Chemisorption of Perfluorooctanoic Acid on Powdered Activated Carbon Initiated by Persulfate in Aqueous Solution

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S *Supporting Information*

ABSTRACT: Perfluorooctanoic acid (PFOA) is a perfluorocarboxylic acid that is difficult to treat by most conventional methods. As a result, it is often removed from solution by adsorption on powdered activated carbon (PAC), followed by incineration of the spent carbon. To provide a new approach for treatment, PFOA was exposed to sulfate radicals ($SO_4^{-\bullet}$) produced by thermolysis of persulfate ($S_2O_8^{2-}$) in the presence of PAC. Under acidic conditions, thermal activation of persulfate resulted in transformation of PFOA to shorter-chain-length perfluorinated compounds, as previously reported. However, when thermolysis of persulfate occurred under circumneutral pH conditions in the presence of PAC, a new removal pathway for PFOA was observed. Under these conditions, the removal of PFOA was attributable to chemisorption, a process in which PAC catalyzed persulfate decomposition and reacted with the transformation products to produce covalently bound PFOA. At PAC concentrations between 200 and 1000 mg/L and an initial PFOA concentration of 0.5 μM, covalent bonding resulted in removal of 10−40% of the PFOA. Under these conditions, the process resulted in removal of more than half of a more hydrophilic perfluoroalkyl acid (i.e., perfluorobutanoic acid, PFBA), which was greater than the amount of PFBA removed by physical adsorption on PAC. Although the high reaction temperatures (i.e., 80 °C) and relatively high doses of PAC used in this study may be impractical for drinking water treatment, this process may be applied to the treatment of these recalcitrant compounds in industrial wastewater, reverse osmosis concentrate, and other waters that contain high concentrations of PFOA and other perfluorocarboxylic acids.

Chemisorption of PFOA on PAC
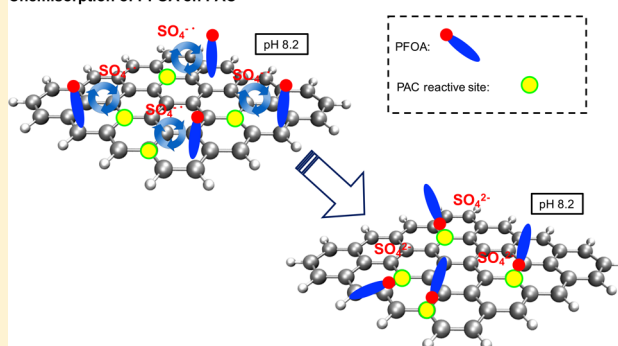
■ INTRODUCTION

Perfluorinated carboxylic acids (PFCAs) are a family of compounds that have been subjected to scrutiny due to their potential for bioaccumulation, their toxicological properties, and a lack of cost-effective treatment technologies.[1−6] Among the PFCAs, perfluorooctanoic acid (PFOA) has attracted the most concern because of its frequent detection in the environment.[7−11] Owing to its perfluorinated carbon backbone, PFOA is extremely stable and resistant to most conventional treatment technologies.[12−14] Several physical treatment technologies can remove PFOA from solution. For example, powdered activated carbon (PAC) can remove PFCAs, but the dose of powdered activated carbon needed is typically high, especially for the treatment of drinking water sources with trace PFCA contamination.[5,15−17] Granular activated carbon (GAC), typically used in a packed bed configuration, can be used to remove PFOA, but it must be refreshed frequently to avoid breakthrough.[18,19] In both cases, PFOA-contaminated solids are produced. Currently, incineration is the most common approach for disposing of spent activated carbon.[5]

Sulfate radical ($SO_4^{-\bullet}$) reacts with PFCAs by removing CF_2 groups to produce shorter-chain-length PFCAs.[5,20−22] A possible mechanism for transformation of PFOA by $SO_4^{-\bullet}$ has been proposed previously.[5,21,23,24] The transformation of PFOA is postulated to start with an electron transfer between $SO_4^{-\bullet}$ and a carboxylic group to generate perfluorooctanoic carboxyl radical (eq 1), which is transformed to perfluoroheptyl radical via decarboxylation (eq 2). Then, the perfluoroheptyl radicals react with oxygen to produce perfluoroheptylperoxy radicals (eq 3). Perfluoroheptyloxy radicals were formed in the reaction between two perfluoroheptylperoxy radicals (eq 4). This intermediate has two reaction pathways: carbonyl fluoride can leave to form perfluorohexyl radicals (eq 5) or hydrogen atom could be abstracted from a donor onto the perfluoroheptyloxy radical to form perfluoroheptanol (eq 6). The perfluorohexyl radical formed in the first pathway will enter
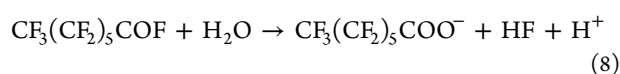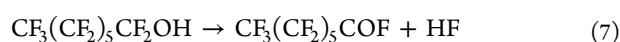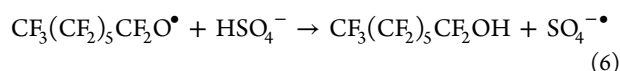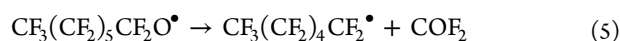
into another round of degradation after reacting with O_2. Perfluoroheptanol can be transformed to perfluoroheptanote via decomposition and hydrolysis (eqs 7 and 8).

$$CF_3(CF_2)_6COO^- + SO_4^{-\bullet} \rightarrow CF_3(CF_2)_6COO^\bullet + SO_4^{2-} \tag{1}$$

$$CF_3(CF_2)_6COO^\bullet \rightarrow CF_3(CF_2)_5CF_2^\bullet + CO_2 \tag{2}$$

$$CF_3(CF_2)_5CF_2^\bullet + O_2 \rightarrow CF_3(CF_2)_5CF_2OO^\bullet \tag{3}$$

$$CF_3(CF_2)_5CF_2OO^\bullet + CF_3(CF_2)_5CF_2OO^\bullet$$
$$\rightarrow 2CF_3(CF_2)_5CF_2O^\bullet + O_2 \tag{4}$$

$$CF_3(CF_2)_5CF_2O^\bullet \rightarrow CF_3(CF_2)_4CF_2^\bullet + COF_2 \tag{5}$$

$$CF_3(CF_2)_5CF_2O^\bullet + HSO_4^- \rightarrow CF_3(CF_2)_5CF_2OH + SO_4^{-\bullet} \tag{6}$$

$$CF_3(CF_2)_5CF_2OH \rightarrow CF_3(CF_2)_5COF + HF \tag{7}$$

$$CF_3(CF_2)_5COF + H_2O \rightarrow CF_3(CF_2)_5COO^- + HF + H^+ \tag{8}$$
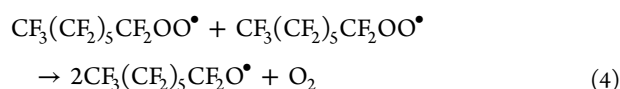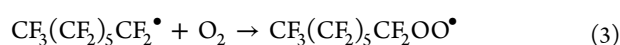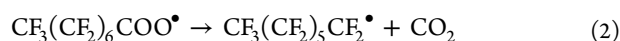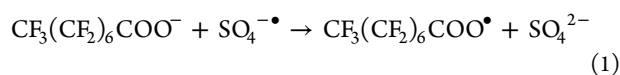
Although previous research has provided insight into the mechanism of PFOA transformation by $SO_4^{-\bullet}$, most studies were conducted in unbuffered systems in which production of acid by decomposition of peroxydisulfate ($S_2O_8^{2-}$) resulted in a large decrease in the solution pH shortly after the experiment began. Because the pH values changed over the course of the experiments, it is difficult to assess the importance of pH on the transformation process. It is possible that transformation by sulfate radicals only occurs under acidic conditions that might be impractical for treatment of water that contains bicarbonate and other buffers. Therefore, experiments conducted under controlled pH conditions are needed to assess the relevance of different approaches that might be employed to treat PFCA-contaminated waters.

In addition to its role as a sorbent, activated carbon is also a versatile catalyst or catalyst support that can enhance the rate at which oxidants (e.g., H_2O_2, O_3) are converted into radicals in advanced oxidation processes.[25,26] Because activation of persulfate involves cleavage of a peroxy bond, activated carbon might also enhance the role of radical generation from persulfate. If this catalytic reaction occurs on the surface of activated carbon in the presence of PFOA, it could serve as a means of transforming PFOA.

To obtain insight into the possibility of using $SO_4^{-\bullet}$ to treat PFOA under conditions relevant to treatment systems, PFOA was exposed to $SO_4^{-\bullet}$ produced by persulfate thermolysis in pH-buffered systems. The potential for using PAC to enhance removal of PFOA from water and to enhance the rate of persulfate activation was also assessed. By monitoring the concentration of PFOA and other PFCAs in solution and on PAC after methanol extraction, it was possible to distinguish PFOA transformation from incorporation into the PAC structure via chemisorption.

■ MATERIALS AND METHODS

Materials. Perfluorooctanoic acid (PFOA) and perfluorobutanoic acid (PFBA) were purchased from Sigma-Aldrich. PAC (type TOG, 50 × 200, Calgon Corp, Pittsburgh, PA) was used after washing with water and methanol twice. All analytical standards and internal standards were purchased from Wellington Laboratories. Potassium persulfate, HPLC-grade water, and Optima methanol were purchased from Fisher Scientific. All other chemicals and solvents were obtained from Fisher Scientific or Sigma-Aldrich. Falcon cell culture flasks, which consist of polystyrene, were used in all experiments. These flasks were chosen because they exhibited the smallest losses of PFCAs and were stable at elevated pH values and temperatures. All flasks were kept in the dark during the experiments.

PFOA Treatment Experiments. PFOA reactions with $S_2O_8^{2-}$ in the presence and absence of PAC were conducted in sealed 40 mL flasks under acidic, neutral, and basic pH conditions with reaction temperatures of 80 °C maintained with a constant-temperature water bath. For most experiments, the initial PFOA concentration was 0.5 μM and the PAC concentration was 200, 500, or 1000 mg/L. Concentrated sulfuric acid or a 150 mM sodium hydroxide solution was used to adjust the pH value to 1.0 or 13.0 for the acidic and basic condition experiments. For experiments conducted at pH 8.2, 100 mM of borate buffer [pH 8.2, $NaB(OH)_4/H_3BO_3$] was used. Five replicates were included in all experiments.

Each set of experiments included treatment experiments, homogeneous oxidation experiments, and adsorption control experiments. Solutions of specific pH values were prepared with HPLC-grade water and sulfuric acid, sodium hydroxide solution, or borate buffer and were preheated in a constant temperature water bath. When the temperatures of the solutions were stable, the other reactants (i.e., PFOA, $S_2O_8^{2-}$) were rapidly introduced into the solutions. For treatment experiments, the reaction was initiated by introduction of 4 mL of 100 mM $K_2S_2O_8$ stock solution (i.e., $[S_2O_8^{2-}]$ = 10 mM). To avoid the direct reaction between activated carbon and $S_2O_8^{2-}$ in the absence of PFOA, the PAC stock suspension solution (10 g/L) was added into the solution before the introduction of the $K_2S_2O_8$ solution. Adsorption control experiments without added $S_2O_8^{2-}$ were conducted to assess the role of persulfate in PFOA removal under neutral pH conditions. To investigate the role of activated $S_2O_8^{2-}$ and oxidative free radicals on PFOA degradation, homogeneous oxidation experiments were conducted in the absence of activated carbon.

Another set of experiments was conducted with sequential additions of persulfate to obtain insight into the effect of pH on PFOA removal in the presence and absence of PAC. Borate buffer [100 mM, pH 8.2, $NaB(OH)_4/H_3BO_3$] was used to maintain the pH under the same reaction conditions used in the buffered treatment experiment. A 400 μL portion of 1 M persulfate stock solution (i.e., the initial concentration of $S_2O_8^{2-}$ was 10 mM) was introduced into the reactor every 3 h. Due to the generation of sulfuric acid from persulfate decomposition, the pH began to drop after the buffer capacity of the solution was exceeded. Thus, basic or circumneutral conditions only existed when the first few aliquots of persulfate decomposed. Samples (i.e., 100 μL) were collected prior to pH measurement and addition of additional persulfate.

To gain insight into the occurrence of covalent binding with PFCAs that have less affinity for PAC, experiments were conducted with PFBA.[27] These experiments were conducted with an initial concentration of PFBA of 0.5 μM, 1000 mg/L PAC, and an initial $S_2O_8^{2-}$ concentration of 10 mM. The solution pH was maintained at 8.2 with 100 mM borate buffer.

Extraction of PFCAs from PAC. Methanol was used both to extract organic compounds (e.g., PFOA and transformation products) from PAC and to scavenge any radicals produced

after sample collection. To recover PFCAs from PAC, 900 μL of methanol was added to a 100 μL sample aliquot in a 1.5 mL polypropylene mini-centrifuge tube. Following collection, the mixture was shaken at 30 °C in an incubator overnight. The mixture was vigorously shaken on a vortex for 1 h prior to separating the PAC from the liquid with a high-speed centrifuge operated at 20 800g for 5 min. After centrifuging, the supernatant was analyzed by HPLC/MS−MS. This method achieved complete recovery of PFOA in adsorption control experiments (without persulfate).

Recovery of Covalently Bound PFCAs. In an effort to break the bond between the covalently bound PFCA and the sorbent, exhausted PAC that had been extracted with methanol was subjected to treatment with hydroxyl radical (OH$^\bullet$). To obtain exhausted PAC samples, treatment experiments with 2.5 μM PFOA, 500 mg/L PAC, 10 mM $S_2O_8^{2-}$, and 100 mM borate buffer (pH 8.2) were conducted. As a control, adsorption was measured in the absence of $S_2O_8^{2-}$. One-milliliter samples were added to 19 mL of methanol and centrifuged to recover the physically adsorbed PFCAs. After methanol extraction, the PAC was dried under nitrogen at room temperature and resuspended in a 10 mL mixture solution of 60 mM $S_2O_8^{2-}$ and 0.125 mM NaOH and heated to 80 °C for 3 h. Under these conditions, any $SO_4^{-\bullet}$ produced from thermolysis of $S_2O_8^{2-}$ was converted to OH$^\bullet$. After treatment by OH$^\bullet$, the sample was dried under nitrogen at room temperature and extracted with methanol to recover the covalently bound PFOA.

Analytical Methods. PFOA and other PFCAs were quantified on an Agilent 1200 HPLC coupled with an Agilent 6410 triple quadrupole mass spectrometer operating in the negative electrospray ionization mode as described previously.[28,29] Prior to the quantification analysis, methanol extraction was applied to all samples.

The concentration of $S_2O_8^{2-}$ was determined by the KI colorimetric method on a Lambda UV spectrophotometer (PerkinElmer Inc.).[30]

To assess the form of PFOA associated with the PAC surface, PAC that had been used for treatment experiments under circumneutral pH conditions was analyzed using a LEO 439 scanning electron microbe (SEM) coupled with a Princeton Gamma-Tech energy dispersive X-ray (EDX) spectrometer. Before characterization, the PAC samples were extracted with methanol and then dried at 50 °C twice to remove all physically adsorbed PFOA from the PAC.

■ RESULTS AND DISCUSSION

Treatment of PFOA by Persulfate in the Presence and Absence of PAC. The presence of 200 mg/L of PAC increased the rate of persulfate decomposition [Figure S1, Supporting Information (SI)]. The promoting effect of PAC on $S_2O_8^{2-}$ decomposition was greater under circumneutral and basic pH conditions. In the presence of 200 mg/L PAC, more than 70% of the initial 10 mM $S_2O_8^{2-}$ disappeared after 3 h compared to 45% in the absence of PAC under circumneutral pH conditions. Due to acid catalysis, PAC only slightly increased the rate of persulfate decomposition under acidic pH conditions.

Results of previous studies suggest that $SO_4^{-\bullet}$ is capable of transforming PFCAs into shorter-chain-length PFCAs via sequential cleavage of carbon−carbon bonds.[5,20,21,31] However, these studies did not specifically address the effect of pH on the reaction. For experiments conducted under acidic pH

conditions (i.e., pH 1.0), we observed the transformation of PFCAs into shorter-chain-length PFCAs irrespective of the presence of PAC (Figure 1). After 3 h, the PFOA concentration
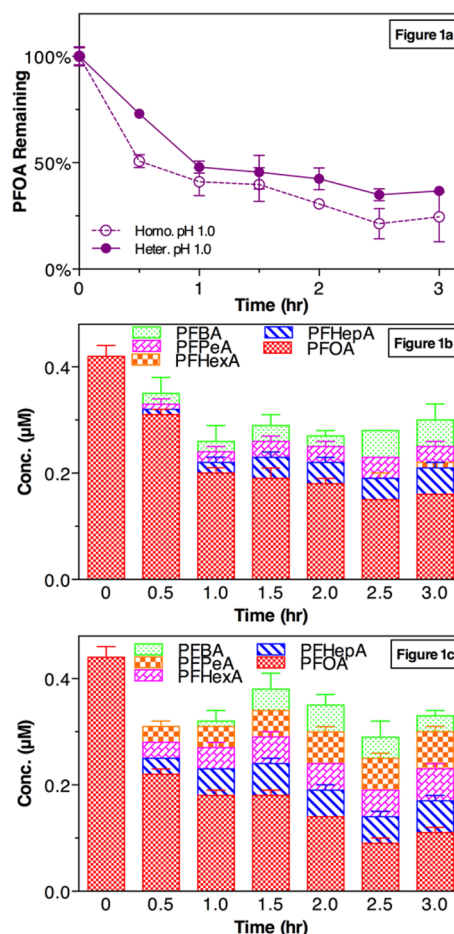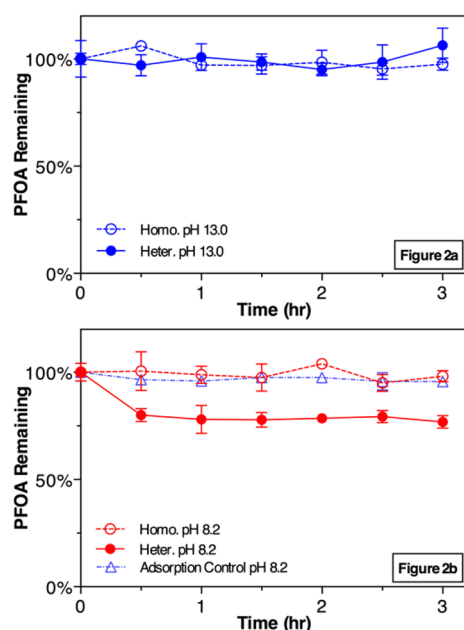

Figure 1. PFOA after exposure to persulfate in the presence and absence of PAC at 80 °C under acidic conditions. Part a shows the results of PFOA removal in homogeneous and heterogeneous treatments under acidic condition. Parts b and c show PFOA transformation into shorter-chain-length PFCAs in homogeneous and heterogeneous systems, respectively. Initial conditions: 0.5 μM PFOA and 10 mM $S_2O_8^{2-}$, and the concentration of PAC in the heterogeneous system was 500 mg/L.

decreased by approximate 80% in the homogeneous system under acidic condition. Shorter-chain-length PFCAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHexA), and perfluoroheptanoic acid (PFHepA), accounted for approximately 65% of the PFOA loss (Figure 1b). In the heterogeneous system under acidic conditions, the PFOA concentration decreased by 60% with shorter-chain-length PFCAs accounting for approximately 50% of the PFOA loss (Figure 1c). Due to acid catalysis at pH values below 3, $S_2O_8^{2-}$ decomposes through an unsymmetrical fission (eq 9) with production of SO_4, which rapidly hydrolyzes to peroxymonosulfuric acid (eq 10).[32−34] Then, peroxymonosulfuric acid is converted into $SO_4^{-\bullet}$ or OH$^\bullet$. Once $SO_4^{-\bullet}$ is generated, the process of sequential cleavage of carbon−carbon bonds is initiated under acidic condition in accordance with the mechanism described previously.

$$S_2O_8^{2-} + H^+ \rightleftharpoons HSO_4^- + SO_4 \qquad (9)$$
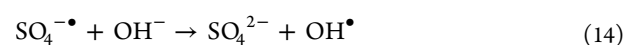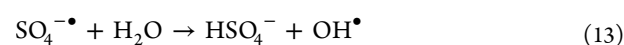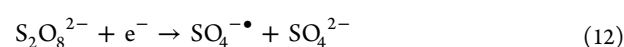
$$SO_4 + H_2O \rightarrow H_2SO_5 \tag{10}$$
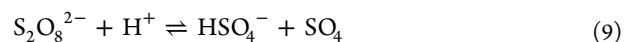
For experiments conducted under basic (i.e., pH 13.0) and circumneutral pH conditions (i.e., pH 8.2), PFOA loss accompanied by the production of shorter-chain-length product was not observed (Figure 2). At pH 13.0, no loss of PFOA was


Figure 2. PFOA after exposure to persulfate in the presence and absence of PAC at 80 °C under basic and circumneutral pH. Parts a and b show the results of PFOA removal in homogeneous and heterogeneous treatments under basic and circumneutral conditions, respectively. Initial conditions: 0.5 μM PFOA and 10 mM $S_2O_8^{2-}$, and the concentration of PAC in the heterogeneous system was 500 mg/L.

observed in the presence or absence of PAC. Under circumneutral pH conditions, the concentration of PFOA decreased by about 20% in the presence of PAC, but the concentration only decreased during the first 30 min, and no shorter-chain-length PFCAs were detected. In adsorption control experiments conducted without added $S_2O_8^{2-}$ under circumneutral pH conditions, the concentration of PFOA did not change (i.e., all of the PFOA was recovered after the methanol extraction). In heterogeneous systems under circumneutral pH conditions, PAC can enhance $S_2O_8^{2-}$ decomposition by serving as an electron donor (eq 12). In addition to reacting with organic compounds, $SO_4^{-\bullet}$ can also react with H_2O (eq 5) and hydroxide ion (eq 6) to form $OH^{\bullet}$.[35−37]

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{-\bullet} \tag{11}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{-\bullet} + SO_4^{2-} \tag{12}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + OH^{\bullet} \tag{13}$$

$$SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \tag{14}$$

Due to the high concentrations of hydroxide ion at pH 13.0, reaction 14 was predominant and $SO_4^{-\bullet}$ was rapidly converted into $OH^{\bullet}$ after generation.[35] Under circumneutral pH conditions, a smaller fraction of the $SO_4^{-\bullet}$ was converted into $OH^{\bullet}$ via reactions 13 and 14.[33,38] Although $OH^{\bullet}$ is also a strong oxidant, it mainly reacts by hydrogen abstraction and cannot transform PFOA.[39]

To further study the effect of pH conditions on treatment of PFOA by persulfate, a set of experiments was conducted with sequential addition of 400 μL of 1 M $S_2O_8^{2-}$ solution in the presence and absence of PAC (Figure 3). A 10 mM aliquot of $S_2O_8^{2-}$ solution was sequentially added every 3 h. Under these conditions, the pH decreased after neutralization of the borate buffer (Figure 3d). The pH change in the homogeneous and
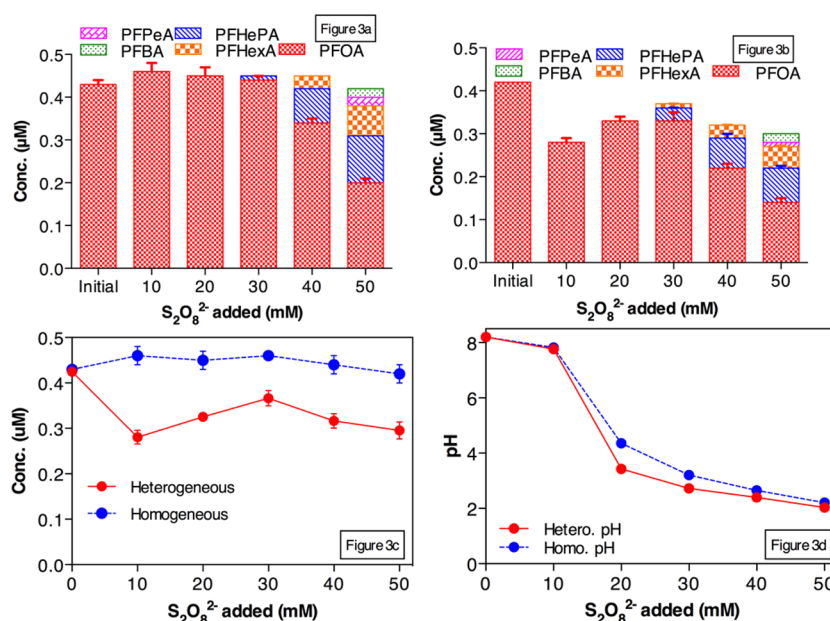
Figure 3. PFOA treatment by sequential addition of persulfate in the presence and absence of PAC. Parts a and b show PFOA conversion into shorter-chain-length PFCAs in the homogeneous and heterogeneous systems, respectively. Part c shows total PFCA concentration in the homogeneous and heterogeneous systems. Part d shows pH value variations of both reaction systems. Initial conditions: 0.5 μM PFOA, 10 mM $S_2O_8^{2-}$, and 100 mM pH 8.2 borate buffer, and concentration of PAC in heterogeneous experiments was 500 mg/L. Addition of 400 μL of 1 M $S_2O_8^{2-}$ stock solution was applied every 3 h.

heterogeneous systems were similar. For the experiments conducted in the absence of PAC, the concentration of PFOA did not change until the third aliquot of persulfate was added. At this time, the pH values of the homogeneous and heterogeneous systems had decreased to 3.2 and 2.7, respectively. After this aliquot of persulfate was activated, only PFHepA was detected as a transformation product in homogeneous system. After the next aliquot was added, other transformation products (i.e., PFHexA, PFPeA, and PFBA) were observed as the PFOA concentration decreased. In the heterogeneous system, approximately 25% of the PFOA was lost without the formation of any transformation products after addition of the first aliquot. Transformation products were not observed until the third aliquot of $S_2O_8^{2-}$ was added and the pH had dropped to 2.7.

Covalent Bonding of PFCAs on PAC. In the heterogeneous reaction systems under circumneutral pH conditions, the absence of shorter-chain-length products upon PFOA removal suggests a different reaction mechanism from that proposed in previous studies (Figure 2b). Our inability to recover the PFOA or its transformation products by methanol extraction could be attributable to incorporation of the compound into the PAC structure by formation of a covalent bond. The unique physiochemical properties of activated carbon are derived from the diverse functional groups located on the PAC (e.g., oxygen, sulfur).[40−43] Upon treatment with $S_2O_8^{2-}$, reactive radicals (e.g., $SO_4^{-•}$, $OH^•$) can react with PAC to form oxidized functional groups on the PAC surface. $SO_4^{-•}$ also might react with the functional groups on the activated carbon surface via a one-electron transfer reaction under circumneutral pH conditions. $SO_4^{-•}$ could also oxidize the carboxylate group of PFOA to form perfluoroalkylcarboxylate radicals or other perfluoroalkyl radicals. As activated carbon could physically adsorb PFOA from solution, these radicals could attach onto the surface of the activated carbon and react with the oxidized sites on the activated carbon to complete a coupling process, in which covalent bonds are formed. A similar phenomenon has been reported, in which phenolic compounds are removed by granular activated carbon under the oxic conditions and converted to species that cannot be recovered by extraction.[41,43−45]

EDX-SEM analysis was used to investigate incorporation of PFOA onto the PAC. Sulfur, silica, and aluminum were detected on the surface of all PAC samples. The EDX spectra of PAC from an adsorption control experiment (Figure S3, SI) was similar to that of the untreated PAC (Figure S2, SI), and no fluorine was detected. This result is in good agreement with complete recovery of PFOA when methanol was used to extract treated samples under acidic or basic pH conditions. For PAC from the experiments conducted under circumneutral pH conditions, fluorine was detected after methanol extraction (Figure S5, SI), indicating that the missing PFOA was most likely incorporated into the PAC structure by covalent bonds.

To determine if the missing PFOA was associated with the PAC structure by an ionic interaction, EDX-SEM analysis was also conducted on PAC pretreated with $S_2O_8^{2-}$ prior to introduction of PFOA at pH 8.2. After the sample was extracted with methanol, the EDX spectrum showed no fluorine, indicating that the compound was not associated with the PAC surface through ion exchange or some other ionic interaction (Figure S4, SI).

The methanol-extracted PAC from the experiments conducted under circumneutral pH conditions was also subjected to treatment with $OH^•$ in an effort to cleave the covalent bond. In this experiment, $S_2O_8^{2-}$ was added under basic pH conditions (pH >13) at 80 °C to convert the $S_2O_8^{2-}$ into $OH^•$. In this experiment, complete recovery of the missing PFOA was observed (Figure 4). The result further supports our hypothesis that the missing PFOA was incorporated into the activated carbon structure by covalent binding.
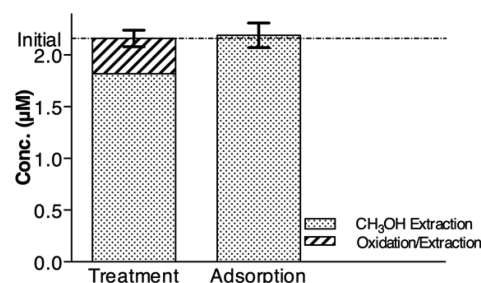
Figure 4. Recovery of PFCAs from used PAC in the presence (left, treatment) and absence (right, adsorption) of persulfate. PFOA was first recovered by extraction with methanol and then oxidation with hydroxyl radicals, followed by extraction with methanol.

To investigate the effect of PAC concentration on the removal of PFOA by covalent binding, experiments were conducted at three different PAC concentrations (Figure 5). As
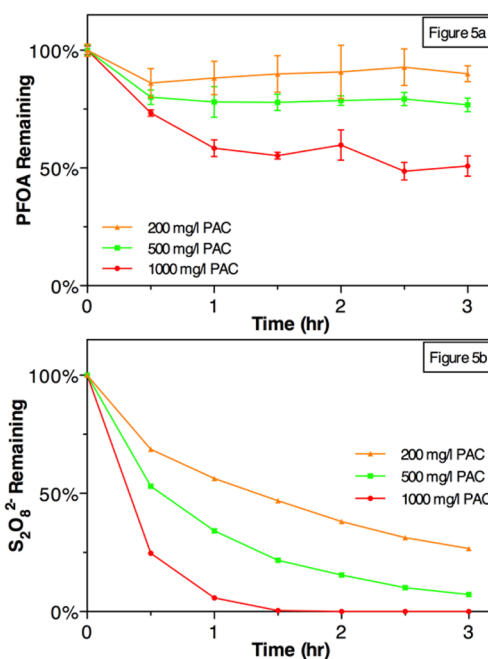

Figure 5. Effect of PAC concentration on PFOA removal by chemisorption (a) and persulfate decomposition (b). Initial conditions: 0.5 μM PFOA, 10 mM $S_2O_8^{2-}$, and 100 mM borate buffer (pH 8.2). The PAC concentrations of the reaction systems were 200, 500, and 1000 mg/L, respectively.

the PAC concentration increased from 200 to 1000 mg/L, the percentage of PFOA removed by covalent binding increased from 15% to 50% (Figure 5a). The higher concentration of PAC also increased the rate of $S_2O_8^{2-}$ decomposition (Figure 5b). In all of the experiments in which PAC was present, the loss of PFOA was completed within the first hour of the

reaction process, despite the fact that between 5% and 30% of the $S_2O_8^{2-}$ decayed during the final 2 h of the experiment.

PFBA is also a member of PFCA family that has a reactivity with $SO_4^{-\bullet}$ similar to that of PFOA. Although PFBA is more hydrophilic and difficult to remove by PAC adsorption, covalent binding still could be a promising treatment method. A similar phenomenon was observed for PFBA in the presence of persulfate and PAC (Figure 6). In the absence of persulfate,
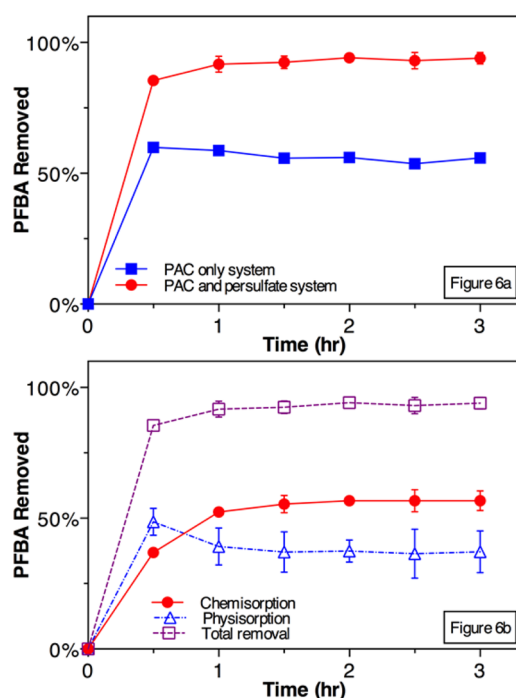
Figure 6. PFBA removal in the PAC adsorption control system and the PAC plus persulfate system. Part a shows PFBA removal in a system containing only the PAC and in PAC and persulfate chemisorption system. Part b shows PFBA removed by chemisorption and physical sorption in PAC plus persulfate reaction system. Initial conditions: 0.5 μM PFBA, 1000 mg/L PAC, and 10 mM and 100 mM borate buffer (pH 8.2). The initial concentration of $S_2O_8^{2-}$ in the PAC plus persulfate system was 10 mM.

approximately 60% of the PFBA was removed from the solution after 0.5 h at a PAC concentration of 1000 mg/L. All of the removed PFBA was completely recovered after extraction with methanol. In the presence of $S_2O_8^{2-}$, the amount of removed PFBA increased to 90% during the first hour of treatment. After methanol extraction, approximately 40% of the PFBA was recovered. Although we did not subject the PAC to oxidation to liberate chemisorbed PFBA, the PFBA that was not recovered was ascribed to covalent binding and not $S_2O_8^{2-}$ destruction.

Although treatment of PFOA by persulfate under circum-neutral pH conditions may not yet be an effective means of treating perfluorinated compound contaminated drinking water sources, the covalent binding described here represents a novel approach for PFCA removal under circumneutral pH conditions. Ultimately, this approach could be useful for treatment of water that contains higher concentrations of PFCAs. The method is also capable of removing PFCAs that have a low affinity for activated carbon (e.g., PFBA). Additional research is needed to identify approaches for increasing the

coverage or reactivity of the functional groups that react with $SO_4^{-\bullet}$ and PFCAs on the PAC surface.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00411.

Figures S1−S5 (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Conder, J. M.; Hoke, R. A.; de Wolf, W.; Russell, M. H.; Buck, R. C. Are PFCAs bioaccumulative? A critical review and comparison with regulatory lipophilic compounds. *Environ. Sci. Technol.* **2008**, *42* (4), 995−1003.

(2) Paul, A. G.; Jones, K. C.; Sweetman, A. J. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. *Environ. Sci. Technol.* **2009**, *43*, 386.

(3) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, Fate and Transport of Perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40* (1), 32−44.

(4) Renner, R. EPA finds record PFOS, PFOA levels in Alabama grazing fields. *Environ. Sci. Technol.* **2009**, *43* (5), 1245−1246.

(5) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Front. Environ. Sci. Eng. China* **2009**, *3* (2), 129−151.

(6) Buhrke, T.; Kibellus, A.; Lampen, A. In vitro toxicological characterization of perfluorinated carboxylic acids with different carbon chain lengths. *Toxicol. Lett.* **2013**, *218* (2), 97−104.

(7) Armitage, J. M.; MacLeod, M.; Cousins, I. T. Modeling the Global Fate and Transport of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct Sources Using a Multispecies Mass Balance Model. *Environ. Sci. Technol.* **2009**, *43* (4), 1134−1140.

(8) Post, G. B.; Cohn, P. D.; Cooper, K. R. Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: A critical review of recent literature. *Environ. Res.* **2012**, *116*, 93−117.

(9) Yeung, L. W. Y.; Miyake, Y.; Taniyasu, S.; Wang, Y.; Yu, H.; So, M. K.; Jiang, G.; Wu, Y.; Li, J.; Giesy, J. P.; et al. Perfluorinated Compounds and Total and Extractable Organic Fluorine in Human Blood Samples from China. *Environ. Sci. Technol.* **2008**, *42* (21), 8140−8145.

(10) 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.

(11) Gorrochategui, E.; Pérez-Albaladejo, E.; Casas, J.; Lacorte, S.; Porte, C. Perfluorinated chemicals: Differential toxicity, inhibition of aromatase activity and alteration of cellular lipids in human placental cells. *Toxicol. Appl. Pharmacol.* **2014**, *277* (2), 124−130.

(12) Goss, K.-U. The p KaValues of PFOA and Other Highly Fluorinated Carboxylic Acids. *Environ. Sci. Technol.* **2008**, *42* (2), 456−458.

(13) Goss, K. U.; Bronner, G.; Harner, T.; Hertel, M.; Schmidt, T. C. The partition behavior of fluorotelomer alcohols and olefins. *Environ. Sci. Technol.* **2006**, *40* (11), 3572−3577.

(14) Takagi, S.; Adachi, F.; Miyano, K.; Koizumi, Y.; Tanaka, H.; Watanabe, I.; Tanabe, S.; Kannan, K. Fate of Perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes. *Water Res.* **2011**, *45* (13), 3925−3932.

(15) Yu, J.; Hu, J. Adsorption of Perfluorinated Compounds onto Activated Carbon and Activated Sludge. *J. Environ. Eng.* **2011**, *137*, 945.

(16) 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.

(17) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*, 318−340.

(18) Thompson, J.; Eaglesham, G.; Reungoat, J.; Poussade, Y.; Bartkow, M.; Lawrence, M.; Mueller, J. F. Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia. *Chemosphere* **2011**, *82* (1), 9−17.

(19) 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.

(20) Hori, H.; Yamamoto, A.; Koike, K.; Kutsuna, S.; Osaka, I.; Arakawa, R. Persulfate-induced photochemical decomposition of a fluorotelomer unsaturated carboxylic acid in water. *Water Res.* **2007**, *41* (13), 2962−2968.

(21) Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S.; Kiatagawa, H.; Arakawa, R. Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant. *Environ. Sci. Technol.* **2005**, *39* (7), 2383−2388.

(22) Kutsuna, S.; Hori, H. Rate constants for aqueous-phase reactions of SO4− with C2F5C(O)O− and C3F7C(O)O− at 298 K. *Int. J. Chem. Kinet.* **2007**, *39* (5), 276−288.

(23) Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K; Ibusuki, T.; Kiatagawa, H; Arakawa, R. Decomposition of Environmentally Persistent Perfluorooctanoic Acid in Water by Photochemical Approaches. *Environ. Sci. Technol.* **2004**, *32*, 6118−6124.

(24) Hori, H.; Nagaoka, Y.; Murayama, M.; Kutsuna, S. Efficient decomposition of perfluorocarboxylic acids and alternative fluoro-chemical surfactants in hot water. *Environ. Sci. Technol.* **2008**, *42* (19), 7438−7443.

(25) Jans, U.; Hoigné, J. Activated Carbon and Carbon Black Catalyzed Transformation of Aqueous Ozone into OH-Radicals. *Ozone: Sci. Eng.* **1998**, *20* (1), 67−90.

(26) Sánchez-Polo, M.; von Gunten, U.; Rivera-Utrilla, J. Efficiency of activated carbon to transform ozone into OH radicals: Influence of operational parameters. *Water Res.* **2005**, *39* (14), 3189−3198.

(27) Goss, K.-U. The pKa Values of PFOA and Other Highly Fluorinated Carboxylic Acids. *Environ. Sci. Technol.* **2008**, *42* (2), 456−458.

(28) Houtz, E. F.; Sedlak, D. L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environ. Sci. Technol.* **2012**, *46* (17), 9342−9349.

(29) 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*, 8187.

(30) Liu, H.; Bruton, T. A.; Doyle, F. M.; Sedlak, D. L. In Situ Chemical Oxidation of Contaminated Groundwater by Persulfate: Decomposition by Fe(III)- and Mn(IV)-Containing Oxides and Aquifer Materials. *Environ. Sci. Technol.* **2014**, *48* (17), 10330−10336.

(31) Lee, Y.-C.; Lo, S.-L.; Chiueh, P.-T.; Liou, Y.-H.; Chen, M.-L. Microwave-hydrothermal decompositionof perfluorooctanoic acid in water by iron-activated persulfate oxidation. *Water Res.* **2010**, *44* (3), 886−892.

(32) Kolthoff, I. M.; Miller, I. K. The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium 1. *J. Am. Chem. Soc.* **1951**, *73* (7), 3055−3059.

(33) Johnson, R. L.; Tratnyek, P. G.; Johnson, R. O. Persulfate Persistence under Thermal Activation Conditions. *Environ. Sci. Technol.* **2008**, *42* (24), 9350−9356.

(34) Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. Rate constants and mechanism of reaction of sulfate radical anion with aromatic compounds. *J. Am. Chem. Soc.* **1977**, *99* (1), 163−164.

(35) Furman, O. S.; Teel, A. L.; Watts, R. J. Mechanism of Base Activation of Persulfate. *Environ. Sci. Technol.* **2010**, *44* (16), 6423−6428.

(36) Liang, C.; Wang, Z. S.; Bruell, C. J. Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere* **2007**, *66*, 106.

(37) Peyton, G. R. The free-radical chemistry of persulfate-based total organic carbon analyzers. *Mar. Chem.* **1993**, *41* (1−3), 91−103.

(38) Sra, K. S.; Thomson, N. R.; Barker, J. F. Persistence of Persulfate in Uncontaminated Aquifer Materials. *Environ. Sci. Technol.* **2010**, *44* (8), 3098−3104.

(39) Schröder, H. F.; Meesters, R. J. W. Stability of fluorinated surfactants in advanced oxidation processes—A follow up of degradation products using flow injection−mass spectrometry, liquid chromatography−mass spectrometry and liquid chromatography−multiple stage mass spectrometry. *J. Chromatogr. A* **2005**, *1082* (1), 110−119.

(40) Seredych, M.; Hulicova-Jurcakova, D.; Lu, G. Q.; Bandosz, T. J. Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance. *Carbon* **2008**, *46* (11), 1475−1488.

(41) Tessmer, C. H.; Vidic, R. D; Uranowski, L. J. Impact of Oxygen-Containing Surface Functional Groups on Activated Carbon Adsorption of Phenols. *Environ. Sci. Technol.* **1997**, *31*, 1872−1878.

(42) Dąbrowski, A.; Podkościelny, P.; Hubicki, Z.; Barczak, M. Adsorption of phenolic compounds by activated carbon—a critical review. *Chemosphere* **2005**, *58* (8), 1049−1070.

(43) Vidic, R. D.; Tessmer, C. H.; Uranowski, L. J. Impact of surface properties of activated carbons on oxidative coupling of phenolic compounds. *Carbon* **1997**, *35* (9), 1349−1359.

(44) Vidic, R. D.; Suidan, M. T.; Brenner, R. C. Oxidative coupling of phenols on activated carbon: impact on adsorption equilibrium. *Environ. Sci. Technol.* **1993**, *27* (10), 2079−2085.

(45) Vidic, R. D.; Suidan, M. T. Role of dissolved oxygen on the adsorptive capacity of activated carbon for synthetic and natural organic matter. *Environ. Sci. Technol.* **1991**, *25* (9), 1612−1618.