

FINAL REPORT

Thermal Decomposition of PFAS on Granular Activated Carbon: Kinetics, Mass Balance, and Reuse of Reactivated Carbon

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14. ABSTRACT In this limited-scope project, we symmetrically investigated the decomposition mechanisms of per- and polyfluoroalkyl substances (PFAS) laden on granular activated carbon (GAC) in various thermal processes. Adsorption to GAC has been frequently used at pilot- and full-scale operations to treat water contaminated by PFAS. The predominant residual from GAC systems is spent or exhausted carbon which contains elevated levels of PFAS. Our primary objectives were (1) investigate the thermal stability of PFAS; (2) determine thermal decomposition mechanisms (temperature and time requirements, thermodynamics, kinetics) of PFAS on spent GAC; (3) tailor GAC to facilitate the adsorption of hydrophobic PFAS anions from water and investigate the long-term performance of raw and tailored GAC after multiple cycles of adsorption-thermal reactivation; and (4) remove PFAS from the brine of nanofiltration and reverse osmosis by GAC. This limited-scope project has yielded numerous innovative and important findings, greatly enhancing our understanding of the thermal stability and degradation mechanisms of PFAS. Without this project, such insightful results would have					
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tests 3 and 4 correspond to a sample prepared in an aluminum foil tube during PPAO treatment; the specific surface areas of these samples were nearly identical. The aluminum foil tube was used to avoid the cracking issue of glass tubes (for scale-up purposes in the future study) and to understand the effect of air oxidation conditions.¹⁸ 61

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List of Acronyms

AFFF: aqueous film-forming foams
BET: Brunauer–Emmett–Teller (gas physical adsorption theory)
BDE: bond dissociation energy
BDL: below the detection limit
CO₂: carbon dioxide
DFT: density functional theory
DoD: Department of Defense
DW: distilled water
ESI: electrospray ionization
 E_A : Arrhenius activation energy
FTIR: Fourier-transform Infrared Spectroscopy
FTOH: fluorotelomer alcohol
FTSA: fluorotelomer sulfonic acid
 ΔG : adsorption free energy
GAC: granular activated carbon
GC: gas chromatography
GCMS: Grand canonical Monte Carlo
GC–Q-trap MSⁿ: gas chromatography coupled with ion trap mass spectrometry
 ΔH : enthalpy change for thermal decomposition
HCl: hydrochloric acid
HFPO-DA: hexafluoropropylene oxide dimer acid
HFPO-TA: hexafluoropropylene oxide trimer acid
HFPO-TeA: perfluoro-2,5,8-trimethyl-3,6,9-trioxadecanoic acid
HTT: heat treatment temperature
HRMS: high-resolution mass spectrometer
IC: ion chromatography
IPR: In Progress Review
 k : thermal phase-transition rate constant
 K_D : water–adsorbent distribution coefficient
MeOH: methanol
MS: mass spectrometry
N₂: nitrogen
NH₄Ac: ammonium acetate
N-Et-FOSSA: *N*-ethyl perfluorooctane sulfonamide acetate acid
NF: nanofiltration
NOM: natural organic matter
O₂: oxygen
PA: polyamide
PCS: porous carbonaceous sorbent
pDADMAC: polydiallyldimethylammonium chloride
PFAS: per- and polyfluoroalkyl substances
PFBA: perfluorobutanoate
PFBS: perfluorobutane sulfonate
PFCA: perfluoroalkyl carboxylate

PFDA: perfluorodecanoate
PFECA: perfluoroalkyl ether carboxylic acid
PFHpA: perfluoroheptanoate
PFHxA: perfluorohexanoate
PFHxS: perfluorohexane sulfonate
PFMPA: Perfluoro(3-methoxypropanoic) acid
PFMeUPA: 4-(Trifluoromethyl)hexafluoropent-2-enoic acid
PFNA: perfluorononanoate
PFO2HpA: Perfluoro-3,6-dioxaheptanoic acid
PFOA: perfluorooctanoate
PFOS: perfluorooctane sulfonate
PFPeA: perfluoropentanoate
PFPrA: perfluoropropionic acid
PFSA: perfluoroalkyl sulfonate
PFUnDA: perfluoroundecanoate
PI: principal investigator
PPAO: post-pyrolysis air oxidation
QA: quality assurance
QC: quality control
QToF-MS: quadrupole time-of-flight mass spectrometry
RO: reverse osmosis
SERDP: Strategic Environmental Research and Development Program
TD-Pyr-GC-MS: thermal desorption pyrolysis gas chromatography-mass spectrometry
TFA: trifluoroacetic acid
TGA: thermogravimetric analysis
UND: University of North Dakota
UPLC: ultrahigh pressure liquid chromatography
USEPA: United States Environmental Protection Agency
WR: water recovery

Keywords

Thermal decomposition, thermal degradation pathways, PFOA, PFOS, GenX, Legacy PFAS, Emerging PFAS, granular activated carbon, ion-exchange resin, reverse osmosis, high-resolution mass spectrometry, gas chromatography

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Abstract

INTRODUCTION AND OBJECTIVES

Adsorption to granular activated carbon (GAC) has been frequently used at pilot- and full-scale operations to treat water contaminated by per- and polyfluoroalkyl substances (PFAS). The predominant residual from GAC systems is spent or exhausted carbon containing elevated levels of PFAS. In this limited-scope project, we symmetrically investigated the decomposition mechanisms of PFAS laden on GAC in various thermal processes. Our primary objectives were focused on analyzing the thermal stability of PFAS, uncovering their decomposition pathways on spent GAC, tailoring adsorbents for enhanced PFAS adsorption in water, and removing PFAS in nanofiltration (NF) and reverse osmosis (RO) brine.

TECHNICAL APPROACH

We employed (1) thermogravimetric analysis to study the thermal stability of PFAS in both oxidative (O₂, CO₂, air) and inert (N₂) atmospheres, (2) a temperature-programmable two-zone tube furnace to simulate the commercial thermal reactivation process of spent GAC, (3) ultra-performance liquid chromatograph (UPLC) coupled with a quadrupole time-of-flight mass spectrometer (QToF-MS/MS) to identify ionizable decomposition products of PFAS on spent GAC heated at different temperatures and durations, and (4) thermal desorption-pyrolysis device (TD-Pyr) connected to a gas chromatograph (GC)-MS system to identify the gaseous thermal decomposition products of PFAS. We also investigated the modification of GAC and evaluated the performance of raw/tailored GAC for PFAS removal from natural waters and NF/RO brine with multiple adsorption-reativation-reuse cycles.

RESULTS

In this limited-scope project, our team has produced numerous novel results and yielded critical insights into PFAS thermal degradation mechanisms. We have detailed the necessary thermal conditions and elucidated the mechanisms of PFAS decomposition in both the thermal regeneration and thermal reactivation processes of GAC. For example, we found that 30-min thermal treatment of spent GAC at ≥ 300 °C achieved $\geq 99\%$ removal of perfluorooctanoate (PFOA). We discovered that the thermal stability of PFAS varies with its structure, particularly impacted by the number of perfluorinated carbons and the presence of ether groups in GenX. We evaluated various strategies for extracting PFAS from spent GAC and discovered that methanol, when amended with salt, yielded promising results in the efficient extraction of PFAS. Our research uncovered novel PFAS thermal degradation mechanisms, including random C-C scission. Many polar and nonpolar thermal degradation products of PFAS were detected and identified for the first time. GAC significantly influenced the decomposition kinetics and pathways of perfluoroalkyl carboxylates (PFCAs), such as PFOA, leading to markedly higher yields of shorter-chained intermediates at lower temperatures. Another breakthrough was the creation of modified sorbents with increased affinity for weakly hydrophobic PFAS anions, marking a substantial advancement in PFAS treatment methodologies. Finally, we explored the removal of PFAS using NF/RO methods and the treatment of PFAS-laden NF/RO brine. Our findings have been detailed in six papers published in prestigious journals, including *Water Research*, *Environmental Science & Technology*, and its sister journals.

BENEFITS

This limited-scope project has yielded numerous innovative and important findings, greatly enhancing our understanding of the thermal stability and degradation mechanisms of PFAS. Without this project, such insightful results would have remained elusive. Understanding PFAS degradation during the thermal regeneration and reactivation of GAC will enable more efficient and cost-effective contaminant removal methods. Identifying PFAS decomposition products will help assess potential environmental risks. This project's insights into PFAS thermal degradation mechanisms, particularly regarding the influence of structural variables and the efficacy of GAC, contribute to the scientific knowledge base. This groundwork is crucial for future explorations into low-temperature PFAS mineralization and the creation of novel treatment approaches. Therefore, the outcomes of this project hold significant real-world implications for addressing PFAS contamination, offering substantial benefits to society.

Executive Summary

INTRODUCTION

In April 2023, the U.S. Environmental Protection Agency (USEPA) identified GAC as one of the three promising treatment technologies for removing PFAS from drinking water sources. However, the regeneration and disposal of spent GAC remain a challenge, and understanding the thermal degradation of PFAS on spent GAC can help address this issue. Hence, this forward-thinking study funded in 2019 on the thermal degradation of PFAS on GAC had important real-world implications in addressing PFAS pollution and water treatment challenges. The primary motivations for conducting such a study were as follows.

- *Environmental and health concerns*: PFAS are a group of man-made chemicals used extensively in various industries since the 1940s. Due to their stability and persistence in the environment, PFAS can accumulate over time, posing potential risks to human health and the environment. A better understanding of the thermal degradation of PFAS on spent GAC could help develop more effective ways to manage and dispose of PFAS-contaminated materials, minimizing their environmental impact.
- *Regeneration and reactivation of spent GAC*: In column systems, which are common use cases in water facilities, GAC particles continuously capture PFAS until they reach capacity or become saturated. Reactivation and reuse of spent GAC by removing PFAS can help prolong its useful life and reduce the cost of water treatment. Studying the thermal degradation of PFAS on spent GAC could help identify optimal conditions for regeneration at low to moderate temperatures and reactivation at elevated temperatures, thereby enhancing the efficiency of these processes.
- *Minimization of secondary contamination*: Inadequate treatment and disposal of spent GAC can lead to secondary contamination, as PFAS can leach back into the environment. Understanding the thermal degradation of PFAS on spent GAC could help identify effective methods for breaking down these contaminants, reducing the risk of secondary contamination.
- *Cost-effective and sustainable solutions*: Developing cost-effective and sustainable methods for PFAS management is essential to address the growing environmental concerns associated with these contaminants. A study on the thermal degradation mechanisms of PFAS can contribute to the development of innovative thermal treatment methods.¹
- *Compliance with regulatory requirements*: USEPA recommends GAC as one of the three treatment technologies for removing PFAS from water. As regulatory agencies worldwide implement stricter standards for PFAS concentrations in drinking water and effluent discharges, water treatment facilities are under increased pressure to ensure compliance.² Understanding the thermal degradation of PFAS on spent GAC could help improve the effectiveness of GAC-based treatment methods and facilitate compliance with these regulations.²

This *limited-scope* project produced numerous innovative and noteworthy results, which have been published in prestigious journals, including *Water Research*, *Environmental Science & Technology*, and its sister journals.^{1, 3-7} These results are highly relevant to removing PFAS from water and decontaminating PFAS-laden GAC.

OBJECTIVES

This project has four objectives, including investigating the thermal stability of PFAS; determining the thermal decomposition mechanisms (temperature and time requirements, thermodynamics, kinetics) of PFAS on spent GAC; tailoring GAC to facilitate the adsorption of weakly hydrophobic PFAS anions; and removing PFAS from the brine of NF and RO by raw/tailored GAC.

We addressed the following major research questions in this limited-scope project:

- a) Did PFAS undergo thermal degradation at low and moderate temperatures, a question highly relevant to the GAC thermal regeneration process? This question had not been addressed in the literature prior to the results of this project.
- b) What were the required temperatures and durations for thermally destabilizing PFAS in different atmospheres, such as in CO₂ used for GAC thermal reactivation?
- c) How quickly were PFAS thermally degraded (kinetics) at a given temperature?

- d) What were the decomposition products of PFAS at low (e.g., 300 °C), moderate (e.g., 500°C), and high (e.g., ≥700 °C) temperatures in various atmospheres (N₂, CO₂, O₂, air)?
- e) What were the thermal decomposition pathways of PFAS in these atmospheres?
- f) What were the effects of GAC properties (e.g., pore size distribution and surface chemistry) and PFAS characteristics (e.g., chain length and functionality) on the GAC adsorption of PFAS?
- g) How could GAC be tailored to enhance the adsorption of negatively charged PFAS species, and what was the long-term performance of raw/tailored GAC after multiple cycles of adsorption and thermal reactivation?
- h) How effective was GAC in removing PFAS from NF/RO brine?"

TECHNICAL APPROACH

We first performed dynamic and isothermal TGA of the acid form of PFCAs and the potassium salt of perfluoroalkyl sulfonates (PFSAs). We then measured the thermal decomposition products of PFCAs and PFSAs using a thermal desorption–pyrolysis device (TD–Pyr) connected to a gas chromatograph (GC) connected to a mass spectrometer (MS).^{3,8} *Unless otherwise specified, PFCAs and PFSAs in the TGA and TD–Pyr–GC–MS experiments and subsequent results refer to the acid forms of PFCAs and the potassium salt forms of PFSAs, respectively.*

We prepared the PFAS-laden GAC samples in the laboratory using sorption experiments.^{3,4} The test solution was the natural surface river water. The river samples underwent a pretreatment mimicking standard drinking water treatment protocols. The adsorption of PFAS onto GAC (Filtrisorb 200, Calgon Carbon Corporation, PA) was assessed in sterile vials, rotated end-over-end to ensure even exposure and distribution. The apparent equilibrium reached within two days.

Following adsorption, the GAC was divided for further analysis and thermal treatment. One portion was freeze-dried and extracted with methanol containing ammonium acetate (NH₄Ac) to determine the initial PFAS mass on the GAC. The concentration of PFAS in the extract was measured using a UPLC coupled with an MS/MS. The other portion was heated in a tube furnace under inert gas flow to simulate the reactivation of spent GAC. In addition to GAC, we also included a few other porous adsorbents (see the main body of the proposal for more information). The heating rates and final temperatures were varied, and the off-gas was captured and analyzed for fluoride ions and residual PFAS.^{3,4,7}

The thermal treatments were classified into three types: T#1 involved thermolysis of PFAS in a closed container heated to specific temperatures and held for different durations. Post-treatment, the container was analyzed for fluoride ions and residual PFAS. T#2 included thermal treatment in the presence of porous adsorbents to study their influence on PFAS degradation. This treatment examined the effects of various carbonaceous materials and a crosslinked polystyrene copolymer resin. T#3 entailed the heating of PFAS pre-adsorbed to GAC from water.

The efficiency of thermal decomposition and the yield of fluoride ions were quantified through equations that factored in the number of fluorine atoms in a PFAS molecule as a measure of how effectively thermal treatments could break down PFAS.^{3,4,7}

Furthermore, the study incorporated a gas-phase adsorption experiment and dynamic heating in a muffle furnace to observe PFAS decomposition under different temperature profiles. The collection and analysis of thermal degradation products were performed using established methods, and computational studies were conducted to investigate the bond dissociation energies of various PFAS using density functional theory (DFT) calculations.⁷

RESULTS AND DISCUSSION

In this project, we made numerous contributions to the field.

- 1. We extended the tools for analyzing PFAS thermal degradation behaviors by innovatively using thermal desorption–pyrolysis–gas chromatograph–mass spectrometry (TD–Pyr–GC–MS) and TGA, traditionally used for the analysis of biomass materials. The application of these ‘new’ tools leads to many interesting observations.**

TGA is a thermal analysis technique that measures the change in mass of a sample as a function of temperature or time under a controlled atmosphere. It is frequently applied in areas such as polymers, pharmaceuticals, food, and environmental samples. By providing valuable information on thermal stability, decomposition, and composition, TGA aids in developing, quality control, and optimizing these materials and processes. TGA had never been used before to study PFAS thermal behaviors prior to this project. In a recent study,³ we innovatively utilized TGA to investigate the thermal stability of PFAS.

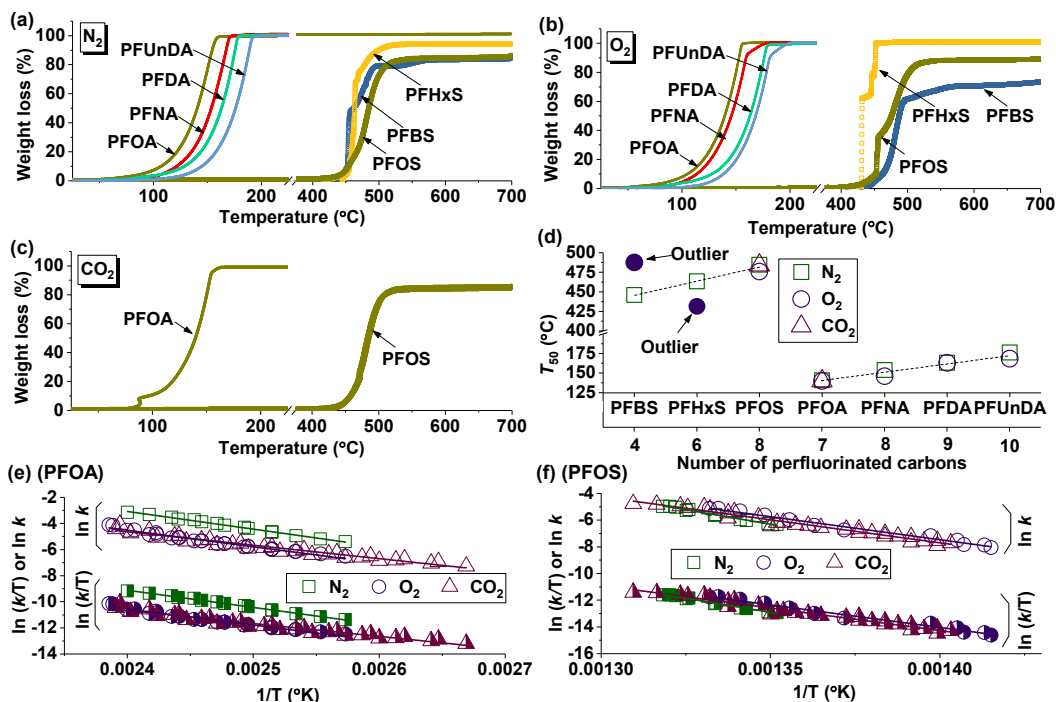


Figure 1. (a)–(c): Dynamic TGA scan curves of the acid form of PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA) and potassium salts of perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and PFOS in different atmospheres.³ (d): Correlation between the temperature at which 50% weight loss was seen (T_{50}) and the number of perfluorinated carbons in PFAS. (e) and (f): Arrhenius- ($\ln k$ vs $1/T$) and Eyring-like ($\ln k/T$ vs $1/T$) plots for PFOA and PFOS based on isothermal TGA scan data.

According to TGA (Figure 1) and thermal degradation (Figure 2) results, PFAS exhibited the following order of thermal stability: PFSAs >> PFUnDA > PFDA > PFNA > PFOA > short-chain PFCAs > hexafluoropropylene oxide dimer acid (HFPO-DA). TGA curves of PFCAs shifted to a higher temperature when the number of perfluorinated carbons (n_{CF_2}) increased (Figure 1).³

The temperature (T_{50} ; °C) corresponding to 50% weight loss of a PFAS in dynamic TGA scans correlates well with n_{CF_2} (Figure 1):

$$T_{50} = 11 \times n_{CF_2} + 63; R^2 = 0.96 \text{ (four PFCAs in Figure 2d)} \quad (1)$$

$$T_{50} = 9 \times n_{CF_2} + 410; R^2 = 0.96 \text{ (three PFSAs in Figure 2d without including two outliers)} \quad (2)$$

An increase in one perfluorinated carbon unit ($-CF_2-$) leads to a rise of T_{50} by approximately 11 and 9 °C for PFCAs and PFSAs, respectively. T_{50} varied insignificantly between different atmospheric environments (N₂, CO₂, O₂) (Figure 1).³

Analysis of isothermal TGA data revealed that the weight loss (destabilization) of PFAS follows first-order kinetics (Figure 1).

2. For the first time, our team demonstrated the degradation of PFCAs (e.g., perfluorobutanoate (PFBA) and PFOA) and HFPO-DA at low temperatures (150–200°C).

3. For the first time, we showed the thermal degradation of recalcitrant PFASs (e.g., PFBS and PFOS) at moderate temperatures ($\geq 450^\circ\text{C}$).

We found that a 20-min thermal treatment achieved $>90\%$ decomposition of PFCAs and PFASs on GAC at 200 and 500°C , respectively. HFPO-DA and PFCAs start to degrade at temperatures as low as 150°C with the presence of GAC (Figure 2).³ A 30-min thermal treatment of spent GAC at $\geq 300^\circ\text{C}$ in either N_2 , CO_2 , or air achieved $\geq 99.9\%$ removal of HFPO-DA and $\geq 99\%$ removal of PFCAs (e.g., PFOA).³ HFPO-DA was more readily decomposed than PFCA with the same n_{CF_2} (i.e., PFBA), indicating that the perfluorinated chain becomes less thermally stable with the inclusion of an ether group. A much higher heat treatment temperature (or HTT) ($\geq 500^\circ\text{C}$) was needed to achieve $\geq 99\%$ decomposition of PFASs (e.g., PFOS) on GAC during a 30-min thermal treatment (Figure 2). According to the measured yields of F^- , significant mineralization of PFOA/PFOS requires an HTT of ≥ 700 – 800°C . For example, the mineralization rate of PFOA on GAC increased sharply to $92.4\text{ mol}\%$ at 700°C from 9.4 – $28.8\text{ mol}\%$ at 150 – 600°C (Figure 2).³ Additionally, we developed an approach for extracting PFAS from spent GAC to measure PFAS on GAC accurately before and after heating.³

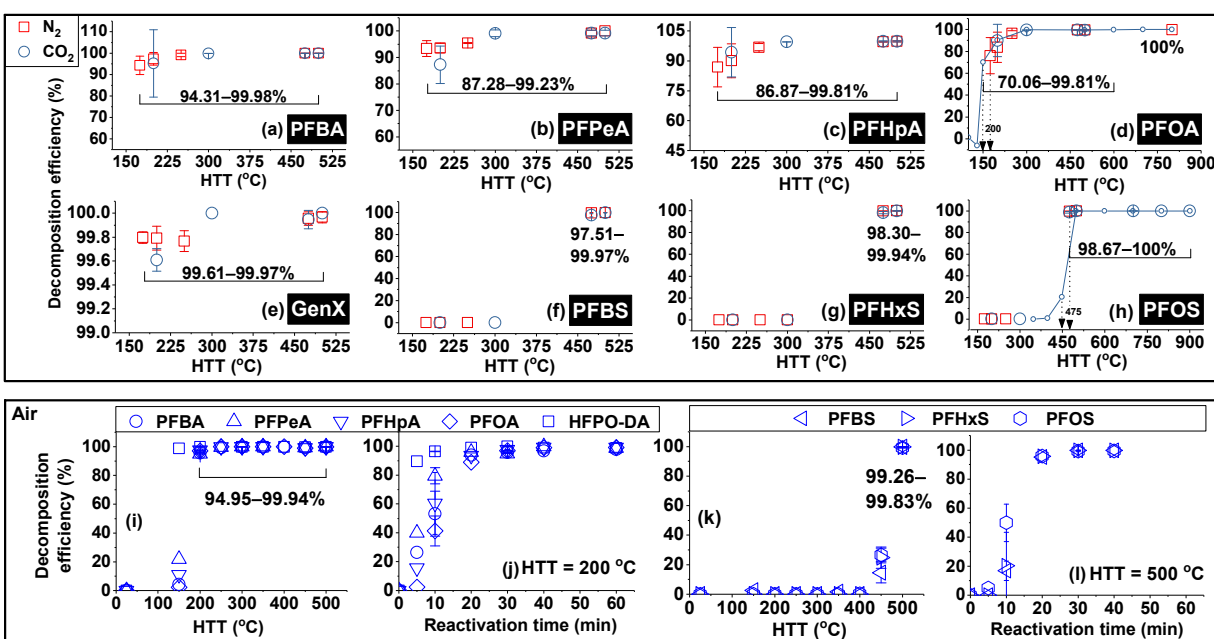


Figure 2. (a–h) Decomposition of PFAS on GAC during 30-min GAC thermal reactivation performed in a tube furnace under a flow of N_2 or CO_2 . The solid lines in (d) and (h) represent independent experiments.³ (i–l) Decomposition of PFAS on GAC in a closed system with air at different HTTs (i; k) or durations (j; l). The adsorption of PFAS on GAC in these experiments was carried out in pretreated surface water. The decomposition efficiency was assigned to 100% if no measurable PFAS was found after thermal treatment.³

4. Our team also discovered the catalytic influence of GAC on the thermal degradation of PFAS for the first time.

We found that the thermal decomposition of PFAS mostly followed first-order kinetics at temperatures of 150 – 250°C , in which the residual PFAS mass ($M_{\text{PFAS},T}$) decreased exponentially as a function of the heating time.⁴ At a higher temperature (300°C), the decomposition of these chemicals can also be described by second-order kinetics, in which a plot of $1/M_{\text{PFAS},T}$ versus heating time was approximately linear.⁴ For comparison purposes, we used the first-order decomposition rate constant (k_{1st} , min^{-1}) in the following discussion.⁴

The value of k_{1st} was below 0.005 min^{-1} for PFCAs at 150 – 250°C in T#1. HFPO-DA appears to be more easily degraded than the PFCA with the same number of perfluorinated carbons (i.e., PFBA).⁴ This

result shows that the perfluorinated chain becomes less thermally stable with the inclusion of a foreign group, such as the ether group.

GAC accelerated the thermal decomposition of HFPO-DA at temperatures as low as 150 °C in T#2 and T#3 conditions. The GAC-induced acceleration was evident for PFCAs at 200 °C, and up to a 60-fold increase in k_{1st} was observed. This acceleration became even more significant at 250 °C, which led to a 150-fold increase in k_{1st} for PFUnDA⁴. The acceleration effect was less pronounced for the short-chain PFAS (PFBA) because the adsorption of PFBA on GAC was much weaker than that of long-chain homologs. The effect of GAC became less marked at higher temperatures of 300 °C and 400 °C at which the substantial thermolysis of PFCAs was seen. Thermal treatment at 300 °C led to near complete decomposition (>99.99%) of PFOA within 60 min.⁴

Because PFCEA and PFCA molecules were not pre-adsorbed on GAC in T#2 treatments, we hypothesize that the accelerated decomposition was caused by the adsorption of gas-phase PFCEA/PFCA on GAC that is much more thermally conductive (0.4–1.36 W/(m•K)) than air (<0.032 W/(m•K) at ≤ 100 °C).^{9, 10} The heat transfer is more efficient on GAC than in air. On the other hand, the thermal conductivity of air increases with temperature. At 400 °C, the effect of GAC amendment on the thermal decomposition rate of PFAS appears to be much less important. To test this hypothesis, we conducted additional experiments with various porous adsorbents, including one non-carbonaceous material (XAD-2 resin), that were co-heated with PFOA. The results show that low adsorption of PFOA on raw charcoals was observed, and the thermal decomposition of PFOA was not accelerated with the addition of raw charcoal samples. The thermal air oxidation of raw charcoals caused pore wall etching and/or unclogging of pores bearing tarry deposits generated during the carbonization step.^{11, 12} This, in turn, widened pores of charcoal and created new surface areas, which relieved steric hindrance for adsorption of PFOA molecules. The thermal decomposition of PFOA increased significantly with the addition of an activated charcoal. Commercial porous materials, GAC (or activated charcoal) and XAD-2 resin, adsorbed PFOA strongly and reduced the thermal decomposition half-life of PFOA from ~400 min to less than 25 min at 200 °C.⁴

5. We identified several novel transient and final thermal degradation products of PFAS.

We identified many transient intermediates during the thermal degradation of PFCAs. PFCAs yielded several transient short-chain intermediates at temperatures as low as 150 °C. The highest-yielding intermediate product for a parent PFCA with n perfluorinated carbons was usually the shorter-chained PFCA with $(n - 1)$ perfluorinated carbons.⁴ For example, PFDA yielded shorter-chain PFCAs in the following order, PFNA > PFOA > perfluoroheptanoate (PFHpA) $\approx$ perfluoropentanoate (PFPeA) $\approx$ PFBA. Similarly, the highest-yielding byproduct of PFOA was PFHpA, whereas PFBA was a trace intermediate product.^{4, 7} This formation pattern seems to agree with the stepwise defluorination mechanism developed for photocatalysis,¹³ reduction by hydrated electrons, and plasma¹⁴ treatments of PFAS. However, a closer look at the results reveals that it is not the predominant mechanism of the thermolysis of PFAS. First, the yield of intermediate PFCAs was low (<5 mol %). Second, a clear stepwise pattern was not observed because all the short-chain intermediates appeared nearly simultaneously.

We found similar phenomena in the thermal decomposition of perfluoroalkyl ether carboxylic acids (PFECAs), such as HFPO-DA.⁷ The evolution of detected transient intermediates from PFECAs can be grouped into two categories: small intermediates and relatively large ones with a UPLC retention time close to that of the parent compound. These transient intermediates were assigned by comparing their UPLC retention time and MS fragmentation patterns with authentic standards.

Three transient organic intermediates (I, II, III) of HFPO-DA were detected by UPLC coupled with a high-resolution mass spectrometer (HRMS).⁷ Compound I with m/z 212.9792 and MS fragments characteristic of PFCAs (C_3F_7 , m/z 168.9894; C_2F_5 , m/z 118.9926) was assigned to be PFBA.⁷ This was further substantiated by an authentic standard. Compounds II and III were identified as PFPrA and TFA, respectively, confirmed with corresponding authentic standards. To our knowledge, these PFCAs were identified for the first time as thermal decomposition products of HFPO-DA.⁷

A novel volatile intermediate (IV) with a molecular weight (m/z 265.9) greater than that of PFBA was also detected.⁷ The fragments at m/z 69.0 (CF_3^+), 119.0 ($C_2F_5^+$), and 169.0 ($C_3F_7^+$) were characteristic

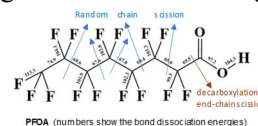
of fluorinated fragments.^{5, 15} The fragments at m/z 146.9 and 196.9 represent the successive loss of the fluorinated fragment CF_2 from IV.⁷ We assigned the ion at m/z 146.9 to be an unsaturated fluorinated fragment with one C replaced by O. The ion at m/z 81.0 represents an unsaturated fluorinated fragment (SMILES: $\text{F}[\text{C}^+]=\text{C}(\text{F})\text{F}$). Taken these results together, we assigned IV to be perfluoro(propyl vinyl ether) (SMILES: $\text{FC}(\text{F})=\text{C}(\text{F})\text{OC}(\text{F})(\text{F})\text{C}(\text{F})(\text{F})\text{C}(\text{F})(\text{F})\text{C}(\text{F})(\text{F})\text{F}$) (library match quality, 74–80%).⁷

6. We identified some novel PFAS thermal degradation mechanisms, such as random C–C scission.

We believed the thermal decomposition of PFAS involves multistep radical chain reactions, including initiation, chain propagation, recombination, and termination.¹⁶ Because of the strong C–F bond, we believed that the thermal decomposition of PFOA was initiated with the homolytic cleavage of the relatively weak C–C bond located next to the carboxyl group of PFOA, or with the C–S bond next to the sulfonate group of PFOS.^{4, 7}

In the absence of GAC, a majority of the thermal PFAS degradation products are nonpolar, gaseous species, including perfluoroalkenes.^{4, 8} The formation of perfluoroalkenes can be well explained by the decarboxylation or end-chain scission pathway.^{4, 7} However, our team found that the addition of GAC significantly altered the degradation pathway, leading to the formation of more polar, short-chain homologs from PFAS, which could not be explained by the decarboxylation mechanism.^{4, 7} For example, at 200 °C, the yield of PFNA from PFDA was maximized after a 30-min treatment when GAC was present, and then disappeared on the same time scale as the parent compound (i.e., PFDA).⁴ At a higher temperature (300 °C), the yield of PFNA from PFDA dropped to <10 mol % after a 5-min treatment and was negligibly low with a longer heating time as PFNA quickly decomposed.⁴

We believe that the formation of polar, short-chained homologs (e.g., PFHpA from PFOA⁴) results from a random-chain scission pathway that is characterized by the homolytic cleavage of C–C bonds along the perfluorinated chain. Recent experimental and computational findings support this mechanism. High-throughput DFT analyses revealed that the most susceptible C–C bond in PFCAs is between the alpha-C (α -C) and beta-C (β -C),⁷ rather than between the α -C and the carboxyl C. This pathway produces perfluorinated radicals that engage in further chain propagation reactions, producing short-chain homologs. Nonetheless, the cleavage site may not be entirely random, as the weakest C–C bond could be adjacent to a radical end.



A similar chain scission pathway was also evident for PFECA thermal degradation. In addition to nonpolar products, we found PFECAs (e.g., HPFO-DA) generate many short-chain PFCAs, which again could not be explained by decarboxylation or end-chain scission pathway.⁷ A pathway for the thermal decomposition of HFPO-DA must take into account: (i) the practically instantaneous formation of TFA, PFPrA, and PFBA upon heating of the parent compound; (ii) the relatively large transient yields of TFA and PFPrA; and (iii) the trace yield of PFBA that rules it out as an intermediate along a primary path.⁷

A pathway consistent with these results was the thermal cleavage of the C–O_{nr} bond, leading to the formation of a perfluoropropyl-oxidanyl radical and a precursor of PFPrA ($\cdot\text{PFPrA-H}$). This result was accomplished by the recombination of the $\cdot\text{PFPrA-H}$ and $\cdot\text{F}$ to form PFPrA, followed by the thermal decomposition of the resulting PFPrA radical to give TFA.⁷ The thermal cleavage of the other stronger C–O ether bond is evidenced by the formation of PFBA from HFPO-DA. HFPO-DA decarboxylation (Pathway C) generates perfluoro(propyl vinyl ether). The DFT simulations predict a few other pathways involving the cleavage of the trifluoromethyl ($-\text{CF}_3$) group, which were not supported by MS spectral evidence; however, this does not preclude the formation of transient intermediates in small amounts in these DFT-predicted pathways.⁷

7. The team compared approaches to efficiently extract PFAS from spent GAC and identified the most promising method.

Investigating and comparing various extraction strategies for the efficient extraction of PFAS from spent GAC is crucial for correctly estimating the residual PFAS on GAC. Furthermore, developing an

efficient extraction method will aid in creating effective solvent-wash-based disposal or remediation techniques.

In our study,³ pure methanol, whether heated (at 60 °C) or not, resulted in low recoveries (30.0–67.8%) of PFAS from GAC (Figure 3). Methanol that was amended with NaOH improved extraction for PFSAAs (71.6–82.5%) but consistently had recoveries greater than 130% for PFCAs. On the other hand, methanol added with NH₄Ac achieved recoveries of 79.2–111.8% for most of the PFAS (Figure 3).

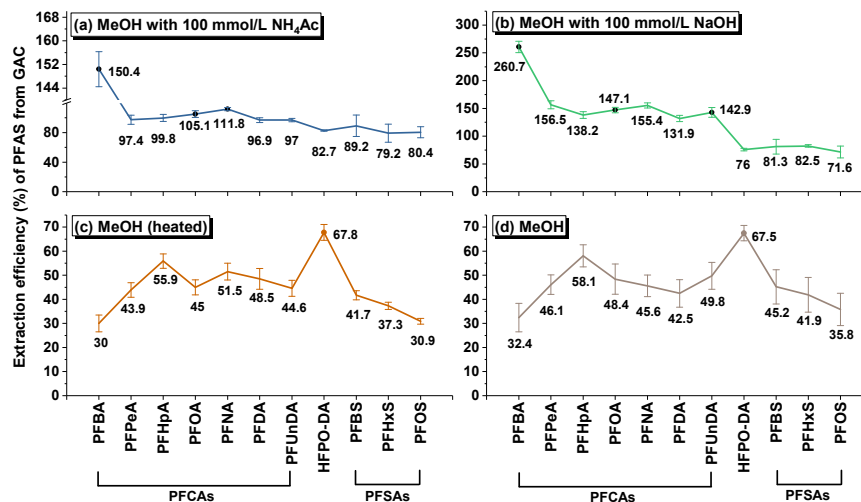


Figure 3. Methanol (MeOH) recovery of PFCAs, PFECA (i.e., HFPO-DA), and PFSAAs from GAC.³

8. We modified adsorbents and studied the removal of PFAS from waste streams of NF/RO.

In this limited-scope project, we modified porous carbonaceous sorbents (PCS) by both thermal and chemical approaches.^{17, 18} Modifying adsorbents with PPAO thermal treatment significantly enhanced PFAS sorption, with up to a 1000-fold increase observed.¹⁷ The PPAO treatment led to a 103-fold increase in the water–adsorbent distribution coefficient (K_D) for individual PFAS in a mixture. This enhancement was more pronounced for longer-chain PFAS, as shown by the differences in $\log K_D$, with $\Delta \log K_D$ being smaller for shorter-chain PFAS. The PPAO treatment's impact on pore structure was also notable, with the enlargement of smaller pores significantly affecting the sorption of longer-chain PFAS compared to shorter-chain ones.

In the chemical modification approach, coating polydiallyldimethylammonium chloride (pDADMAC) to PCS suspensions resulted in a charge reversal, with the zeta potential of PCS shifting from -51 mV to +7.5 mV. This modification led to more effective removal of longer-chain PFAS like PFNA and PFOS than shorter-chain ones like PFBS and PFPeA. The sorption of PFOS or PFNA increased as more pDADMAC was added, correlating with the zeta potential changes.¹⁸

Finally, the RO membrane SW30 exhibited the highest PFAS rejection rates, all above 98.5%, but had the lowest flux rate due to smaller and tighter pores. NF membranes NF90 and NFX showed high PFAS rejections (>97%), while DK and NF270 membranes had lower removal efficiencies, especially for short-chain PFAS. The NF90 membrane, with high rejection rates for all PFAS and a relatively high flux rate, was recommended for PFAS removal. This selection was based on balancing flow flux, PFAS rejection, and adsorption characteristics of the membranes.

In summary, prior to this research, there was a considerable degree of uncertainty within the environmental science community regarding the possibility of degrading 'forever chemicals' at low temperatures. The findings from our *limited-scope* project, consisting of a series of studies, have provided enlightening insights into this matter. Below are a number of noteworthy results and conclusions from this project:

1. TGA was successfully used to study the thermal stability of PFAS. The study found that the order of thermal stability of PFAS was as follows: PFSAAs (potassium salts) >> PFCAs > HFPO-DA. TGA curves of PFCAs shifted to a higher temperature when the number of perfluorinated carbons increased.³

2. The temperature corresponding to 50% weight loss of a PFAS (T50) in TGA experiments correlated well with the number of perfluorinated carbons. An increase in one perfluorinated carbon unit leads to a rise of T50 by approximately 11 and 9 °C for PFCAs and PFSA, respectively.³

3. The weight loss of PFAS under isothermal conditions followed first-order kinetics, as revealed by the analysis of isothermal TGA data.³

4. Various extraction strategies were compared for the efficient extraction of PFAS from spent GAC. We found that methanol, especially when amended with NH₄Ac, showed promising results in the extraction of PFAS. However, the extraction efficiency varied among different types of PFAS.³

5. A 30-min thermal treatment of spent GAC at ≥ 300 °C achieved $\geq 99.9\%$ removal of HFPO-DA and $\geq 99\%$ removal of PFCAs (e.g., PFOA). To achieve $\geq 99\%$ decomposition of PFSA (e.g., PFOS), a higher temperature of ≥ 500 °C was needed.³

6. The thermal decomposition of PFAS followed mostly first-order kinetics at temperatures of 150–250 °C. However, at a higher temperature (300 °C), the decomposition can also be described by second-order kinetics.⁴

7. The perfluorinated chain in PFAS became less thermally stable with the inclusion of an ether group, making PFCEA (HFPO-DA) more easily degradable than PFCA with the same number of perfluorinated carbons (i.e., PFBA).⁴

8. GAC was found to accelerate the thermal decomposition of HFPO-DA and PFCAs at temperatures as low as 150 °C and 200 °C respectively, with the acceleration effect becoming insignificant at ≥ 300 °C.⁴

9. The accelerated decomposition was hypothesized to be caused by the adsorption of gas-phase PFCEA/PFCA on GAC, which is much more thermally conductive than air, enhancing heat transfer.⁴

10. Other porous carbonaceous materials also accelerated the thermal decomposition of PFOA, with the effect more pronounced with thermally air-activated charcoal, commercial GAC, and XAD-2 resin.⁴

11. The thermal degradation of PFCAs yielded several transient PFCA intermediates. We discovered that the stepwise defluorination mechanism is not the primary process, as evidenced by the low yield and the concurrent emergence of short-chain intermediates in the absence of GAC.⁴

12. The presence of GAC altered the decomposition pathway of PFAS, significantly increasing yields of shorter-chained PFCA intermediates at lower temperatures.⁴

13. Significant mineralization of PFOA/PFOS, as indicated by measured yields of F⁻, required high thermal treatment (HTT) of ≥ 700 –800 °C, with the mineralization rate not significantly differing in CO₂ or air at a given HTT.³

14. The thermal decomposition of PFAS was believed to involve a series of radical chain reactions, including initiation, propagation, recombination, and termination. This process is initiated by the cleavage of a relatively weak C–C or C–S bond, forming a nonfluorinated moiety and a perfluoroalkyl biradical.^{4,7}

15. We believed that the perfluoroalkyl biradical underwent chain propagation reactions, yielding shorter-chained perfluoroalkyl radicals, which may recombine with carboxyl groups/radicals, producing PFCA intermediates. These chain reactions ultimately result in very short, or "dead," fluorinated units.^{4,7}

16. Further experimentation on individual PFECAs led to the identification of three transient organic intermediates of HFPO-DA (PFBA, PFPrA, TFA) and a novel volatile intermediate IV, suggesting that HFPO-DA undergoes thermal decomposition to form these transient intermediates.⁷

17. The thermal decomposition of other PFECAs, such as hexafluoropropylene oxide trimer acid (HFPO-TA) and perfluoro-2,5,8-trimethyl-3,6,9-trioxadecanoic acid (HFPO-TeA), also generated significant quantities of PFPrA and TFA, suggesting a similar decomposition pathway. A pathway consistent with the results suggests the thermal cleavage of the ether C–O bond (C–O_{nr}) closer to the carboxyl group, leading to the formation of certain radicals and intermediates.⁷

18. The project developed a database of pure water isotherms with PFAS on commercial GAC, which will be crucial for water facilities requiring PFAS control. Adsorption isotherms of PFAS on GAC showed strong nonlinearity, and the adsorption strength increased with increasing PFAS chain length.¹⁹

19. The adsorption of PFAS onto GAC was found to depend on the surface area of the GAC and the molecular dimensions of the adsorbate and the distribution of accessible surface area in nanopores. This

result indicates that the internal surface area of GAC determined by N₂ porosimetry may not be accessible to PFAS molecules, leading to potential inconsistencies in adsorption capacity.^{17, 18}

20. GAC derived from different feedstocks showed varying effectiveness in PFAS removal. In particular, bituminous GACs showed better performance than coconut shell and lignite coal GACs, leading to the selection of F200, a bituminous GAC, for subsequent experiments.^{17, 18}

21. A new strategy for using pyrogenic carbonaceous materials for PFAS removal was developed. This strategy involved post-pyrolysis air oxidation, which enlarges pore size, increases surface area, and can enhance the adsorption capacity of individual PFAS by up to three orders of magnitude. After thermal reactivation, the biochars showed even higher PFAS adsorption values, suggesting this was effective for PFAS removal and allowed for material reuse.^{17, 18}

22. An increase in pyrolysis temperature led to a decrease in H/C and O/C atomic ratios and an increase in CO₂-specific surface area and porosity, indicating a progressive conversion to materials with greater hydrophobicity, higher nanoporosity, and a more condensed aromatic structure. The process of thermal oxidation, termed 'pore reaming', opened pore networks, increasing pore volume and specific surface area.¹⁷

23. Sorption experiments in multisolute-PFAS systems showed inconsistent effects of pyrolysis temperature on the adsorption value, except for samples heated to 600°C, which exhibited larger surface areas, porosities, and thus greater adsorption values. Post-pyrolysis air oxidation treatment significantly enhanced PFAS adsorption, especially for longer-chain PFAS. This treatment also increased the oxygen content of the carbons, which, despite increasing surface charge repulsion, did not counteract the beneficial effects of pore reaming.¹⁷

24. Competitive adsorption of PFAS on GAC was observed. Longer-chain PFAS had a greater affinity for carbon and thus compete more effectively for sorption sites than shorter-chain compounds.

25. Coating pDADMAC on PCS reversed the surface charge and increased the anionic exchange capacity, thereby enhancing PFAS adsorption.¹⁸

26. The surface chemistry of the adsorbent played a crucial role in the sorption of PFAS. Sorption of pDADMAC to carbons led to a charge reversal, enhancing the sorption capabilities of the carbon spheres.¹⁸

IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Benefits

This limited-scope project has yielded numerous innovative and important findings, greatly enhancing our understanding of the thermal stability and degradation mechanisms of PFAS. Without this project, such insightful results would have remained elusive. Understanding PFAS degradation during the thermal regeneration and reactivation of GAC will enable more efficient and cost-effective contaminant removal methods. Identifying PFAS decomposition products will help assess potential environmental risks. This project's insights into PFAS thermal degradation mechanisms, particularly regarding the influence of structural variables and the efficacy of GAC, contribute to the scientific knowledge base. This groundwork is crucial for future explorations into low-temperature PFAS mineralization and the creation of novel treatment approaches. Therefore, the outcomes of this project hold significant real-world implications for addressing PFAS contamination, offering substantial benefits to society.

Expected beneficiaries of this project include the DoD, water treatment professionals, soil/groundwater remediation professionals, communities concerned with PFAS presence in water, research and education communities, and their stakeholders. The successful completion of this limited-scope project has established a solid foundation for a larger-scale study, focusing on maximizing PFAS mineralization at low temperatures, treatment of volatile organofluorine compounds, and sustainable use and disposal of fluoride ions generated from PFAS thermal decomposition.

Future work

This research provided a comprehensive investigation into the thermal degradation of PFAS on spent media such as GAC. The findings revealed exciting possibilities for the following future research tasks (#1–#8), with a focus on achieving more efficient PFAS degradation, optimizing extraction strategies, and understanding the kinetics of thermal decomposition.

1) This limited-scope project centered on perfluorinated compounds and GenX. Future research could focus on determining the optimum temperature for the degradation of various PFAS. The understanding of the thermal stability of different PFAS could also be expanded to include more compounds (e.g., cationic and zwitterionic precursors) and conditions (e.g., with or without moisture), which will provide a more comprehensive understanding of the thermal behavior of PFAS. A crucial area requiring deeper exploration is the thermal stability and degradation of emerging compounds, including precursors and various PFAS types present in AFFFs and sites contaminated with PFAS.

2) The thermal decomposition of PFAS under isothermal conditions followed first-order kinetics at low temperatures, suggesting that the degradation process may be predictable and manageable. However, the observation of second-order kinetics at higher temperatures suggested that the process might be more complex than currently understood. Future research should delve deeper into the kinetics of thermal degradation of PFAS, as a better understanding of these kinetics could lead to the development of more efficient and predictable degradation methods.

3) Likewise, a future research task could be the optimization of thermal degradation conditions for PFAS, especially in real-field conditions. This task would focus on adapting our laboratory findings to practical scenarios in a pilot-scale combustor or incinerator, where dynamic conditions and convective gas movements are prevalent. We would aim to determine the effective decomposition temperatures in these environments, investigating if they may be higher than those observed in laboratory (e.g., TGA) experiments. This research would not only enhance the practical applicability of our findings but also contribute to the development of more efficient and feasible strategies for PFAS degradation in real-world thermal treatment facilities.

4) Furthermore, while we found that GAC accelerated the thermal decomposition of PFAS, the mechanism behind this acceleration is still uncertain. We hypothesized that it was due to the higher thermal conductivity of GAC than air at low and moderate temperatures.⁴ However, other factors, such as rare minerals on GAC, may also play a role.⁴ Future research should focus on understanding the exact mechanism of this acceleration. Also, the impact of other porous carbonaceous materials and porous resins on the thermal decomposition of PFAS should be investigated further. These studies could lead to the discovery of novel media for PFAS degradation.

5) The research also demonstrated that GAC altered the decomposition pathway of PFAS, increasing yields of shorter-chained PFCA intermediates at lower temperatures. This observation points to a possible direction for future research, which could focus on manipulating the decomposition pathway of PFAS to enhance the production of shorter-chained intermediates, thereby speeding up the degradation process. A future research endeavor should investigate how GAC properties, such as surface area, microporosity, mesoporosity, surface functional groups, and pore size distribution, influence the acceleration of PFAS degradation during thermal treatment.

6) The transient organic intermediates identified during the thermal decomposition of individual PFECAs could also provide a starting point for future research to mineralize intermediates.

7) Future research should also focus on understanding the relative importance of surface chemistry and pore size distribution in the adsorption of PFAS. In this limited-scope project, we showed that the adsorption capabilities of carbon spheres can be enhanced by reversing the surface charge. However, the exact mechanism behind this enhancement is still unknown. A better understanding of this process could lead to the development of novel sorbents with enhanced PFAS adsorption capabilities.

8) Finally, the results of this study suggested the possibility of using thermally reactivated biochars as an affordable alternative to GAC for PFAS removal. Further research should be undertaken to enhance the adsorption of shorter-chain PFAS and to reduce the loss of the carbonaceous sorbent during thermal reactivation.

In summary, this research has shed light on various aspects of the thermal degradation of PFAS on spent media such as GAC. Future research should focus on optimizing thermal degradation conditions, understanding the kinetics of degradation, optimizing extraction strategies, and exploring the role of surface chemistry in PFAS adsorption. Furthermore, the development of affordable and efficient alternatives to GAC for PFAS removal is another promising direction for future research.

Main Body of the Report

1. Objectives

This SERDP proposal was submitted in response to the SERDP Statement of Need (EPSON-21-C1), seeking an improved understanding of the effectiveness and sustainability of thermal destruction technologies for treating materials containing PFAS. Our long-term goal was to develop sustainable thermal treatment technologies to decompose PFAS effectively. In this limited-scope project, we focused on the thermal treatment (reactivation and combustion) of spent GAC laden with PFAS and addressed the following key objectives:

- 1) Investigation of the thermal stability of PFAS;
- 2) Determination of the thermal decomposition mechanisms (temperature and time requirements, thermodynamics, kinetics) of PFAS on spent GAC;
- 3) Modification of GAC to facilitate the adsorption of weakly hydrophobic PFAS anions, especially short-chain PFAS, from water;
- 4) Investigation of the long-term performance of raw and tailored GAC after multiple cycles of adsorption–thermal reactivation and removing PFAS from the brine of NF/RO by raw/tailored GAC.

We studied the thermal stability of PFAS from the room temperature (non-heating control) to 900 °C. Decomposition behaviors of PFAS during the thermal reactivation (in N₂ or CO₂) or combustion (in O₂ or air) of PFAS-laden GAC were thoroughly examined. PFAS decomposition products were identified by quadrupole time-of-flight MS (QToF-MS/MS) and thermal desorption/programmed pyrolysis GC–MS (TD–Pyr–GC–MS). Furthermore, we compared ammoxidation- and impregnation-based modification approaches to develop tailored GAC with an enhanced adsorption capacity of anionic PFAS species. Lastly, we evaluated the performance of raw/tailored GAC for removing PFAS from concentrate streams of NF and RO with or without the pre-ozonation treatment of NF/RO brine. This limited-scope project primarily examined various PFAS, including PFASs (e.g., PFOS), PFCAs (e.g., PFOA), and PFECAs (e.g., HFPO-DA, the acid form of GenX).

2. Background

2.1. PFAS REMOVAL FROM WATER

PFAS are synthetic organic chemicals widely used for a range of consumer and industrial products, including nonstick cookware, AFFFs, and paint materials.²⁰⁻²² Polyfluoroalkyl compounds are subject to chemical²³ and biological²⁴⁻²⁷ degradation, while PFCAs and PFASs are chemically and biologically recalcitrant. PFASs and PFCAs are two specific subclasses of PFAS that have received scholarly attention since 2001. Once released to the natural environment,^{25, 28, 29} long-chain (≥ 7 perfluorocarbons) PFASs (e.g., PFOS) and PFCAs (e.g., PFOA) can bioaccumulate and biomagnify through food webs.³⁰⁻³³ In particular, PFOS and PFOA have been reported in >95% of blood samples collected during multiple U.S. national surveys³⁴ at concentrations that are a risk to human health.³⁵⁻³⁸ PFAS-contaminated drinking water is an important source of exposure for the general population.³⁹⁻⁴³ The USEPA recently set a drinking water advisory on the combined level of PFOS and PFOA at 0.070 µg/L, making the removal of these chemicals from drinking water a health priority.⁴⁴⁻⁴⁶

PFOS and PFOA cannot be easily removed from water during conventional water and wastewater treatment.^{44, 47-49} PFOS, PFOA, and many other PFAS are ionic or ionizable,

moderately hydrophobic, and soluble in water. PI Xiao⁴⁵ reported that the average removal of PFOS and PFOA was often <10% during conventional coagulation and flocculation. Removals close to 25% were achieved in the enhanced coagulation domain characterized by a relatively high coagulant dosage (e.g., >60 mg alum/L) and (thus) a low coagulated water pH.⁴⁵ In another study, PI Xiao analyzed the concentrations of PFCAs and PFSA in the influent and effluent from 37 wastewater treatment plants serving more than 40 cities/towns across Minnesota.²⁵ This study demonstrated that certain conventional and advanced/tertiary treatment technologies (e.g., UV sterilization) are not effective in PFAS removal from wastewater.²⁵ In fact, PFOA and PFOS can be generated from precursor compounds during drinking water and municipal wastewater treatment.^{23, 25}

Recently, various advanced technologies have been reported to degrade PFOA and PFOS in water under specialized conditions, such as B₁₂-mediated reduction,⁵⁰ photocatalysis,^{51, 52} electrochemical approaches,^{49, 53} reduction by hydrated electrons under completely anaerobic conditions,^{54, 55} hydrothermal decomposition at alkaline pH,⁵⁶ and plasma treatment.¹⁴ While progress is continually being made in these advanced treatment technologies, most approaches will likely prove unsuitable to scale up for the treatment of natural waters or concentrated waste streams of membrane filtration that contain colloidal particles and dissolved organic matter. At pilot- and full-scale operations, GAC adsorption continues to be the most frequently used approach for treating PFAS-contaminated water.⁴⁷ The predominant residual from GAC systems is spent or exhausted carbon containing PFAS. Removal/destruction of PFAS on spent GAC was the focus of this limited-scope project.

2.2. GAC

GAC is a versatile adsorbent that has widely been used in drinking-water treatment for removing organic contaminants, including precursors of disinfection byproducts, i.e., natural organic matter (NOM).^{57, 58} It has also been frequently employed in advanced or tertiary treatment of domestic wastewater.⁵⁹⁻⁶¹ Unlike powdered activated carbon that is activated by chemical approaches, GAC is produced by the carbonization of feedstocks at 800 °C or less in N₂ and activated thermally in CO₂ or steam at high temperatures. The loss of substances of feedstock during carbonization leads to the creation of pores in the carbon matrix.⁶² During activation, gases (i.e., CO₂) enter the pores, remove obstructions such as tarry deposits, and open more pore networks for access by the solute. The accessible pores account for the internal surface area of GAC.

The adsorptive properties of GAC are determined by its porosity (physical adsorption) and surface chemistry, which are determined by the feedstock of GAC and carbonization/activation conditions (e.g., temperature and activation gases used in thermal activation). The largest producer of GAC (e.g., the Filtrasorb[®] series) in the United States is Calgon Carbon Corporation; the main activation process is thermal, and the main feedstocks of GAC are bituminous coal and coconut shell. The second largest producer is Norit Americas, Inc. (now a part of Cabot Corporation), producing GAC (e.g., Hydrodarco[®] and Darco[®] series) by thermal activation of charcoal made from lignite and bituminous coal. This limited-scope project included mainstream GAC products from these dominant GAC manufacturers.

2.3. THERMAL DECOMPOSITION OF PFAS ON SPENT GAC

Spent GAC is usually (1) thermally reactivated or regenerated, (2) used as a fuel for combustion, or (3) landfilled, depending on whether the spent GAC is deemed non-hazardous.⁶³ Conventional thermal reactivation of spent GAC is achieved by heating at >700 °C under N₂, CO₂, or steam.⁶⁴ Air may be inadvertently or intentionally introduced during the reactivation process to

cool the reactor.⁶⁴ The fate of PFAS in thermal processes such as those occurring during GAC reactivation (in N₂ or CO₂) and combustion (in air or O₂) is poorly understood. Filling this key knowledge gap will accomplish the following: (a) promote the development of effective and sustainable thermal decomposition technologies for PFAS loaded on GAC; and (b) enhance our understanding of PFAS fate during the incineration of PFAS-containing biosolids and municipal solid wastes. PFAS (e.g., PFOA) are commonly believed to be thermally stable. However, very few studies have been conducted on thermal stabilities and decomposition products of PFAS on GAC. To our knowledge, only one study is available in the literature⁶⁵ on this topic prior to our first thermal PFAS degradation study.³ Watanabe et al. determined the decomposition efficiency of PFOA, perfluorohexanoate (PFHxA), and PFOS on GAC at 700 °C.⁶⁵ The authors determined the recovery of mineralized fluorine to be 51, 74, and 70% for PFOA, PFHxA, and PFOS, respectively, associated with GAC.⁶⁵ However, the degradation rates of these three PFAS were not provided.⁶⁵ Furthermore, it is also unclear how the PFHxA (C6) gives a higher yield of fluoride ions than its long-chained homolog (i.e., PFOA (C8)) in Ref.⁶⁵. Lastly, the mineralization rates at other temperatures were not determined in Ref.⁶⁵. All these questions were clarified in our first,³ second,⁴ and third⁵ studies on this topic.

2.4. MODIFICATION OF PCS

Adsorption of PFAS to PCS is mainly driven by the hydrophobic effect and a pore-filling process. The pores of PCS can be divided into three basic varieties based on their size:⁶⁷ *micropores* (< 20 Å), *mesopores* (20–500 Å), and *macropores* (>500 Å).⁶⁴ PCS such as GAC possesses all three varieties of pores simultaneously, but is normally nanoporous having apertures within the range of solute molecular diameters. PFAS are typically <10 Å in their longest dimension. Adsorption should take place primarily in micropores (< 20 Å) of GAC. However, not all micropores of PCS are available for adsorbate molecules. PI Xiao discovered that mesopores serve as an important passage to micropores where the steric hindrance may restrict the entrance of adsorbate molecules into micropores.⁶⁸ Steric hindrance can impact adsorption thermodynamically or kinetically that may become more severe as the ratio of pore aperture to the adsorbate molecular size decreases.⁶⁹

PCS particles carry a negative charge in the water at circumneutral pH owing to the surface carboxyl and acidic hydroxyl groups.^{70, 71} The total adsorption free energy of PFCA/PFSA anions can be partitioned into terms for hydrophobic (ΔG^h), electrostatic repulsion ($\Delta G^{e,r}$) between PFAS anions and the negatively charged GAC surface, and a lumped term (ΔG^0) for all other interactions, including dipolar, quadrupolar, and steric hindrance:

$$-RT\ln K_{\text{PFAS anion}} = \Delta G^h + \Delta G^{e,r} + \Delta G^0 \quad (3)$$

In this proposal, we altered the surface charge of PCS to lower the electrostatic repulsion ($\Delta G^{e,r}$). PCS modification has been extensively studied in the literature.^{72, 73} The most widely used approach is to change the density of oxygen- and nitrogen-containing functional groups on the PCS surface. The basicity of PCS is associated with (i) resonating electrons of the polyaromatic units of the PCS surface that attract protons and (ii) basic surface functionalities that are capable of binding with protons.⁷² Nitrogen functionalities generally provide basic properties and enable the PCS particles to be less negatively charged, which may mitigate the electrostatic repulsion between the PCS surface and PFAS anions. In this proposal, we explored approaches to alter the surface chemistry of PCS and evaluated the long-term performance of the tailored PCS after multiple adsorption and reactivation cycles.

3. Materials and Methods

3.1. TASK 1—INVESTIGATION OF THERMODYNAMICS AND KINETICS OF THERMAL PFAS DECOMPOSITION IN BOTH INERT AND OXIDATIVE ATMOSPHERES

We studied seven PFCAs and three PFSA: PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, and potassium salts of PFBS, PFHxS, and PFOS. The test set also included one PFECA, HFPO-DA.³ The ammonium salt of HFPO-DA (trade name, GenX²²) is an alternative to PFOA/PFOS. The test solution was surface water collected from the Red River (Grand Forks, ND) (dissolved organic carbon = 7.8 mg/L; specific ultraviolet absorbance = 3.2 L/mg/cm; pH = ~7.8; turbidity = 14.3 NTU). The water sample was spiked with PFAS to a known concentration, equilibrated for 48 h at room temperature (~22 °C), and pretreated with processes simulating typical drinking water physicochemical treatment processes.^{45, 74} Adsorption of PFAS in the pretreated water to GAC (Filtrisorb 200, Calgon Carbon Corporation, PA) (BET surface area: 691.4 m²/g; microporosity: 0.3 cm³/g; mesoporosity: 0.07 cm³/g) was performed in 50-mL Thermo Scientific NuncTM sterile polypropylene vials that were rotated end-over-end at 40 rpm for four days at ~22 °C. The apparent adsorption equilibrium was reached within two days. We also prepared unspiked controls.³

After adsorption, the PFAS-laden GAC particles were split into two portions. One portion of GAC particles was freeze-dried, weighed, and extracted using methanol (V_{extr} , mL) with 100 mmol/L NH₄Ac to determine the PFAS mass on GAC before thermal treatment ($M_{\text{PFAS,GAC,initial}}$) by eq 4.³

$$M_{\text{PFAS,GAC}} = (C_{\text{extr}} \times V_{\text{extr}})/E \quad (4)$$

where E (%) is the extraction efficiency and C_{extr} (μmol) is the concentration of PFAS in the extract measured using a Waters Acuity ultrahigh pressure liquid chromatograph (UPLC) coupled with a Waters QToF-MS/MS (Synapt G2-S, Waters Corporation, Milford, MA, USA).

The other portion of PFAS-laden GAC particles was transferred to a porcelain crucible and heated in a temperature-programmable two-zone quartz tube furnace (MTI Corporation, CA) under a flow of N₂ or CO₂ (200 mL/min) to simulate the industrial reactivation process of spent GAC. The sample was heated at 10 °C/min to the desired final heat treatment temperature (HTT = room temperature (non-heating control) to 900 °C) and held for 30 min. Off-gas from the furnace was passed through a series of six beakers containing 50-mL fluoride ions (F⁻)-free deionized water (DW) (#1–5) and methanol (#6). After the thermal treatment and cool down, the crucible was placed in a known volume of DW (#7) and ultrasonicated for 30 min. Concentrations of F⁻ in DW samples and residual PFAS in DW and methanol samples were determined and their mass ($M_{\text{F-,total}}$ and $M_{\text{PFAS,liquid,residual}}$, μmol) were calculated. Concentrations of F⁻ were determined by the standard SPADNS method.⁷⁵ To verify the results obtained in the tube furnace (an open system under a flow of N₂ or CO₂) and to investigate the effect of O₂, certain reactivation experiments were also performed in a closed system in an air atmosphere.³

The above-mentioned adsorption and heating experiments were repeated. After thermal treatment, GAC was extracted by methanol with 100 mmol/L NH₄Ac added to determine the residual concentration of PFAS on GAC ($C_{\text{extr,GAC,residual}}$) and remaining mass ($M_{\text{PFAS,GAC,residual}}$, μmol).³

The thermal decomposition efficiency was calculated by

$$\text{Decomposition (\%)} = \left[1 - \frac{(C_{\text{extr}} \times V_{\text{extr}}/E)_{\text{PFAS,GAC,residual}} + M_{\text{PFAS,liquid,residual}}}{(C_{\text{extr}} \times V_{\text{extr}}/E)_{\text{PFAS,GAC,initial}}} \right] \times 100\% \quad (5)$$

After thermal treatment, if no measurable residual PFAS was detected on GAC and in liquid samples #1–#7, the values of $C_{\text{extr,GAC,residual}}$ and $M_{\text{PFAS,liquid,residual}}$ in eq 5 were assigned to zero or the decomposition efficiency was assigned to 100%.

The yield of F^- from a PFAS with $(2n + 1)$ F atoms during thermal decomposition was calculated with the following equation:³

$$\text{Yield (F}^-) = \frac{M_{\text{F-total}}}{(2n+1)[M_{\text{PFAS,GAC,initial}} - M_{\text{PFAS,GAC,residual}} - M_{\text{PFAS,liquid,residual}}]} \times 100\% \quad (6)$$

Furthermore, we conducted dynamic and isothermal TGA experiments on PFAS powders and identified decomposition products of PFOA using a TD–Pyr–GC–MS system (Agilent GC 7890 and 5975C MS; Santa Clara, CA).

3.2. TASK 2—DETERMINATION OF THE EFFECT OF GAC ON PFAS THERMAL DECOMPOSITION DURING THERMAL REACTIVATION AND COMBUSTION AS A FUEL OF PFAS-LADEN GAC

3.2.1. Thermal treatments (T#1)

The thermal decomposition of the studied PFAS was performed in a closed borosilicate glass container³ in three conditions (T#1, without GAC; T#2, PFAS with GAC; T#3, PFAS pre-adsorbed on GAC). Before the thermal treatment in T#1 (thermolysis), a known quantity (1.2×10^{-5} mol or 0.005 g PFOA) of PFAS powders or solution (in the case of PFBA and HFPO-DA) was added into a pre-cleaned container and air-dried at 25 °C.⁴ The measurement of the weight or volume of PFAS became less accurate below 1.2×10^{-5} mol of PFAS. The container with PFAS was then capped with a ground glass stopper. Next, we set a muffle furnace (Neytech., Vulcan 3-550, USA) to a predetermined temperature (150 °C, 200 °C, 250 °C, 300 °C, or 400 °C), and then quickly put the container with PFAS inside the furnace for an isothermal treatment for up to 180 min. After heat treatment and cooldown, the container was added with DW or methanol (amended with 100 mmol/L NH_4Ac)³ and sonicated for 30 min.⁴ Concentrations of fluoride ions (F^-) in DW and residual PFAS in methanol were determined,³ and their masses (M_{F} and $M_{\text{PFAS,T}}$, mol) were calculated in the manner described previously.³ Our extraction method (methanol with NH_4Ac) achieved recoveries ranging from 80.4% to 111.8% for most of the PFAS involved in this study.³ Concentrations of F^- were determined by the standard SPADNS method.⁷⁵ The analysis of PFAS was carried out on a Waters UPLC system coupled with a Waters ToF-MS²³ (Synapt G2-S, Waters Corporation, Milford, MA, USA).

The thermal decomposition efficiency was calculated by comparing the residual mass of PFAS in heated samples ($M_{\text{PFAS,T}}$, mol) with that in the non-heated controls ($M_{\text{PFAS,i}}$, mol).

The yield of F from a PFAS with $(2n + 1)$ F atoms during thermal decomposition was calculated with the following equation:⁴

$$\text{Yield (F)} = \frac{M_{\text{F}}}{(2n+1)[M_{\text{PFAS,i}} - M_{\text{PFAS,T}}]} \times 100\% \quad (7)$$

The yield of transient intermediates from a parent compound was calculated by⁴

$$\text{Yield (intermediate)} = \frac{M_{\text{intermediate,formed}}}{[M_{\text{PFAS,i}} - M_{\text{PFAS,T}}]} \times 100\% \quad (8)$$

3.2.2. Thermal treatments (T#2)

The thermal treatment in T#2 was performed similarly to that in T#1, except for the addition of a small amount of a porous adsorbent.⁴ The mixture in the container was shaken manually for homogenization before thermal treatment. These porous adsorbents included GAC (Filtrisorb 200, Calgon Carbon Corporation, PA), raw charcoals ($n = 4$), and thermally air-oxidized charcoals ($n = 4$). Two charcoal samples were made from a cellulose-rich feedstock (Maple wood) at a heat treatment temperature of 350 °C (referred as M350) or 600 °C (M600) following a previously published procedure.^{68, 76} Another two charcoal samples were produced from a lignin-rich feedstock (pecan shells) at a heat treatment temperature of 350 °C (P350) or 700 °C (P700). We also prepared porosity-enhanced charcoals by oxidizing raw charcoals in air at 400 °C for 30 min.^{11, 77} The surface areas (SAs) of these PCS were measured with N₂ at 77 K (Autosorb-iQ, Quantachrome, Boynton Beach, FL),⁷⁸ and calculated by the 11-point Brunauer–Emmett–Teller (BET) method. In addition to these carbonaceous materials, we also included a crosslinked polystyrene copolymer resin (Amberlite® XAD-2, Sigma–Aldrich, St. Louis, MO) as an adsorbent in a T#2 experiment. Finally, to examine the possible effect of borosilicate glass, a sample of PFOA was thermally treated along with five 2-mL borosilicate vials (available surface area (SA): 0.0027 m² per vial) to increase the available SA of the borosilicate glass container (0.025 m²) by ~50%.

3.2.3. Thermal treatments (T#3)

To prepare the thermal treatment in T#3, a PFAS chemical was pre-adsorbed to a porous adsorbent in water. We could not conduct gas-phase adsorption experiments because the thermal decomposition of PFCA vapor is inevitable with increasing temperature to or above 150 °C. The test solution was prepared with distilled water containing 1.0×10^{-3} mol/L NaHCO₃ as a buffer and 1.0×10^{-3} mol/L NaCl. The adsorption experiment was performed in 50-mL Thermo Scientific Nunc™ sterile polypropylene vials rotated end-over-end at 10 rpm for four days at ~22 °C.⁴

After adsorption, PFAS-laden adsorbent particles were split into two portions. The first portion was freeze-dried, weighed, and extracted using methanol (V_{extr} , mL) amended with 100 mmol/L NH₄Ac³ to determine the mass before thermal treatment ($M_{\text{PFAS},i}$). The one-point K_D was defined as the ratio of the adsorbed concentration (C_s) to the dissolved concentration at equilibrium (C_w). The second portion of the PFAS-laden adsorbent particles was placed in a closed container and heated in an air environment within a muffle furnace (Neytech., Vulcan 3-550, USA) at a predetermined temperature. After heat treatment and cooldown, the sample was processed in the same way as described above for the T#1 experiment.⁴

3.2.4. Other thermal treatments

We also performed thermal decomposition in the atmosphere of N₂. In this experiment, the sample to be heated was first placed into a container, and purged with N₂ for 15 min to remove air. The container was then capped with a ground glass stopper and heated in the muffle furnace at a predetermined temperature.⁴

In addition to isothermal treatment, we also examined the decomposition of PFAS in a dynamic thermal environment. Briefly, a known quantity of PFOA/PFOS chemical powders was placed in a closed container and heated dynamically in the muffle furnace at a 10 °C/min heating rate. This heating rate was used previously in TGA.³ After heat treatment and cooldown, the samples were treated in the same manner as the T#1 experiment.

Finally, the thermal decomposition of PFOA³ and PFOS at low and moderate temperatures (≤ 500 °C) was also studied by means of TD-Pyr-GC-MS (Agilent GC 7890 and 5975C MS; Santa Clara, CA).^{3,7}

3.3. TASK 3—DEVELOPMENT OF TAILORED GAC TO FACILITATE THE ADSORPTION OF PFAS FROM WATER

3.3.1. Sorbent Preparation and Characterization

From the PCS family, we selected biochar as a candidate because of its cost-effectiveness and the ready availability of feedstocks.^{17, 18} The PCS (biochars) were prepared by pyrolyzing softwood shavings (mixed species) at 300, 400, 500, or 600 °C for 2 h under N₂ flow.⁷⁹ The samples were named SWXXX, where SW is softwood feedstock, and XXX the temperature. Portions were subjected to post-pyrolysis air oxidation (PPAO) by placing them in open 60-mL glass vials (0.10 g per vial) in a muffle furnace at 400 °C for 30 min in air.⁸⁰ The PPAO-treated products were named with the appendage -PPAO. Another portion of SW500 was coated with pDADMAC (Sigma) by equilibrating the raw biochar with a pDADMAC solution and thoroughly rinsing the collected solid;⁸¹ it was labeled as SW500-PD. Previously we found that pDADMAC adsorption on an activated carbon was essentially irreversible,⁸¹ and the coated amount was 23.1 mg pDADMAC per gram SW500-PD.⁷⁹ A portion of SW500 was first PPAO-treated and then coated with pDADMAC; this sample was labeled SW500-PPAO-PD. Gas porosimetry was performed with CO₂ at 273 K and with N₂ at 77 K on an Autosorb iQ (Anton Paar). Pore size distribution was simulated by Non-local Density Functional Theory (DFT) for CO₂ adsorption isotherm and Barrett-Joyner-Halenda theory (relative pressure $P/P_0 = 0.35\text{--}0.92$) for N₂ adsorption isotherm using built-in software. Non-local DFT also simulated total pore volume. DFT simulation was not used for N₂ adsorption isotherm because data cannot be obtained at very low P/P_0 ($= 10^{-7}$) with the biochars, due to diffusion limitation of N₂ at the cryogenic temperature.⁸³ Zeta potential was measured using a Malvern Zetasizer Nano ZS90. Additional data on surface chemical properties, morphology, and structure of the sorbents are available elsewhere.⁷⁹

3.3.2. PFAS Adsorption Experiments

We tested HFPO-DA, PFBA (C₄, or 4 carbons in the structure), PFPeA (C₅), PFHpA (C₇), PFOA (C₈), PFNA (C₉), PFDA (C₁₀), PFUnDA (C₁₁), PFBS (C₄), PFHxS (C₆), and PFOS (C₈). The chemicals were from Sigma-Aldrich except for GenX and PFHpA, which were from Fisher Scientific. Solutions were prepared in ultrapure water containing 1 mM NaCl and buffered at pH 7.4 with 1 mM NaHCO₃ (-PPAO series and their controls) or at pH 7.0 with 3 mM phosphate (-PD series and their controls).^{17, 18}

The -PPAO series (except for SW500-PPAO) were equilibrated with PFAS mixtures, sometimes including just the shorter-chain compounds or the longer-chain compounds. The -PD series were equilibrated with individual solutes (PFPeA, PFNA, PFBS, or PFOS).¹⁷

Adsorption was performed by placing 100–400 mg unmodified or modified biochar in contact with 10, 15, or 25 mL PFAS solution (unless otherwise specified) in 50-mL sterile polypropylene vials at prescribed initial PFAS concentrations (0.0687–8.53 μM). The vials were shaken end-over-end at 22 °C for 2, 4 or 14 days. The aqueous phase was filtered through a 0.45- μm nylon membrane for analysis. Controls were prepared in the biocide-added test solution. Sorbent-free controls were spiked with a PFAS at the same initial dose as in the corresponding test

vials. These control samples were manipulated in the same manner as test samples. The sorbed level (q , $\mu\text{mol/g}$) was computed by subtracting the concentration in the test vial (C_{aq} , μM) from that in the corresponding control vial and then normalizing for the sorbent mass in the test vial. The distribution ratio K_D (L kg^{-1}) is defined as the ratio of sorbed concentration ($\mu\text{g kg}^{-1}$) to the solution concentration in the test vials. Adsorption isotherms were fit to the Freundlich model,

$$q = K_F \times C_{\text{aq}}^n \quad (9)$$

where K_F is the affinity coefficient, and n is the linearity exponent. The K_F and n were obtained by linear regression of the log-transformed expression of eq. 9. The K_F equals the solid-to-solution distribution ratio K_D (L kg^{-1}) at a unit dissolved concentration ($1 \mu\text{M}$).

3.3.3. Analysis of PFAS

PFAS were analyzed by UPLC–HRMS using either a Waters Acquity UPLC coupled with a Synapt G2-S hybrid quadrupole time-of-flight HRMS.

3.4. TASK 4—REMOVAL OF PFAS FROM CONCENTRATE STREAMS GENERATED FROM NF AND RO

Five commercial thin film composite polyamide (PA) membranes were used, including four NF membranes (NF270, NF90, NFX, and DK) and one RO membrane (SW30). NFX was purchased from Synder Filtration (Vacaville, CA), and DK was obtained from Osmonics GE Water (Trevose, PA). NF90, NF270, and SW30 were supplied by Dow FilmTec (Minneapolis, MN). Six PFAS and HFPO-DA were from Sigma Aldrich (St. Louis, MO). Methanol (optima grade), NaCl, and NaHCO_3 were supplied by Fisher Scientific (Santa Clara, CA), and NOM (Suwannee River Natural Organic Matter) was from the International Humic Substance Society (St. Pual, MN). Ultrapure water (UPW) was obtained from a Milli-Q system (Millipore, Billerica, MA).

3.4.1. Concentration test for membrane selection

PFAS rejection and concentration were conducted in duplicates by a custom-assembled crossflow filtration cell (Sterlitech, Auburn, WA) with an active membrane area of 42 cm^2 . Dry flat membrane coupons were first rinsed and soaked in the UPW for 24 h to completely wet and stretch the pores, and then precompacted for 2 h under the operation pressure by UPW to ensure a stable operation condition. Subsequently, the feed solution with $1 \mu\text{M}$ PFAS in 1.5 L synthetic groundwater containing 1 mM NaCl, 2 mM NaHCO_3 , and 1 mg/L NOM was introduced into the system. The water recovery (WR) and flux were obtained by monitoring the weight of permeate. The operation pressure for PFAS concentration was 8 bar and the temperature was kept at 25°C . The concentration experiments continued until a WR of 90% was achieved.

$$WR = \frac{F_p}{F_f} \times 100\% \quad (10)$$

where F_p and F_f are flow rates of permeate and feed solution (L/min), respectively. PFAS rejection rate (R) was calculated as follows:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (11)$$

where c_p and c_f are PFAS concentrations in permeate and feed solution (μM), respectively.

3.4.2. Static adsorption of PFAS on membranes

The static adsorption of six PFAS on five membranes was duplicated in 50 mL high-density polyethylene bottles (Thermo Scientific Nalgene) containing 25 mL PFAS (1 μ M) solution and 10 cm² membrane pieces. The bottles were kept at 25 °C for 24 h to reach a steady state. After that, membranes were removed, and PFAS were extracted with 10 mL methanol amended with NH₄Ac. Control adsorption tests without membranes were duplicated to eliminate the influence of containers.

3.4.3. PFAS concentrate from NF

The NF90 was selected to obtain the PFAS concentrate for subsequent treatment considering the PFAS rejection, adsorption, and flux. The NF90 membrane was housed on a spiral-wound membrane module (Sterlitech, Auburn, WA) with a 2.6 m² active membrane area.

Synthetic groundwater solution (10 L) with 1 μ M PFAS and HFPO-DA was introduced to the feed tank under the same operation condition as the concentration test part to obtain 1-L concentrate.

4. Results and Discussion

4.1. TASK 1—INVESTIGATION OF THERMODYNAMICS AND KINETICS OF THERMAL PFAS DECOMPOSITION IN BOTH INERT AND OXIDATIVE ATMOSPHERES

We started this project by employing TGA to determine the temperature needed to volatilize PFAS in three different atmospheres (O₂, CO₂, and N₂).

4.1.1. Thermal stability of PFAS – TGA

TGA is a thermal analysis technique that measures the weight loss of a sample as a function of temperature or time. It is widely used in fields such as polymer science, biomass technology, and chemical engineering. However, its application in studying the thermal behavior of PFAS is unprecedented prior to this research. In a recent study,³ we innovatively applied TGA to study the thermal stability of PFAS, and the results revealed very interesting and novel results. In one instance, we performed *dynamic* TGA scans from room temperature to a predetermined temperature. The other TGA experiment was devoted to the calculation of the weight loss of PFAS under *isothermal* conditions.³

According to TGA (Figure 1) and thermal degradation (Figure 2) results, PFAS exhibited the following order of thermal stability: PFSAs >> PFUnDA > PFDA > PFNA > PFOA > short-chain PFCAs > HFPO-DA. TGA curves of PFCAs shifted to a higher temperature when the number of perfluorinated carbons (*n*CF₂) increased (Figures 1a–1c).³

An increase in one perfluorinated carbon unit (–CF₂–) led to a rise of *T*₅₀ by approximately 11 and 9 °C for PFCAs and PFSAs, respectively. *T*₅₀ varied insignificantly between different atmospheric environments (N₂, CO₂, O₂) (Figure 1d).³

Analysis of isothermal TGA data revealed that the weight loss (destabilization) of PFAS follows first-order kinetics (Figure 1). Figures 1e and 1f show Arrhenius- and Eyring-like plots for first-order weight-loss rate constants (*k*) of PFOS and PFOA.³

4.1.2. Extraction of PFAS from spent GAC

Investigating and comparing various extraction strategies for the efficient extraction of PFAS from spent GAC is crucial for determining the thermal degradation rate of PFAS. In our study, pure methanol, whether heated (at 60 °C) or not, resulted in low recoveries (30.0–67.8%) of PFAS from GAC (Figure 3). Methanol that was amended with NaOH improved extraction for PFASs (71.6–82.5%) but consistently had recoveries greater than 130% for PFCAs. On the other hand, methanol added with NH₄Ac achieved recoveries ranging from 79.2 to 111.8% for most of the PFAS.³

4.1.3. PFAS Degradation during GAC Thermal Reactivation

We then determined PFAS degradation during the conventional GAC thermal reactivation and identified and quantified PFAS thermal degradation products. Commercial GAC is a highly porous pyrogenic carbonaceous material produced from bituminous coal, wood, or coconut shell which is activated at 700 °C and above in CO₂ or steam. Spent GAC can be thermally reactivated or regenerated, used as a fuel for combustion, or landfilled, depending on whether the spent GAC is deemed nonhazardous. During thermal reactivation, the exhausted carbon is heated for ~30 min with hot inert gases (e.g., N₂), CO₂, or steam.⁴

We found that a 20-min thermal treatment achieved >90% decomposition of PFCAs and PFASs on GAC at 200 and 500 °C, respectively (Figure 2). A 30-min thermal treatment of spent GAC at ≥300 °C in either N₂, CO₂, or air achieved ≥99.9% removal of HFPO-DA and ≥99% removal of PFCAs (e.g., PFOA) (Figure 2). HFPO-DA was more readily decomposed than PFCA with the same *n*_{CF₂} (i.e., PFBA) (Figure 2), indicating that the perfluorinated chain became less thermally stable with the inclusion of an ether group. A much higher heat treatment temperature (or HTT) (≥500 °C) is needed to achieve ≥99% decomposition of PFASs (e.g., PFOS) on GAC during a 30-min thermal treatment (Figure 2). According to the measured yields of F⁻, significant mineralization of PFOA/PFOS requires an HTT of ≥700–800 °C. For example, the mineralization rate of PFOA on GAC increased sharply to 92.4 mol% at 700 °C from 9.4–28.8 mol% at 150–600 °C (Figure 2).⁴

4.1.4. Thermal decomposition kinetics of PFAS

The thermal decomposition of PFAS was investigated in three conditions (#1, #2, and #3; see Figure 4). In condition #1, PFAS was heated without the presence of GAC, while a known amount of GAC was heated together with PFAS in condition #2.⁴ In condition #3, PFAS was pre-adsorbed to GAC particles.⁴ More details can be found in our previous publication.⁴ We found that the thermal decomposition of PFAS mostly followed first-order kinetics at temperatures of 150–250 °C, in which the residual PFAS mass (*M*_{PFAS,T}) decreased exponentially as a function of the heating time (Figure 4). At a higher temperature (300 °C), the decomposition of these chemicals can also be described by second-order kinetics, in which a plot of 1/*M*_{PFAS,T} versus heating time was approximately linear. For comparison purposes, we used the first-order decomposition rate constant (*k*_{1st}, min⁻¹) in the following discussion.⁴

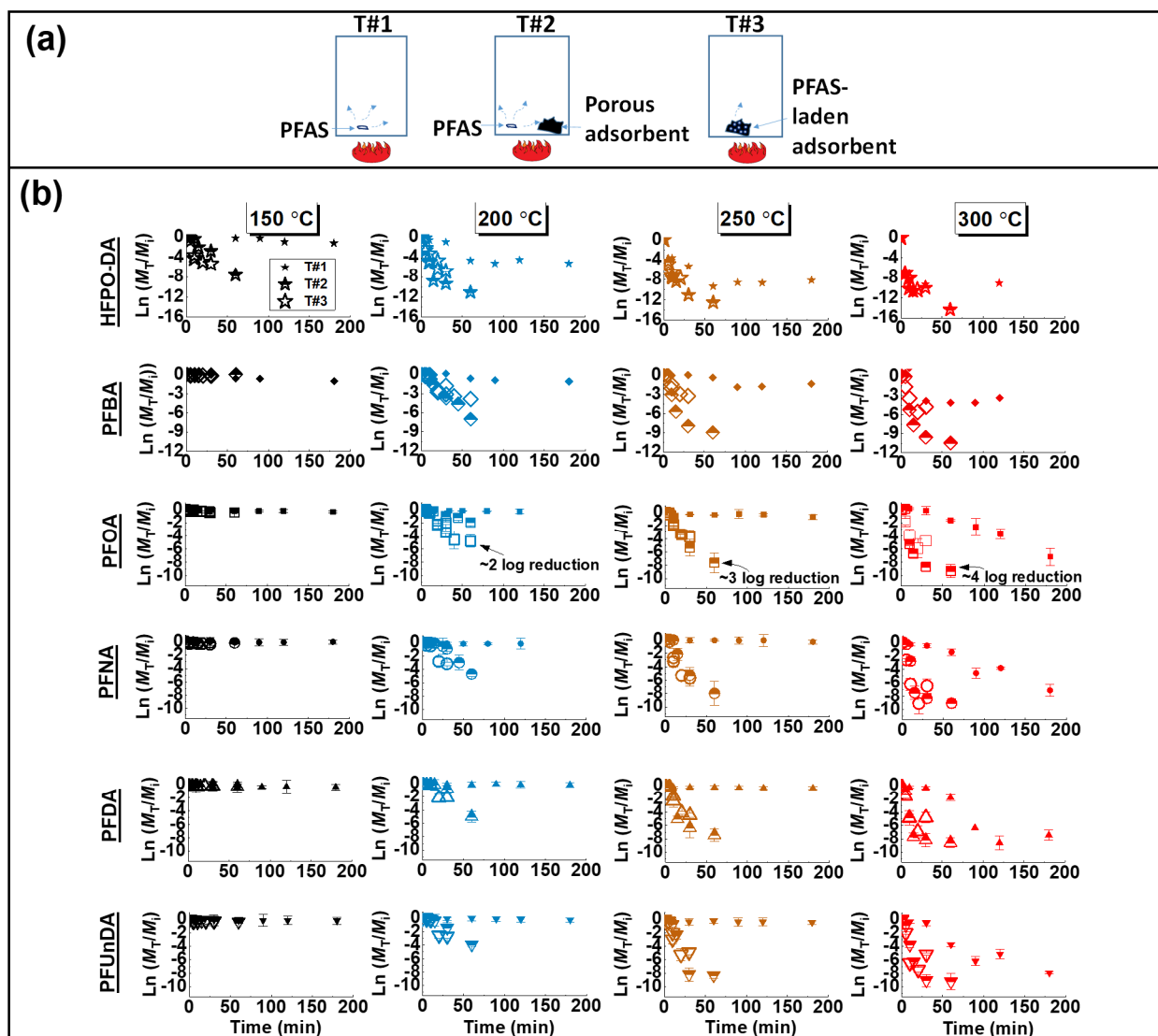


Figure 4. (a) A schematic of PFAS thermal decomposition experiments in a closed system in three conditions (T#1, T#2, T#3). (b) Degradation of studied PFAS and a PFAS alternative (HFPO-DA) at various temperatures.⁴ Thermal treatments were triplicated for PFOA, PFNA, PFDA, and PFUnDA. The error bars represent the standard deviation (1-sigma) of three trials. Some points without visible error bars have errors that are smaller than the symbol. T#1 (closed symbols): PFAS only (initial PFAS mass: 1.2×10^{-5} mol). T#2 (half-open symbols): PFAS (1.2×10^{-5} mol) with the presence of 0.1 g GAC. T#3 (open symbols): 0.1 g of GAC laden with $3.0\text{--}4.5 \times 10^{-7}$ mol PFAS. M_T and M_i are the residual mass of PFAS in heated samples and the initial mass in non-heated controls, respectively. The degradation of studied PFAS at 150 °C occurred at a slow rate.

The value of k_{1st} was below 0.005 min^{-1} for PFCAs at 150–250 °C in T#1. PFECA (HFPO-DA) appears to be more easily degraded than the PFCA with the same number of perfluorinated carbons (i.e., PFBA) (Figure 4). This shows that the perfluorinated chain becomes less thermally stable with the inclusion of a foreign group, such as the ether group.⁴

4.2. TASK 2—DETERMINATION OF THE EFFECT OF GAC ON PFAS THERMAL DECOMPOSITION DURING THERMAL REACTIVATION AND COMBUSTION AS A FUEL OF PFAS-LADEN GAC

After determining the temperatures and time needed for thermally degrading PFAS on GAC, we moved on to understand the thermal decomposition kinetics, products, and mechanisms of PFAS.

4.2.1. Effect of GAC on the Thermal Decomposition Kinetics of Long-chain PFCAs

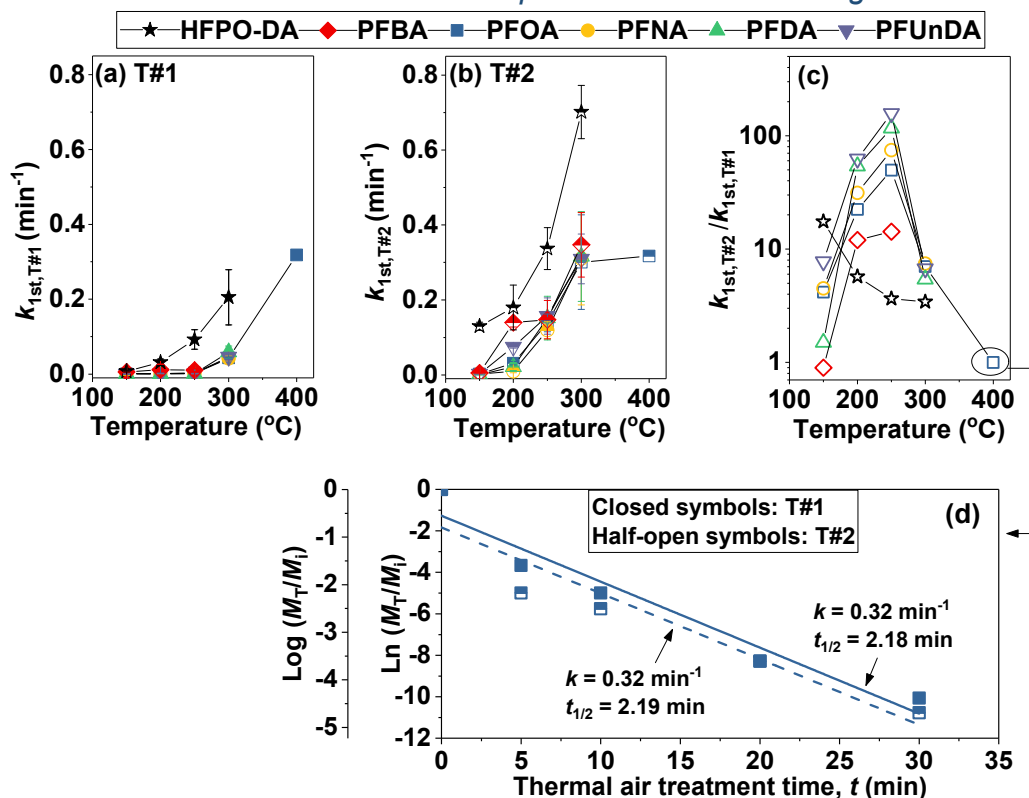


Figure 5. (a–c) First-order decomposition rate constants (k_{1st} , min^{-1}) of PFCAs (1.2×10^{-5} mol) treated at different temperatures in conditions of T#1 (thermolysis; closed symbols) and T#2 (with the presence of 0.1 g of GAC; half-open symbols). (d) Thermal decomposition of PFOA (1.2×10^{-5} mol) in T#1 and T#2 (with the presence of 0.1 g GAC) in a closed container at 400 $^{\circ}\text{C}$. Lines in (d) represent the best fit to the decomposition data using the first-order kinetic model.⁴

As illustrated in Figure 5, GAC accelerated the thermal decomposition of HFPO-DA at temperatures as low as 150 $^{\circ}\text{C}$ in T#2 and T#3 conditions. The GAC-induced acceleration was evident for PFCAs at 200 $^{\circ}\text{C}$, and up to a 60-fold increase in k_{1st} was observed (T#2 and T#3) (Figure 5). This acceleration became even more significant at 250 $^{\circ}\text{C}$, which led to a 150-fold increase in k_{1st} for PFUnDA (Figure 5). As displayed in Figure 5, the acceleration effect was less pronounced for the short-chain PFAS (PFBA) because the adsorption of PFBA on GAC was much weaker than that of long-chain homologs. The effect of GAC became less marked at higher temperatures of 300 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$ at which the significant thermolysis (T#1) of PFCAs was seen (Figure 5). Thermal treatment at 300 $^{\circ}\text{C}$ in T#2 led to near complete decomposition (>99.99%) of PFOA within 60 min. No attempt was made to maximize the thermal decomposition of PFCAs.⁴

Because PFCEA and PFCA molecules were not pre-adsorbed on GAC in T#2 treatments, we hypothesized that the accelerated decomposition was caused by the adsorption of gas-phase PFCEA/PFCA on GAC that is much more thermally conductive ($0.4\text{--}1.36\text{ W}/(\text{m}\cdot\text{K})$) than air ($<0.032\text{ W}/(\text{m}\cdot\text{K})$) at $\leq 100\text{ }^{\circ}\text{C}$).^{9, 10} The heat transfer is more efficient on GAC than in air. On the other hand, the thermal conductivity of air increased with temperature. At $400\text{ }^{\circ}\text{C}$, the effect of GAC amendment on the thermal decomposition rate of PFAS appeared to be much less important.⁴

4.2.2. Effect of Other Porous Carbonaceous Materials and Porous Resin

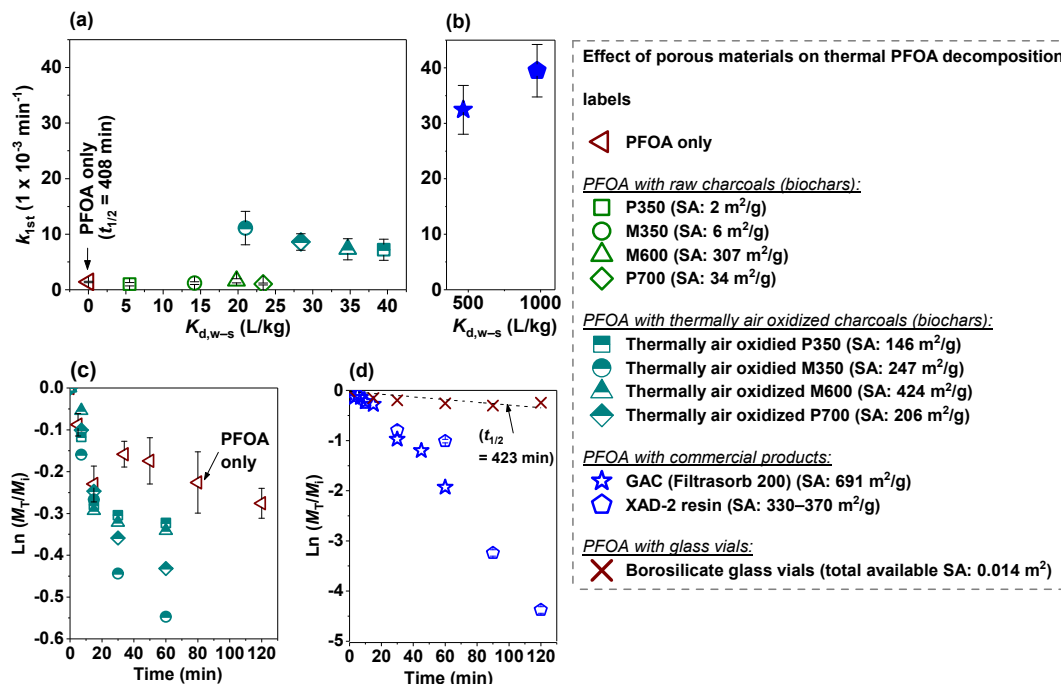


Figure 6. (a) and (b): First-order decomposition rate constants (k_{1st} , $1 \times 10^{-3} \text{ min}^{-1}$) of PFOA ($1.2 \times 10^{-5} \text{ mol}$) treated at $200\text{ }^{\circ}\text{C}$ in T#1 (thermolysis) or in T#2 with the presence of a raw charcoal sample (M350, M600, P350, or P700) (0.5 g), a thermally air-oxidized charcoal (0.1 g), GAC (Filtrisorb 200) (0.1 g), a non-carbonaceous porous material (XAD-2 resin) (0.1 g), or five 2-mL borosilicate vials ($11.1 \pm 0.01 \text{ g}$). (c) and (d): Thermal decomposition of PFOA in different conditions at $200\text{ }^{\circ}\text{C}$. The dashed line in (d) represents the best fit to the decomposition data using the first-order kinetic model. The N_2 B.E.T. SA of XAD-2 resin was obtained from the literature.^{84, 85} The N_2 B.E.T. SAs of nine PCM adsorbents were measured in this study.⁴

We then conducted T#2 experiments with various PCSs of different surface areas and one non-carbonaceous material, XAD-2 resin. The results were plotted as a function of the K_D of PFOA (Figure 6). Charcoals have a higher thermal conductivity, $0.08\text{--}0.18\text{ W}/(\text{m}\cdot\text{K})$,^{86, 87} than air. However, raw charcoals are primarily microporous ($\leq 20\text{ \AA}$).¹¹ Steric hindrance can result from narrow pore throats, internal obstructions, or pore blockage by occluded non-covalently bound matter such as pyrolysis tars.^{68, 88} The length of PFOA molecules is approximately $10\text{ \AA}$.⁸⁹ The steric bulk of PFOA molecules may limit their access to the interior micropore SA of raw charcoal that is available to N_2 molecules. Therefore, low adsorption of PFOA on raw charcoals was observed (Figure 6), and the thermal decomposition of PFOA was not accelerated with the addition of a raw charcoal sample (M350, M600, P350, or P700).

The thermal air oxidation of raw charcoals caused pore wall etching and/or unclogging of pores bearing tarry deposits generated during the carbonization step.^{11, 12} This, in turn, widened pores of charcoal and created new SA, which helped relieve steric hindrance for adsorption of PFOA molecules (Figure 6). As illustrated in Figure 6, the thermal decomposition of PFOA increased significantly with the addition of a thermally air-oxidized charcoal. Commercial porous materials, GAC (or activated charcoal) and XAD-2 resin, adsorbed PFOA strongly (Figure 6) and reduced the thermal decomposition half-life of PFOA from ~400 min to less than 25 min at 200 °C (Figure 6). The N₂ B.E.T. SA of the XAD-2 resin (330–370 m²/g) was lower than that of the thermally air-oxidized M600; however, the XAD-2 resin is characterized by a broad pore size distribution and a mean pore size of 90 Å. Mesopores (20–500 Å) have shown to be important for molecules to access deeper and smaller pores of adsorbents.⁶⁸ Finally, the borosilicate glass appeared to have no significant effect on the thermal decomposition of PFOA (Figure 6).

4.2.3. Identification and Quantification of Decomposition Products of Long-chain PFCAs With and Without the Presence of GAC

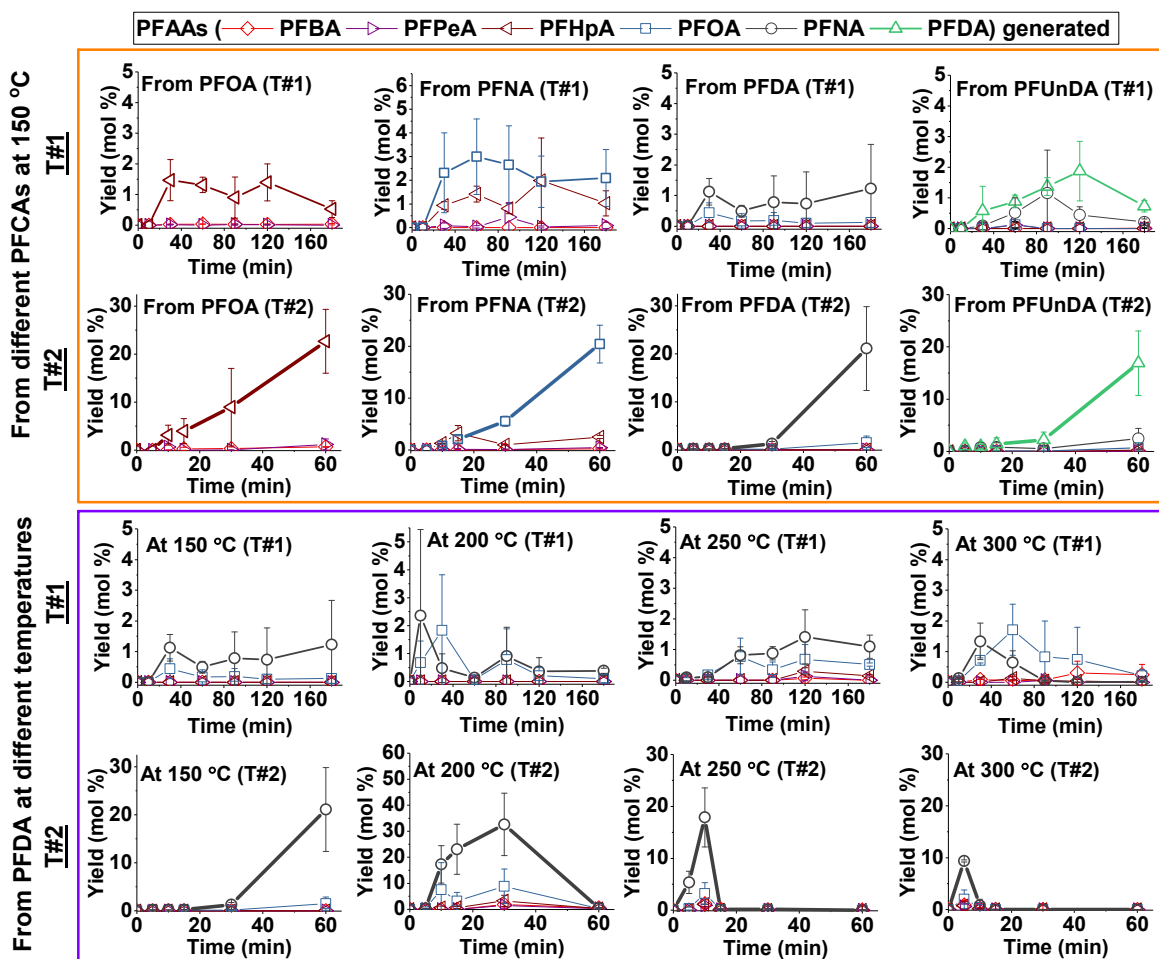


Figure 7. Generation (and subsequent decomposition) of intermediate short-chain PFCAs from parent compounds treated with (T#2) or without (T#1) GAC. Note the difference in y-axis scales.⁴

We identified many transient intermediates during the thermal degradation of PFCAs. PFCAs yielded several transient short-chain intermediates at temperatures as low as 150 °C (Figure

7). The highest-yielding intermediate product for a parent PFCA with n perfluorinated carbons was usually the shorter-chained PFCA with $(n - 1)$ perfluorinated carbons (Figure 7). For example, PFDA yielded shorter-chain PFCAs in the following order, PFNA > PFOA > PFHpA $\approx$ PFPeA $\approx$ PFBA. Similarly, the highest-yielding byproduct of PFOA was PFHpA, whereas PFBA was a trace intermediate product. This formation pattern seems to agree with the stepwise defluorination mechanism (Pathway II in Figure 8) that has been developed for photocatalysis,¹³ reduction by hydrated electrons, and plasma¹⁴ treatments of PFAS. However, a closer look at the results reveals that it is not the predominant mechanism of the thermolysis of PFAS. First, the yield of intermediate PFCAs was low (<5 mol %). Second, a clear stepwise pattern was not observed because all the short-chain intermediates appeared nearly simultaneously.^{4, 7}

4.2.4. Thermal Decomposition Pathways of Long-chain PFCAs

We believed the thermal decomposition of PFAS involved multistep radical chain reactions, including initiation, chain propagation, recombination, and termination.¹⁶ Because of the strong C–F bond, we believed that the thermal decomposition of PFOA was initiated with the homolytic cleavage of the relatively weak C–C bond located next to the carboxyl group of PFOA, or with the C–S bond next to the sulfonate group of PFOS. The C–C or C–S bond split, forming a nonfluorinated moiety and a perfluoroalkyl biradical such as $\cdot\text{C}_7\text{F}_{14}$ (m/z 350.0) from PFOA or $\cdot\text{C}_8\text{F}_{16}$ (m/z 399.9) from PFOS. The perfluoroalkyl radical further underwent a series of defluorination, or radical chain propagation reactions, generating shorter-chained perfluoroalkyl radicals (Figure 8). These perfluoroalkyl radicals might recombine with carboxyl group/radical successively yielding PFCA intermediates. Eventually, these chain propagation reactions were terminated by producing the “dead,” or very short, fluorinated units. In Pathway I (Figure 8), transient PFCA intermediates were the minor product.⁴

The presence of GAC altered the decomposition pathway of PFCAs and significantly increased yields of shorter-chained PFCA intermediates at 150 °C. At 200 °C, the yield of PFNA from PFDA was maximized after a 30-min treatment when GAC was present, and then disappeared on the same time scale as the parent compound (i.e., PFDA). At a higher temperature (300 °C), the yield of PFNA from PFDA dropped to <10 mol % after a 5-min treatment and was negligibly low with a longer heating time as PFNA quickly decomposed.⁴

Decarboxylation or end-chain scission is commonly referenced in existing literature as the predominant mechanism for the degradation of PFCAs.^{90, 91} However, it cannot explain the formation of shorter-chained homologs from PFCAs. We believed that random-chain scission was an effective mechanism leading to the degradation of PFCAs in the presence of GAC. Random scission is characterized by the homolytic cleavage of C–C bonds at unpredictable locations along the perfluorinated chain, resulting in perfluorinated radicals of different chain lengths. Our recent experimental and computational findings supported this mechanism.^{4, 7} High-throughput DFT analyses revealed that the most susceptible C–C bond is between the α -C and β -C, rather than between the α -C and the carboxyl C. This pathway produced perfluorinated radicals that engage in further chain propagation reactions.⁷

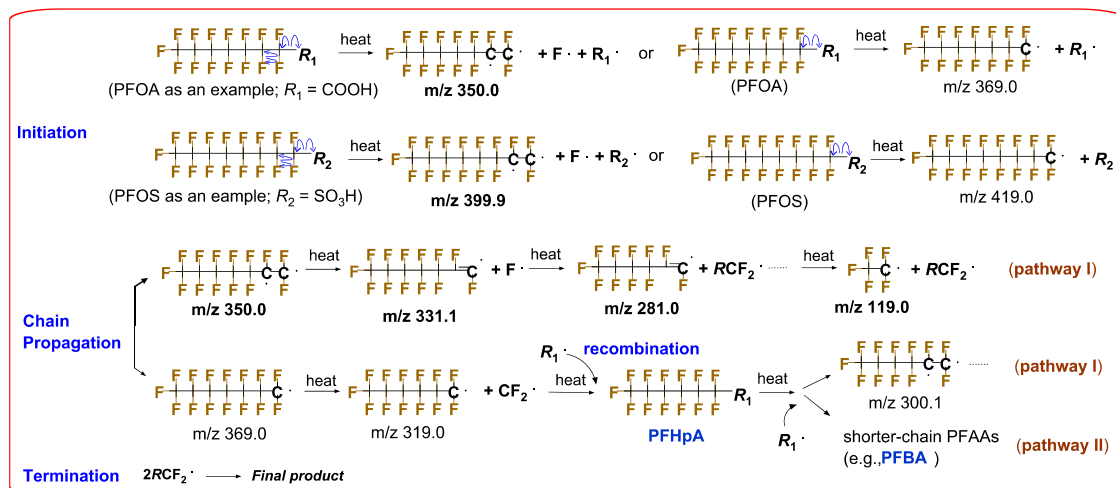


Figure 8. Possible “unzip” decomposition pathways of perfluoroalkyl substances during thermal treatment. Species with m/z 399.9, 350.0, 331.1, 281.0, and 119.0 were shown in TD–Pyr–GC–MS spectra of PFOA and PFOS. We found no MS spectral evidence for $\cdot\text{C}_7\text{F}_{14}$ (m/z 300.1), $\cdot\text{C}_6\text{F}_{13}$ (m/z 319.0), $\cdot\text{C}_7\text{F}_{15}$ (m/z 369.0), and $\cdot\text{C}_8\text{F}_{17}$ (m/z 419.0), but this does not preclude their formation in small amounts.⁴

4.2.5. Thermal Decomposition PFECAs and Short-chain PFCAs

The chain-scission mechanism also applies to the thermal degradation of PFECAs, such as HFPO-DA.⁷ Figures 9 and 10 illustrate the thermal degradation of PFECAs and short-chain PFCAs pre-adsorbed on adsorbents. In selected experiments, a high initial mass (up to 75.9 $\mu\text{mol/g}$) of PFECAs was directly added to AmberChrom® 1X8 to estimate the maximum percentage removal (Figure 10). Regardless of concentrations of PFAS in the resin, all these PFAS compounds exhibited near-complete degradation (>98.59%) in as little as 30 min at 500 °C. Deformation of the resin beads was seen at 300 °C and above. No attempt was made to reuse the decontaminated resin beads as they are intended for single use only.⁷

Upon heating PFECAs and PFCAs at 500 °C, no new noteworthy peaks emerged in UPLC–HRMS chromatograms of full scans and HRPIS, signifying rapid degradation of both parent compounds and transient intermediates at this temperature.^{3, 8} For example, Yao et al. demonstrated that perfluoroheptene, a notable thermal decomposition product of PFOA, starts to degrade at a temperature as low as 200 °C.⁸

PFECAs were more prone to degradation than PFCA counterparts. HFPO-DA had a half-life of 4.3 min at 200 °C compared to 13 min for PFBA (Figure 9a). The half-lives of both chemicals decreased as the heating temperature increased (e.g., 5.0 min for PFBA at 400 °C).⁶ The relatively long half-lives of parent PFAS at low temperatures allowed us to compare the thermal stability and capture transient thermal decomposition products. The thermal degradation rate constants declined in the following order: PFECAs > PFCAs > unsaturated PFCA (i.e., PFMeUPA). The most notable features of Figure 9—as well as a side-by-side comparison of Figures 9a and 9b—are the significant yields of TFA, PFPrA, and HFPO-DA when a mixture of studied PFECAs and PFCAs was heated at low temperature (Figures 9b and 9c). These results indicate the formation of TFA, PFPrA, and HFPO-DA during thermal treatments.⁷

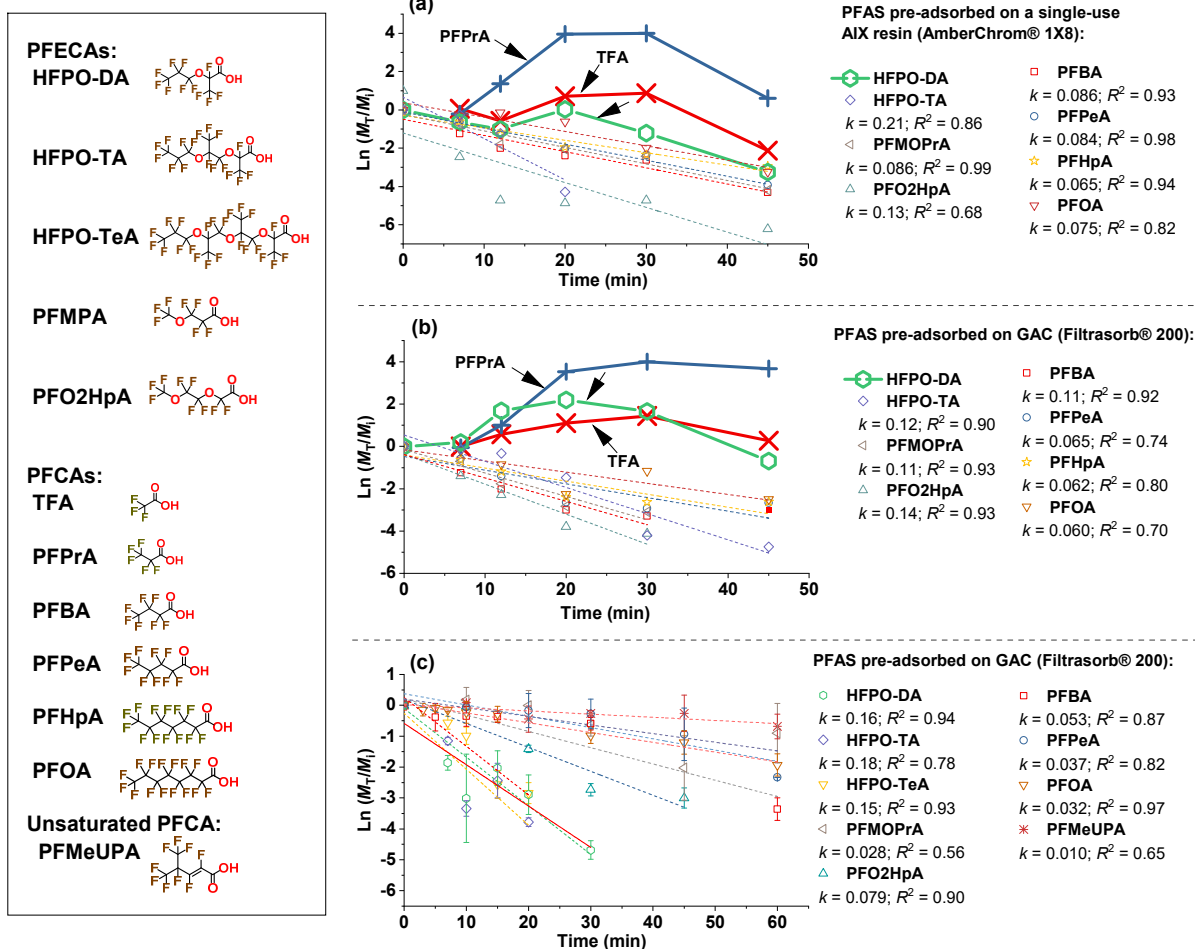


Figure 9. Thermal degradation of PFECAs and PFCAs on adsorbents at 200 °C for up to 60 min in N₂. In panels a and b, the adsorbent was laden with a mixture of the PFAS, whereas the adsorbent was laden with one PFAS chemical in panel c. Initial PFAS loading on GAC (μmol/g): HFPO-DA, 5.9–7.6; HFPO-TA, 21.2–42.6; HFPO-TeA, 18.0; perfluoro(3-methoxypropanoic) acid (PFMPA), 1.2–2.5; perfluoro-3,6-dioxahexanoic acid (PFO2HpA), 1.7–2.6; PFBA, 1.5–2.1; PFPeA, 1.9–3.5; PFHpA, 3.1–4.9; PFOA, 7.2–12.5. The generation and subsequent degradation of TFA, PFPrA, and HFPO-DA during the treatment were illustrated by arrows in this figure. M_i and M_t refer to the mass of PFAS (μmol/g) before and after the thermal treatment, respectively (eq 1); for TFA and PFPrA, M_i was the mass after 7-min of heating. The dashed lines represent the best linear fits, assuming a pseudo-first-order degradation. The degradation rate constants (k , min⁻¹) were given. After heating for over 30 min, the residual PFECAs were typically below the detection limits of the method.⁷

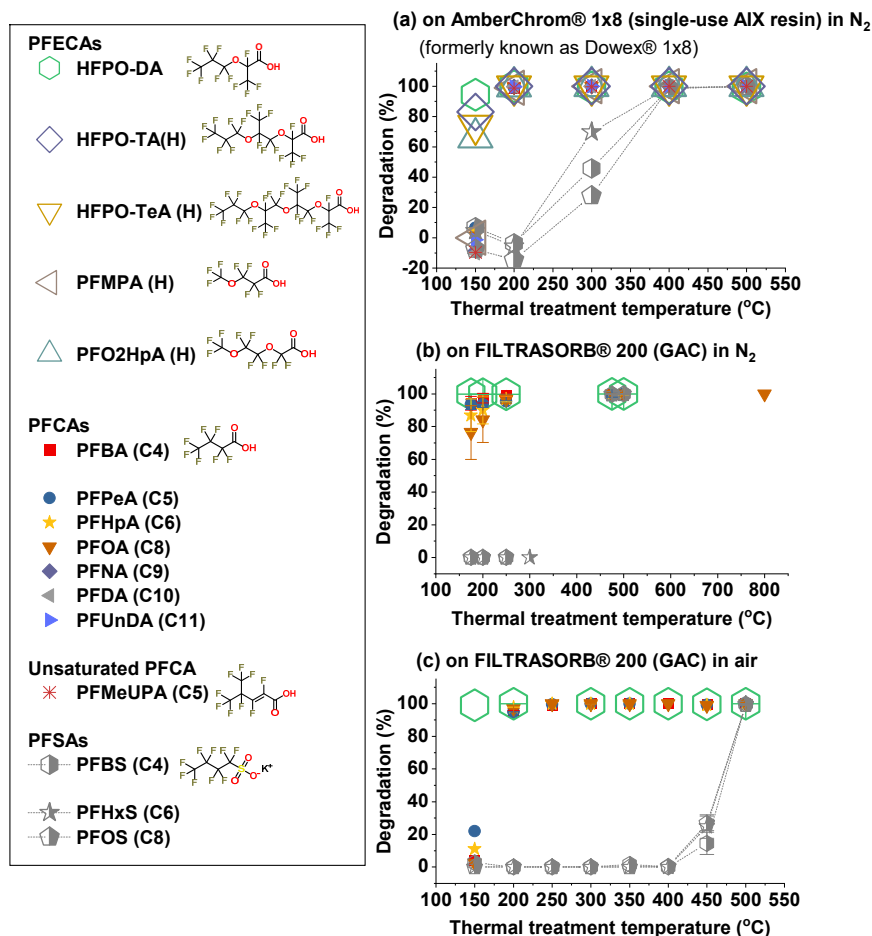


Figure 10. Thermal decomposition of a mixture of HPFO-DA, PFCAs, and PFSA pre-adsorbed on (a) a single-use resin and (b, c) GAC.³ Thermal treatment was conducted at different temperatures for 30 min. In selected experiments, a high (H) initial mass of a mixture of PFECAs (e.g., PFMPA (H)) was directly added to the resin to estimate the maximum percentage removal of PFCEAs upon heating.⁷

4.2.5. Thermal Decomposition Products of PFECAs

We conducted additional thermal treatment experiments on individual PFECAs (Figure 9c) to capture short-lived transient intermediates of PFECAs and short-chain PFCAs. Figure 11 displays the evolution of detected transient intermediates from PFECAs, which can be grouped into two categories: small intermediates and relatively large ones with a UPLC retention time close to that of the parent compound. These transient intermediates were assigned by comparing their UPLC retention time and MS fragmentation patterns with authentic standards.⁷

Three transient organic intermediates (I, II, III) of HFPO-DA were detected by UPLC–HRMS. Compound I with m/z 212.9792 and MS fragments characteristic of PFCAs (C_3F_7 , m/z 168.9894; C_2F_5 , m/z 118.9926) was assigned to be PFBA. This was further substantiated by an authentic standard. Compounds II and III were identified as PFPrA and TFA, respectively, confirmed with corresponding authentic standards. Figures 9 and 11 show that they built up rapidly but decomposed within 60 min. To our knowledge, these PFCAs were identified for the first time as thermal decomposition products of HFPO-DA.⁷

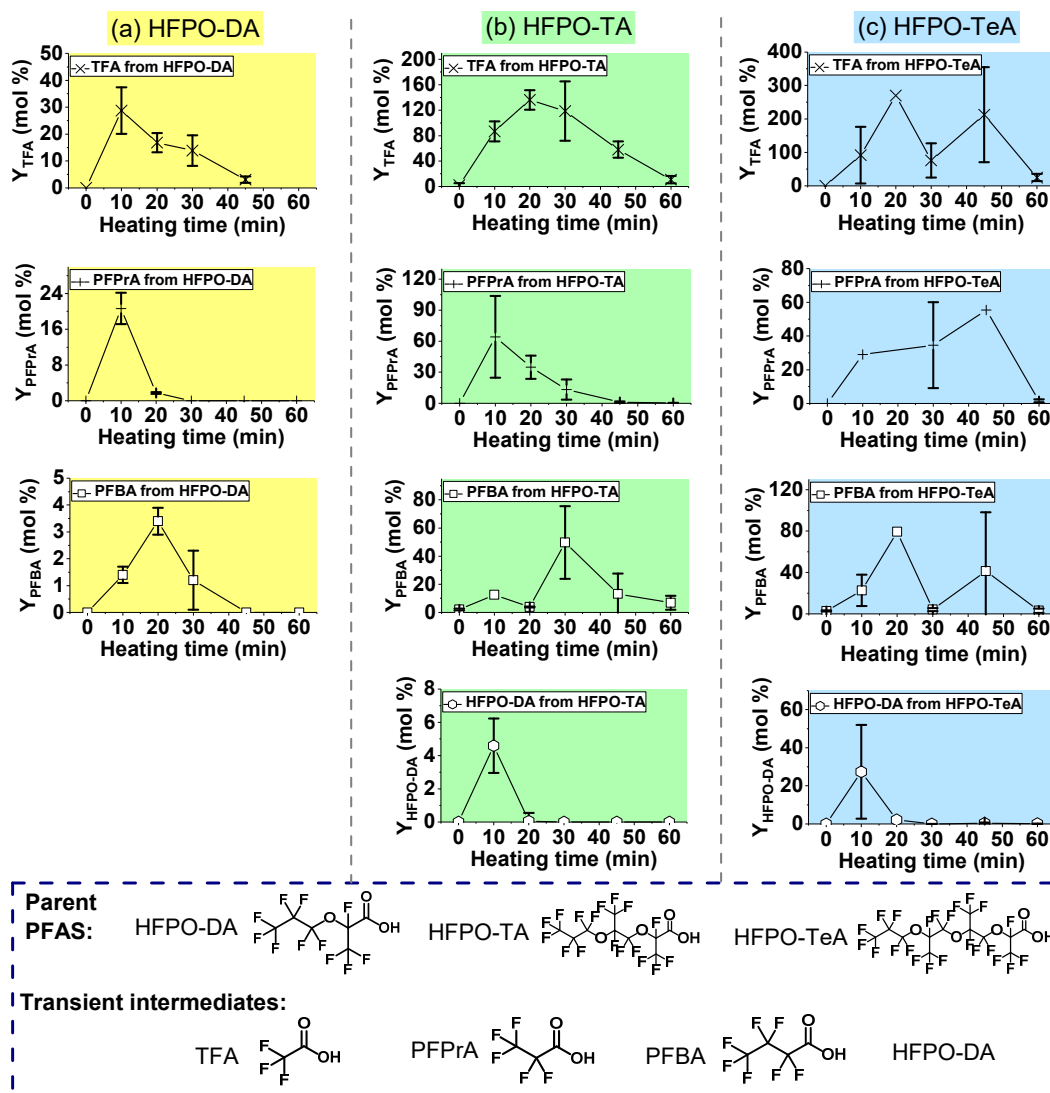


Figure 11. Yields of intermediates from a single PFECA pre-adsorbed on GAC after heating at 200 °C for different durations.⁷

A novel volatile intermediate (IV) with a molecular weight (m/z 265.9) greater than that of PFBA was also detected (Figures 12–14).⁷ The fragments at m/z 69.0 (CF_3^+), 119.0 (C_2F_5^+), and 169.0 (C_3F_7^+) are characteristic of fluorinated fragments.^{5, 15} The fragments at m/z 146.9 and 196.9 represent the successive loss of the fluorinated fragment CF_2 from IV. We assigned the ion at m/z 146.9 to be an unsaturated fluorinated fragment with one C replaced by O (SMILES: $\text{FC(F)=[O+]} \text{C(F)=C(F)F}$). The ion at m/z 81.0 represents an unsaturated fluorinated fragment (SMILES: F[C+]=C(F)F). Taken these results together, we assigned IV to be perfluoro(propyl vinyl ether) (SMILES: $\text{FC(F)=C(F)OC(F)(F)C(F)(F)C(F)(F)F}$) (library match quality, 74–80%).

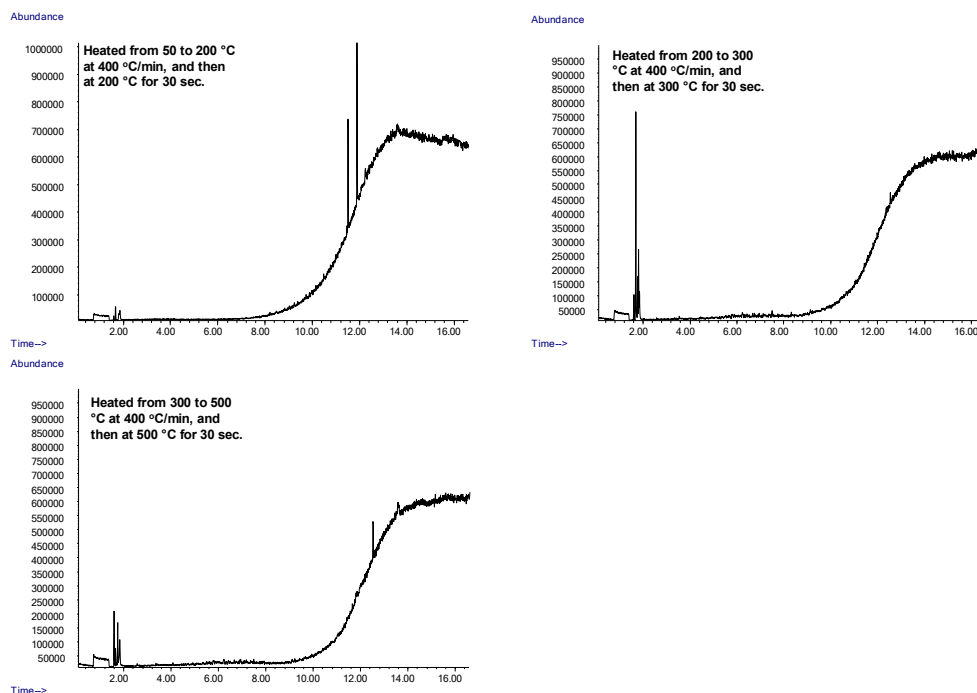


Figure 12. TD-Pyr-GC-MS chromatograms of HFPO-DA at 200–500 °C.⁷

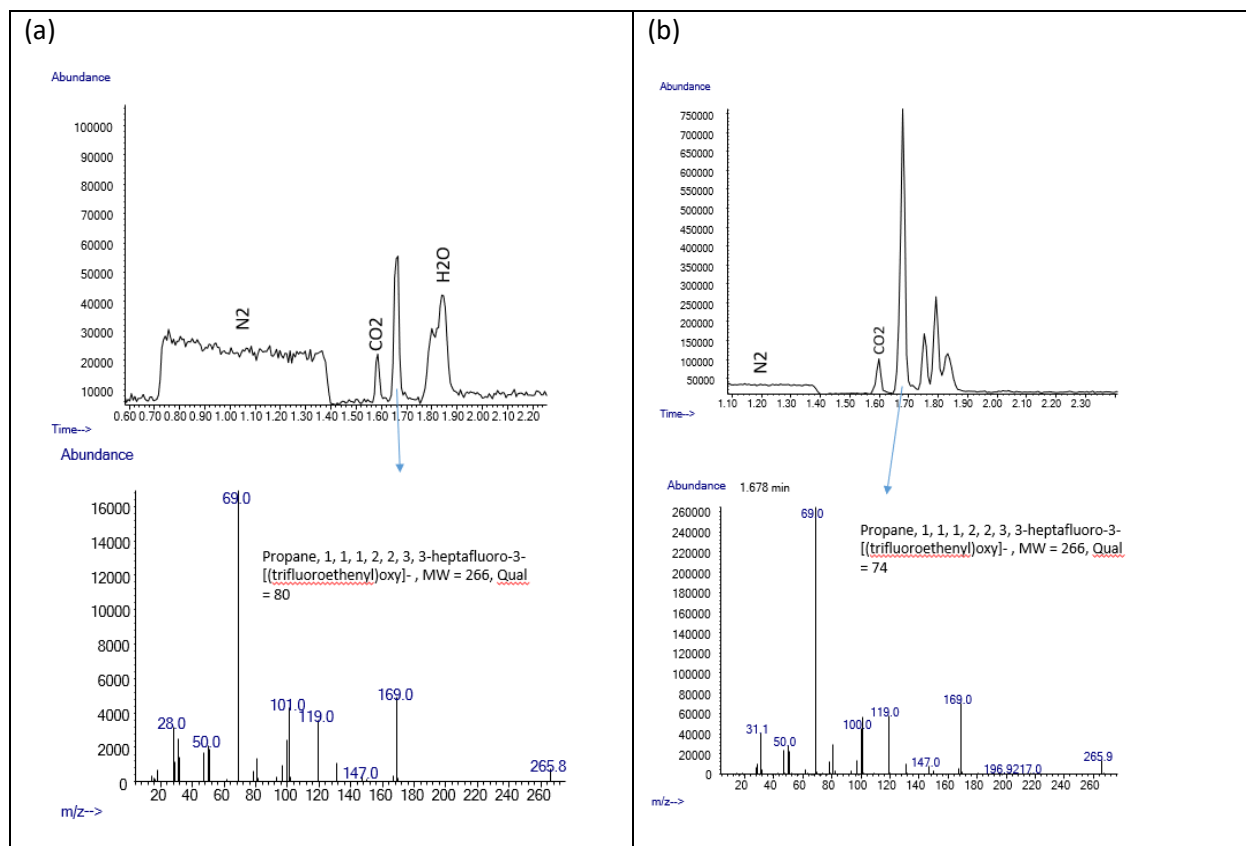


Figure 13. (a) TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 200 °C. (b) TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 300 °C.⁷

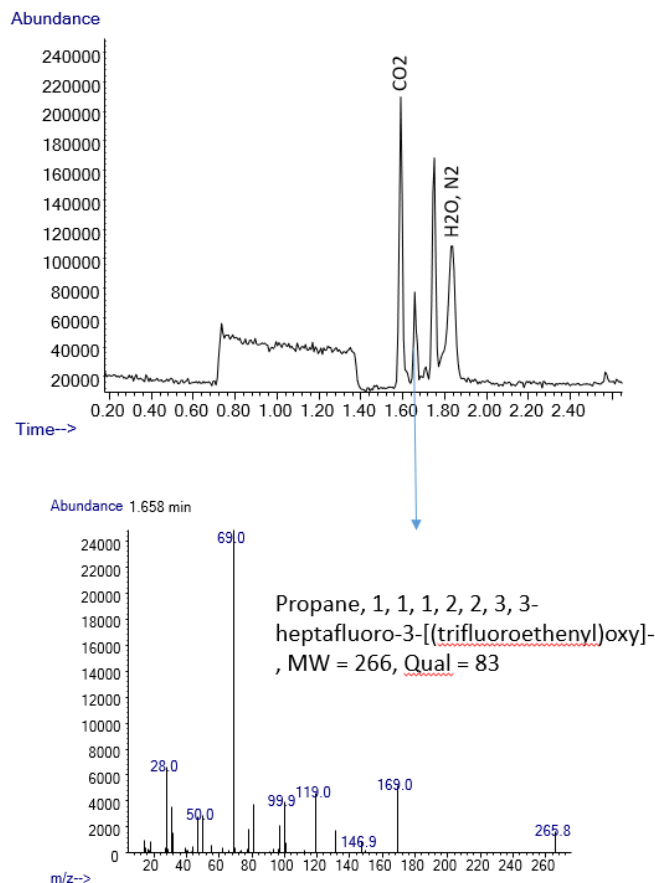


Figure 14. TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 500 °C.⁷

The yields of transient intermediates from HFPO-DA are shown in Figure 11, except for perfluoro(propyl vinyl ether), which was not quantified due to the lack of an authentic standard. TFA, PFPrA, and PFBA were generated quantitatively from HFPO-DA (Figure 11). TFA was formed in 30% maximum yield but disappeared on the same time scale as HFPO-DA. PFBA was a minor product of HFPO-DA, which disappeared after a slight lag compared to PFPrA.⁷

HFPO-TA and HFPO-TeA may be thermally decomposed by a similar pathway, judging by the significant quantities of PFPrA and TFA produced during their degradation (Figure 11).⁷ The yields of TFA and PFBA from HFPO-TA and HFPO-TeA were much higher than those from HFPO-DA because multiple C–O bonds can break off in HFPO-TA and HFPO-TeA (Figure 11). Interestingly, HFPO-DA was a minor thermal decomposition product of its long-chain homologs (i.e., HFPO-TA and HFPO-TeA).

4.2.5. Thermal Decomposition Products of Short-chain PFCAs

TFA and PFPrA evolved quantitatively from PFBA after 10 min in 4.6% maximum yield but disappeared on the same time scale as PFBA (Figure 15). A novel gaseous thermal decomposition product (V) of PFBA was detected with an empirical formula of C₃F₆. It has two fewer F atoms than perfluoropropane, with a fragmentation pattern identical to perfluoropropene (CAS No.: 116-15-4).⁹² Therefore, a reasonable but tentative assignment of compound V is perfluoropropene (library match quality, 74–81%) (Figure 16).⁷

The transformation of PFPeA was similar to that of PFBA. Within minutes of thermal treatment at ≥ 200 °C, almost 100% of PFPeA was removed from spent GAC and resins (Figures 9 and 10). TFA, PFPrA, and PFBA—whose identities were confirmed with authentic standards—were formed from PFPeA but rapidly degraded with a longer treatment time (Figure 9). A novel gaseous product (VI) of PFPeA, perfluoro-1-butene (C_4F_8), was detected (library match quality, 84–94%) (Figure 17).⁷

Where comparisons could be made, the yield of shorter-chain homologs from a PFCA declines with the chain length of this PFCA. Perfluoroheptanoic acid (C7) formed in ~30 mol % yield from PFOA (C8) under the experimental conditions, whereas the yields of PFBA (C4) from PFPeA (C5) and PFPrA (C3) from PFBA were both less than 10 mol % (Figure 15).⁷

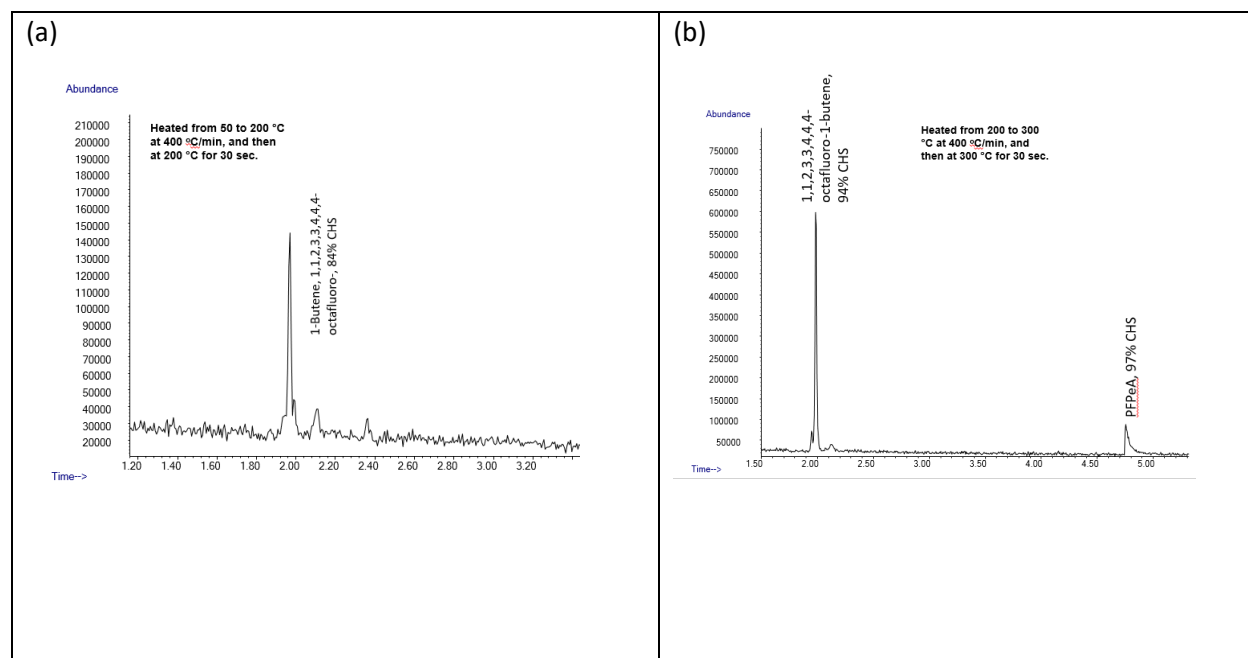


Figure 17. (a) TD-Pyr-GC-MS chromatogram of PFPeA heated at 200 °C. (b) TD-Pyr-GC-MS chromatogram of PFPeA heated at 300 °C.⁷

4.2.6. DFT calculation results

BDE, also known as the bond enthalpy, provides critical information on which bonds in PFAS are likely to break off upon thermal, chemical, and physical treatments. Degradation of a PFCEA or PFCA molecule might occur as soon as the temperature is high enough to initiate bond breaking. The bond that is more easily broken is favored. Tables A1–A7 of Appendix A give the DFT calculation details of C–C, C–F, C–O, O–H, and C=C BDEs. These computational results, in combination with the experimental data, yielded several interesting and novel observations. *i*) The C–C bonds in the perfluorinated backbone of PFPeA and PFBA are generally weaker than the bond (α -C–COOH) connecting the α -C and the carboxyl-C (Figure 18).⁷ Therefore, in addition to decarboxylation, the random C–C scission in the perfluorinated chain is a very likely mechanism that dissociates PFPeA and PFBA. *ii*) BDE data on PFPeA, PFMPA, and HFPO-DA indicate that the α -C–COOH BDE increases with an electron-donating ether O in the perfluorinated chain but declines with the electron-withdrawing $-CF_3$ moiety attached to the α -C (Figure 18). The result suggests that the side trifluoromethyl group may aid in the decarboxylation of HFPO-DA. *iii*) The

C=C double bond strengthens the adjacent C–C bonds, including the α -C–COOH bond (Figure 18). *iv*) In HFPO-DA, the C–O ether bond (C–O_{away}) away from the electron-withdrawing carboxyl group is stronger than the C–O ether bond (C–O_{nr}) closer to the carboxyl group (Figure 18). The result indicates the preferential thermal cleavage of the C–O_{nr} bond, supported by experimental data; the minor yield of PFBA (Figure 11) rules out the cleavage of the C–O_{away} bond (pathway B in Figure 19) as a primary thermal degradation pathway for HFPO-DA. The results differed from a previous study by Bentel et al., which found that the C–O_{nr} bond had a considerably higher BDE than the C–O_{away} bond in HFPO-DA.⁹³ The discrepancy could be caused by the different DFT methods (e.g., M06-2X/Def2-TZVP in this study). And *v*) the difference in C–O BDEs in PFECAs decreases with increasing chain length (Figure 18).⁷

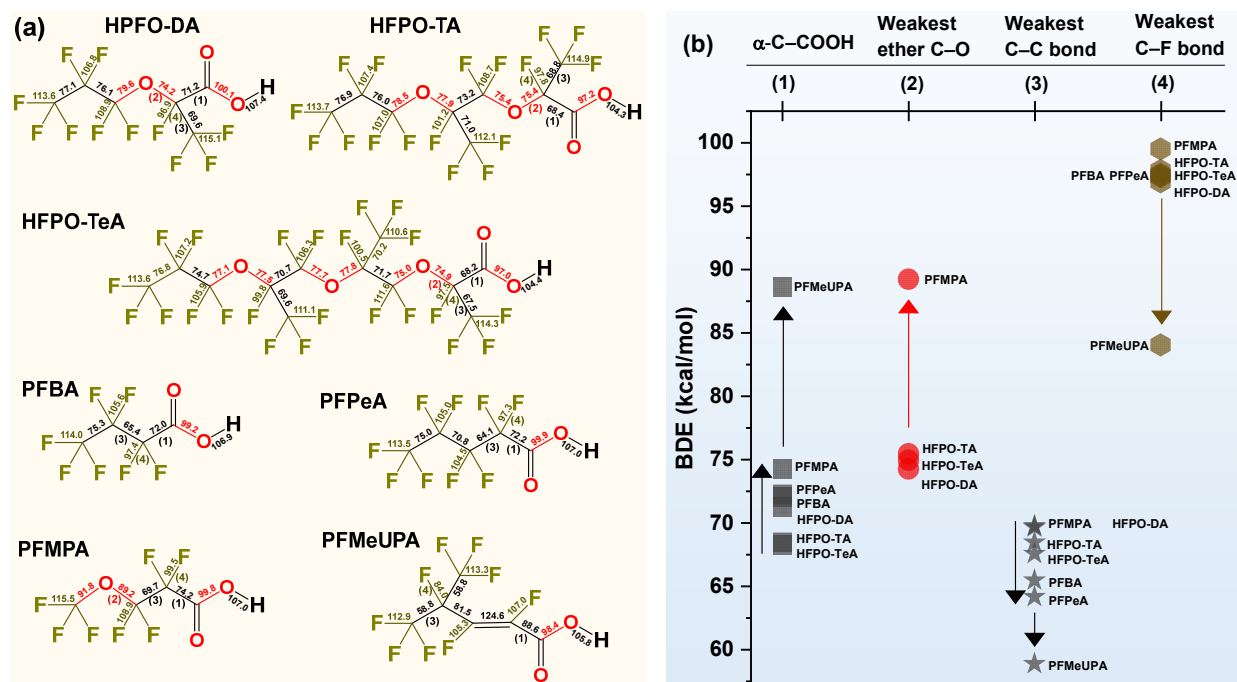


Figure 18. Bond dissociation energies (BDEs) of PFAS calculated at the M06-2X/Def2-TZVP level of theory using high-performance computing resources.⁷

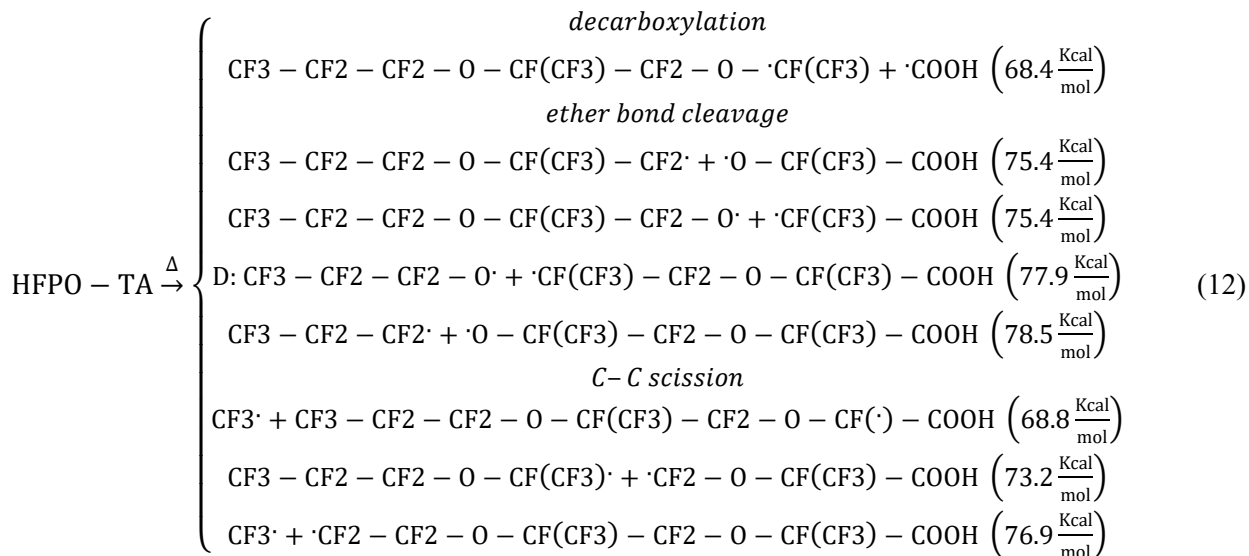
4.2.7. Thermal Decomposition Pathways of PFECAs.

With these experimental and computational results, we developed explicit thermal degradation pathways for HFPO-DA. PFBA, PFPrA, and TFA were not considered thermal decomposition products of HFPO-DA in previous computational studies.^{94, 95} Therefore, the detection of these short-chain PFCAs from HFPO-DA upon heating indicates a novel thermal degradation pathway that was not considered previously.⁷

A pathway for the thermal decomposition of HFPO-DA must take into account: (i) the practically instantaneous formation of TFA, PFPrA, and PFBA upon heating of the parent compound; (ii) the relatively large transient yields of TFA and PFPrA; and (iii) the trace yield of PFBA that rules it out as an intermediate along a primary path.

A pathway consistent with these results is the thermal cleavage of the C–O_{nr} bond, leading to the formation of a perfluoropropyl-oxidanyl radical and a precursor of PFPrA ($\cdot$ PFPrA-H) (Pathway A in Figure 19). This result is accomplished by the recombination of the $\cdot$ PFPrA-H and $\cdot$ F to form PFPrA (Figure 19), followed by the thermal decomposition of the resulting PFPrA

generation of PFOS from 8:2 fluorotelomer sulfonate also likely involved the recombination of perfluoroalkyl radicals with the sulfonate group.⁵



4.2.8. Thermal Decomposition Pathways of Short-chain PFCAs.

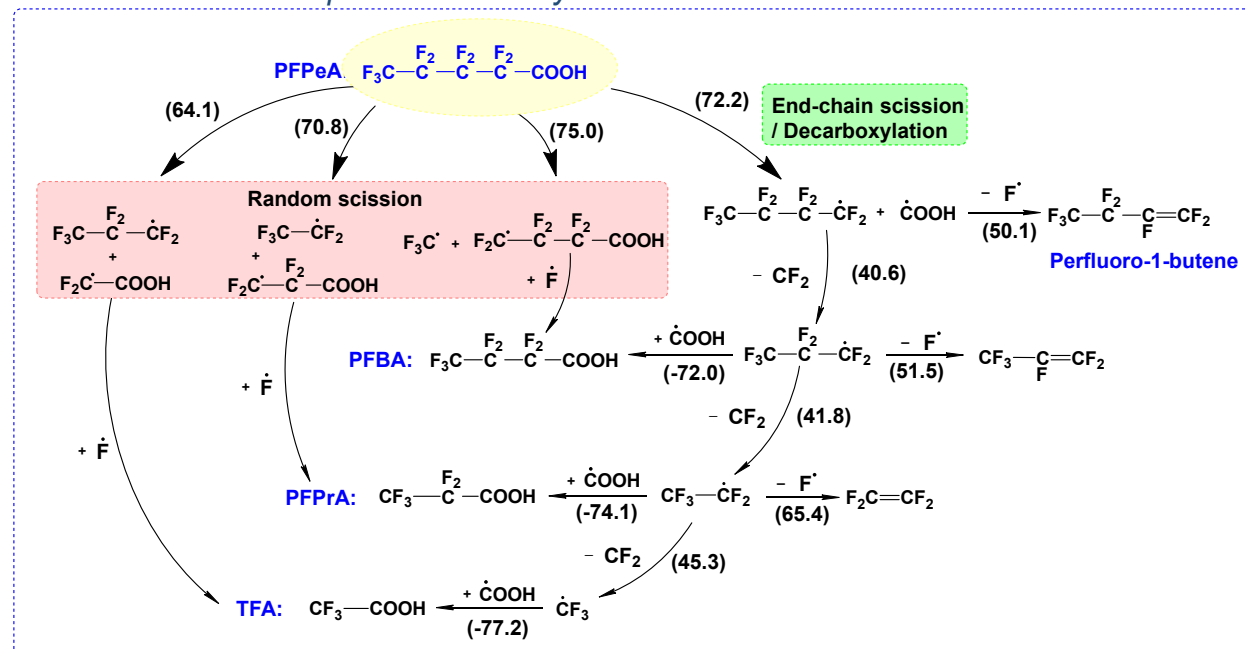


Figure 20. Proposed thermal decomposition pathways of PFPeA. PFBA, PFPrA, TFA, and perfluoro-1-butene are detected as thermal decomposition products of PFPeA. The three-digit numbers (e.g., 70.8) indicate the DFT-calculated enthalpy change (kcal/mol).⁷

Because of the strong C-F bond, the thermal decomposition of short-chain PFCAs should be initiated by the cleavage of the relatively weak C-X bond in which X stands for elements such as C other than F. For PFCAs, only two types of C-X bonds can break: (1) the α -C-COOH bond connecting the perfluorinated chain and the carboxyl group and (2) the C-C covalent bond on the perfluorinated backbone. The bonds that tend to break first are the weakest in the structure. Xiao

et al. previously interpreted HRMS data of PFOA and PFOS thermal degradation products in an ‘unzip’ mechanism involving the end-chain scission and random C–C scission at seemingly random points in the perfluorinated chain.^{4, 5} The experimental and computational data obtained in this study supported this mechanism. Figure 20 illustrates the degradation pathways of two short-chain PFCAs (i.e., PFBA and PFPeA) through both pathways. End-chain scission occurs through decarboxylation that breaks PFCAs' α -C–COOH bond (Figures 19 and 20). The weakest C–C bond in both PFPeA and PFBA, however, is the one connecting the α -C and the β -C. The β -C– γ -C bond is also weaker than the α -C–COOH bond in PFPeA. Therefore, both computational and experimental results suggested random scission in the perfluorinated chain as a degradation mechanism for these short-chain PFCAs (Figure 20).⁷

4.3. TASK 3—DEVELOPMENT OF TAILORED GAC TO FACILITATE THE ADSORPTION OF PFAS FROM WATER

4.3.1. Detailed adsorption isotherms of PFAS on GAC

Another objective of this project was to tailor GAC to facilitate the adsorption of PFAS anions. We first investigated the effect of feedstocks of GAC on PFAS removal in buffered organic-free water. To ensure cross-data comparability, GAC isotherm tests were conducted using organic pure water to minimize the effects of competition from background organic constituents. The organic-free isotherms provided a good starting point for GAC selection. We then constructed isotherms for several PFAS on GAC in organic-free water, surface water, landfill leachate, and ozonated landfill leachate, and analyzed the influence of background constituents.⁹⁶

Developing a database of pure water isotherms with PFAS would be of great importance to water facilities requiring PFAS control, as it would provide a reliable basis for GAC product selection. We initially compared the adsorption of various PFAS species in organic-free water by GAC from different suppliers (Table 1 and Figure 21). Table 2 gives Freundlich parameters of PFAS adsorption isotherms on these five GAC samples. As depicted in Figure 21, the adsorption isotherms of PFAS on these GACs all exhibited strong nonlinearity, with most nonlinear indices below 0.4. Additionally, the nonlinear indices of each PFAS on different GAC sources did not show much variation. For instance, the nonlinearity index of PFOA ranged from 0.23 to 0.32, while the nonlinearity index of GenX varied between 0.19 and 0.29. Due to the closeness of the nonlinear indices of various types of PFAS, it is possible to compare their K_F values visually. A comparison of the magnitude of the K_F values across the different PFAS species revealed an increasing trend with increasing chain length.

Table 1. Properties of GAC samples used in this study.⁹⁶

Adsorbent	Manufacturer	Type	SA, m ² /g	Micro-V, cm ³ /g	Meso-V, cm ³ /g	References
Filtrisorb 200 (F200)	Calgon	Bituminous coal	840	0.38	0.08	97
			691.4	0.30	0.07	3
Filtrisorb 400 (F400)	Calgon	Bituminous coal	900 -1100	0.401	0.164	98
			1035	0.37	N/A	99
			785	0.404	0.149	73
				0.08	0.17	100
Norit GAC 400	Norit	Bituminous coal	963	0.05	0.19	100
			770	0.031	0.153	101
			862	42%	57%	102

Hydrosorb [®] 4000	Norit	Lignite coal	650 607	0.171 0.15	0.535 0.37	98 103
Aquasorb [®] CX	Jacobi	Coconut shell	1056 1009.71	0.618 N/A	0.007 N/A	104 105

SA: surface area; micro-V: micropore volume; meso-V: mesopore volume.

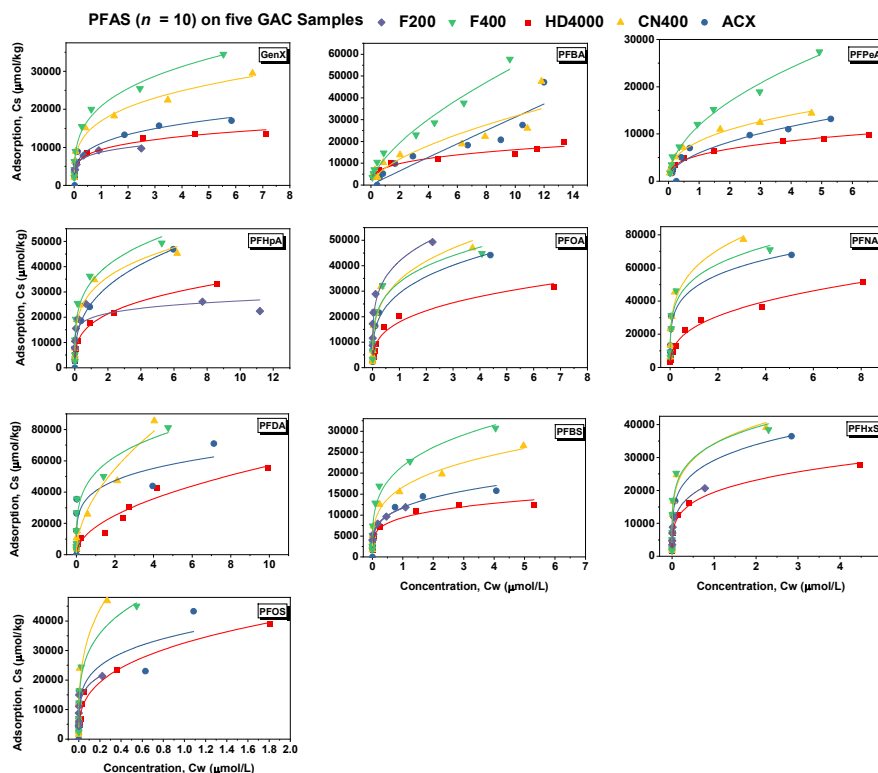


Figure 21. Adsorption isotherm of PFAS onto five different used GAC in organic-free water. The symbols are the measured concentrations, and the fitted line is the Freundlich model.⁹⁶

Table 2. Freundlich parameters of PFAS adsorption on different types of GACs in organic-free water.⁹⁶

PFAS	GAC	$K_F \pm SE$	$n \pm SE$	R^2
PFBA	HD4000	7.9 ± 0.66	0.32 ± 0.038	0.95
	ACX	3.3 ± 2.1	0.97 ± 0.27	0.86
	CN400	7.8 ± 3.1	0.61 ± 0.18	0.81
	F400	12 ± 1.6	0.64 ± 0.068	0.97
PFPeA	HD4000	5.5 ± 0.19	0.32 ± 0.022	0.98
	ACX	6.0 ± 0.72	0.48 ± 0.087	0.90
	CN400	8.5 ± 0.27	0.36 ± 0.024	0.99
	F400	12 ± 0.46	0.51 ± 0.030	0.99
PFHpA	HD4000	17 ± 0.45	0.30 ± 0.014	0.99
	ACX	25 ± 1.3	0.34 ± 0.029	0.98
	CN400	30 ± 1.4	0.25 ± 0.023	0.97
	F400	34 ± 2.2	0.25 ± 0.032	0.94
	F200	20 ± 1.4	0.13 ± 0.027	0.79
PFOA	HD4000	18 ± 0.95	0.32 ± 0.030	0.97
	ACX	29 ± 1.6	0.29 ± 0.029	0.97
	CN400	34 ± 2.5	0.28 ± 0.035	0.92
	F400	34 ± 2.5	0.25 ± 0.036	0.93

	F200	42 ± 3.0	0.23 ± 0.027	0.92
PFDA	HD4000	18 ± 2.1	0.51 ± 0.065	0.95
	ACX	41 ± 6.5	0.22 ± 0.064	0.74
	CN400	38 ± 4.4	0.52 ± 0.094	0.95
	F400	52 ± 5.1	0.26 ± 0.047	0.88
PFNA	HD4000	24 ± 0.78	0.36 ± 0.019	0.99
	ACX	48 ± 3.1	0.22 ± 0.027	0.96
	CN400	59 ± 3.8	0.25 ± 0.032	0.95
	F400	53 ± 3.3	0.23 ± 0.029	0.96
PFBS	HD4000	9.4 ± 0.35	0.22 ± 0.021	0.97
	ACX	12 ± 0.82	0.26 ± 0.042	0.93
	CN400	17 ± 0.42	0.27 ± 0.015	0.99
	F400	22 ± 0.70	0.27 ± 0.018	0.98
	F200	12 ± 0.12	0.23 ± 0.0052	0.99
PFHxS	HD4000	19 ± 0.42	0.25 ± 0.010	0.991
	ACX	29 ± 0.98	0.22 ± 0.014	0.99
	CN400	34 ± 1.5	0.22 ± 0.015	0.97
	F400	34 ± 2.1	0.20 ± 0.021	0.96
	F200	23 ± 1.1	0.25 ± 0.017	0.97
PFOS	HD4000	33 ± 1.6	0.33 ± 0.029	0.97
	ACX	36 ± 4.6	0.23 ± 0.055	0.84
	CN400	72 ± 7.0	0.31 ± 0.030	0.94
	F400	54 ± 2.8	0.25 ± 0.017	0.98
	F200	30 ± 6.4	0.21 ± 0.047	0.71
HFPO-DA	HD4000	9.4 ± 0.35	0.22 ± 0.020	0.97
	ACX	11 ± 0.88	0.27 ± 0.046	0.91
	CN400	17 ± 0.56	0.27 ± 0.018	0.98
	F400	21 ± 0.63	0.29 ± 0.017	0.98
	F200	8.7 ± 0.30	0.19 ± 0.018	0.95

Note: The isotherms of PFBA, PFPeA, PFDA, and PFNA on F200 did not pass the quality control standards of our laboratory, and therefore, their Freundlich parameters were not included in this table.

The K_D values were also calculated for three different C_w concentrations, taking into account the nonlinearity of the adsorption process (Figure 22). To make a more visible comparison, the vertical coordinates in Figure 22 were set to the same range of values. PFOA adsorption was stronger than PFHpA, which in turn was stronger than PFBA, and the same trend was followed for PFBS and PFHxS. K_D values were higher at low concentrations than at high C_w .

However, the B.E.T. N_2 SA ranking (Table 1) and the K_D ranking did not agree with each other. Adsorption of PFAS onto GAC is fundamentally related to SA; however, it is also dependent on the adsorbate's molecular dimensions and the distribution of accessible SA throughout nanopores of varying dimensions due to size-exclusion (steric) effects. Consequently, the internal surface area of GAC determined by N_2 porosimetry may not be accessible to PFAS molecules. As such, the adsorption of PFAS onto GAC did not invariably correspond with the B.E.T. N_2 SA. Previous studies have also reported such inconsistencies related to the adsorption of other types of organic compounds to biochar.^{11, 68, 106} Therefore, it is recommended that isotherms, either as K_D or as graphics for PFAS, be used as a measure of GAC adsorption capacity in place of B.E.T. N_2 surface area. Organic pure water isotherms provided a suitable reference point for comparison of different GAC products, and truly reflected the inherent adsorption potential of carbon.

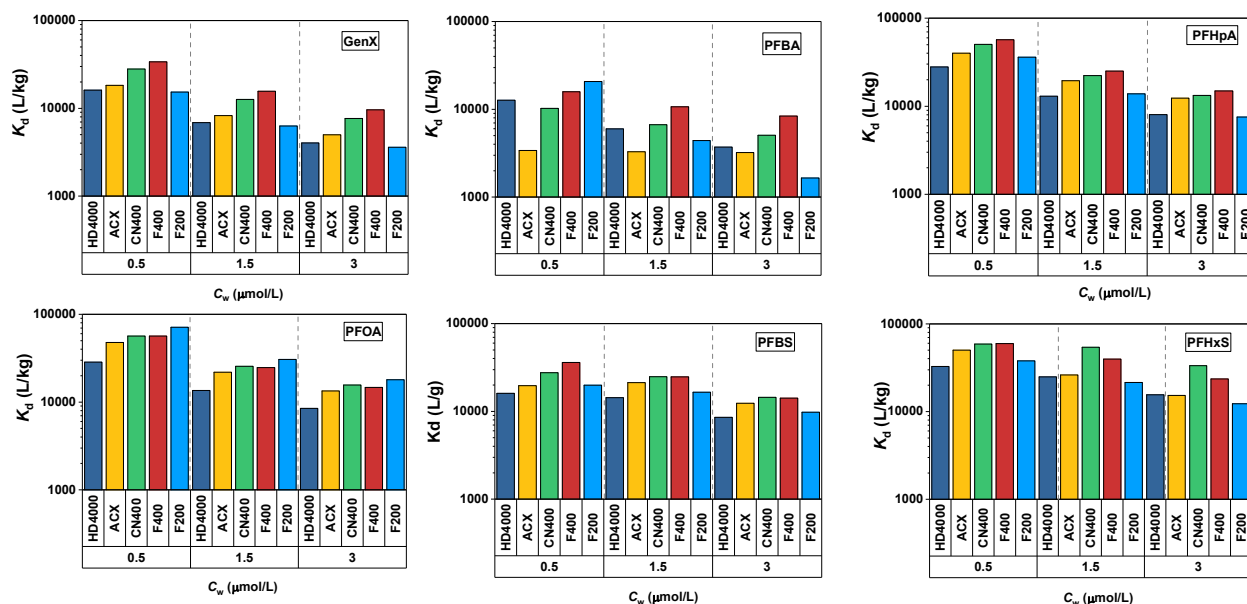


Figure 22. Absorption distribution of PFAS on different GACs in organic-free water.⁹⁶

GAC can be produced from various feedstocks, each having unique properties that influence their effectiveness in PFAS removal. Coal-based GAC is made from bituminous coal or lignite. It is known for its high hardness, large surface area, and highly developed pore structure. The pore sizes of coal-based GAC can range from micropores to mesopores (Table 1), making it suitable for adsorbing a wide range of PFAS. Coconut shell-based GAC is derived from the shells of coconuts, a renewable and abundant resource. This type of GAC is characterized by its high hardness, low ash content, and a predominantly microporous structure (Table 1).¹⁰⁷ It should be noted that restricted diffusion of organic molecules is manifested more in micropores due to the steric effect than in mesopores.^{11, 68, 106} In this study, bituminous GACs showed better performance than coconut shell and lignite coal GACs, though the difference was less than one order of magnitude (Figure 22). Consequently, F200, a bituminous GAC prepared from bituminous coal and with decades of experience in water and wastewater treatment, was chosen for subsequent experiments.

4.3.2. Modification of PCS

We explored how GAC properties influenced PFAS adsorption and developed a strategy for using pyrogenic carbonaceous materials in PFAS removal. This approach integrated post-pyrolysis modification to significantly enhance adsorptive effectiveness, coupled with a reactivation step that facilitates material reuse.¹⁷ Modification entailed brief post-pyrolysis air oxidation at 400 °C, which considerably enlarged pore size and surface area and increases the solid-to-water distribution ratio, K_D , of individual PFAS by as much as three orders of magnitude. In some cases (e.g., PFOA), the K_D was comparable to a commercial GAC.¹⁷ Residual sorbed PFAS could be decomposed by brief thermal reactivation of the spent biochar at 500 °C in N₂ or air. After thermal reactivation in air the biochars exhibited even greater PFAS K_D values. While thermal reactivation of GAC in air could be achieved as well, adsorption affinity for the shorter-chain PFAS was noticeably reduced. Overall, this study points to a new strategy of using pyrogenic carbonaceous materials for PFAS removal.¹⁷

With increasing pyrolysis HTT from 300 to 600 °C, SW biochars showed decreasing H/C atomic ratio (0.785 to 0.251), decreasing O/C atomic ratio (0.250 to 0.0553), increasing CO₂-specific surface area (CO₂-SSA; 219-698 m²/g), and increasing porosity (0.069–0.188). The maple biochars showed the same trends.¹⁰⁸ These trends reflect progressive conversion to materials with greater hydrophobicity, higher nanoporosity, and a more condensed aromatic (graphitic micro-crystallite) structure.¹⁰⁹

Thermal oxidation during PPAO treatment opened pore networks by burning away tarry deposits and pore wall matter.¹¹ We termed this effect ‘pore reaming’.¹¹ Pore reaming was confirmed here by the increases in pore volume and specific surface area after PPAO treatment for biochars corresponding to each HTT. The increases are as follows: SW300, 0.069 to 0.178 cm³/g and 219 to 671 m²/g; SW400, 0.106 to 0.184 cm³/g and 395 to 689 m²/g; and SW600, 0.188-0.231 cm³/g and 698-811 m²/g. Generally, PPAO treatment enriched O and depleted H content. Among all PPAO-treated biochars, SW600-PPAO had the lowest H/C (0.220) and O/C (0.141).

Adsorption experiments were carried out in multisolute-PFAS systems (mixture of longer-chain and shorter-chain PFAS). The effect of pyrolysis temperature (HTT) on the 2-d K_D value was inconsistent, except that SW600 and SW600-PPAO samples showed greater K_D values than the corresponding lower-HTT samples (Figures 23 and 24, respectively), concordant with their notably larger surface areas and porosities. For these reasons, the further study focused on the 600 °C biochars. When possible to compare K_D at different contact times, K_D was greater for the 14-day than the 2-day contact time in some cases (PFBA and PFPeA), but unaffected by contact time in others (e.g., GenX, PFDA, PFBS, and PFHxS). Further kinetic evaluation is essential because adsorption rates affect the practicality of using biochar.

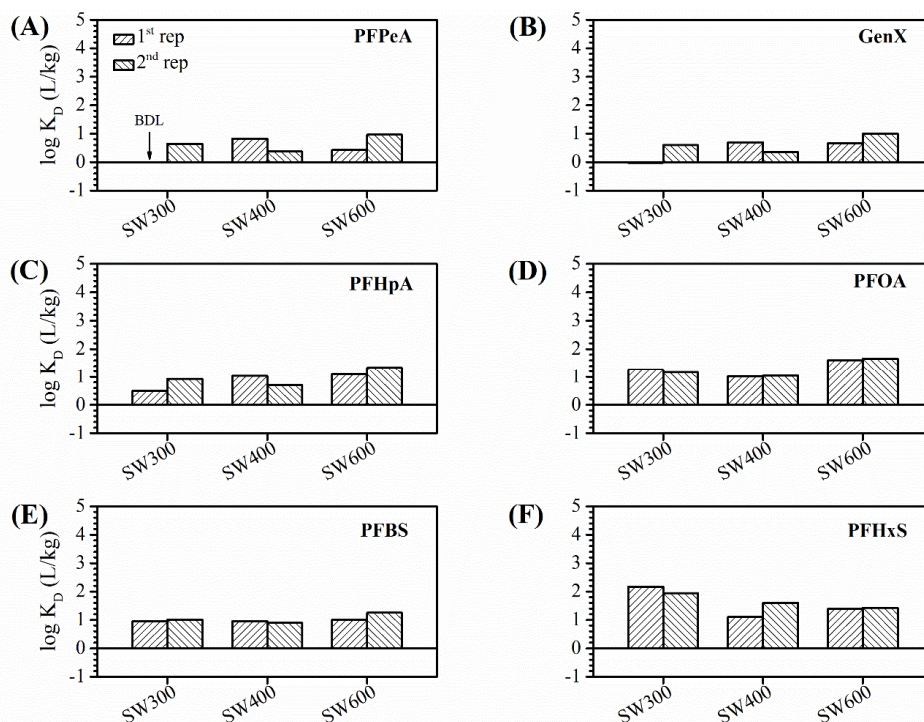


Figure 23. Single-point K_D values for a mixture of PFAS sorbed for 2 days to unmodified softwood biochars as a function of pyrolysis temperature, 300, 400, or 600 °C. BDL signifies below the detection limit because the difference between initial and final dissolved concentrations was too small to give a reliable value.¹⁷

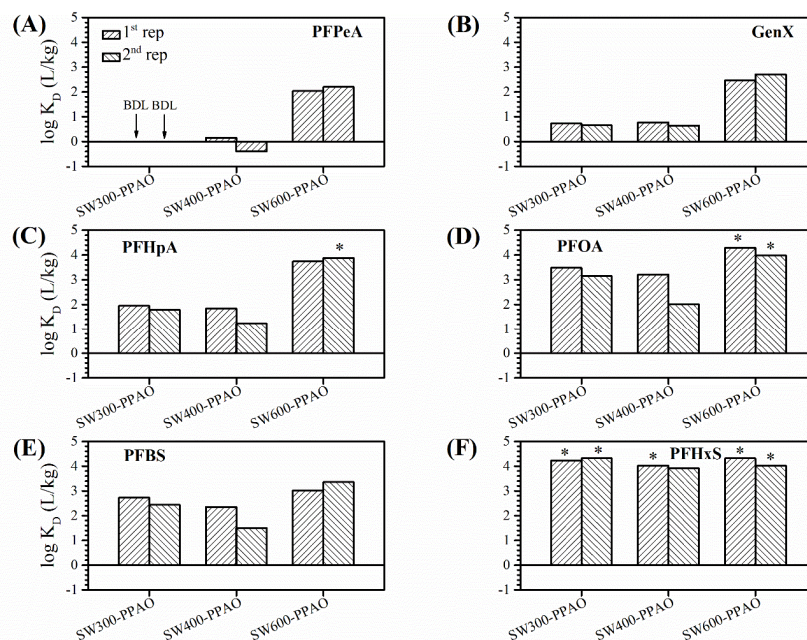


Figure 24. Single-point K_D values for a mixture of PFAS sorbed for 2 days to PPAO-treated softwood biochars as a function of pyrolysis temperature, 300, 400, or 600 °C. BDL signifies below the detection limit because the difference between initial and final dissolved concentrations was too small to give a reliable value. The asterisk (*) signifies the displayed bar is the lower limit because the final dissolved concentration was below the detection limit.¹⁷

Figure 25 above shows individual 2-d $\log K_D$ values for a PFAS mixture sorbed to M600 or SW600 compared to the corresponding PPAO-treated biochar.¹⁷ The K_D increased as a function of perfluorocarbon chain length, and for the same chain length, was greater for sulfonates than carboxylates in agreement with previous studies of GACs and anion exchange resins.^{110, 111}

The most striking feature of the plots in Figure 25, as well as a side-by-side comparison of Figures 23 and 24, is that *adsorption was greatly enhanced by PPAO treatment, by as much as 10^3* . In cases where confident comparison was possible, adsorption of PFAS with longer chains was more effectively enhanced by PPAO treatment than PFAS with shorter chains within each class, carboxylate or sulfonate.¹⁷ Apart from freeing up additional surface and pore space for incoming molecules, PPAO treatment also increased the O content of the carbons.^{11, 108} Some of the O content is carboxyl, which exists largely in deprotonated form at the experimental pH, and as other studies show, resulted in a downward shift in the zeta potential (to more negative values).^{11, 108} Evidently, charge repulsion of PFAS anions by the additional surface oxidation/charge did not outweigh pore reaming effects. Pore reaming may explain the greater effect of PPAO treatment on adsorption affinity of longer-chain compounds if it can be assumed that steric restriction is more effectively alleviated by reaming for longer- than shorter-chain homologs.¹⁷

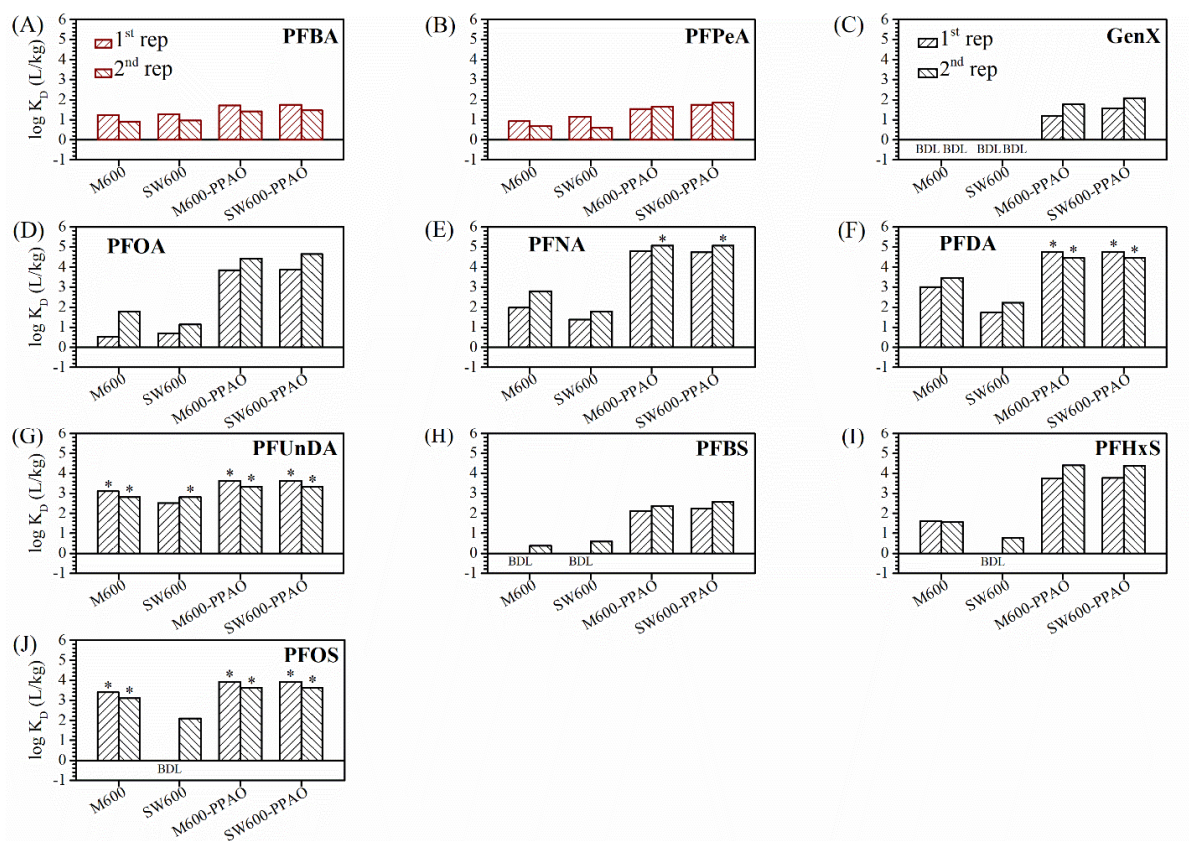


Figure 25. Single-point K_D values for a mixture of PFAS sorbed for 14 days (A-B) or 2 days (C-J) to unmodified compared to PPAO-treated M600 and SW600 (see 2-day K_D values for PFBA and PFPeA). The dual bars represent separate experiments. BDL signifies below the detection limit because the difference between initial and final dissolved concentrations was too small to give a reliable K_D value for that replicate. The asterisk (*) signifies a lower limit of K_D because the final dissolved concentration was below the detection limit.¹⁷

4.3.3. Competitive adsorption of PFAS on GAC

Competitive adsorption was observed. Competitive adsorption among PFAS on carbons^{111, 112} and kaolinite⁸⁹ has been reported. Because the longer-chain compounds have a greater affinity for the carbon, they are expected to compete more effectively for adsorption sites than the shorter-chain compounds.¹¹³ To test whether competition was manifested, we compared 2-day adsorption for a mixture that contained just shorter-chain-PFAS (called S-mix) and compared the results with the mixture containing both longer-chain and shorter-chain PFAS (called LS-mix) (Figure 26). In cases where confident comparison was possible, adsorption of a given shorter-chain PFAS (PFBA, PFPeA, or GenX) was weaker in LS-mix than S-mix systems in four out of five cases. The fifth case, which gave mixed results, applies to the shortest of the three shorter-chain compounds (PFBA), suggesting that PFBA was partially displaced by the other two shorter-chain compounds present in the S-mix system. Thus, our results are consistent with other reports of competitive effects in anionic PFAS mixtures.¹⁸

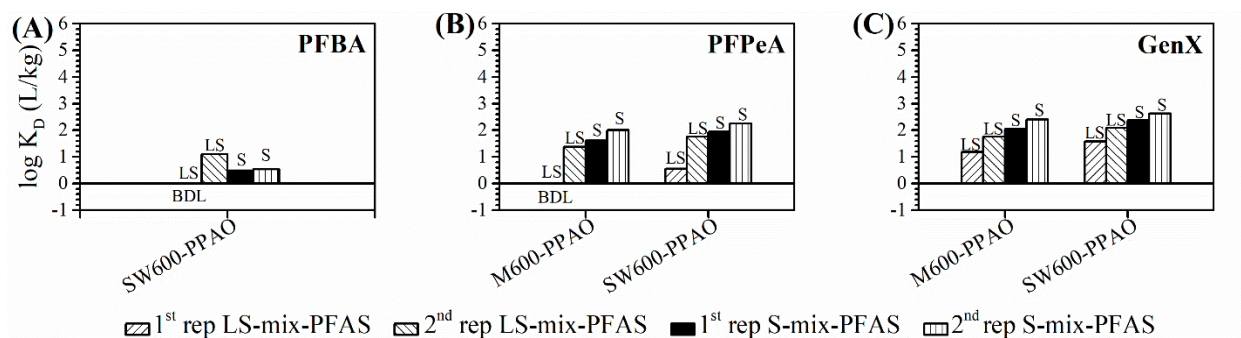


Figure 26. Competitive effects. Adsorption after 2d of PFBA, PFPeA, and GenX either in a mixture with long-chain PFOA, PFNA, PFDA, and PFUnDA or without long-chain. BDL signifies below the detection limit because the difference between initial and final dissolved concentrations was too small to give a reliable value. The letter LS above the bar represents the LS-mix-PFAS system and S the S-mix-PFAS system.¹⁸

Coating pDADMAC on PCS reversed the surface charge and increased the anionic exchange capacity. For a given chain length, regardless of size, the positively-charged surface favors adsorption of sulfonates over carboxylates due to the stronger hydrophobicity and polarizability of the sulfonate group.¹⁸ The reason for the extraordinary enhancement of PFAS adsorption by pDADMAC coating of the PCS of our study in comparison to the activated carbons of other reports¹¹⁴ (including our own preliminary results) is unknown and deserves further study. Regenerability of the sorbent is an important issue. PCSs can be regenerated thermally, an advantage for this family of materials. After regenerating SW600-PPAO in air at 500 °C, it sorbed more PFAS than before regeneration.¹¹⁵

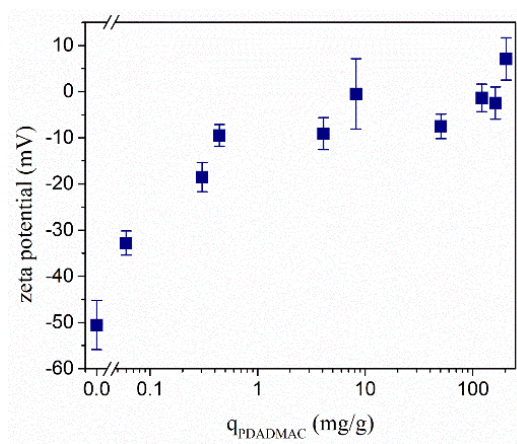


Figure 27. Zeta potential of SW500 (1 g/L) as a function of the amount of pDADMAC added to the buffered solution (pH 7.0; 3 mM phosphate) per g sorbent. The left-most point represents value in the absence of added pDADMAC. The error bar represents triplicate samples.¹⁸

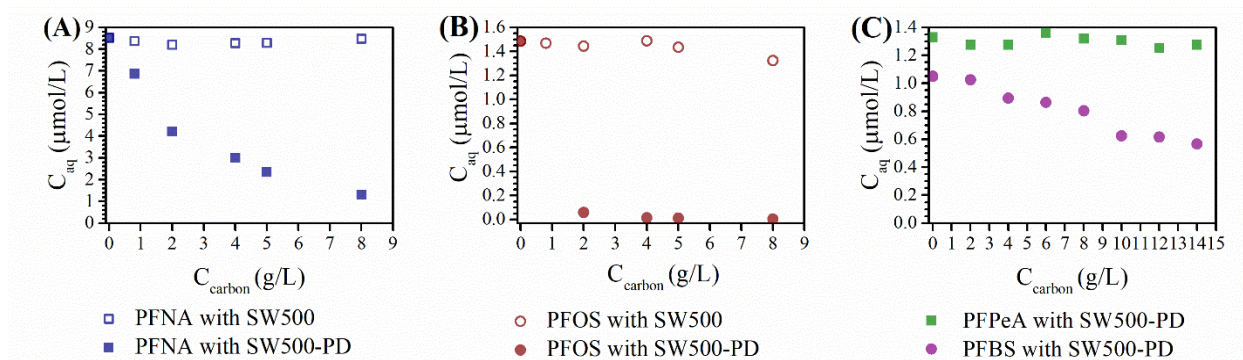


Figure 28. Adsorption of (A) PFNA, (B) PFOS, and (C) PFPeA, PFBS, by pDADMAC-coated or uncoated PCS (SW500-PD or SW500, respectively) at pH 7.0 (3 mM phosphate) as a function of carbon dose. Four-day contact period.¹⁸

Several researchers have emphasized the importance of PCS surface chemistry in the adsorption of PFAS.¹¹⁶⁻¹²⁰ For example, Zhi and Liu found that the electrostatic repulsion between negatively charged carbon surface and PFAS anions resulted in low adsorption.¹¹⁸ In this study, the adsorption of pDADMAC to carbons led to charge reversal. This is shown here by the experiment in Figure 27 where addition of increasing amounts of pDADMAC to an aqueous suspension of SW500 particles at pH 7.0 causes the zeta potential to progressively shift from -51 mV to +7.5 mV. Figures 28A and 28B reveal that pDADMAC-coated PCS (SW500-PD) more effectively removed micromolar concentrations of PFNA or PFOS from the solution than its uncoated counterpart (SW500). Furthermore, SW500-PD more effectively removed PFOS than PFNA, which had the same perfluorocarbon chain length (8). The shorter-chain compounds, PFBS and PFPeA, were much less effectively removed by SW500-PD than were the longer-chain compounds, PFOS and PFNA, while the order sulfonate > carboxylate for the same perfluorocarbon chain length (4 in this case) was maintained (Figure 28C). The shorter-chain carboxylate PFPeA was not noticeably sorbed by suspensions of SW500-PD up to 14 g-SW500-PD/L. Neither of the shorter-chain compounds were appreciably sorbed by SW500, even at 8 g-SW500/L.

Adsorption of PFOS or PFNA increased as the amount of pDADMAC added to the aqueous suspension of SW500 increases (Figures 29A or 29C, respectively), and the sorbed concentration in each case correlates with the zeta potential of the suspended particles (Figures 29B or 29D, respectively). These results indicate that adsorption is a function of surface charge neutralization and the introduction of positively charged sites by pDADMAC. The isotherms on SW500-PD in Figure 30 show that PFOS adsorption is more nonlinear and favorable than PFNA adsorption: the Freundlich n were 0.344 and 0.465, respectively, and the K_D (i.e., K_F at $C_{aq} = 1 \mu\text{M}$) were 1,204 and 714 L kg^{-1} , respectively. The isotherms in Figure 30 also revealed that the difference between the sulfonate and the carboxylate for the same chain length diminished as concentration increased.¹⁸

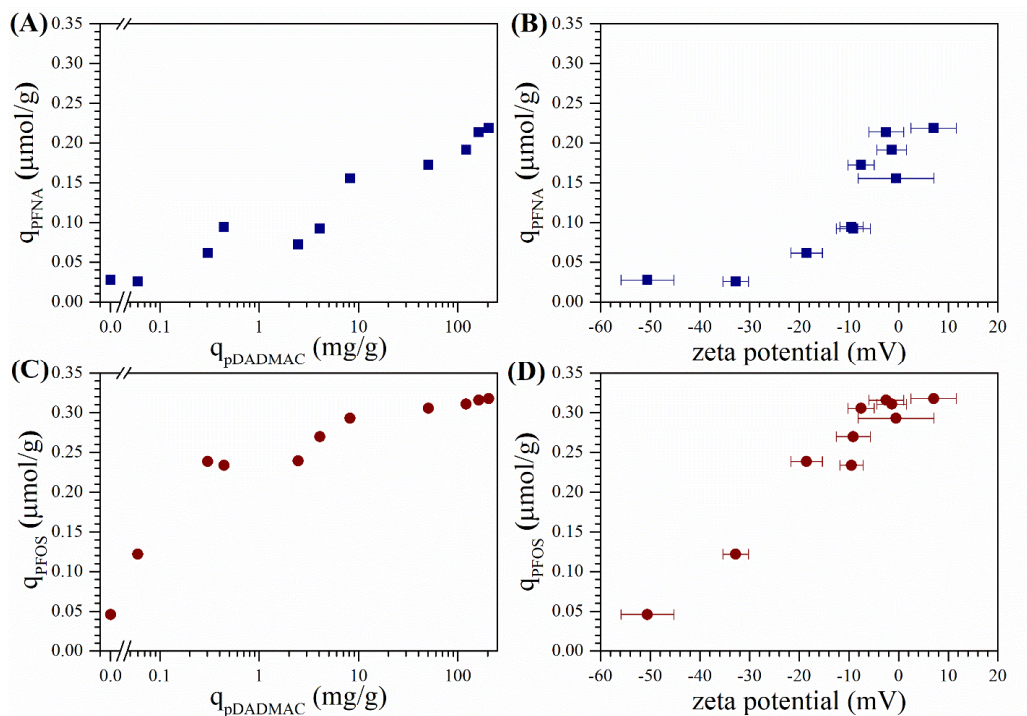


Figure 29. Adsorption of PFNA and PFOS by SW500 at different nominal sorbed concentrations of pDADMAC (A and C) and different zeta potential of the particle suspension (B and D). q_{pDADMAC} refers to the mass of pDADMAC added to the buffered solution per g sorbent. The left-most points represent values in the absence of added pDADMAC. Carbon dose, 5 g/L; initial PFNA, 1.2 μM ; initial PFOS, 1.6 μM ; pH = 7.0 (3 mM phosphate). The error bar represents triplicate samples.¹⁸

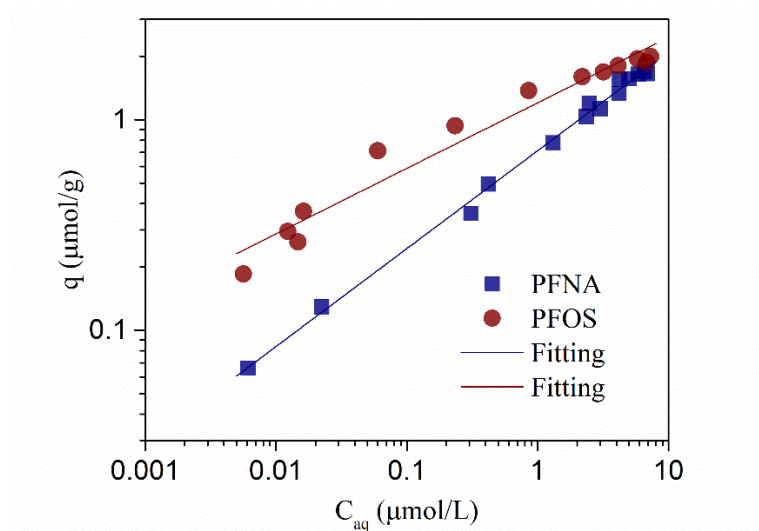


Figure 30. Adsorption isotherms of PFNA and PFOS on SW500-PD at pH 7.0 (3 mM phosphate). Lines are linear fit of the data to the log-transformed Freundlich equation; $R^2 = 0.961$ for PFOS and $R^2 = 0.996$ for PFNA. Four-day contact period.¹⁸

It is possible that the K_D for the pDADMAC-coated PCS were minimum values, since the buffer ion, phosphate—present in large molar excess over the PFAS—binds strongly to pDADMAC-coated PCS,⁷⁹ and may have been competitive. Competition is supported by the following: with phosphate, PFBS and PFPeA did not show evidence of adsorption to SW500, nor did PFPeA to SW500-PD (Figure 29C); yet without phosphate both PFBS and PFPeA sorb to SW300, SW400, and SW600), albeit moderately. The competitive effect of phosphate has also been observed on other materials, including powdered activated carbon,¹²¹ anion exchange resin,¹²² and ferrihydrite.¹²³

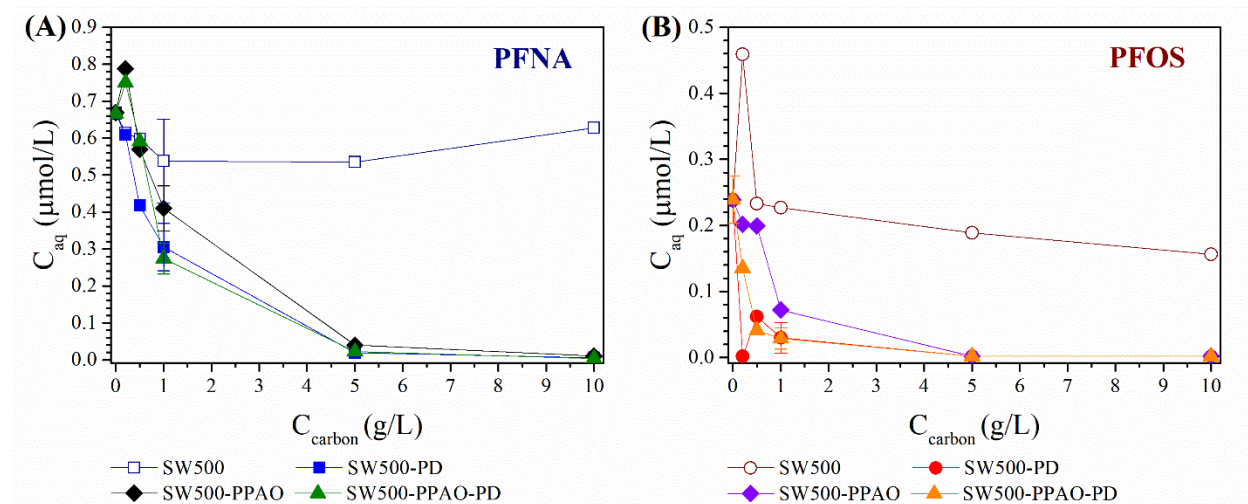


Figure 31. Adsorption of (A) PFNA or (B) PFOS to unmodified, pDADMAC-coated, or thermally oxidized SW500; pH 7.0 (3 mM phosphate). The error bar represents triplicate samples. Lines connect points to guide the eye. Four-day contact period.¹⁸

It is possible that pDADMAC blocks some pores. The CO_2 -SSAs of SW500 and SW500-PD (579 and 571 m^2/g , respectively), were quite close, suggesting at first that it does not.¹⁸ However, CO_2 might not well represent PFAS access because it is a much smaller molecule. In addition, gas porosimetry was carried out in the absence of water molecules, which could assist pore obstruction by clustering around charged sites on the pDADMAC strands. Nevertheless, pDADMAC coating greatly increased PFAS adsorption despite possible pore blockage.

Single-solute experiments on PFNA and PFOS sought to compare the effectiveness of thermal oxidation and quaternary ammonium derivatization (i.e., SW500-PPAO vs SW500-PD), and to determine whether the two treatments are additive. Figure 31 shows that at pH 7.0 in 3 mM phosphate buffer, quaternary ammonium derivatization is slightly more effective than thermal oxidation under the same conditions, all in the presence of phosphate. However, the two treatments did not appear to be additive, as the curves for SW500-PD and SW500-PPAO-PD practically overlap.

In particular, we evaluated the long-term performance of the adsorbent (up to 14 days).¹⁸ Differences in PFAS uptake between the 2-day and 14-day contact times were small and showed no trend, suggesting very fast adsorption kinetics of PFAS on the studied adsorbents, including GAC. We also investigated the adsorption of PFAS to thermally reactivated GAC. Lastly, GAC is produced by thermal activation of carbonized feedstock (e.g., charcoal or biochar). In order to understand the effect of feedstock properties, we also made biochars at different temperatures,

activated them by thermal air oxidation, and compared laboratory-produced activated biochar (or activated charcoal) with commercial activated charcoal (i.e., GAC).¹⁸

An increase in pyrolysis temperature resulted in a decrease in O/C (0.250 to 0.0553), a decrease in H/C (0.785 to 0.251), and an increase in CO₂-specific surface area (CO₂-SSA; 219 to 698 m²/g) of the unmodified biochar samples.¹⁷ These trends are consistent with those of many other studies and reflect the progressive conversion of biochar to a more condensed aromatic structure.^{109, 124} Pore reaming by PPAO treatment as addressed in detail previously^{11, 108} was confirmed by the increases in CO₂-pore volume and CO₂-SSA, the increase in O/C, and the decrease in H/C. Previous work found that PPAO increased acidic functionality, specifically carboxyl groups.^{11, 108}

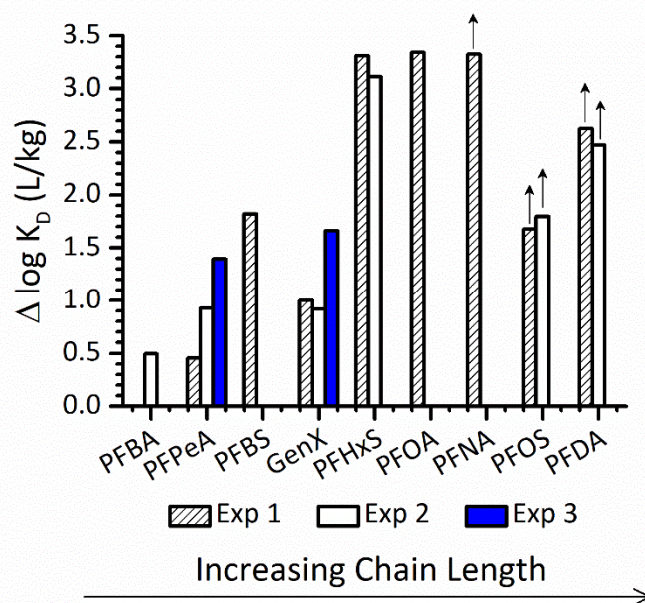


Figure 32. The difference in log K_D values after and before PPAO treatment for the SW600 biochars. Each bar represents an average of duplicate tests. The arrows signify that the bar represents an estimated minimum value. Exp 1 (hatched bar): experiment 1 with mix of shorter- and longer-chain PFAS and 2-day contact time. Exp 2 (open bar): experiment 2 with mix of shorter- and longer-chain PFAS and 14-day contact time. Exp 3 (blue bar): experiment 3 with mix of only shorter-chain PFAS and 2-day contact time. Bars are missing either because the experiment was not carried out for that compound, or because there was a BDL limitation. Screening test is conducted to select the best set of biochar (SW600 and SW600-PPAO) for a separate test involving more PFAS with results shown in this figure.¹⁸

Differences in PFAS uptake between the 2-day and 14-day contact times were small and showed no trend. Samples pyrolyzed at 600 °C (SW600 and SW600-PPAO) showed correspondingly greater K_D values than those pyrolyzed at lower temperatures, consistent with their larger CO₂-SSA and porosity. Additional data were presented in the preliminary report.¹²⁵ The difference in log K_D between the PPAO-treated and unmodified 600 °C-biochar, which was proportional to the difference in adsorption free energy, could be computed for some compounds. Figure 32 shows that $\Delta \log K_D$ tends to be smaller for shorter-chain than for longer-chain PFAS. Our previous report noted that longer-chain PFAS were noticeably competitive against shorter-chain PFAS for adsorption sites.^{89, 125}

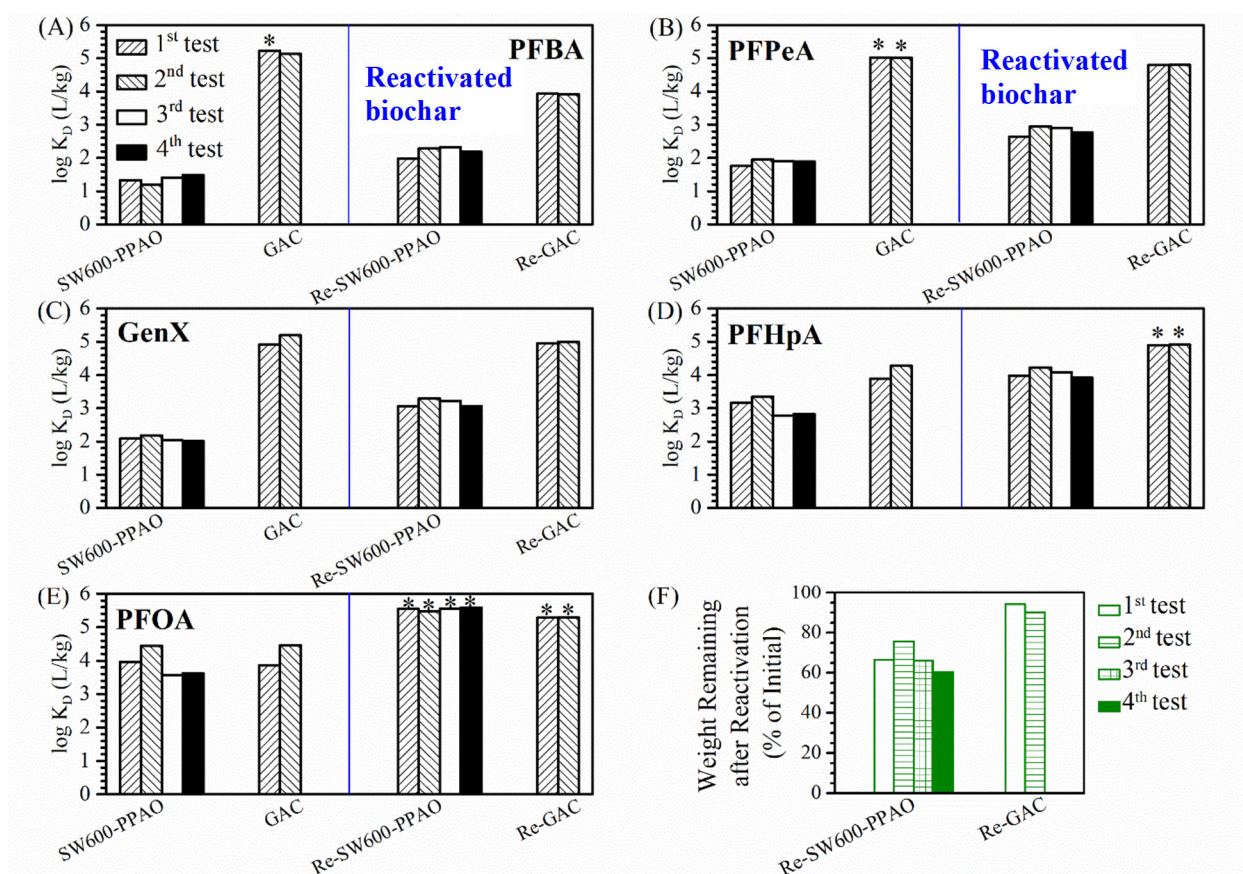


Figure 33. (A)–(E) Single-point K_D values for each compound in a mixture of PFCA sorbed for 2 days to PPAO-treated biochars and unmodified PCS, compared to reactivated counterparts (at 500 °C for 30 min under air). “Re-” denotes reactivated-. The asterisk (*) signifies that the displayed bar is the lower limit because the final dissolved concentration was below the method detection limit. (F) Sorbent weight remaining after air reactivation (normalized to initial weight). For SW600-PPAO, tests 1 and 2 correspond to a sample prepared in open glass vials, whereas tests 3 and 4 correspond to a sample prepared in an aluminum foil tube during PPAO treatment; the specific surface areas of these samples were nearly identical. The aluminum foil tube was used to avoid the cracking issue of glass tubes (for scale-up purposes in the future study) and to understand the effect of air oxidation conditions.¹⁸

Furthermore, how thermal treatment affects sorptivity of PFAS had never been tested prior to this study, despite that the answer bears critically on whether the biochar can be reused for PFAS removal from water. We tested the potential for thermal reactivation of SW600-PPAO biochar in comparison with a GAC. The materials were first allowed to sorb a mixture of PFCAs, PFSA, and GenX and then the dried materials were heated to 500 °C for 30 min in air to remove the PFAS. The reactivated biochars and GAC were then re-tested for their ability to sorb a mixture of PFBA, PFPeA, GenX, PFHpA, or PFOA. The results (Figures 33A–33E) clearly indicate that biochars can be reactivated for PFAS adsorption. In fact, in almost all cases, the K_D of each PFAS for the reactivated biochar was greater than that for the original. The results for the biochar contrast with those for the GAC: thermal reactivation of GAC under the same conditions as the biochar results in an increase in K_D of PFHpA and PFOA, but a decrease or no change in K_D of the shorter-chain PFAS (PFBA, PFPeA, and GenX). Further research is necessary to determine the cause of the differences. Enhanced removal caused by the thermal reactivation step may be due to additional

pore reaming, whereas decreased removal may be due to decreased hydrophobicity of the surface via introduction of oxygen groups. We speculate that for the biochars the former effect predominates generally, while for the GAC the net effect depends more on the specific compound. Thermal reactivation of the biochar SW600-PPAO, however, came at the expense of partial burn-off of the carbonaceous sorbent (24.4–39.6%), which was much less for the GAC (5.78–9.86%) (Figure 33F).¹⁸

Modified PCS generally had larger PFAS adsorption capacity than pristine PCS due to its greater specific surface area and more condensed aromatic character.^{126, 127} However, the K_D values of the longer-chain PFAS (PFHpA and PFOA) for SW600-PPAO biochar were comparable to those for GAC (Figure 33). Contingent on further improvement in adsorption of shorter-chain PFAS, PPAO might make biochar a more affordable alternative to GAC for PFAS removal.

4.4. TASK 4—REMOVAL OF PFAS FROM CONCENTRATE STREAMS GENERATED FROM NF AND RO

Lastly, we identified the proper NF/RO membrane for PFAS removal and assessed its performance with a complex feed solution. Six commercial NF and RO membranes were tested for their adsorption and removal of PFAS in the presence of NOM. Furthermore, we also investigated the adsorption of PFAS in NF/RO brine by commercial GAC and thermally regenerate the PFAS-laden GAC. The results indicated a high removal efficiency of PFAS from brine by GAC, likely due to the ion pair adsorption and the electrostatic interactions. Thermal treatment of GAC after adsorption of PFAS from brine showed near-complete degradation/removal of PFAS from GAC.

4.4.1. Performance of RO/NF membranes

The flux rates and rejections of PFAS by five membranes were shown in Table 3 and Figure 34. Overall, RO membrane SW30 had the highest PFAS rejection (all >98.5%) and lowest flux rate due to its smaller and tighter pores. As for NF membranes, NF90 and NFX gained high PFAS rejections (>97%), while DK and NF270 had lower PFAS removal, especially for short-chain PFAS such as PFBA, PFBS, and PFHxS. This might be because of the larger pore of NF270 and the relatively positive-charged surface of DK, where the latter weakens the electrostatic repulsion between the anionic PFAS and negatively charged PA layer. In addition, PFAS rejections for each membrane showed the following trends: the rejections decreased as the length of C-F chain is reduced due to the higher steric exclusion; rejections of PFASs were higher than PFCAs of the same carbon-chain length. The greater electrostatic repulsion between the sulfonic head group of PFASs and the PA layer than that between the carboxylic head group of PFCAs and the PA layer might explain the latter. To gain a deeper understanding of the removal mechanism in this process, we conducted static adsorption tests to assess the contribution of adsorption to rejection. The findings are presented in Table 3. Additionally, Figure 35 illustrates the percentage of PFAS adsorbed onto the membrane from the solution, as determined through mass balance calculations. Adsorption of PFOS contributed the most among all PFASs, which may be owing to the strong hydrophobic effect from its C-F chain and the membrane surface. Besides, adsorption contributed the most for NFX, which indicates the potential of scaling and the different rejection mechanisms of PFAS by NFX. In conclusion, considering the flow flux, PFAS rejection and adsorption, NF90 with high rejection rates for all PFASs and relatively high flux was selected to generate the concentrate of PFAS for subsequent treatment.

Table 3. Flux of NF/RO Membranes and Adsorption Capacities of PFAS.

Membrane	Flux (LMH/ 8bar)	Adsorption capacity ($\mu\text{M}/\text{m}^2$)				
		PFBS	PFBA	PFHxS	PFOS	PFOA
NF270	1014.5	0.061	0.322	0.159	1.840	0.175
NF90	120.4	0.047	0.190	0.198	2.175	0.924
NFX	33.5	2.267	0.456	4.248	8.315	3.141
DK	378.3	0.063	0.222	0.264	2.151	0.716
SW30	10.5	0.101	0.379	0.415	1.513	0.985

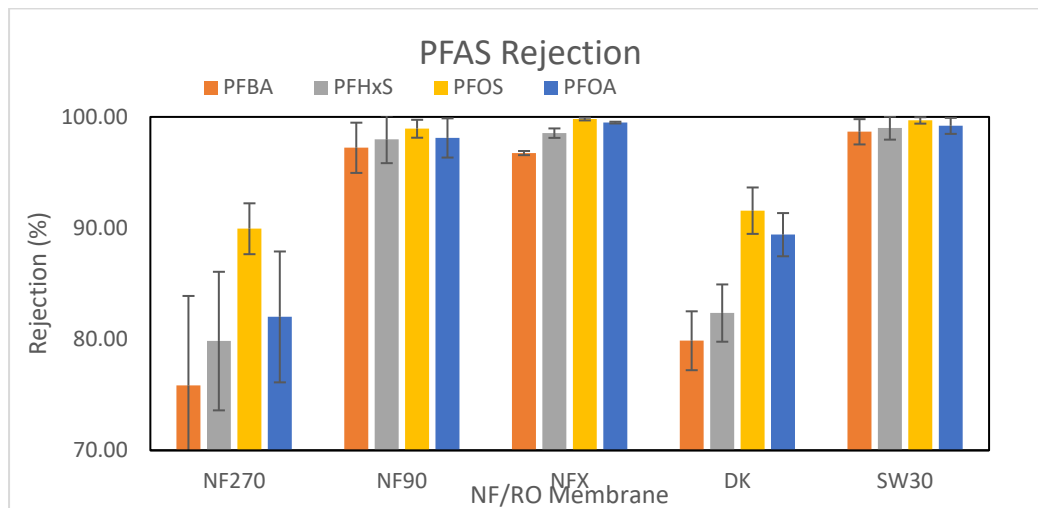


Figure 34. Rejection rates of PFAS by five NF/RO membranes under the operation pressure of 8 bar and temperature of 25 °C (unpublished results).

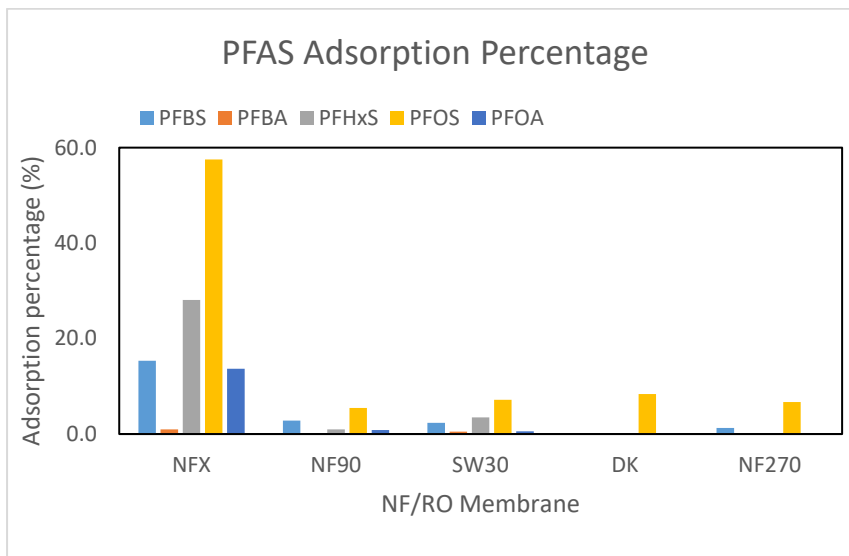


Figure 35. Percentages of PFAS adsorbed onto the membranes to that in the water from static adsorption tests (unpublished results).

4.4.2. Adsorption of PFAS on GAC in RO brine

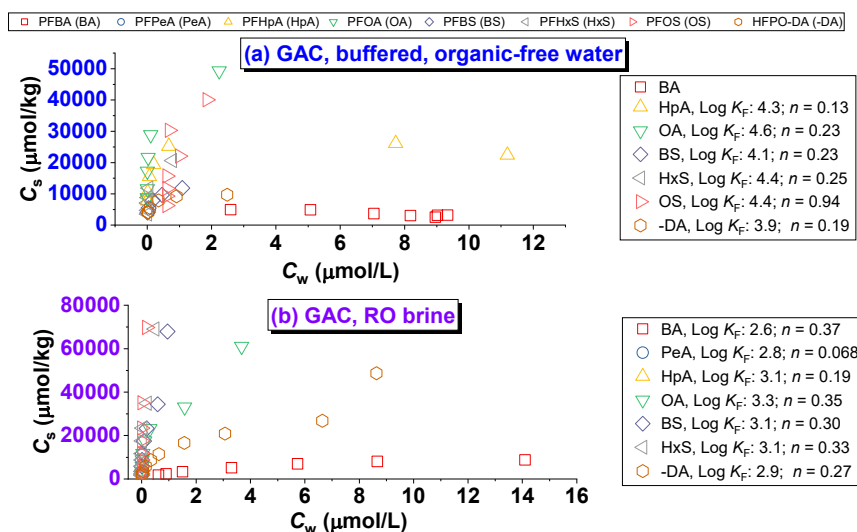


Figure 36. Adsorption isotherms of PFAS on GAC in buffered, organic-free water and RO brine (unpublished results).

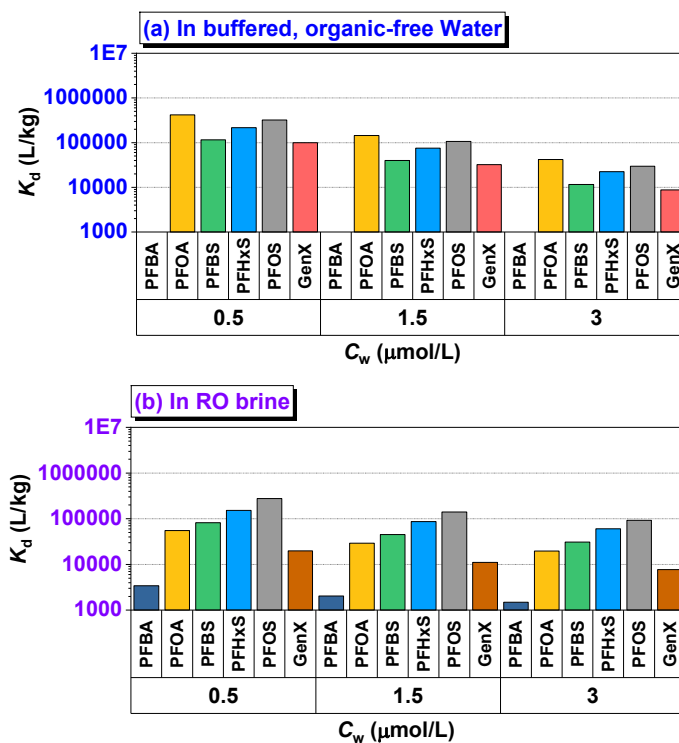


Figure 37. Single-point adsorption coefficients of PFAS on GAC in buffered, organic-free water and RO brine (unpublished results).

We further assessed the adsorption of PFAS on GAC (F200) in RO brine. It appeared that the brine background constituents did not inhibit the adsorption of PFAS on GAC (Figures 36 and 37). For certain PFAS, the adsorption was even high in RO brine than in organic-free water. We believed this is due to the ion-pair adsorption of PFAS anions with a counterion in solution (M^+_{aq}) (eq 13):



F200 GAC had few positive (anion-exchange) sites under non-acidic conditions. Despite the background NOM in RO brine, the adsorption of PFAS by the ion pair mechanism was not diminished by the influence of NOM. Thus it was reasonable to conclude that anion-exchange adsorption was minor and that PFAS anions were mainly bound by the ion-pair adsorption mechanism for F200 GAC.

5. Conclusions and Implications for Future Research/Implementation

5.1. CONCLUSIONS

Prior to this research, there was a considerable degree of uncertainty within the environmental science community regarding the possibility of degrading 'forever chemicals' at low temperatures. The findings from our *limited-scope* project, consisting of a series of studies, have provided enlightening insights into this matter. Below are a number of noteworthy results and conclusions from this project:

1. TGA was successfully used to study the thermal stability of PFAS. The study found that the order of thermal stability of PFAS was as follows: PFSA (potassium salts) >> PFCAs > HFPO-DA. TGA curves of PFCAs shifted to a higher temperature when the number of perfluorinated carbons increased.³
2. The temperature corresponding to 50% weight loss of a PFAS (T50) in TGA experiments correlated well with the number of perfluorinated carbons. An increase in one perfluorinated carbon unit leads to a rise of T50 by approximately 11 and 9 °C for PFCAs and PFSA, respectively.³
3. The weight loss of PFAS under isothermal conditions followed first-order kinetics, as revealed by the analysis of isothermal TGA data.³
4. Various extraction strategies were compared for the efficient extraction of PFAS from spent GAC. We found that methanol, especially when amended with NH₄Ac, showed promising results in the extraction of PFAS. However, the extraction efficiency varied among different types of PFAS.³
5. A 30-min thermal treatment of spent GAC at ≥300 °C achieved ≥99.9% removal of HFPO-DA and ≥99% removal of PFCAs (e.g., PFOA). To achieve ≥99% decomposition of PFSA (e.g., PFOS), a higher temperature of ≥500 °C was needed.³
6. The thermal decomposition of PFAS followed mostly first-order kinetics at temperatures of 150–250 °C. However, at a higher temperature (300 °C), the decomposition can also be described by second-order kinetics.⁴
7. The perfluorinated chain in PFAS became less thermally stable with the inclusion of an ether group, making PFCEA (HFPO-DA) more easily degradable than PFCA with the same number of perfluorinated carbons (i.e., PFBA).⁴
8. GAC was found to accelerate the thermal decomposition of HFPO-DA and PFCAs at temperatures as low as 150 °C and 200 °C respectively, with the acceleration effect becoming insignificant at ≥300 °C.⁴
9. The accelerated decomposition was hypothesized to be caused by the adsorption of gas-phase PFCEA/PFCA on GAC, which is much more thermally conductive than air, enhancing heat transfer.⁴

10. Other porous carbonaceous materials also accelerated the thermal decomposition of PFOA, with the effect more pronounced with thermally air-activated charcoal, commercial GAC, and XAD-2 resin.⁴

11. The thermal degradation of PFCAs yielded several transient PFCA intermediates. We discovered that the stepwise defluorination mechanism is not the primary process, as evidenced by the low yield and the concurrent emergence of short-chain intermediates in the absence of GAC.⁴

12. The presence of GAC altered the decomposition pathway of PFAS, significantly increasing yields of shorter-chained PFCA intermediates at lower temperatures.⁴

13. Significant mineralization of PFOA/PFOS, as indicated by measured yields of F^- , required high thermal treatment (HTT) of ≥ 700 – 800 °C, with the mineralization rate not significantly differing in CO_2 or air at a given HTT.³

14. The thermal decomposition of PFAS was believed to involve a series of radical chain reactions, including initiation, propagation, recombination, and termination. This process is initiated by the cleavage of a relatively weak C–C or C–S bond, forming a nonfluorinated moiety and a perfluoroalkyl biradical.^{4, 7}

15. We believed that the perfluoroalkyl biradical underwent chain propagation reactions, yielding shorter-chained perfluoroalkyl radicals, which may recombine with carboxyl groups/radicals, producing PFCA intermediates. These chain reactions ultimately result in very short, or "dead," fluorinated units.^{4, 7}

16. Further experimentation on individual PFECAs led to the identification of three transient organic intermediates of HFPO-DA (PFBA, PFPrA, TFA) and a novel volatile intermediate IV, suggesting that HFPO-DA undergoes thermal decomposition to form these transient intermediates.⁷

17. The thermal decomposition of other PFECAs, such as hexafluoropropylene oxide trimer acid (HFPO-TA) and perfluoro-2,5,8-trimethyl-3,6,9-trioxadecanoic acid (HFPO-TeA), also generated significant quantities of PFPrA and TFA, suggesting a similar decomposition pathway. A pathway consistent with the results suggests the thermal cleavage of the ether C–O bond (C–O_{nr}) closer to the carboxyl group, leading to the formation of certain radicals and intermediates.⁷

18. The project developed a database of pure water isotherms with PFAS on commercial GAC, which will be crucial for water facilities requiring PFAS control. Adsorption isotherms of PFAS on GAC showed strong nonlinearity, and the adsorption strength increased with increasing PFAS chain length.¹⁹

19. The adsorption of PFAS onto GAC was found to depend on the surface area of the GAC and the molecular dimensions of the adsorbate and the distribution of accessible surface area in nanopores. This result indicates that the internal surface area of GAC determined by N_2 porosimetry may not be accessible to PFAS molecules, leading to potential inconsistencies in adsorption capacity.^{17, 18}

20. GAC derived from different feedstocks showed varying effectiveness in PFAS removal. In particular, bituminous GACs showed better performance than coconut shell and lignite coal GACs, leading to the selection of F200, a bituminous GAC, for subsequent experiments.^{17, 18}

21. A new strategy for using pyrogenic carbonaceous materials for PFAS removal was developed. This strategy involved post-pyrolysis air oxidation, which enlarges pore size, increases surface area, and can enhance the adsorption capacity of individual PFAS by up to three orders of magnitude. After thermal reactivation, the biochars showed even higher PFAS adsorption values, suggesting this was effective for PFAS removal and allowed for material reuse.^{17, 18}

22. An increase in pyrolysis temperature led to a decrease in H/C and O/C atomic ratios and an increase in CO₂-specific surface area and porosity, indicating a progressive conversion to materials with greater hydrophobicity, higher nanoporosity, and a more condensed aromatic structure. The process of thermal oxidation, termed 'pore reaming', opened pore networks, increasing pore volume and specific surface area.¹⁷

23. Sorption experiments in multisolute-PFAS systems showed inconsistent effects of pyrolysis temperature on the adsorption value, except for samples heated to 600°C, which exhibited larger surface areas, porosities, and thus greater adsorption values. Post-pyrolysis air oxidation treatment significantly enhanced PFAS adsorption, especially for longer-chain PFAS. This treatment also increased the oxygen content of the carbons, which, despite increasing surface charge repulsion, did not counteract the beneficial effects of pore reaming.¹⁷

24. Competitive adsorption of PFAS on GAC was observed. Longer-chain PFAS had a greater affinity for carbon and thus compete more effectively for sorption sites than shorter-chain compounds.

25. Coating pDADMAC on PCS reversed the surface charge and increased the anionic exchange capacity, thereby enhancing PFAS adsorption.¹⁸

26. The surface chemistry of the adsorbent played a crucial role in the sorption of PFAS. Sorption of pDADMAC to carbons led to a charge reversal, enhancing the sorption capabilities of the carbon spheres.¹⁸

5.2. IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

This research provided a comprehensive investigation into the thermal degradation of PFAS on spent media such as GAC. The findings revealed exciting possibilities for the following future research tasks (#1–#8), with a focus on achieving more efficient PFAS degradation, optimizing extraction strategies, and understanding the kinetics of thermal decomposition.

9) This limited-scope project centered on perfluorinated compounds and GenX. Future research could focus on determining the optimum temperature for the degradation of various PFAS. The understanding of the thermal stability of different PFAS could also be expanded to include more compounds (e.g., cationic and zwitterionic precursors) and conditions (e.g., with or without moisture), which will provide a more comprehensive understanding of the thermal behavior of PFAS. A crucial area requiring deeper exploration is the thermal stability and degradation of emerging compounds, including precursors and various PFAS types present in AFFFs and sites contaminated with PFAS.

10) The thermal decomposition of PFAS under isothermal conditions followed first-order kinetics at low temperatures, suggesting that the degradation process may be predictable and manageable. However, the observation of second-order kinetics at higher temperatures suggested that the process might be more complex than currently understood. Future research should delve deeper into the kinetics of thermal degradation of PFAS, as a better understanding of these kinetics could lead to the development of more efficient and predictable degradation methods.

11) Likewise, a future research task could be the optimization of thermal degradation conditions for PFAS, especially in real-field conditions. This task would focus on adapting our laboratory findings to practical scenarios in a pilot-scale combustor or incinerator, where dynamic conditions and convective gas movements are prevalent. We would aim to determine the effective decomposition temperatures in these environments, investigating if they may be higher than those observed in laboratory (e.g., TGA) experiments. This research would not only enhance the

practical applicability of our findings but also contribute to the development of more efficient and feasible strategies for PFAS degradation in real-world thermal treatment facilities.

12) Furthermore, while we found that GAC accelerated the thermal decomposition of PFAS, the mechanism behind this acceleration is still uncertain. We hypothesized that it was due to the higher thermal conductivity of GAC than air at low and moderate temperatures.⁴ However, other factors, such as rare minerals on GAC, may also play a role.⁴ Future research should focus on understanding the exact mechanism of this acceleration. Also, the impact of other porous carbonaceous materials and porous resins on the thermal decomposition of PFAS should be investigated further. These studies could lead to the discovery of novel media for PFAS degradation.

13) The research also demonstrated that GAC altered the decomposition pathway of PFAS, increasing yields of shorter-chained PFCA intermediates at lower temperatures. This observation points to a possible direction for future research, which could focus on manipulating the decomposition pathway of PFAS to enhance the production of shorter-chained intermediates, thereby speeding up the degradation process. A future research endeavor should investigate how GAC properties, such as surface area, microporosity, mesoporosity, surface functional groups, and pore size distribution, influence the acceleration of PFAS degradation during thermal treatment.

14) The transient organic intermediates identified during the thermal decomposition of individual PFECAs could also provide a starting point for future research to mineralize intermediates.

15) Future research should also focus on understanding the relative importance of surface chemistry and pore size distribution in the adsorption of PFAS. In this limited-scope project, we showed that the adsorption capabilities of carbon spheres can be enhanced by reversing the surface charge. However, the exact mechanism behind this enhancement is still unknown. A better understanding of this process could lead to the development of novel sorbents with enhanced PFAS adsorption capabilities.

16) Finally, the results of this study suggested the possibility of using thermally reactivated biochars as an affordable alternative to GAC for PFAS removal. Further research should be undertaken to enhance the adsorption of shorter-chain PFAS and to reduce the loss of the carbonaceous sorbent during thermal reactivation.

In summary, this research has shed light on various aspects of the thermal degradation of PFAS on spent media such as GAC. Future research should focus on optimizing thermal degradation conditions, understanding the kinetics of degradation, optimizing extraction strategies, and exploring the role of surface chemistry in PFAS adsorption. Furthermore, the development of affordable and efficient alternatives to GAC for PFAS removal is another promising direction for future research.

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Appendix A (Supporting Data)

Table A 1. BDEs of HFPO-DA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
HFPO-DA	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-COOH	-1553.312539	
	CF ₃ -CF ₂ -CF ₂ ·	-813.233055	79.6
	·O-CF(CF ₃)-COOH	-739.952607	
	CF ₃ -CF ₂ -CF ₂ -O·	-888.451761	74.2
	·CF(CF ₃)-COOH	-664.74252	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)·	-1364.093419	71.2
	·COOH	-189.105688	
	CF ₃ ·	-337.614015	77.1
	·CF ₂ -CF ₂ -O-CF(CF ₃)-COOH	-1215.575725	
	CF ₃ -CF ₂ ·	-575.426334	76.1
	·CF ₂ -O-CF(CF ₃)-COOH	-977.764859	
	CF ₃ -CF ₂ -CF ₂ -O-CF(·)-COOH	-1215.58953	69.6
	CF ₃ ·	-337.612099	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CO·	-1477.41267	100.1
	·OH	-75.74036	
	·F	-99.748541	
	·CF ₂ -CF ₂ -CF ₂ -O-CF(CF ₃)-COOH	-1453.382954	113.6
	CF ₃ -CF(·)-CF ₂ -O-CF(CF ₃)-COOH	-1453.393842	106.8
	CF ₃ -CF ₂ -CF(·)-O-CF(CF ₃)-COOH	-1453.390428	108.9
	CF ₃ -CF ₂ -CF ₂ -O-C(·)(CF ₃)-COOH	-1453.409519	96.9
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₂ (·))-COOH	-1453.380619	115.1
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-COO·	-1552.632638	107.4
	·H	-0.508793	
	PFBA:CF ₃ -CF ₂ -CF ₂ -COOH	-1002.453442	-72.0
	CF ₂	-237.740076	41.8
	CF ₃ -CF ₂ ·	-575.426332	
	PFPrA:CF ₃ -CF ₂ -COOH	-764.650124	-74.1
	CF ₃ -CF ₂ -OH	-651.327167	-100.7
	CF ₃ -CF ₂ -O·	-650.646133	108.1
	CF ₃ -COF	-550.8659	1.3
	CF ₃ -CF ₂ -CO·	-688.747647	101.7
	CF ₃ -CH ₂ -CO·	-490.243044	15.8
	CH ₂	-39.123645	1.3
	CF ₃ -CH ₂ -COOH	-566.140985	18.6
	TFA:CF ₃ -COOH	-526.842746	109.6
	CF ₃ -CF ₂ -CF ₂ -O-CF=CF ₂	-1264.243824	63.4

Table A 2. BDEs of HFPO-TA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
HFPO-TA	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2341.964749	
	CF ₃ -CF ₂ -CF ₂ ·	-813.233055	78.5
	·O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1528.606552	
	CF ₃ -CF ₂ -CF ₂ -O·	-888.451761	77.9
	·CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1453.388777	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ ·	-1601.890257	75.4
	·O-CF(CF ₃)-COOH	-739.954354	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O·	-1677.10784	75.4
	·CF(CF ₃)-COOH	-664.736712	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)·	-2152.750138	68.4
	·COOH	-189.105688	
	CF ₃ ·	-337.614015	76.9
	·CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2004.228208	
	CF ₃ -CF ₂ ·	-575.426334	76.0
	·CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1766.417313	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)·	-1364.088423	73.2
	·CF ₂ -O-CF(CF ₃)-COOH	-977.759719	
	CF ₃ -CF ₂ -CF ₂ -O-CF(·)-CF ₂ -O-CF(CF ₃)-COOH	-2004.237566	71.0
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(·)-COOH	-2004.241153	68.8
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CO·	-2266.069485	97.2
	·OH	-75.74036	
	·F	-99.748541	
	·CF ₂ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2242.034955	113.7
	CF ₃ -CF(·)-CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2242.044995	107.4
	CF ₃ -CF ₂ -CF(·)-O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2242.045754	107.0
	CF ₃ -CF ₂ -CF ₂ -O-C(·)(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-2242.054898	101.2
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₂ (·))-CF ₂ -O-CF(CF ₃)-COOH	-2242.037578	112.1
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF(·)-O-CF(CF ₃)-COOH	-2242.043057	108.7
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-C(·)(CF ₃)-COOH	-2242.060282	97.8
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₂ (·))-COOH	-2242.033061	114.9
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COO·	-2341.289742	104.3
	·H	-0.508793	

Table A 3. BDEs of HFPO-TeA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
HFPO- TeA	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)-COOH	-3130.620629	
	CF ₃ -CF ₂ -CF ₂ ·	-813.233055	
	·O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)- COOH	-2317.264657	77.1
	CF ₃ -CF ₂ -CF ₂ -O·	-888.451761	
	·CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)- COOH	-2242.045307	77.5
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ ·	-1601.890257	
	·O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1528.606559	77.7
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O·	-1677.10784	
	·CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1453.388766	77.8
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ ·	-2390.546803	
	·O-CF(CF ₃)-COOH	-739.954354	75.0
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O·	-2465.764497	
	·CF(CF ₃)-COOH	-664.736712	74.9
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)·	-2941.406309	
	·COOH	-189.105688	68.2
	CF ₃ ·	-337.614015	
	·CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ -O- CF(CF ₃)-COOH	-2792.88427	76.8
	CF ₃ -CF ₂ ·	-575.426334	
	·CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ -O- CF(CF ₃)-COOH	-2555.075269	74.7
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)·	-1364.088424	
	·CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-COOH	-1766.419561	70.7
	CF ₃ -CF ₂ -CF ₂ -O-CF(·)-CF ₂ -O-CF(CF ₃)-CF ₂ -O- CF(CF ₃)-COOH	-2792.895628	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)·	-2152.746618	69.6
	·CF ₂ -O-CF(CF ₃)-COOH	-977.759727	71.7
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(·)-CF ₂ -O- CF(CF ₃)-COOH	-2792.894759	
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(·)-COOH	-2792.89898	70.2
	CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)-CO·	-3054.725719	
	·OH	-75.74036	97.0
	·F	-99.748541	
	·CF ₂ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)-COOH	-3030.691078	113.6

CF ₃ -CF(·)-CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)- CF ₂ -O-CF(CF ₃)-COOH	-3030.70118	107.2
CF ₃ -CF ₂ -CF(·)-O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)- CF ₂ -O-CF(CF ₃)-COOH	-3030.703336	105.9
CF ₃ -CF ₂ -CF ₂ -O-C(·)(CF ₃)-CF ₂ -O-CF(CF ₃)- CF ₂ -O-CF(CF ₃)-COOH	-3030.713093	99.8
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₂ (·))-CF ₂ -O-CF(CF ₃)- CF ₂ -O-CF(CF ₃)-COOH	-3030.695099	111.1
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF(·)-O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)-COOH	-3030.702729	106.3
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-C(·)(CF ₃)-CF ₂ - O-CF(CF ₃)-COOH	-3030.711961	100.5
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₂ (·))- CF ₂ -O-CF(CF ₃)-COOH	-3030.695904	110.6
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF(·)- O-CF(CF ₃)-COOH	-3030.694184	111.6
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-C(·)(CF ₃)-COOH	-3030.716696	97.5
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₂ (·))-COOH	-3030.689959	114.3
CF ₃ -CF ₂ -CF ₂ -O-CF(CF ₃)-CF ₂ -O-CF(CF ₃)-CF ₂ - O-CF(CF ₃)-COO·	-3129.945458	104.4
·H	-0.508793	

Table A 4. BDEs of PFMeUPA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
PFMeUPA	F ₃ C-CF(CF ₃)-CF=CF-COOH	-1278.332983	58.8
	F ₃ C·	-337.614015	
	F ₃ C-CF(·)-CF=CF-COOH	-940.625237	
	F ₃ C-C(F)(CF ₃)·	-813.24455	81.5
	·CF=CF-COOH	-464.958501	
	F ₃ C-CF(CF ₃)-CF	-951.134437	124.6
	CF-COOH	-326.999959	
	F ₃ C-CF(CF ₃)-CF=CF·	-1089.086052	88.6
	·COOH	-189.105688	
	F ₃ C-CF(CF ₃)-CF=CF-CO·	-1202.435888	98.4
	·OH	-75.74036	
	·F	-99.748541	
	F ₂ C(·)-CF(CF ₃)-CF=CF-COOH	-1178.404586	112.9
	F ₃ C-C(CF ₃)(·)-CF=CF-COOH	-1178.450607	84.0
	F ₃ C-CF(CF ₃)-C(·)=CF-COOH	-1178.416649	105.3
	F ₃ C-CF(CF ₃)-CF=C(·)-COOH	-1178.414004	107.0
	F ₃ C-CF(CF ₃)-CF=CF-COO·	-1277.655641	105.8
	·H	-0.508793	

Table A 5. BDEs of PFMPA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
PFMPA	F ₃ C-O-CF ₂ -CF ₂ -COOH	-1077.697526	91.8
	F ₃ C·	-337.614015	
	·O-CF ₂ -CF ₂ -COOH	-739.937232	
	F ₃ C-O·	-412.837209	89.2
	·CF ₂ -CF ₂ -COOH	-664.718096	
	F ₃ C-O-C(F ₂)·	-650.663558	69.7
	·CF ₂ -COOH	-426.92295	
	F ₃ C-O-CF ₂ -C(F ₂)·	-888.473636	74.2
	·COOH	-189.105688	
	F ₃ C-O-CF ₂ -CF ₂ -CO·	-1001.798102	99.8
	·OH	-75.74036	
	·F	-99.748541	
	F ₂ C(·)-O-CF ₂ -CF ₂ -COOH	-977.76497	115.5
	F ₃ C-O-CF(·)-CF ₂ -COOH	-977.77539	108.9
	F ₃ C-O-CF ₂ -CF(·)-COOH	-977.790429	99.5
	F ₃ C-O-CF ₂ -CF ₂ -COO(·)	-1077.018232	107.0
	·H	-0.508793	

Table A 6. BDEs of PFBA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
PFBA	PFBA:CF ₃ -CF ₂ -CF ₂ -COOH	-1002.453442	
	CF ₃ -CF ₂ -CF ₂ ·	-813.233055	72.0
	·COOH	-189.105688	
	CF ₃ ·	-337.614015	75.4
	·CF ₂ -CF ₂ -COOH	-664.719353	
	CF ₃ -CF ₂ ·	-575.426334	65.4
	·CF ₂ -COOH	-426.922951	
	·F	-99.748541	
	·CF ₂ -CF ₂ -CF ₂ -COOH	-902.523309	114.0
	CF ₃ -CF(·)-CF ₂ -COOH	-902.53657	105.6
	CF ₃ -CF ₂ -CF(·)-COOH	-902.549616	97.4
	·H	-0.508793	106.9
	CF ₃ -CF ₂ -CF ₂ -COO·	-1001.774246	
	CF ₃ -CF ₂ -CF ₂ -CO·	-926.554975	99.2
	·OH	-75.74036	

Table A 7. BDEs of PFPeA.

PFAS	Sequence	G(T)	BDE (Kcal/mol)
PFPeA	CF ₃ -CF ₂ -CF ₂ -CF ₂ -COOH	-1240.258555	
	CF ₃ -CF ₂ -CF ₂ -CF ₂ ·	-1051.037884	72.2
	·COOH	-189.105688	
	CF ₃ ·	-337.614015	75.0
	·CF ₂ -CF ₂ -CF ₂ -COOH	-902.525015	
	CF ₃ -CF ₂ ·	-575.426334	70.8
	·CF ₂ -CF ₂ -COOH	-664.719353	
	CF ₃ -CF ₂ -CF ₂ ·	-813.233475	64.1
	·CF ₂ -COOH	-426.922951	
	CF ₃ -CF ₂ -CF ₂ -CF ₂ -CO·	-1164.359065	99.9
	·OH	-75.74036	
	·F	-99.748541	
	CF ₂ (·)-CF ₂ -CF ₂ -CF ₂ -COOH	-1140.329073	113.5
	CF ₃ -CF(·)-CF ₂ -CF ₂ -COOH	-1140.342679	105.0
	CF ₃ -CF ₂ -CF(·)-CF ₂ -COOH	-1140.343539	104.5
	CF ₃ -CF ₂ -CF ₂ -CF(·)-COOH	-1140.354964	97.3
	CF ₃ -CF ₂ -CF ₂ -CF ₂ --COO·	-1239.579189	107.0
	·H	-0.508793	
	CF ₃ -CF ₂ -CF=CF ₂	-951.209463	50.1
	CF ₂	-237.740076	40.6
	CF ₃ -CF ₂ -CF ₂ ·	-813.233055	
	PFBA: CF ₃ -CF ₂ -CF ₂ -COOH	-1002.453442	-72.0
	CF ₃ -CF=CF ₂	-713.402379	51.5
	CF ₃ -CF ₂ ·	-575.426332	41.8

PFPrA: CF ₃ -CF ₂ -COOH	-764.650124	-74.1
CF ₂ =CF ₂	-475.573578	65.4
·CF ₃	-337.614015	45.3
TFA: CF ₃ -COOH	-526.842746	-77.2

Appendix B (List of Scientific/Technical Publications)

1. Alinezhad, A., Shao, H., Litvanova, K., Sun, R., Kubatova, A., Zhang, W., Li, Y., **Xiao, F.***. “Mechanistic Investigations of Thermal Decomposition of Perfluoroalkyl Ether Carboxylic Acids and Short-chain Perfluoroalkyl Carboxylic Acids” *Environmental Science & Technology* (accepted).
2. Wang, Z., Alinezhad, A., Sun, R., **Xiao, F.***, **Pignatello, J.J.***. “Pre- and postapplication thermal treatment strategies for sorption enhancement and reactivation of biochars for removal of perfluoroalkyl substances from water” *ACS ES&T Engineering*. 3, 193–200, 2023.
3. Wang, Z., Alinezhad, A., Nason, S., **Xiao, F.***, **Pignatello, J.J.***. “Enhancement of per- and polyfluoroalkyl substances removal from water by pyrogenic carbons: Tailoring carbon surface chemistry and pore properties” *Water Research*, 229, 119467, 2023.
4. **XIAO, F.***, “A review of biochar functionalized by thermal air oxidation” *Environmental Functional Materials*, 1, 187–195, 2022.
<https://doi.org/10.1016/j.efmat.2022.03.001>.
5. CHALLA SASI, P., Alinezhad, A., YAO, B., KUBÁTOVÁ, A. GOLOVKO, S., GOLOVKO, M., **XIAO, F.*** “Effect of Granular Activated Carbon and Other Porous Materials on Thermal Decomposition of Per- and Polyfluoroalkyl Substances: Mechanisms and Implications for Water Purification” *Water Research*, 200, 117271, 2021. <http://doi.org/10.1016/j.watres.2021.117271>
6. Alinezhad, A., CHALLA SASI, P., ZHANG, P., YAO, B., GOLOVKO, S., GOLOVKO, M. KUBATOVA, A., **XIAO, F.***, “An Investigation of Thermal Air Degradation and Pyrolysis of PFAS and PFAS Alternatives in Soil” *ACS ES&T Engineering* 2, 198–209, 2022. <https://doi.org/10.1021/acsestengg.1c00335>.