>104.8</td>
</tr>
<tr>
<td>Landfill groundwater</td>
<td>N</td>
<td>66.7</td>
<td>112.8</td>
<td>63.6</td>
<td>62.7</td>
<td>32.3</td>
<td>80.2</td>
<td>6.60</td>
<td>315.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> \(R^2 > 0.99\) for all regressions.
Comparison of the chain length dependence of GAC sorption kinetics is not as straightforward. In Figure 5, we have plotted \( A(US)/A(\text{mix}) \) versus chain length, where \( A(US) \) represents \( q_e \), \( v_0 \), and \( f_2 \) values in the presence of ultrasound, and \( A(\text{mix}) \) represents those values in the absence of ultrasound. Thus, \( A(US)/A(\text{mix}) \) is the ultrasound-mediated sorption kinetics enhancement factor. The ultrasound kinetic enhancement for groundwater samples is equal to or greater than Milli-Q samples, suggesting ultrasound may reduce kinetic competition of groundwater organics for GAC sorption sites. Interestingly, the kinetic enhancement generally increases with increasing PFC chain length. Because molecular diffusion is inversely proportional to molecular weight, \( D \propto (1/MW)^{1/2} \), the species with the slowest bulk diffusion constant is observed to have the greatest ultrasound sorption kinetics enhancement. This is consistent with the conclusion that ultrasound primarily mediates PFC diffusion into GAC nanopores (\( d = 0.5–3 \text{ nm} \)).

**CONCLUSIONS**

GAC is observed to be effective for the sorption of four PFCs, PFOS, PFOA, PFBS, and PFBA, from deionized water and landfill groundwater in the absence and presence of 20 kHz ultrasound. The adsorption kinetics were well-represented by a pseudo second-order model, with maximum monolayer sorption capacity and initial sorption rate values increasing with PFC chain length. The equilibrium PFC sorption constants and the sorption capacity also increased with increasing PFC chain length. The equilibrium PFC sorption constants enhancement in puriﬁed water than in landﬁll groundwater, indicating competition for sorption sites by natural and cocontaminant groundwater organics. Ultrasonic irradiation significantly increased the PFC–GAC sorption kinetics by a factor of 2.5–9, and slightly increased the extent of PFC equilbrium adsorption by a factor of 1.05–1.5. The extent of the ultrasonic PFC–GAC sorption kinetics enhancement increased with increasing PFC chain length, indicating ultrasound acts to increase PFC diffusion into the GAC nanopores. Thus, application of ultrasonic irradiation may improve the utility of GAC filters for the removal of PFCs from waste streams. For example, a municipal WWTP in Minnesota that also treats PFC industrial waste and groundwater containing PFCs has installed GAC filtration as a tertiary treatment. The GAC filter is effective for PFOS removal, >95%, but not as effective for shorter-chain PFC removal, 40–70%, resulting in continued PFC discharge to the Mississippi River. Although the liquid residence time of the WWTP GAC filter is unknown, it is likely less than days required for equilibrium sorption, indicating simultaneous ultrasonic irradiation could improve PFC removal efficacies. Future works should focus on optimizing the ultrasonic parameters such as frequency and power density to minimize energetic requirements, investigating how the PFCs are interacting with and sorbing to the GAC nanopores at a molecular level, and designing devices that can incorporate ultrasonic irradiation into conventional GAC columns.

**ASSOCIATED CONTENT**

Supporting Information. A table of the landfill groundwater constituents (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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