Regeneration of PFAS-laden Granular Activated Carbon by Modified Supercritical CO_2 Extraction

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Abstract

Granular activated carbon (GAC) is widely used to treat contaminated per- and polyfluoroalkyl substances (PFAS) waste streams, resulting in the accumulation of large quantities of spent GAC that need to be landfilled or regenerated. A novel modified supercritical CO_2 ($scCO_2$) extraction for regeneration of spent GAC is developed. With the addition of organic solvents and acid modifiers, the procedure yielded > 97% perfluorooctanoic acid (PFOA) desorption after a 60-minute treatment in a continuous flow reactor. The mild extraction conditions at T ~ 100°C do not trigger the formation of volatile organic fluorine or changes in GAC sorbent properties. Mechanistically, the high miscibility of co-solvent/$scCO_2$ eliminates diffusion transport limitations, enabling rapid reagent and PFAS transport in a single-phase (gas-like) medium. The introduction of organic co-solvent and the absence of water reverses hydrophobic interactions between GAC and the PFAS. The acid modifier minimizes the electrostatic PFOA/ GAC interactions by protonating the perfluorooctanoate ion and providing competition for active GAC sites. The approach offers an economically effective regeneration scheme, enabling the reuse of sorbents and yielding effluent with a high loading of PFAS that is amenable to subsequent end-of-life treatment technologies.

Keywords: PFAS; PFOA; granular activated carbon; GAC regeneration; supercritical CO_2; modified supercritical fluid extraction

Synopsis: Supercritical CO_2 with minimal co-solvents regenerates PFOA-laden GAC with > 99.9% desorption efficiency.

1 Introduction

Granular activated carbon (GAC) is used to treat contaminated waters with per- and polyfluoroalkyl substances (PFAS). [1] While widespread adoption of GAC offers a cost-effective solution, it also creates a pressing need for managing the accumulation of spent GAC. Sorbent regeneration unlocks the potential for sustainable, large-scale treatment of PFAS-contaminated streams. [2] Thermal regeneration utilizes high temperatures, ~600-1000°C, to desorb PFAS and other contaminants. The higher temperatures can also effectively destroy PFAS in situ; however, the process is energy-demanding and can lead to GAC degradation and loss. [3] Recent studies also show that thermal degradation yields the formation of volatile organo-fluorine (VOF) compounds that could re-enter the environment as gases or aerosols. [4]

Motivated by the development of various end-of-life PFAS destruction technologies [5, 6], the effective PFAS transport from sorbents into concentrated liquid feedstock becomes highly desirable. Approaches that can desorb PFAS without forming VOFs while preserving GAC's structural and adsorptive properties are highly desirable. Several reported low-temperature methods rely on organic solvents [7-10] or aqueous solutions [8]. The application of these methods for the desorption of long-chain (C-8) PFAS is challenging due to their strong affinity to surfaces, and the large quantities of solvents required for GAC treatment hinder large-scale implementation (Table S1). [11]

Above its critical point (31°C, 7.4 MPa), CO_2 becomes a supercritical fluid ($scCO_2$)–a nonpolar solvent with low dielectric constant and negligible molecular dipole moment. [12] Supercritical fluid extraction (SFE) temperatures ($T < 100\,°C$) would not trigger volatile fluorinated species formation via thermal degradation. [6, 13] SFE is used in commercial applications for removing

organics from solid matrices, e.g., botanical extraction, surface sterilization, food pasteurization, and material synthesis. [12, 14] In analytical chemistry, the SFE enables quantitative PAH recovery from sorbent traps at $T = 45\,^{\circ}C$. [15] There is also a report on $scCO_2$ use to extract PFOA and PFOS from nonporous materials such as paper, fabrics, and sand. [16]

This study is the first investigation of low-temperature spent GAC regeneration using $scCO_2$ extraction with the addition of co-solvents and acid modifiers. Perfluorooctanoic acid (PFOA) was chosen for this study due to its environmental persistence and high adsorption affinity, yet our modified SFE approach yielded >99% desorption after 1 hour of GAC treatment.

2 METHODS AND MATERIALS

All chemicals and solvents used in this study are described in Section S1 in Supporting Information (SI). The analytical methods for PFAS analysis are described in Section S2 in SI. Each GAC sample was weighed (0.71 ± 0.01 g) and mixed with 19.0 mL of an aqueous solution of PFOA at 20 ppm. After 5 days, the GAC was removed, and the liquid was analyzed using LC-MS/MS. The GAC pellets were dried in an oven at 70°C for 12 hours. The spent GAC sub-samples were extracted into 20 mL of ethanol (EtOH) + 0.15% NH_4OH solution [11] to determine the amount of PFOA sorbed onto GAC. After 24 hours, the GAC was removed, and the liquid was analyzed using LC-MS/MS.

Figure S1 describes the laboratory continuous flow reactor used in this study. The CO_2 from the gas cylinder is condensed to the liquid phase in a calcium chloride cold bath (-10 to -5°C) CO_2 and pumped at 25 mL/min. The co-solvent (MeOH, or MeOH + 1% v/v H_2SO_4) injected at 1 mL/min, T~20°C, is mixed with $scCO_2$ before entering the reactor section. The CO_2 and solvent post-mixing become a supercritical single-phase fluid if the organic solvent does not exceed its solubility limit in the $scCO_2$. [17] P = 20.3 MPa, T = 110 - 120°C were chosen as the

operational parameters to satisfy single-phase conditions. After performing SFE for 60 minutes, the column contents were dried in an oven at 70°C for 24 hours. The sample was divided into two sub-samples: one was subjected to extraction by soaking in EtOH and ammonium hydroxide, followed by LC-MS/MS; the other was loaded with PFOA again and underwent a second regeneration cycle. Each experiment was performed in triplicates. The desorption efficiency (DE) was calculated as:

$$DE = \frac{[PFAS \in spent\ GAC] - [PFAS \in GAC\ after\ regeneration]}{[PFAS \in spent\ GAC]} \times 100\,\%,$$

where *[PFAS in spent GAC]* is the PFOA concentration (mg/g) in the spent sorbent, and *[PFAS in GAC after regeneration]* is the PFOA concentration (mg/g) in the regenerated sorbent.

3 RESULTS AND DISCUSSION

3.1 Modified $scCO_2$ method for GAC regeneration

PFOA exhibits strong adsorption onto GAC due to hydrophobic and electrostatic interactions, which present challenges for conventional techniques. [18] The modified $scCO_2$ extraction yielded near complete desorption of PFOA (Figure 1) by counteracting both forces. First, the method takes advantage of the transition from a polar aqueous to a nonpolar $scCO_2$ environment, which weakens/eliminates hydrophobic interactions. Once in $scCO_2$, PFOA miscibility decreases compared to the shorter fluorinated molecules. [19] Due to the high polarity of the perfluorooctanoate ion, $C_8F_{15}O_2^-$, electrostatic interactions become the dominant force; therefore, in pure $scCO_2$, desorption efficiency was limited to < 30% (Figure 2).

The addition of organic co-solvents can enhance PFAS solubility in $scCO_2$. E.g., Chen et al. [16] reported that the $scCO_2$/ MeOH mixture was effective in extracting PFOA and PFOS from nonporous materials. Table S1 shows that organic solvent-based extraction (MeOH, EtOH,

Acetone) in the batch GAC/ C-8 PFAS systems reach the DE ~ 40-95% after 12-24 hours. [7, 8] MeOH extraction showed the best results. Chularueangaksorn et al. utilized a column flow reactor and MeOH, reporting DE = 67% desorption of PFOA from GAC 400 after 24 hours of treatment. [9] The solubility of PFAS in alcohols generally decreases for longer PFAS molecules and longer carbon chain lengths of alcohol. [20] For example, the solubility of PFOS in MeOH is ~ 37 g/L; it is ~ 5 times higher than in EtOH (~ 7 g/L). The solubility of PFOA in MeOH is 37.1 g/L, similar to PFOS's. Thus, in this proof-of-concept study, MeOH is used as a co-solvent. In our experiment, adding MeOH alone did not significantly affect PFOA desorption (Figure 1), indicating that scCO2 is an effective agent for disrupting the hydrophobic interaction. A slight increase in desorption efficiency from 18.7% to 26.3% in the second cycle might be attributed to carryover from the previous cycle. While dipolar organic solvents can disrupt hydrophobic interactions [18, 21], they are unlikely to affect the electrostatic interactions between PFAS molecules and GAC surfaces. [16] Lacking hydrophobic PFOA/GAC interaction in $scCO_2$ and $scCO_2$/MeOH mixtures, the low desorption is contributed to electrostatic interactions, which can be weakened by introducing an ionic agent. Thus, adding sulfuric acid (1% vol in MeOH) increased the desorption efficiency to >97%.

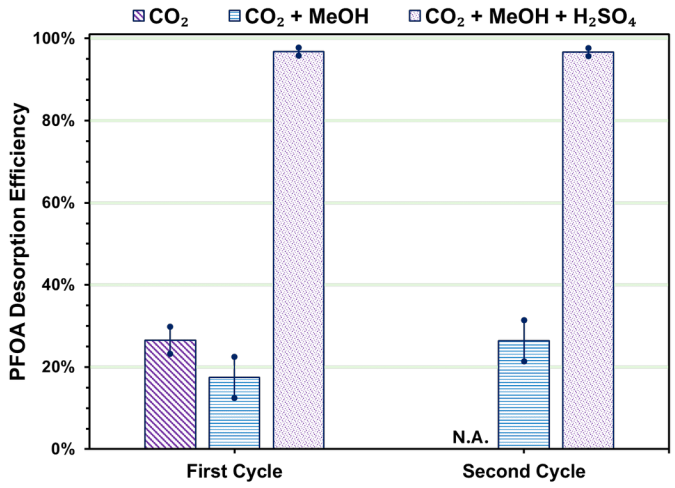

Figure 1. PFOA desorption from GAC using only $scCO_2$, scCO2 + MeOH, and $scCO_2$ + MeOH/H_2SO_4. Experimental conditions are 110°C, 10 MPa, and an exposure time of 60 min. The second cycle of desorption in CO_2 was not conducted. Error bars are standard deviations from triplicated experiments.

The modified SFE regeneration method yielded significantly faster and more efficient PFAS removal compared to conventional solvent-based techniques (Table S1). Treatment time was 1 hour, compared to 5-24 hours for traditional methods, yielding >97% PFAS removal (max DE~99.9%). Notably, solvent consumption was decreased to ~ 4% of other reported solvent-based methods, presenting an environmentally friendly and cost-effective approach for GAC regeneration. The synergistic result of combining $scCO_2$, a co-solvent, and an acid modifier achieves remarkable desorption results and complete restoration of GAC properties (Table 1).

3.2 Proposed mechanisms for modified supercritical CO_2 GAC regeneration

PFOA/GAC interaction is governed by two key forces, which must be effectively counteracted. Specifically, the Filtrasorb 400 GAC has a point of zero charge (pH_{pzc}) of 8.65, [1] characteristic of activated carbons with low oxygen content. [22] The low oxygen content is reflected in the measured concentration of oxygen-containing groups (phenolic, carboxylic, lactonic) of 0.21 mmol/g. [23] The measured pH during adsorption in this study (~ 4.8) was below the pH_{pzc}. Under such conditions, the surface of the activated carbon becomes positively charged due to the protonation of surface groups, enhancing electrostatic interactions with negatively charged PFAS anions. The shift to the $scCO_2$ environment weakened hydrophobic interactions, leading to a change from a predominantly surface-aligned orientation to a perpendicular orientation. This reorientation, consistent with the classical work of Zisman and colleagues [24], minimizes the contribution of hydrophobic forces, leaving electrostatic interactions as the dominant force between the monovalent PFOA anion and the GAC surface in the $scCO_2$ environment.

Route I is enabled by the high dielectric permittivity of $scCO_2$, facilitating proton availability from PFOA dissociation. This can lead to the association of PFOA molecules (Figure 2, Route I) and subsequent desorption in its protonated form. However, this route exhibits limited efficacy for PFOA, DE < 30% (Figure 1). The effectiveness of this route may vary in other systems**.**

Route II involves the interaction of CO_2 molecules with water retained in the GAC pores, leading to the formation of bicarbonate ions. While the bicarbonate ion is typically a weak competitor for PFAS on GAC under normal conditions, the high concentration of CO_2 and small pore volume may enhance the effect (Figure 2, Route II). However, the presence of water within the pores can also promote hydrophobic interactions, potentially hindering the efficacy of Route II.

Route III is based on disrupting the electrostatic forces between GAC and PFAS. The $scCO_2$ or methanol cannot effectively weaken the electrostatic interaction between GAC and PFOA. Figure 1 shows no significant change in desorption efficiency from $scCO_2$ to $scCO_2$/ MeOH experiments. On the other hand, adding the MeOH/ acid mixture yields significant improvement in the PFOA desorption. The MeOH assists in introducing sulfuric acid to a single-phase supercritical mixture and ultimately inside the sorbent's pores. Mechanistically, a divalent sulfate ion exhibits a stronger affinity to the active sites on the GAC surface, causing the release of a weaker PFOA monovalent perfluorooctanoate ion, $C_8F_{15}O_2^-$ (Figure 2, Route III). Moreover, sulfuric acid (pKa = -3) can protonate PFOA (pKa = - 0.2 – +3.8). [25] The long-chain PFAS may form micelles/hemi-micelles [18, 26] in an aqueous environment that can interact with the GAC surface during sorption; however, it is unclear if these structures interact in a scCO2/organic co-solvent environment in the absence of liquid water. We expected that micelle formation is negligible in a nonpolar solvent and does not significantly affect the proposed mechanism of

hydrophobic and electrostatic forces disruption in the $scCO_2$ environment. Though beyond the scope of the current report and the subject of ongoing work, we suspect that Route III should also hold for other PFAS.

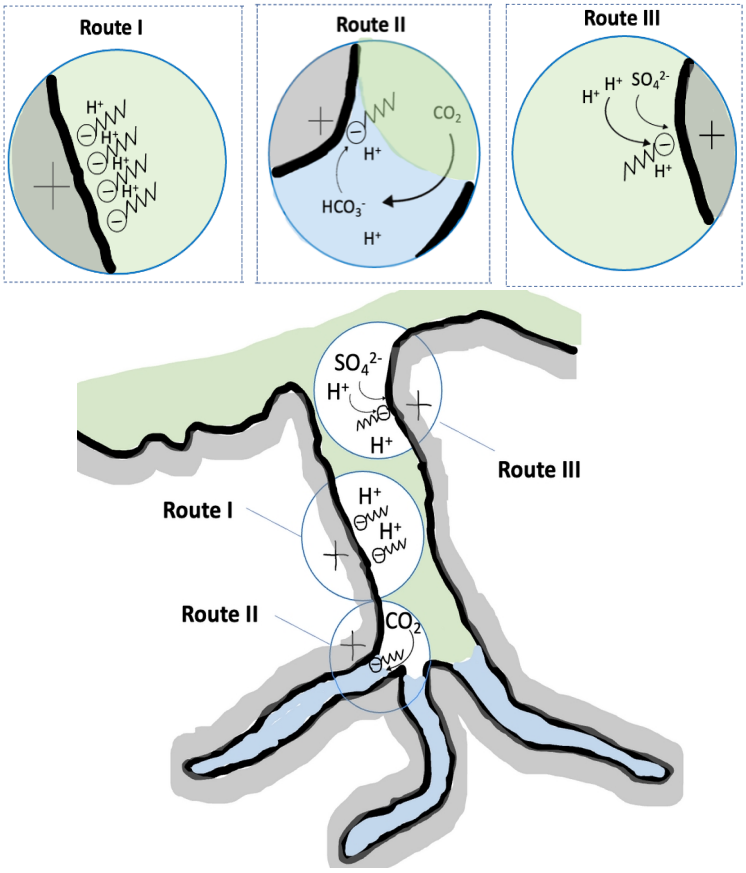

Figure 2: PFOA desorption routes from GAC, blue – porous water, green – $scCO_2$. Route I - in pure $scCO_2$, high dielectric permittivity and subsequent proton association lead to partial PFOA protonation; Route II - in pure $scCO_2$, bicarbonate ions formed from CO_2 interaction with retained water compete with PFOA for adsorption sites; Route III - in $scCO_2$/ MeOH/ H_2SO_4 (i) competition of the sulfate ion for GAC active site and (ii) PFOA protonation.

3.3 Impacts of co-solvent concentration on regeneration efficiency

Increasing the concentration of acid-modified co-solvent in $scCO_2$ yielded the highest desorption efficiency of 99.9% (Figure S2). In these experiments, the CO_2 flow rate was constant (25 mL/min), and the co-solvent flow rate varied from 0.2 to 6.8 mL/min. The results showed only marginal improvement for high MeOH flow rates. This corroborates that the hydrophobic interaction does not play a significant role in the $scCO_2$ environment, and the disruption of

electrostatic attraction by the pH surface modifier is the dominant mechanism. Further research is needed to optimize the acid concentration in the $scCO_2$/ MeOH mixture and substitute MeOH with more environmentally friendly solvents.

From a practical perspective, these observations suggest that the process can yield a very concentrated effluent, reducing consumption of co-solvent and, in turn, reducing the volume of effluent that needs to be treated in the end-of-life destruction step. In a binary CO_2/ solvent system, the pressure, temperature, and mole fractions of each solvent determine the phase of the overall fluid mixture. Based on data extrapolation from Reighard et al.[27], at $X_{MeOH}=0.1792$ and 10 MPa, the dew point of the CO_2/ MeOH mixture is at ~ 110°C. Assuming that a trace concentration of sulfuric acid does not affect the solubility of MeOH in CO_2, a lower X_{MeOH} would lead to a single-phase supercritical gas-like mixture of MeOH completely dissolved in CO_2, while a higher X_{MeOH} would lead to a two-phase mixture of liquid MeOH and the gas-like $scCO_2$. Adjusting the flow rates controls MeOH concentration and mixture phase during regeneration. Though limiting the concentration of MeOH produces more concentrated effluent, the presence of a liquid interface at the GAC surface may improve the desorption and regeneration efficiency, as seen in the experiment at 6.8 mL/min, where the experimental condition was close to the MeOH dew point.

3.4 Assessment of GAC properties after regeneration

A sustainable PFAS regeneration approach must also maintain GAC's structural integrity and adsorption capacity after regeneration. Table 1 shows that BET surface area and micropore volume of spent GAC decreased (971 to 922 m^2/g), indicating the occupation of active sorption sites and pore blockage by PFOA molecules. After the regeneration step, the BET surface area and micropore volume slightly increased (971 to 1012 m^2/g) compared to the virgin GAC.

Though it is unclear what fraction of PFOA molecules resided within the micropores or on the surface, the modified SFE could desorb PFOA from all active sites, preserving the GAC porous structure. The adsorption capacity of regenerated GAC was 0.52 ± 0.02 mg/g—nearly identical to the virgin GAC. We inferred that sulfate ions that competed with the $C_8F_{15}O_2^-$ ion in the $scCO_2$ environment entered the aqueous phase during the next adsorption cycle, allowing reuse of regenerated GAC.

Table 1: Characteristics of the porous structure of virgin GAC, PFOA-laden GAC, and regenerated GAC

	Virgin GAC	PFOA-laden GAC	Regenerated GAC
BET Surface Area (m^2/g)	973.1	922.1	1012.2
Micropore Surface Area (m^2/g)	573.7	544.3	609.8
Micropore Volume (cm^3/g)	0.287	0.271	0.299

4 Environmental Implications

Traditional waste management approaches often involve the disposal of contaminated adsorbents, leading to substantial environmental and economic burdens. This unsustainable practice necessitates the development of efficient and environmentally friendly spent sorbent regeneration approaches. Our $scCO_2$-based sorbent regeneration method holds significant promise for mitigating the environmental impact of PFAS contamination, offering a sustainable alternative to traditional practices. Mild temperature conditions minimize energy consumption and reduce the risk of sorbent degradation. Though the CO_2 was naturally aspirated during the experiment, it can be captured and reused in practical applications. After dropping the temperature and pressure below supercritical conditions, the MeOH, H_2SO_4, and PFOA mixture naturally separates to form a concentrated liquid effluent.

The modified SFE process offers significant environmental benefits. The need for disposal is minimized by regenerating the GAC, reducing landfill waste, and reducing the associated environmental impact. Reusable GAC practices lessen the demand for new materials, promoting

resource conservation and minimizing the environmental impact of production. Furthermore, the process produces a concentrated PFAS effluent, facilitating efficient and cost-effective downstream end-of-life PFAS (and other contaminant) destruction. Future research should focus on expanding the applicability of this method to a broader range of PFAS compounds and optimizing operational parameters (e.g., temperature, exposure time, and co-solvent formulation). The potential of this approach extends beyond GAC regeneration, with applications for other sorbents, such as ion-exchange resins.

Supporting Information –

S1. Experimental setup, chemicals, and reagents

S2. Analytical method

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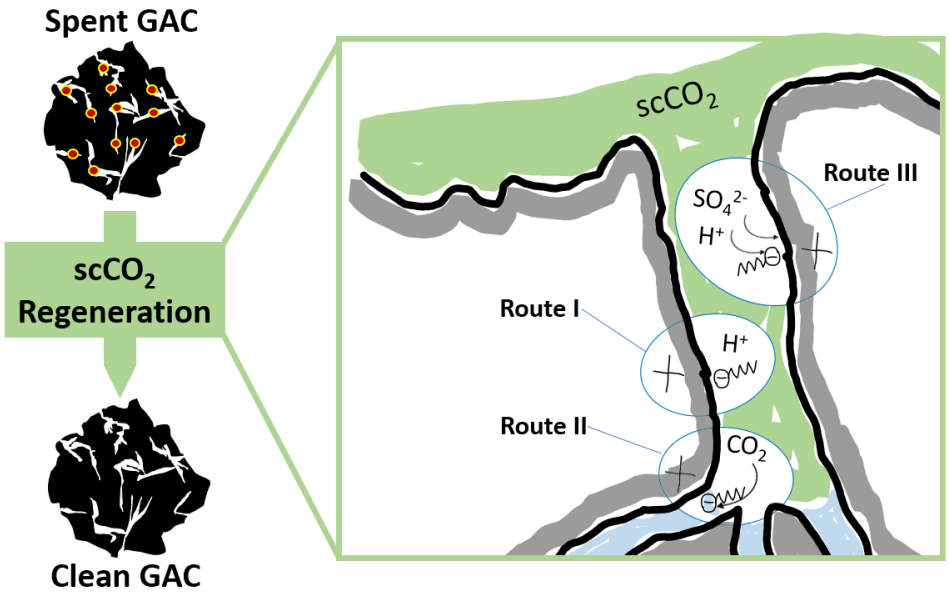
413 *Graphical abstract:*



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