

Regeneration of PFAS-laden Granular Activated Carbon in Modified Supercritical CO₂ Extraction

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Abstract

Granular activated carbon (GAC) is used widely to treat PFAS-contaminated streams, resulting in large quantities of spent GAC that are landfilled or regenerated for future use. Herein, we report the development and application of supercritical CO₂ (scCO₂) extraction modified with organic solvent and acid modifier. The method yields > 97% desorption efficiency of PFOA after ~60 minutes of treatment in a continuous flow reactor. The mild extraction conditions at ~100 °C do not trigger the formation of volatile organic fluorine or the alteration of the GAC sorbent properties. Another benefit of using scCO₂ in the extraction is the high miscibility of co-solvent/scCO₂, which eliminates diffusion transport limitations, enabling rapid PFAS extraction into a single-phase (gas-like) medium. The introduction of an organic co-solvent and the absence of water as a solvent limit hydrophobic interactions between the sorbent and the adsorbate. At the same time, the addition of acid modifiers reduces the electrostatic interactions between PFAS and sorbents. Supercritical fluid extraction (SFE) may prove effective for other types of sorbents, including various ion-exchange resins. The modified SFE process can be an economically effective regeneration scheme, leading to the reuse of sorbents in future adsorption cycles and achieving high PFAS concentration in the effluent for end-of-life treatment technologies.

Keywords: PFAS, PFOA, granular activated carbon, regeneration, supercritical fluid extraction, supercritical CO₂, co-solvent, modifier, mineral acid, adsorption, desorption, repeated cycles

1 Introduction

Granular activated carbon (GAC) is widely used to treat PFAS-contaminated streams [1]. The result of this application is the accumulation of large quantities of spent GAC, which necessitates the development of efficient regeneration technologies. The regeneration of the sorbent will allow it to be used in one or even multiple regeneration cycles, which improves the sustainability of the adsorption process for removing PFAS from contaminated water.

Regeneration of GAC contaminated with PFAS has been studied at length, [2][3], and the industry has implemented several approaches. In thermal regeneration, the spent GAC is subjected to elevated temperatures of 600 – 1000°C, enabling the desorption of PFAS and other adsorbed contaminants. The higher temperatures can effectively destroy PFAS; however, they result in GAC degradation and require high amounts of energy. [4] Recent studies show that thermal degradation of PFAS yields the formation of volatile organo-fluorine (VOF) compounds that could re-enter the environment in a gaseous or aerosol state after partitioning onto the atmospheric particles. [5, 6] Despite the development of various end-of-life PFAS destructive technologies [7-25], the effective removal of PFAS from sorbents poses a significant barrier to treating PFAS-contaminated matrices. Approaches that avoid high temperatures and can desorb PFAS without forming VOFs while preserving GAC's structural and adsorptive properties for subsequent use are highly desirable. Several methods were proposed, such as solvent-based GAC regeneration; however, the large quantities of required solvents, particularly methanol, limit their large-scale implementation. [26]

Above its critical point (31°C, 7.4 MPa), CO₂ becomes a supercritical fluid; scCO₂ is a nonpolar solvent due to the low dielectric constant and negligible molecular dipole moment. It is used in commercial applications, such as botanical extraction, cleaning nanostructures, surface

sterilization, food pasteurization, and nanoparticle synthesis. [27-31] Supercritical fluid extraction (SFE) procedures for removing organic species from solid samples have been discussed in the literature. For example, in analytical chemistry, the SFE enables quantitative recovery of polycyclic aromatic hydrocarbons (PAHs) from solid samples and sorbent traps at $T = 45^{\circ}\text{C}$. [32] Typical temperatures of scCO_2 extraction ($T < 100^{\circ}\text{C}$) are insufficient for PFAS destruction or formation of intermediate VOFs. [25] It is unclear at what levels fluorinated organics can dissolve in scCO_2 . Most studies were limited to small molecules C1-C2, and the literature provides some evidence of PFOA solubility in scCO_2 [33].

The regeneration of spent GAC by scCO_2 has not been reported in the literature; it may offer significant advantages for extracting and recovering organic substances due to the enhanced mass transfer based on high molecular diffusion and low surface tension. However, the carboxyl and sulfonic groups impart polarity to PFAS, limiting their solubility in scCO_2 . A scCO_2 /organic solvent mixture with an acidic or alkaline modifier can improve sorbent regeneration. PFAS has strong hydrophobic and electrostatic interactions with carbon-based structures due to the strong electronegativity of the fluorine atoms [34]. Therefore, it may be advantageous to use a small amount of organic co-solvents, such as methanol, which increases the solubility of PFAS in scCO_2 . For example, Chen et al. [35] demonstrated that scCO_2 with MeOH was effective in extracting PFOA and PFOS from nonporous materials (e.g., paper, fabrics, and sand). Although dipolar organic solvents can disrupt the hydrophobic interaction between PFAS molecules and GAC surfaces [36], this process is slow [34], and it requires the addition of a catalyst/pH adjuster.

This study investigates the feasibility of low-temperature desorption of PFAS from the surface of spent GAC using supercritical carbon dioxide extraction with the addition of co-solvents.

Perfluorooctanoic acid (PFOA) was chosen as the PFAS of interest due to its persistence in the environment and significant regulatory concerns.

2 METHODS AND MATERIALS

2.1 Chemicals and reagents

PFOA ($\geq 95\%$, Sigma Aldrich, China) and Deionized (DI) water (resistivity, $\rho = 18.2 \text{ M}\Omega\text{-cm}$) from ELGA PURELAB® Option-Q (Woodridge, IL, USA) lab water purification system was used for preparing solutions for adsorption. CO_2 (99.5%, Linde, Danbury, CT, USA), ACS reagent grade methanol (99.8%, Thermo Fisher Scientific, Waltham, MA, USA), H_2SO_4 (95.0-98.0%, Avantor Performance Material LLC, Radnor, PA, USA), ethanol (200 Proof, Decon Labs, Inc., King of Prussia, PA, USA), and NH_4OH (28-30%, MilliporeSigma, Darmstadt, Germany) were used for sorbent treatment. LC/MS Grade methanol ($>99.9\%$, Thermo Fisher Scientific, Waltham, MA, USA) and HPLC Grade ammonium acetate ($>98\%$, Thermo Fisher Scientific, Waltham, MA, USA) were used for LC-MS/MS samples. Granular activated carbon (Filtrisorb-400) was obtained from Calgon Carbon (Pittsburgh, PA).

2.2 Sorption conditions

Each sample of GAC was weighed ($0.70 \pm 0.01 \text{ g}$) and mixed with 19.0 mL 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 samples were extracted into 20 mL of EtOH + 0.5% NH_4OH solution, similar to ref [26], 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.

2.3 Regeneration in supercritical CO₂ conditions

The diagram of the laboratory SFE setup is shown in Figure 1. The CO₂ from the gas cylinder is condensed to the liquid phase in a calcium chloride cold bath (-10 to -5°C) before entering the HPLC pump. CO₂ is pumped at 25 mL/min. The co-solvent (MeOH, or MeOH + 1% v/v H₂SO₄) is injected at 1 mL/min at ~20°C through a separate line and mixed with the heated scCO₂ before entering the reactor section. The CO₂ and solvent post-mixing become supercritical single-phase fluid if the flow rate of the organic solvent does not exceed its solubility limit in the scCO₂. Critical points for a two-phase system depend on mixture fraction and the type of organic co-solvent. These critical conditions can be obtained experimentally, but the data are limited to a few solvents. [37, 38] P = 20.3 MPa, T = 110°C were chosen as the operational parameters for these experiments to satisfy single phase conditions (Table 1), the extraction time, τ = 60 min. The reactor section for the GAC placement is a 3.5-inch long, ID = 1/4-inch stainless steel tube with 149-micron frits on both sides to hold the sorbent in place. 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 parts: one part was subjected to extraction by soaking in ethanol and ammonium hydroxide followed by LC-MS/MS, and the second part underwent a second regeneration cycle. The regenerated GAC sample set aside for the second regeneration cycle was loaded with PFOA again. Each experiment was performed in triplicates. The desorption efficiency (%DE) was calculated as:

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

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

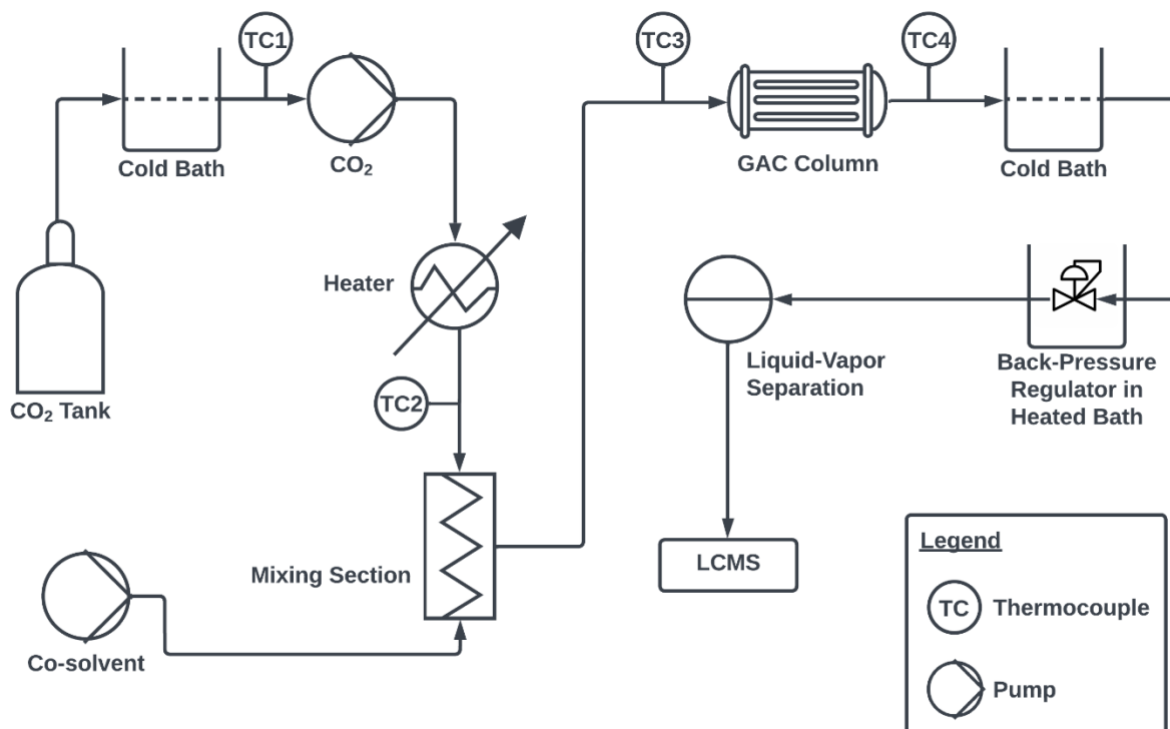


Figure 1: Flow diagram of the SFE setup and thermocouple (TC) locations. A gas cylinder supplies CO₂, which is condensed to the liquid phase in a cold bath (TC1), pumped, and heated before entering the mixing section (TC2) and mixed with EtOH. The fluid temperature in the reactor section is measured (TC3 and TC4). The fluid passes through a 40°C cold bath before entering the BPR to avoid rapid throttling and damaging the diaphragm. After exiting the BPR, the effluent was collected in a flask while gaseous CO₂ separated naturally.

2.4 Analytical methods

The quantitative analysis of PFOA in all the liquid samples was performed by Quattro Micro quadrupole tandem mass spectrometer, 2795 Alliance HT LC system (Waters Corporation, Milford, MA, USA) equipped with a Kinetex-C18 column (4.6 * 50 mm, 2.6 μm, Phenomenex, Torrance, CA, USA). Before each analysis, the samples were diluted with LC-MS grade methanol and water in a volumetric ratio of 60:40. The calibration curves in the 0.1 – 50 ppb range for each PFAS were obtained using PFAC30PAR standard solutions. The mobile phase for LC consisted of: (A) 10 mM ammonium acetate in Optima® HPLC-grade water and (B) 10 mM ammonium acetate in Optima® HPLC-grade methanol. The eluent flow rate was 0.20 mL/min, and the

gradient timetable contained 5 entries: 0 min (50 % A, 50 % B), 5 min (5 % A, 95 % B), 7 min (5 % A, 95 % B), 7.5 min (50 % A, 50 % B), and 13 min (50 % A, 50 % B). MS protocols were previously reported. [39] The analytical detection limit for PFOA in LC-MS/MS analysis is 0.05 ppb. The GAC's surface areas and pore size distributions were determined using nitrogen adsorption at 77 K with a Micromeritics 3Flex analyzer, following the Brunauer-Emmett-Teller (BET) analysis of surface area and pore sizes.

3 RESULTS AND DISCUSSION

3.1 Application of modified supercritical CO₂ for PFOA desorption

The solubility of PFAS generally decreases with the number of carbons in the PFAS molecule structure, along with an increase in the carbon chain length of alcohol. [40] The solubility of PFOS (C8) in methanol (~37 g/L) is 5 times higher than in ethanol (~7 g/L); thus, in this proof-of-concept study, methanol is used as a co-solvent.

The results of PFOA extraction from spent GAC using scCO₂ in the presence of co-solvents (methanol, methanol + acid) are presented in Fig. 2. The extraction efficiency of ~33% in pure scCO₂ can be explained by the fact that this solvent is relatively nonpolar and has limited affinity for polar molecules due to its large molecular quadrupole. [35] Mechanistically, scCO₂ may aid in extracting PFOA by protonating its carboxylate groups and providing competing ions. In conventional solvents (methanol, etc.), the fully deprotonated, negatively charged carboxylate groups of PFOA interact with the positively charged GAC through electrostatic force, while the H⁺ ions diffuse into the solvent. However, due to the low dielectric constant of CO₂, the H⁺ ions are more likely to pair with the carboxylate groups, thereby weakening the electrostatic interaction between GAC and PFOA. In addition, CO₂ may react with the small amount of water on the GAC

pore structure to form HCO_3^- , which can compete with perfluorooctanoate ion $\text{C}_8\text{F}_{15}\text{O}_2^-$ for electrostatic interaction with GAC.

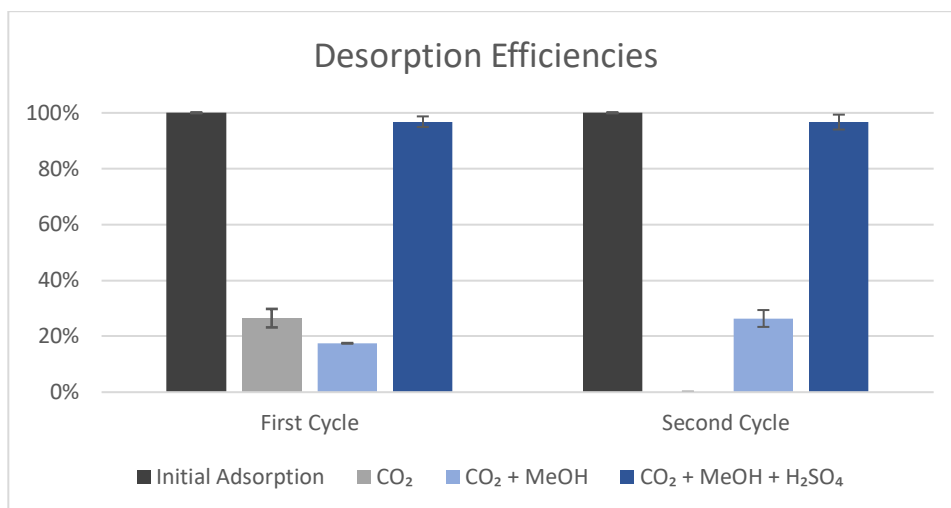


Figure 2: PFOA desorption efficiencies from spent GAC using scCO₂ in pure Sc-CO₂ and in the presence of methanol, methanol + acid (110°C, 10 MPa, time of 60 min). The second cycle of desorption in CO₂ was not conducted.

The best extraction (~98 – 99%) occurred in acid-modified SFE cases with co-solvent (MeOH with 1% vol H₂SO₄). These results suggest the prevailing PFOA desorption mechanism from GAC surfaces is related to pH surface charge. The literature reports the point of zero charge of Filtrasorb 400 GAC, $\text{pH}_{\text{pzc}} = 8.65$. [1] This value is consistent for an activated carbon with low oxygen content [41]. The concentration of oxygen-containing groups for Filtrasorb 400 was found to be 0.21 mmol/g. [42] When an adsorbent is present at a pH lower than its pH_{pzc} , its surface is positively charged, influencing electrostatic interactions with PFAS anions.

3.2 Proposed mechanism of PFOA desorption from GAC surface

The hydrophobic and electrostatic interactions are the two major forces governing PFAS adsorption by GAC. [1][43][44] Hydrophobic interactions arise between the hydrophobic surface of the GAC and the nonpolar tail of PFAS molecules, while electrostatic interactions occur between the anionic functional groups of PFAS and the positively charged surface of the GAC.

These two mechanisms that retain the PFAS molecule on the surface must be counteracted to trigger the desorption. Organic solvents, such as methanol, attenuate hydrophobic interactions in aqueous solutions. At the same time, introducing a strong acid that dissociates into ions will alter the solution's ionic strength and weaken the electrostatic interaction of the PFAS polar group with the sorbent. In the scCO₂ environment, the hydrophobic interactions are insignificant; thus, adding solvent alone does not enhance the extraction. The co-solvent plays the role of a transport media delivering a pH modifier to the single-phase scCO₂ mixture. Overcoming diffusion limitations, scCO₂ enables the rapid transport of co-solvent and acid to the surface. Once the electrostatic interaction is weakened by acid and the PFOA molecule is released, the scCO₂/solvent mixture facilitates rapid removal of the PFOA molecule from the surface.

In this work, the divalent sulfate ion has a stronger affinity to the active sites on the GAC surface, causing the release of a weaker PFOA monovalent perfluorooctanoate ion, C₈F₁₅O₂⁻. Moreover, inhibition of PFOA dissociation occurs in the presence of a stronger sulfuric acid (pK_a = -3). The pK_a of PFOA is reported to be in the range from -0.2 to +3.8 [45]. Consequently, in the presence of sulfuric acid, the perfluorooctanoate ion becomes protonated, i.e., forcing PFOA to its neutral form, weakening the electrostatic attraction to the positively charged GAC surface, thus enhancing the desorption efficiency. The authors recognize that long-chain PFFAS will likely form micelles/hemi-micelles [46][34] in an aqueous environment that can interact with the GAC surface during sorption. It is unclear if these structures interact in a scCO₂/organic co-solvent environment in the absence of liquid water. However, the presence of micelles should not significantly affect the general mechanism of hydrophobic and electrostatic forces disruption in the proposed desorption mechanism.

3.3 Optimizing co-solvent flow rate in scCO₂ for PFAS desorption

Table 1 shows that the concentration of acid-modified co-solvent in scCO₂ did not significantly affect the extraction, which collaborates with the hypothesis that the hydrophobic interaction does play a significant role in the desorption in the scCO₂ environment and that the disruption of electrostatic attraction by pH modifier is the dominant mechanism in SFE scenario. In these experiments, the CO₂ flow rate was held constant (25 mL/min), and the co-solvent flow rate was varied from 0.2 to 6.8 mL/min. From a practical perspective, it suggests 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.

When utilizing a co-solvent system, the pressure, temperature, and mole fractions of each solvent determine the phase of the overall fluid mixture running through the GAC during regeneration. According to Reighard et al., at $X_{MeOH} = 0.1792$ and 10 MPa, the dew point of the CO₂ and MeOH is ~110°C. [47] Assuming the sulfuric acid does not affect the solubility of MeOH in CO₂ and vice versa, a lower X_{MeOH} would lead to a single-phase supercritical gas-like mixture of MeOH completely dissolved in CO₂ while a higher X_{MeOH} would lead to a 2-phase mixture of liquid MeOH with some CO₂ dissolved and the gas-like scCO₂ with some MeOH dissolved. Adjusting the flow rates of MeOH allows us to control the mole fraction of MeOH during regeneration.

Table 1: Extraction efficiency of PFOA-laden GAC for different flow rates.

ScCO ₂ Flow rate (mL/min)	Co-solvent and amendment	Co-solvent flow rate (mL/min)	X_{MeOH} MeOH + H ₂ SO ₄	T (°C)	Extraction efficiency, %
25	MeOH + 1% v/v H ₂ SO ₄	0.2	0.0089	120	96.9
25	MeOH + 1% v/v H ₂ SO ₄	1.0	0.0430	110	98.0
25	MeOH + 1% v/v H ₂ SO ₄	6.8	0.2338	120	99.9

3.4 Assessment of GAC properties after regeneration

To ensure the sustainability of the developed approach, we need not only to obtain concentrated PFAS solutions under mild conditions that prevent the formation of VOFs but also to verify that the GAC retains its textural and adsorption properties after regeneration. Table 2 presents the BET surface area of Filtrasorb 400 virgin GAC, PFOA-loaded GAC, and regenerated GAC (after Cycle 1) in the $scCO_2$ / MeOH/ H_2SO_4 mixture. BET surface area and micropore volume decreased after the sorption of PFOA after the first cycle, indicating pore blockage during sorption. However, after the regeneration step, the BET surface area and micropore volume were restored and even increased compared to the virgin Filtrasorb 400. Though it is unclear if the PFOA molecule is captured within the micropores or on the surface, the proposed modified SFE allows for nearly complete GAC regeneration, preserving its porous structure for subsequent adsorption cycles.

Table 2 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)	973.15	922.05	1012.16
Micropore Surface Area (m^2/g)	573.75	544.26	609.75
Micropore Volume (cm^3/g)	0.2865	0.2711	0.2993

4 CONCLUSION

The modified SFE method allows for nearly complete desorption of PFOA from spent GAC under mild temperature conditions, avoiding the formation of VOFs and deterioration of the sorbent properties. Our main hypothesis for using $scCO_2$ to extract PFAS from sorbents is that the high miscibility of co-solvent/ $scCO_2$ eliminates diffusion transport limitations, enabling rapid PFAS extraction into a single-phase (gas-like) medium. Additionally, $ScCO_2$ can facilitate the extraction of PFOA by protonating its carboxylate groups and supplying competing ions. The introduction of an organic co-solvent and the absence of water as a solvent removes hydrophobic interactions

between the sorbent and the adsorbate, while the addition of acid modifiers further protonates $C_8F_{15}O_2^-$ ion, reducing the electrostatic interactions between PFAS and sorbent surface. Future research should focus on optimizing PFAS extraction from GAC by varying operational parameters such as temperature, exposure time, and the addition of co-solvents. Additionally, supercritical extraction may prove effective for other types of sorbents, including various ion-exchange resins. Based on our findings, the modified SFE process can be an economically effective regeneration scheme, leading to the reuse of sorbents and achieving high PFAS concentration in the effluent for end-of-life treatment technologies.

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