Regeneration of PFAS-laden granular activated carbon by modified supercritical CO$_2$ extraction☆

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HIGHLIGHTS

- Low-temperature GAC sorbent regeneration with >99.9 % PFAS desorption efficiency.
- Supercritical CO$_2$ extraction is enhanced by acid modifier.
- Mechanisms disrupting the interaction between PFAS and sorbent are elucidated.
- Mild temperature extraction preserved GAC properties for consequent sorption cycles.

GRAPHICAL ABSTRACT
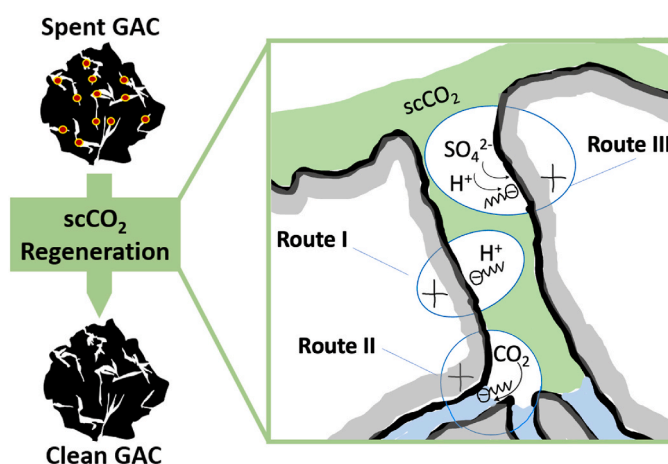
ABSTRACT

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 >99% perfluorooctanoic acid (PFOA) desorption after a 60-min 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.

1. Introduction

Granular activated carbon (GAC) is used to treat contaminated waters with per- and polyfluoroalkyl substances (PFAS) (Zhang et al., 2023). 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 (Vakili et al., 2024; Gagliano et al., 2023). Thermal regeneration utilizes high temperatures, ranging from 600 to 1000 °C, to desorb PFAS and other contaminants from spent GAC. 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 (Smith et al., 2023a; Lin et al., 2022).

Motivated by the development of various end-of-life PFAS destruction technologies (Sahu et al., 2018; Kalra et al., 2021; Singh et al., 2019; Smith et al., 2023b; Austin et al., 2023, Austin, 2024; Li et al., 2022, 2023; Yang et al., 2023; Hori et al., 2008; Wu et al., 2019; Pinkard et al., 2021, 2023; Pinkard, 2022; Hao et al., 2021, 2022, 2023; Soker et al., 2023; Endo et al., 2023), 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 (Du et al., 2016; Deng et al., 2015; Chularueangaksorn et al., 2014; Senevirathna et al., 2010) or aqueous solutions (Deng et al., 2015). 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) (Siriwardena et al., 2021).

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 (Beckman, 2004). Supercritical fluid extraction (SFE) temperatures ($T < 100°C$) would not trigger volatile fluorinated species formation via thermal degradation (Austin, 2024; Verma et al., 2023). SFE is used in commercial applications for removing organics from solid matrices, e.g., botanical extraction, surface sterilization, food pasteurization, and material synthesis (Beckman, 2004; Schantz et al., 1986; López-Periago et al., 2015, 2017; Portolés-Gil, 2018; Kubovics et al., 2021). In analytical chemistry, the SFE enables quantitative PAH recovery from sorbent traps at $T = 45°C$ (Hawthorne et al., 1986). There is also a report on $scCO_2$ use to extract PFOA and PFOS from nonporous materials such as paper, fabrics, and sand (Chen et al., 2012).

Unlike traditional solvent-based or aqueous desorption methods, $scCO_2$ regeneration operates at relatively low temperatures, which not only reduces energy consumption but also minimizes the risk of sorbent degradation. Furthermore, this technique prevents the formation of VOFs typically associated with high-temperature thermal regeneration, offering a safer and more sustainable alternative for PFAS treatment. 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 h of GAC treatment.

2. Materials and methods

Granular activated carbon (Filtrasorb-400) for experiments was obtained from Calgon Carbon (Pittsburgh, PA). 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.

2.1. Sorption conditions

After 5 days, the GAC was removed, and the liquid analyzed using LC-MS/MS. The GAC pellets were dried in an oven at 70 °C for 12 h. Subsamples were extracted into 20 mL of ethanol (EtOH) + 0.15% NH_4OH solution (Siriwardena et al., 2021) to determine the amount of PFOA sorbed onto GAC. The PFOA loading on virgin GAC was 0.52 ± 0.02 mg/g under the described conditions. After 24 h, the GAC was removed by centrifugation, and the liquid analyzed using LC-MS/MS.

2.2. Regeneration in supercritical CO_2 conditions

The diagram of the laboratory SFE setup is shown in Fig. 1. The CO_2 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. CO_2 is pumped at 25 mL/min. The co-solvent (methanol (MeOH), or MeOH + 2.3% v/v H_2SO_4) is injected at 1 mL/min at ~20 °C through a separate line and mixed with the heated $scCO_2$ before entering the reactor section. The CO_2 and solvent post-mixing become a supercritical single-phase fluid if the flow rate of the organic solvent does not exceed its solubility limit in the $scCO_2$. Critical points for a two-phase system depend on mixture fraction and the type of organic co-solvent. These critical transition points can be obtained experimentally, but the data are limited to only a few solvents (Wu et al., 2006; Chatwell et al., 2021). The operational parameters for these experiments were chosen as P = 10.0 MPa and T = 110–120 °C to ensure single-phase conditions, with an extraction time of t = 60 min.

The reactor has a volume of 1.29 mL, a length of 63.5 mm, and consists of a stainless steel tube with an inner diameter of 5.1 mm and an outer diameter of 6.35 mm, fitted with 149-μm frits on both ends to contain the sorbent. After performing SFE for 60 min, the column contents were dried in an oven at 70 °C for 24 h. The sample was divided into two sub-samples: one was subjected to extraction by soaking in ethanol and ammonium hydroxide, followed by LC-MS/MS, and the other 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:

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

where *[PFAS in spent GAC]* is the PFOA loading (mg/g) in the spent sorbent, and *[PFAS in GAC after regeneration]* is the residual PFAS 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 (Du et al., 2014). The modified scCO$_2$ extraction yielded near complete desorption of PFOA (Fig. 2) 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 (Dardin et al., 1998). 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% (Fig. 2).

The addition of organic co-solvents can enhance PFAS solubility in scCO$_2$. For example, Chen et al. (2012) 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 h (Du et al., 2016), (Deng et al., 2015). 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 h of treatment (Chularueangaksorn et al., 2014). The solubility of PFAS in alcohols generally decreases for longer PFAS molecules and longer carbon chain lengths of alcohol (Meng et al., 2017). 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 (Fig. 2), indicating that scCO$_2$ 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 (Du et al., 2014; Dutta et al., 2019), they are unlikely to affect the electrostatic interactions between PFAS molecules and GAC surfaces (Chen et al., 2012). Lacking hydrophobic PFOA/GAC interaction in scCO$_2$ and scCO$_2$/MeOH mixtures, the low
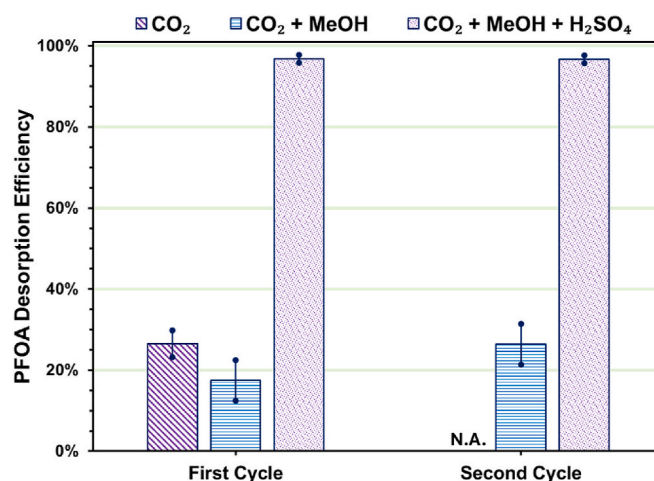

Fig. 2. PFOA desorption from GAC using only scCO$_2$, scCO$_2$ + MeOH, and scCO$_2$ + MeOH/H$_2$SO$_4$. Experimental conditions are 110 °C, 10 MPa, and an exposure time of 60 min. The second cycle of desorption in CO$_2$ was not conducted. Error bars are standard deviations from triplicated experiments.

desorption is contributed to electrostatic interactions, which can be weakened by introducing an ionic agent. Thus, adding sulfuric acid (2.3% vol in MeOH) increased the desorption efficiency to >97%.

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 h, compared to 5–24 h 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
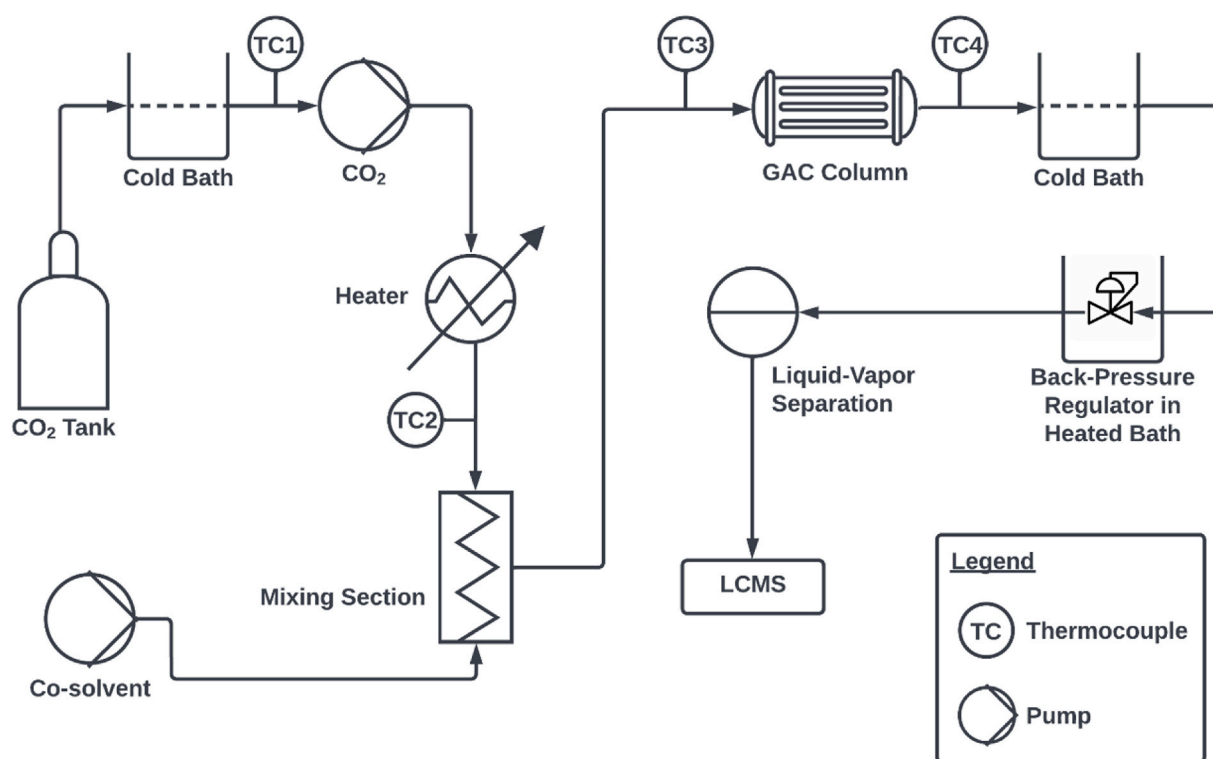
Fig. 1. SFE process flow diagram and thermocouple (TC) locations. A gas cylinder supplies CO$_2$, which is condensed to the liquid phase in a cold bath (TC1), pumped, and heated before entering the mixing section (TC2) and mixed with MeOH. The fluid is cooled to ~40 °C before entering the back pressure regulator (BPR) placed in a warm water bath to avoid rapid throttling and diaphragm damage. After exiting the BPR, the effluent was collected in a flask while gaseous CO$_2$ separated naturally.

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 (Zhang et al., 2023), characteristic of activated carbons with low oxygen content (Morlay et al., 2012). The low oxygen content is reflected in the measured concentration of oxygen-containing groups (phenolic, carboxylic, lactonic) of 0.21 mmol/g (Liu Mei et al., 2008). The measured pH during adsorption in this study ($\sim$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 (Shafrin et al., 1962), 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 (Fig. 3, Route I) and subsequent desorption in its protonated form. However, this route exhibits limited efficacy for PFOA, DE < 30% (Fig. 2). 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 (Fig. 3, 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. Fig. 2 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, $C_8F_{15}O_2^-$ (Fig. 3, Route III). Moreover, sulfuric acid (pKa = -3) can protonate PFOA (pKa = $-0.2 - +3.8$) (Burns et al., 2008). The long-chain PFAS may form micelles/hemi-micelles (Du et al., 2014; Uriakhil et al., 2021) in an aqueous environment that can interact with the GAC surface during sorption; however, it is unclear if these structures interact in a $scCO_2$/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.

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% (Fig. 4). 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. (1996), at $X_{MeOH} = 0.1792$ and 10 MPa, the dew point of the CO_2/MeOH mixture is at $\sim$ 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 due to the excess liquid MeOH that doesn't dissolve into $scCO_2$. 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 increased amount of MeOH shifts the dew point to below experimental conditions.

3.4. Assessment of GAC properties after regeneration

A sustainable PFAS regeneration approach must not only produce a concentrated PFAS effluent and prevent the formation of VOFs but also maintain GAC's structural integrity and adsorption capacity after regeneration. Table 1 presents the BET surface area of virgin GAC, PFOA-loaded GAC, and regenerated GAC with the modified $scCO_2$ extraction. It is shown that BET surface area and micropore volume of spent GAC decreased (971–922 m²/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 (971–1012 m²/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 for subsequent use. This was further verified by testing the adsorption capacity and confirming no changes compared to the virgin GAC at 0.52 ± 0.02 mg/g. This suggests that sulfate ions, which compete with the $C_8F_{15}O_2^-$ ion during desorption in the $scCO_2$ environment, are transferred to the aqueous phase during the next adsorption cycle, allowing the regenerated GAC to function effectively.

4. Conclusion

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

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

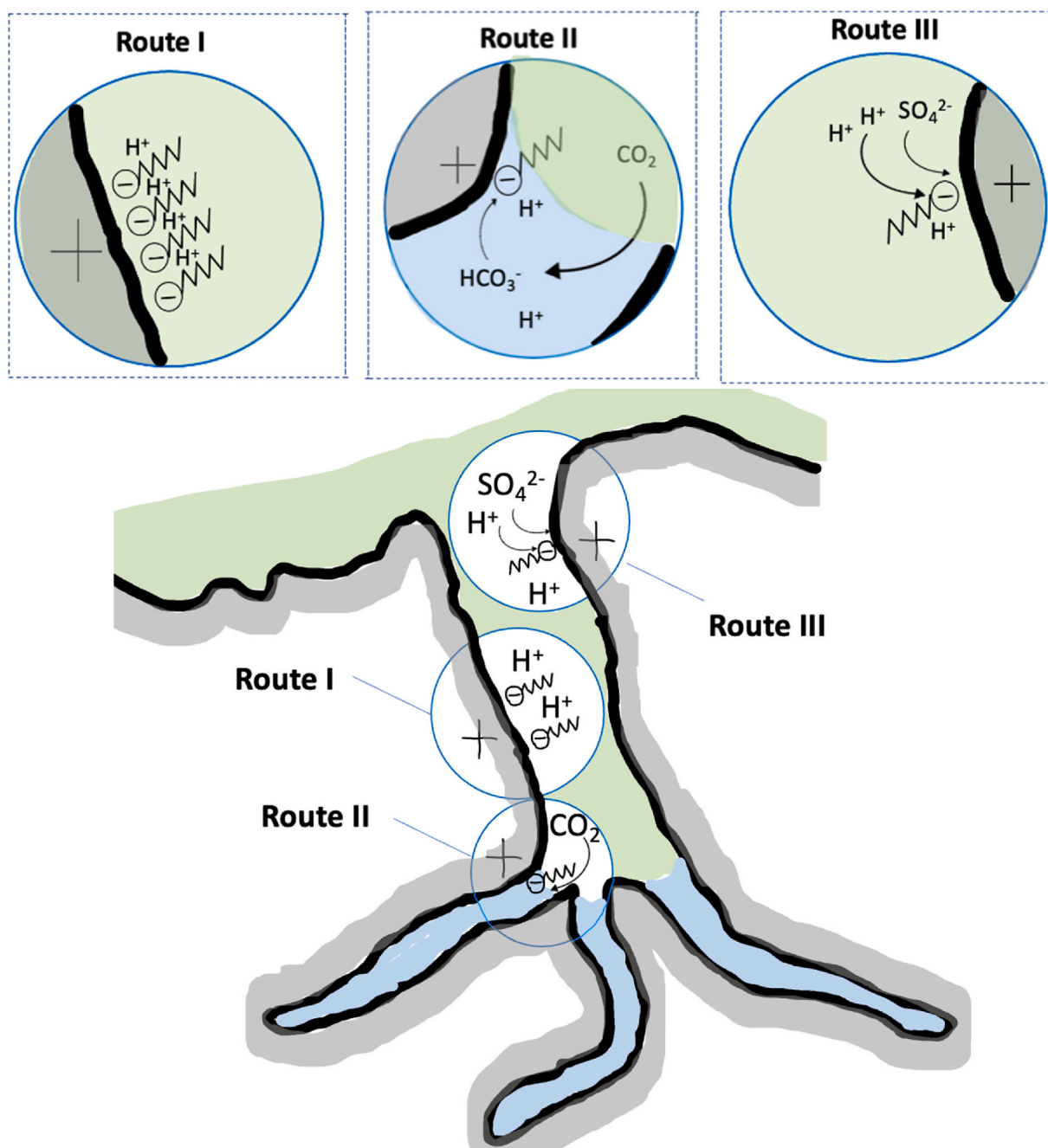|	Virgin GAC	PFOA-laden GAC	Regenerated GAC
BET Surface Area (m²/g)	973.1	922.1	1012.2
Micropore Surface Area (m²/g)	573.7	544.3	609.8
Total Pore Volume (cm³/g)	0.522	0.492	0.532
Micropore Volume (cm³/g)	0.287	0.271	0.299

Fig. 3. 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$_2$SO$_4$ (i) competition of the sulfate ion for GAC active site and (ii) PFOA protonation.

method holds significant promise for mitigating the environmental impact of PFAS contamination, offering a sustainable alternative to traditional practices. This method operates under mild temperature conditions, minimizing energy consumption and reducing the risk of sorbent degradation. Furthermore, the absence of water in the scCO$_2$ environment effectively eliminates hydrophobic interactions between the sorbent and the adsorbate, facilitating the release of PFOA molecules. While scCO$_2$ alone proves effective in disrupting hydrophobic interactions, achieving complete PFOA desorption requires additional strategies. To overcome the electrostatic barrier, we introduce sulfuric acid modifier, which plays a dual role: it protonates the PFOA anion (C$_8$F$_{15}$O$_2^-$), reducing its electrostatic attraction to the GAC surface, and the divalent sulfate ion exhibits a stronger affinity for the active sorption

sites on the GAC surface, effectively competing with the PFOA anion and displacing it from the sorbent. This synergistic approach, combining scCO$_2$, a co-solvent, and an acid modifier, achieves remarkable results, yielding a desorption efficiency of 99.9% while fully restoring the GAC's adsorption capacity.

The modified SFE process offers significant environmental benefits. By regenerating the GAC, the need for disposal is minimized, reducing landfill waste and associated environmental risks. The reusable GAC reduces 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 destruction technologies such as supercritical water oxidation (Smith et al., 2023b; Austin et al., 2023; Li et al.,
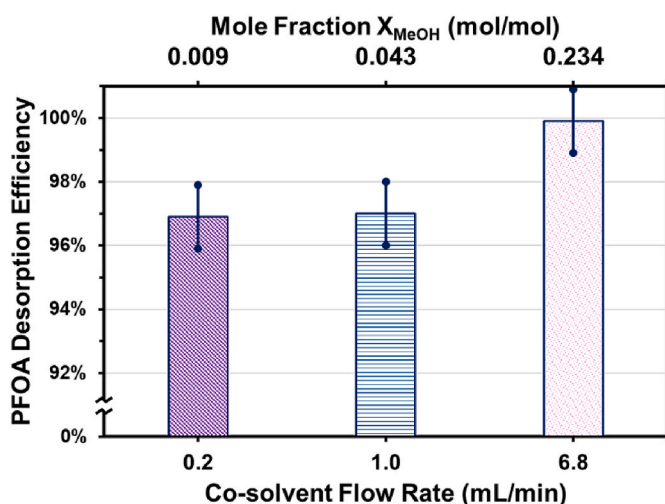
Fig. 4. Desorption efficiency of PFOA-laden GAC for varying the flow rate of the co-solvent (MeOH + 2.3% v/v H_2SO_4) and constant flow rate of $scCO_2$ at 25 mL/min. The value of the flow rate of the co-solvent determines the molar fraction of methanol (X_{MeOH}) in the mixture and affects its state in the supercritical or subcritical condition.

2023; Pinkard et al., 2021; Du et al., 2016) hydrothermal alkaline treatment (Wu et al., 2019; Hao et al., 2021, 2023; Endo et al., 2023) and ball milling (Yang et al., 2023; Ateia et al., 2021). Future research should focus on expanding the applicability of this method to a wider range of PFAS compounds and optimizing operational parameters (temperature, exposure time, co-solvent selection) for enhanced efficiency. The potential of this technology extends beyond GAC, with promising applications for regenerating other adsorbents, such as ion-exchange resins.

CRediT authorship contribution statement

Tatiana Didenko: Writing – review & editing, Writing – original draft, Visualization, Methodology. **Almond Lau:** Validation, Investigation, Data curation. **Anmol L. Purohit:** Investigation, Data curation. **Ji Feng:** Methodology, Data curation. **Brian Pinkard:** Writing – review & editing. **Mohamed Ateia:** Writing – review & editing, Visualization, Methodology. **Igor V. Novosselov:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143986.

Data availability

Data will be made available on request.

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