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**Efficient PFAS Removal from Contaminated Soils through Combined Washing and
Adsorption in Soil Effluents**

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Abstract

This study investigates soil washing as a viable strategy to remove poly- and perfluoroalkyl substances (PFAS) from contaminated soils using various washing agents including water, methanol, ethanol, and cyclodextrin ((2-Hydroxypropyl)- β -cyclodextrin HPCD)). Water was less effective (removing only 30% of PFAS), especially for long-chain hydrophobic PFAS. Methanol (50% v/v) or HPCD (10 mg g⁻¹ soil) achieved >95% PFAS removal regardless of PFAS type, soil size fraction (0–400 μ m or 400–800 μ m), or experimental setups (batch or column, at liquid/solid (L/S) = 1). Column optimization studies revealed improved efficiency at L/S = 10 with diluted washing solutions, where HPCD exhibited rapid PFAS mobilization even at lower concentrations (1 mg mL⁻¹). We then applied a first-order decay model to effectively predict PFAS breakthrough curves and mobilization within soil columns. Subsequent treatment of wash effluents by activated carbon and biochar effectively reduced PFAS concentrations below detection limits. The performance of both soil washing and subsequent adsorption was found to depend strongly on the specific characteristics of PFAS compounds. These findings highlight the significant potential of methanol and HPCD in soil washing and the effectiveness of integrated soil washing and adsorption for optimizing PFAS removal.

Keywords: Poly- and perfluoroalkyl substances (PFAS); Soil Washing; Cyclodextrin; Adsorption; Modeling

36 **Environmental implications**

37 Per- and polyfluoroalkyl substances (PFAS) are hazardous pollutants known for their
38 persistence bioaccumulation, and determinantal impacts. This research investigates an
39 efficient soil washing approach integrating subsequent treatment of wash effluents via
40 adsorption onto carbonaceous adsorbents (activated carbon or biochar). We compared
41 various washing agents, finding methanol and cyclodextrin to be most effective (>95%
42 removal) across PFAS types and soil fractions, using batch and dynamic flow conditions.
43 PFAS mobilization was accurately predicted by first-order decay model. This study presents
44 a promising method for PFAS remediation, combining optimized soil washing with efficient
45 effluent treatment for comprehensive removal.

46

1. Introduction

Poly- and perfluoroalkyl substances (PFAS), a family of about 10000 chemicals, are highly persistent and widespread in the environment, posing significant risks to human health and the environment. Soils constitute a long-term environmental sink and a crucial reservoir of PFAS contamination, slowly releasing these contaminants to the hydrosphere and allowing uptake in biota (Evich et al., 2022). PFAS contamination in soils originates from sources like firefighting foams (Dauchy et al., 2019), landfill leachate (Wei et al., 2019), wastewater (Caniglia et al., 2022), solid biowastes (Caniglia et al., 2022; Munoz et al., 2022), and atmospheric depositions (Johansson et al., 2019; Sha et al., 2022). Regional investigations (Anderson et al., 2019) and global surveys (Brusseau et al., 2020; Rankin et al., 2016; Söregård et al., 2022; Strynar et al., 2012) have revealed widespread PFAS contamination in soils worldwide. These studies, analyzing between 28 and 2500 sites at regional or global scales, consistently found PFAS contamination in various environments, even in areas distant from known contamination sources, including urban and remote areas at global scale (Brusseau et al., 2020), army installations in US (Anderson et al., 2019), and background forest soils in Sweden (Söregård et al., 2022). These studies provide compelling evidence that soils serve as a persistent environmental reservoir for PFAS contamination, emphasizing the urgent need for remediation efforts.

Remediation of PFAS contaminated soils has proven to be challenging and expensive due to the extreme persistence and diverse properties of PFAS. Few techniques have been reported to remediate PFAS-contaminated soils including thermal degradation, immobilization/stabilization, and soil capping (Bolan et al., 2021; Liu et al., 2023). Although efficient, thermal degradation can be limited by higher treatment cost, the need for off-site transportation of large soil volumes, and its energy-intensive nature (Sun et al., 2024). Immobilization/stabilization, capping, or encapsulation methods raise concerns about the long-term effectiveness, as PFAS may persist in the soil and potentially leach out over time (Mahinroosta et al., 2020). Moreover, the efficiency of soil immobilization techniques for PFAS

compounds may be compromised in the presence of other PFAS or heavy metals, potentially altering their mobility and raising concerns in mixed-contamination scenarios (Cai et al., 2023; Liu et al., 2023). For example, our recent study revealed an elevated release of GenX (an alternative PFAS to PFOA) when both PFOA and GenX were immobilized together in soil (Liu et al., 2023). In addition to the inherent challenges posed by strong stability and persistence of PFAS, remediation of contaminated soils is further limited by the complex interactions of pollutants with soil matrix, restricted pollutant accessibility, and the presence of non-target compounds (Usman et al., 2022).

Soil washing, a method historically used for contaminated soils, employs physical and/or chemical separation to reduce waste volume and concentrate contaminants into a smaller liquid phase for easier and flexible treatment (Bolan et al., 2021; Usman et al., 2022). Despite its potential, very few studies explored the use of soil washing for PFAS-contaminated soils (Grimison et al., 2023; Høisæter et al., 2021; Pang et al., 2022; Uwayezu et al., 2024). Existing studies primarily use water as the main washing agent (Grimison et al., 2023; Høisæter et al., 2021; Quinnan et al., 2022; Uwayezu et al., 2024) occasionally combined with gas/foam fractionation (Pang et al., 2022) or soil fractionation for separate treatments of coarse and fine soil fractions (Grimison et al., 2023; Quinnan et al., 2022). Given the diverse array of PFAS compounds with varying characteristics (hydrophobic/hydrophilic, short-chained vs. long chained, sulphonic vs. carboxylic heads etc.), exploring alternative washing agents is crucial for PFAS removal from contaminated soils.

Thus, the aim of this study was to investigate the efficiency of various washing agents including water, methanol, ethanol, and cyclodextrin (as an environmentally friendly alternative to organic solvents) in different concentrations to remove PFAS from contaminated soil. While cyclodextrins (CDs) are recognized as eco-friendly, biomass-derived co-solvents (Talvenmäki et al., 2021; Usman et al., 2012; Viglianti et al., 2006), their application in the washing of PFAS-contaminated soils has not previously investigated to our knowledge. Cyclodextrins offer some advantages over organic solvents like their natural origin based on starch, non-toxic nature,

and biodegradability (Sikder et al., 2019). CDs are characterized by a distinct hydrophobic non-polar interior cavity, which forms host-guest complexes with thousands of organic molecules improving their solubility (Crini et al., 2018). This study used (2-Hydroxypropyl)- β -cyclodextrin (HPCD), a hydroxyalkyl derivative CD, recognized for its improved water solubility and higher pollutant desorption capacity compared to traditional CDs (α -, β - and γ -cyclodextrins) (Sikder et al., 2019; Viglianti et al., 2006). These washing solutions have been used to remove PFAS from the coarse and fine fractions of an agricultural soil spiked with five different PFAS, including legacy PFAS (PFOA, PFOS) and their newer substitutes (GenX and 6:2 FTAB, respectively), along with PFDA as a long-chained PFAS. Soil washing experiments were conducted in both batch and flow-through column settings, including open-loop and closed-loop column setups. Subsequently, the soil washing effluent was treated using activated carbon and biochar for PFAS adsorption. Activated carbon remains a highly effective adsorbent for PFAS removal in contaminated water and wastewater (Gagliano et al., 2020; Pauletto et al., 2022). Similarly, biochar has demonstrated viable potential as an alternative adsorbent to activated carbon (Karunakaran et al., 2022). However, there exists limited information regarding the efficacy of these carbonaceous adsorbents in the treatment of effluents generated by soil washing processes. Notably, this study represents the first reported application of biochar for the adsorption of PFAS from soil washing effluents.

2. Experimental section

2.1. Chemicals and reagents

Perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorodecanoic acid (PFDA) were obtained from Sigma-Aldrich. Perfluoro-2-propoxypropanoic acid (GenX) and N-(carboxymethyl)-N,N-dimethyl-N-[3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-yl]ammonium (6:2 FTAB) were purchased from Manchester Organics Limited and Wellington Laboratories, respectively. Commercially available activated carbon (Sigma Aldrich) and biochar (ÉlémentTerre, France) were used. Analytical grade ethanol, methanol, and (2-Hydroxypropyl)- β -cyclodextrine (HPCD) were obtained from Sigma-Aldrich and were used

without further purification. Unless otherwise stated, all solutions were prepared using deionized (DI) water (Elga PURELAB Chorus, 18.2 M Ω -cm).

2.2. Target soil

In this study, a non-contaminated agricultural soil was spiked with tested PFAS compounds (GenX, PFOA, PFOS, PFDA and 6:2 FTAB). This soil was of silt loam type (20.5, 59.8 and 19.7 wt % of sand, silt and clay, respectively) with pH of 6.9. The major characteristics of this soil are provided in Table S1 and a detailed description is provided in the context of our previous study (Liu et al., 2023). Preliminary assays employing the same extraction and analysis methods as described below revealed non-detectable PFAS concentrations in this soil, i.e. below the instrument detection limit. This soil was sieved to achieve two particle size fractions of 0–400 μ m and 400–800 μ m, which were then used in the subsequent experiments. Both of these fractions were artificially contaminated by spiking with five different PFAS compounds, namely PFOA, PFOS, PFDA, 6:2 FTAB, and GenX in methanol to obtain a concentration of 200 μ g kg⁻¹ for each PFAS (total PFAS concentration of 1000 μ g kg⁻¹ dry weight). This solution was allowed to evaporate under continuous mixing to ensure homogeneous contaminant distribution. Spike-recovery tests of PFAS using methanol as the extraction agent resulted in >99% recovery of the target PFAS.

2.2. Soil washing

Soil washing has been evaluated under three different experimental setups used in this study including a) batch conditions, b) open-loop column under water-saturated conditions and c) closed-loop column under water-saturated conditions. A visual representation of these setups is shown in Figure 1, and a summary of experimental conditions is presented in Table 1. Further details are provided below:

The preliminary batch experiments compared the washing efficiency of water, ethanol (10, 25 and 50% v/v), methanol (10, 25 and 50% v/v) and HPCD (1, 5 and 10 mg g⁻¹ soil w/w) for PFAS removal from soil. For this, 2 g of PFAS contaminated soil was mixed with the tested washing solutions at liquid-to-solid ratios (L/S) of 1. This L/S ratio was chosen to get closer to

column and ultimately real field conditions (Monfort et al., 2019; Rybnikova et al., 2017) while minimizing the volume of final effluent requiring further treatment. These soil slurries were placed on shaker at 200 rpm for 24 h, centrifuged, decanted, filtered (0.2 μm PES filter) and prepared for the analysis of the target compounds. All batch experiments were performed in triplicates, at room temperature and in amber glass bottles to avoid any photolytic degradation by light. Batch experiments were conducted for both soil fractions sieved through 0-400 μm and 400-800 μm .

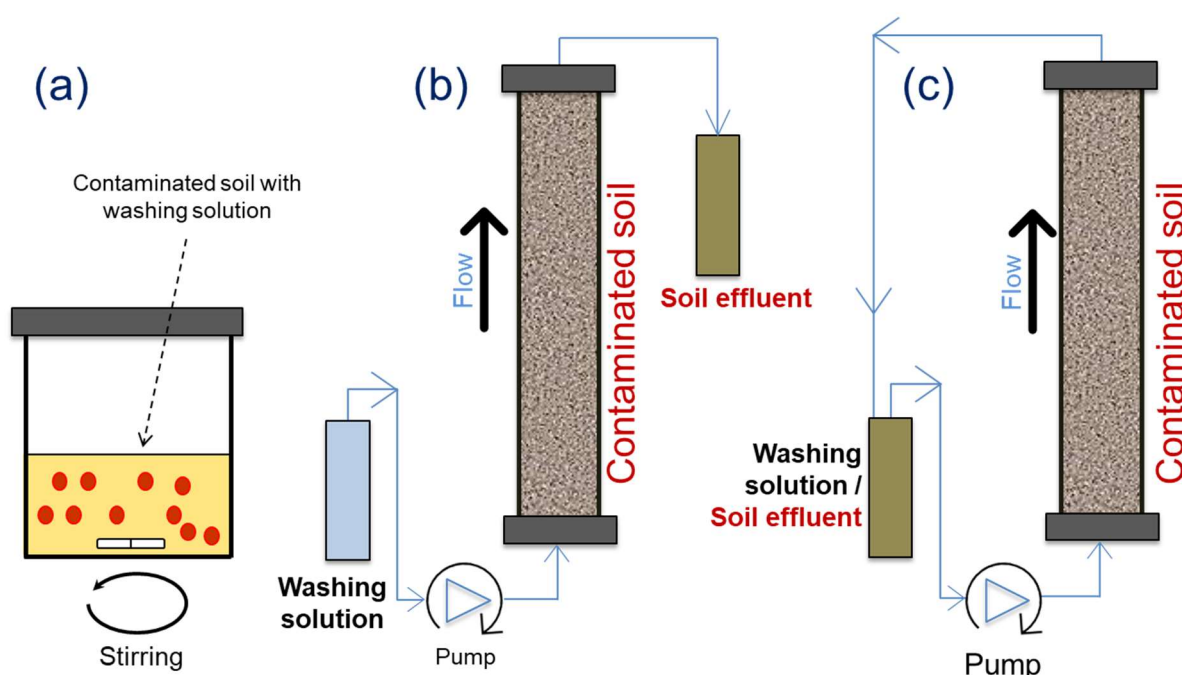


Figure 1: Schematic illustration of the experimental setups utilized in this study: a) batch conditions, b) open-loop column under water-saturated conditions, and c) closed-loop column under water-saturated conditions. In open-loop experiments, the washing solution was injected through the column until the entire influent solution had been introduced, followed by completion of the outflow from the column (Figure 1b). Closed-loop columns maintained similar conditions, with the effluent continuously collected and re-injected through the column in a continuous loop for three cycles.

For column experiments, 10 g soil was packed into a glass column with an internal diameter (D_{int}) of 1.6 cm and a bed length (L) of 4.7 cm. The bulk density of the packed soil was 1.45 g/cm^3 . The pore volume ($PV = 7.5$) was estimated by weight differences before and after the

saturation of the dry column. For column experiments, 10 mL of washing solutions (L/S of 1) were injected at a constant flow rate of 0.1 mL min⁻¹. In open-loop experiments, the washing solution was injected through the column and the experiment was stopped when the entire influent solution had been injected (in about 100 minutes at 0.1 mL min⁻¹) and the outflow from the column was completed by injecting air once the washing solution was exhausted to capture the maximum amount of washing effluent (Figure 1b). In closed loop columns, similar conditions were maintained (10 mL of washing solution at 0.1 mL min⁻¹). However, the effluent was continuously collected and re-injected through the column in a continuous loop at the same flow rate (i.e., 0.1 mL min⁻¹) for approximately three injection cycles, with a total duration of 300 minutes (Figure 1c). Closed-loop system allows higher reaction/contact time as compared to the open-loop column system (Rybnikova et al., 2017). Further experiments were conducted at a higher L/S ratio of 10, while maintaining the total amount of methanol or HPCD comparable to this system as explained in Section 3.3. Blank experiments were conducted in the same way, using deionized water as the washing solution.

2.3. PFAS adsorption on carbonaceous adsorbents

PFAS adsorption experiments were performed using biochar (1 g L⁻¹) or activated carbon (1 g L⁻¹) using 10 mL of soil washing effluents (bearing methanol 5% v/v or HPCD 1 mg mL⁻¹) in amber glass bottles. Experiments were also performed in water with similar contents of washing agents (methanol 5% v/v or HPCD 1 mg mL⁻¹) spiked with higher PFAS concentrations (0.2 or 1 mg L⁻¹). After stirring for 24 h to reach equilibrium, the samples were centrifuged at ~4000 g for 30 min, and aliquots of the resulting supernatants were transferred into sampling LC vials for PFAS analyses. Blank samples of equal solution chemistry but without the adsorbents were also collected for quality assurance, and aqueous losses to the reactor walls were verified to be <5%, which was considered in calculating the adsorption of PFAS.

2.4. PFAS quantifications and quality control

The target PFAS (PFOA, PFOS, PFDA, 6:2 FTAB, and GenX) were analyzed using a liquid chromatography-tandem mass spectrometry (LC-MS/MS) system with a limit of quantification of 1 ppb as detailed previously (Liu et al., 2023). Background and instrumental contamination of PFAS was removed by installing a PFAS delay column (PFAS analyses kit, Waters) that effectively delayed instrumental contribution of PFAS from pump, solvent lines and solvents. A continuous calibration verification sample was analyzed after every 30 samples with blank runs after every 10 samples. A 10-point calibration was used for sample quantification ($R^2 > 0.99$). The detailed description of the analytical procedure has been provided in our previous study (Liu et al., 2023).

210 **Table 1:** A summary of the experimental work performed in this study regarding soil washing and subsequent adsorption of PFAS from soil
 211 washing effluents.

a) Soil washing setups					
System	Soil fractions (μm)	System	Soil washing agent/dose	L/S ratio	Target PFAS
Freshly contaminated agricultural soil	1) 0 – 400 or 2) 400 – 800	Batch	Water	1	GenX, PFOA, PFOS, PFDA, 6:2 FTAB
			Ethanol/Water: 10, 25, and 50% v/v	1	
			Methanol/Water: 10, 25, and 50% v/v	1	
			HPCD (1, 5, and 10 mg g ⁻¹ soil w/w)	1	
	400 – 800	Column (Open-loop)	Methanol/Water: 50% v/v	1	
			HPCD (10 mg g ⁻¹ soil w/w)	1	
		Column (Closed-loop)	Methanol/Water: 50% v/v	1	
			HPCD (10 mg g ⁻¹ soil w/w)	1	
		Column (Open-loop)	Water	10	Breakthrough release of GenX, PFOA, PFOS, PFDA, 6:2 FTAB
			Methanol/Water: 5% v/v	10	
			HPCD (10 mg g ⁻¹ soil w/w = 1 mg mL ⁻¹)	10	
b) PFAS adsorption experiments					
System	Adsorbent	System	Reagent doses	Target PFAS	
Aqueous solution (soil washing effluents or artificially contaminated water)	Activated carbon Or Biochar	Batch	PFAS concentration: 0.02, 0.2 and 1 mg L ⁻¹ Adsorbent dosage: 1 g L ⁻¹ Adsorption time: 24 h	GenX, PFOA, PFOS, PFDA, 6:2 FTAB	

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3. Results and discussion

3.1. Batch washing of PFAS-contaminated soil

Figure 2 presents the recovery of 5 PFAS (GenX, PFOA, PFOS, PFDA, and 6:2 FTAB) after washing both size fractions (0-400 μm and 400-800 μm) of agricultural soil spiked with the PFAS mixture. The efficiency of different washing solutions including water, ethanol (1, 25, and 50% v/v), methanol (1, 25, and 50% v/v) and HPCD (1, 5 and 10 mg g^{-1} w/w) was compared. Water was able to remove about 65-75% of GenX and <45% of PFOA but showed negligible efficiency against PFOS, PFDA and 6:2 FTAB. Higher washing efficiency of GenX in water compared to other PFAS can be linked to its high water solubility and lower binding affinity towards soil constituents (Heidari et al., 2021; Liu et al., 2023). Our recent column study indicated lower binding capacity of GenX compared to PFOA in a pristine as well as amended soil (Liu et al., 2023). Higher recovery of GenX with water, though beneficial in context of soil washing, could threaten the groundwater resources due to its higher leaching in groundwater in contaminated soils. This highlights the concerns over the safety and environmental mobility of GenX as an alternative of PFOA. Moreover, 6:2 FTAB and long-chained PFDA were the most resistant to soil washing using water which is consistent with previous studies showing poorer soil washing efficiency for long-chain compounds, especially $>\text{C}_8$ (Grimison et al., 2023) and with previous reports on PFAS desorption from aqueous film forming foam (AFFF)-contaminated soils (Kabiri et al., 2021; Kabiri et al., 2022). The resistance of longer chain PFAS to soil washing is linked to the increase in sorption with increase in number of C-F_2 moieties, their low solubility in water and high hydrophobicity (Grimison et al., 2023; Nguyen et al., 2020; Oliver et al., 2019; Uwayezu et al., 2024). In addition to chain length, the results indicate that the type of functional groups (sulfonate and carboxylic groups) also affected the efficiency of soil washing. The lower removal of PFOS compared to PFOA, despite having the same carbon chain length, may be attributed to the hydrophobic nature of PFOS and its greater retention in soil, possibly due to the CF_2 unit in sulfonates (Uwayezu et al., 2024). Numerous soil immobilization and adsorption studies have

reported higher sorption of PFOS compared to PFOA (Knight et al., 2021; Rodrigo et al., 2022).

The inefficiency of water against hydrophobic or long-chained PFAS indicates the need for an additional washing solution. The inclusion of all the tested washing agents, even at low concentrations, improved the PFAS removal efficiency compared to water. Among them, methanol (50%) and HPCD (10 mg g^{-1}) showed particularly higher washing efficiencies to remove all the target PFAS ranging from 92-98%. An increase in the dose of methanol and HPCD improved the PFAS recovery. For example, the removal of PFOS increased from 51%, 75%, and 99% using 1, 5 and 10 mg g^{-1} HPCD. The optimum concentration of methanol and HPCD were 50% (v/v) and 10 mg g^{-1} , respectively. The optimum concentration of methanol (50%) is consistent with previous studies showing the optimum desorption of PFOS from soil (Senevirathna et al., 2021) and granular activated carbon for the successful regeneration of this adsorbent (Deng et al., 2015).

PFAS removal was slightly higher (4-6% higher) in coarse soil fractions (Figure 2a) than the fine soil fractions (Figure 2b). This can be linked to the higher sorption capacity of clay in fine soil fractions compared to the coarse fraction (Abou-Khalil et al., 2023; Mahinroosta et al., 2020). This difference was remarkable in a recent and similar - but mobile - soil washing study where washing efficiencies were greater for gravel and sand fractions, up to 98% and 96% respectively, compared to fine (clay) soil fractions, maximum 62% removal efficiency (Quinnan et al., 2022). Due to PFAS's strong sorption affinity for fine soil fractions, traditional soil washing studies have proposed separating these fractions (Grimison et al., 2023; Hubert et al., 2023; Quinnan et al., 2022). Despite the recognized role of clay particles in affecting the mobility of PFAS (Abou-Khalil et al., 2023), our study clearly demonstrates the robust effectiveness of the tested washing solutions in removing PFAS from coarse as well as fine soil fractions. This suggests that PFAS elimination from the soil can be achieved without the need to separate distinct soil fractions, as required in traditional soil washing strategies. It is worth noting that though partitioning coefficients of PFAS can vary according to their chain length (Ahrens et al., 2010), similar recoveries between different PFAS were observed in our

study highlighting the strong efficiency of methanol and HPCD in washing PFAS contaminated soils.

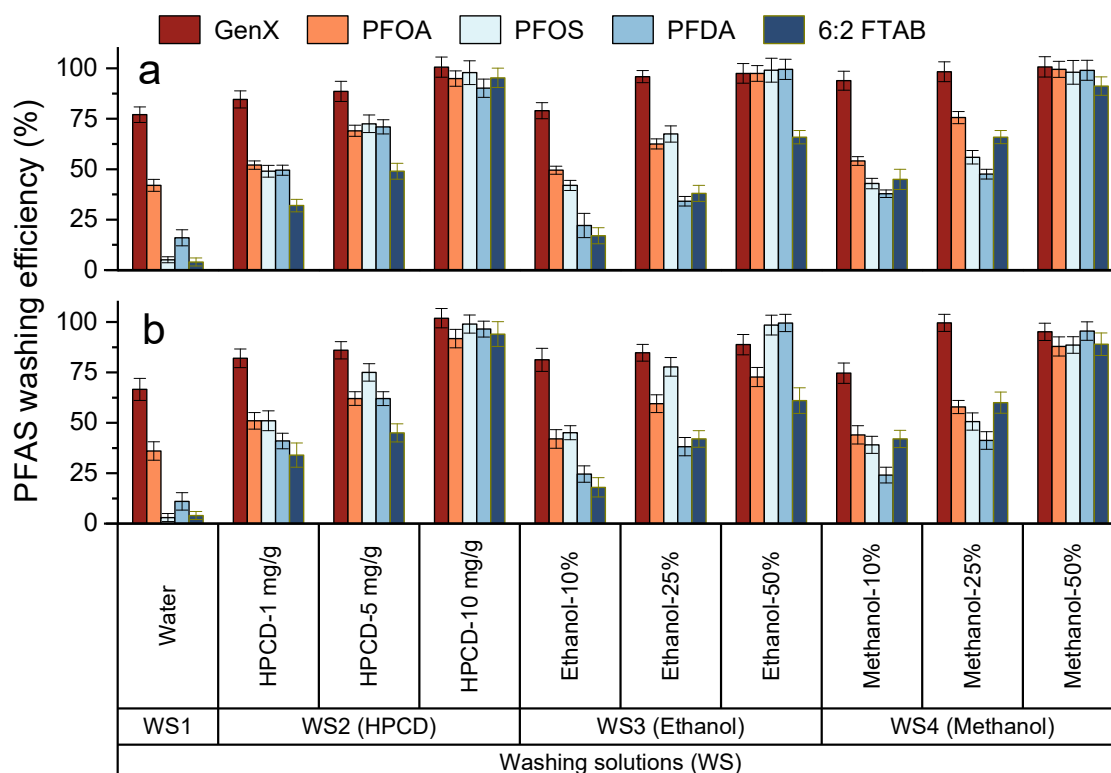


Figure 2: Washing efficiency for 5 PFAS (GenX, PFOA, PFOS, PFDA and 6:2 FTAB) in two size fractions, including a) 400-800 µm and b) 0-400 µm, of an agricultural soil spiked with an initial concentration of 200 µg kg⁻¹ soil for each PFAS under batch conditions. Each bar and error bars are means and standard deviations of triplicates, respectively. Washing solutions include deionized water along with HPCD, ethanol and methanol at different concentrations (L/S ratio of 1).

3.2. Column washing of a PFAS-spiked soil

Column experiments were performed to assess the efficiency of the soil washing solutions in removing PFAS from the target soil under conditions closer to field investigations. Experiments were performed at a constant flow rate of 0.1 mL min⁻¹ that was consistently verified throughout the study. Column experiments performed with 0-400 µm fraction were halted due to the column clogging caused by the higher amount of fine soil particles (data not shown). Therefore, only the results obtained with spiked coarse soil fractions (400-800 µm) are presented in Figure 3. Like batch experiments, both washing solutions exhibited >90% removal for all the target PFAS under column conditions. Typically, closed-loop system offers

extended reaction time leading to improved treatment efficiency, a trend observed in previous studies on the chemical oxidation or sorption of pollutants (Rybnikova et al., 2017). However, in our case, both systems resulted in comparable treatment efficiency. The comparable washing efficiency under both open and closed loop systems, even similar to the batch systems, indicates the quick and efficient role of these washing solutions in removing PFAS. It is important to note that in soil washing facilities, L:S ratios are typically higher compared to our laboratory study (L/S ratio of 1), such as 5:1 (Quinnan et al., 2022), 18:1 (Grimison et al., 2023) and 2-40:1 (Uwayezu et al., 2024). Therefore, the selection of appropriate washing agents may also help decrease the volume of final effluent requiring treatment. It is, however, important to acknowledge that our study utilized spiked soil samples. In these samples, the PFAS have been in contact with the soil for a relatively short period compared to historically contaminated sites. This recent contact may lead to higher desorption efficiencies compared to aged contamination scenarios (Nguyen et al., 2022; Usman et al., 2022). Moreover, the role of varying soil properties and experimental conditions (particularly flow rate which has been 0.1 mL min⁻¹ in our study) should also be considered for a more comprehensive comparison of the treatment efficiency.

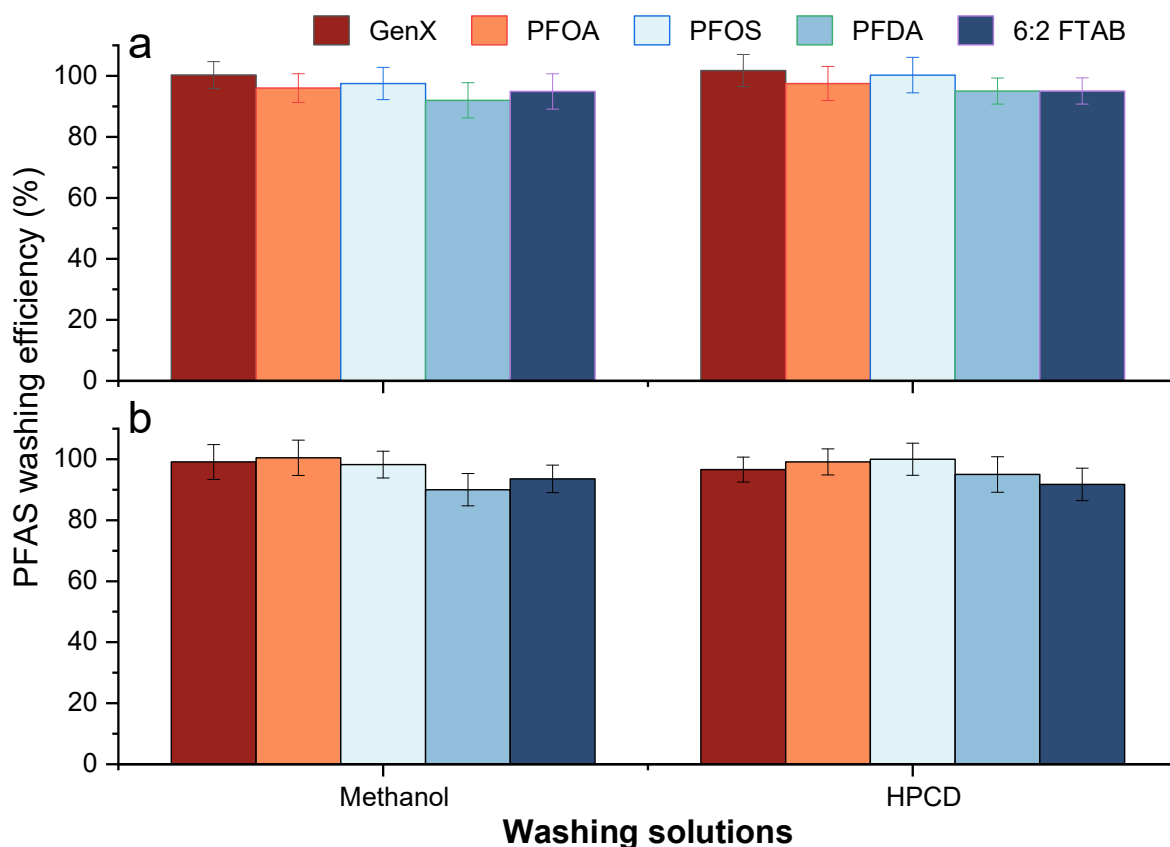


Figure 3: Washing efficiency for 5 PFAS (GenX, PFOA, PFOS, PFDA and 6:2 FTAB) in an agricultural soil spiked with an initial concentration of $200 \mu\text{g kg}^{-1}$ soil for each PFAS under flow-through conditions including open-loop (Figure 3a) and closed-loop columns (Figure 3b). In open-loop experiments, the washing solution was injected through the column until the entire influent solution had been introduced, followed by completion of the outflow from the column (Figure 1b). Closed-loop columns maintained similar conditions, with the effluent continuously collected and re-injected through the column in a continuous loop for three cycles. Soil washing solutions including methanol (50% v/v) and HPCD (10 mg g^{-1} soil w/w) were injected at a flow rate of 0.1 mL/min L/S ratio of 1). Error bars are relative standard deviations of duplicates.

3.3. Column optimization of the loading of washing solutions

Although washing solutions containing 50% methanol or 10 mg g^{-1} HPCD (equivalent to 10 mg mL^{-1} at L/S ratio of 1) effectively removed the target PFAS with minimal effluent volume, the discharge of effluents with high concentrations of solvents, particularly methanol at 50%, can raise concerns for both health and environmental impacts (Lau et al., 2014). Additionally, the high solvent concentrations may hinder PFAS removal through subsequent adsorptive

processes, given its role in solubilizing pollutants, as previously reported (Deng et al., 2015; Rodrigo et al., 2022; Senevirathna et al., 2021).

To address these concerns, additional experiments were conducted at a higher L/S ratio of 10, while maintaining the total amount of methanol or HPCD constant. This involved increasing the volume of the washing solution tenfold to lower the concentrations of methanol and HPCD while maintaining a similar overall amount of washing agent. The objective was to assess whether diluted solutions of methanol (10 mL of 5% solution instead of 1 mL of 50% methanol solution per gram of soil) or HPCD (1 mg mL⁻¹ in L/S of 10 instead of 10 mg mL⁻¹ in L/S of 1, equaling 10 mg/g of soil in both cases) could effectively remove PFAS. Additionally, this approach addresses whether a specific solution concentration is necessary or if the total amount of washing reagents is the determining factor. For this, column experiments were performed using coarse soil fractions (400-800 µm) under saturated open loop conditions. The kinetic release of target PFAS was evaluated by taking samples at regular intervals. The obtained results are illustrated in Figure 4 presenting the residual PFAS concentrations in the soil after washing with respect to injection volume and the number of elution volumes per column pore volume (V/V_p).

The use of washing solutions demonstrated varying degrees of effectiveness in removing PFAS contaminants from the soil (Figure 4). Like batch experiments, the use of water alone removed PFAS by 90% (GenX), 70% (PFOA), 30% (PFOS) <10% (for both PFDA and 6:2 FTAB). PFAS removal mostly occurred in the first five PV hinting the quick removal of easily mobilized PFAS fractions by water. No significant increase beyond that point hints the strong sequestration of the hydrophobic PFAS in soil (Grimison et al., 2023; Nguyen et al., 2020; Rayner et al., 2022) and limited ability of water against these fractions. However, the efficiency of PFAS removal by water was higher as compared to that in batch conditions which can be linked to higher L/S ratios used in this column experiment. These findings are consistent with Uwayezu et al. (2024) who reported a 50-70% improvement in PFOS removal with an increase in the L/S ratio from 2 to 40. The use of methanol (5%) or HPCD (1 mg mL⁻¹) significantly improved the PFAS removal efficiency. For methanol, both GenX and PFOA were removed in

the first PV while PFOS, PFDA and 6:2 FTAB exhibited continuous removal along subsequent injected volume. The washing efficiency was, however, lower compared to the column experiments performed at higher methanol concentration (50% at L/S ratio of 1). This suggests that for methanol, concentration and amount of washing reagent is a critical parameter. HPCD (same amount per g of soil was used at different liquid/solution ratios) exhibited quick and significantly higher removal of all the PFAS as evident from the drop in residual concentration in soil in the first three PV (Figure 4c). The observed plateau in PFAS release suggests a possible existence of two-stage, an initial rapid release, followed by a slower release of PFAS with lower availability. This variability in PFAS availability is likely due to sorption processes within the soil components, where some molecules are strongly bound to soil particles, limiting their release (Liu et al., 2023; Usman et al., 2022).

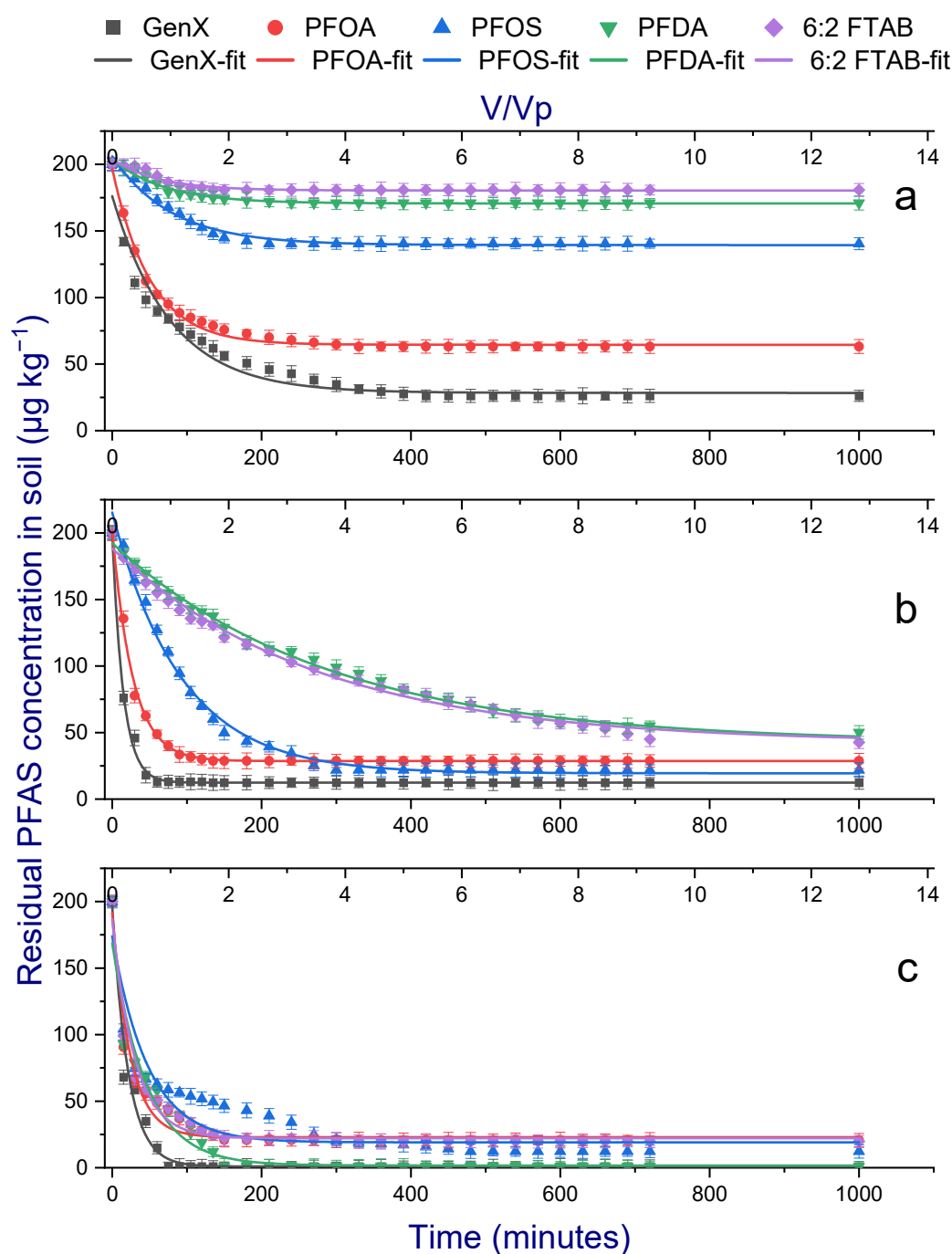


Figure 4: Evolution of PFAS concentration in contaminated soil columns over time (lower x-axis) and V/V_p , with the release of PFAS washing with three solutions including (a) water, (b) 5% methanol, and (c) HPCD (1 mg mL^{-1}). The upper axis (V/V_p) represents the ratio of the injected solution volume to the pore volume. The initial concentration of each PFAS (GenX, PFOA, PFOS, PFDA, and 6:2 FTAB) was $200 \mu\text{g kg}^{-1}$ of soil. Flow rate: 0.1 mL min^{-1} , $L/S = 10$. The solid lines represent the fit of a one-phase decay exponential model to the data. Error bars are standard deviations of duplicates.

To get further insights into the washing efficiency in soil columns, we employed a one-phase first order exponential decay model. This model is commonly used to describe the decay of pollutants in many chemical and biological processes (Zhang et al., 2024). We adapted the model to describe the soil washing to mobilize PFAS from soils using the following simplified equation:

$$C = (C_0 - p)e^{-kt} + p$$

Where C is the concentration of PFAS in soil at any time t ($\mu\text{g kg}^{-1}$), C_0 is the initial concentration of PFAS in soil ($200 \mu\text{g kg}^{-1}$), k is the first-order mobilisation rate constant (min^{-1}), and p is the plateau representing C value at infinite times ($\mu\text{g kg}^{-1}$). The model yielded great values of R^2 (≥ 0.92) and the fitted values of k and p are shown in Table 2. Fitting curves are in good agreement with the experimental data, suggesting that PFAS mobilization using washing agents can be described through a first-order process in soil columns. The modeling data also confirmed the significant discrepancy in terms of mobilization rate among washing agents. Although p can be strongly dependent on PFAS type as well as extracting agent, time to reach the plateau can be the same regardless of PFAS compound.

Table 2: Fitting results of the one-phase exponential decay model adapted for soil washing data presented in Figure 4.

		GenX	PFOA	PFOS	PFDA	6:2 FTAB
Washing agent						
Water	k (min^{-1})	0.013	0.020	0.013	0.014	0.016
	p ($\mu\text{g kg}^{-1}$)	28.4	64.5	139.4	170.7	180.4
Methanol	k (min^{-1})	0.068	0.036	0.011	0.003	0.004
	p ($\mu\text{g kg}^{-1}$)	12.3	28.6	19.4	42.5	42.2
HPCD	k (min^{-1})	0.047	0.041	0.021	0.022	0.033
	p ($\mu\text{g kg}^{-1}$)	0.9	22.9	19.1	1.6	22.2

3.4. Adsorption of PFAS from soil washing effluents using carbonaceous adsorbents

Following the successful removal of PFAS from contaminated soil through soil washing, attention turned to addressing the environmental implications posed by the significant PFAS levels present in the washing effluents. This phase of the research focused on adsorbing the separated PFAS onto two carbonaceous adsorbents: activated carbon and biochar. While previous studies have demonstrated the efficacy of activated carbon in removing PFAS from soil washing effluent (Grimison et al., 2023; Uwayezu et al., 2024), they typically used water alone for soil washing, unlike our study, which utilized methanol and HPCD to enhance pollutant solubility. Additionally, our study explored the use of biochar as a cost-effective and sustainable alternative to activated carbon.

Batch experiments using activated carbon or biochar effectively eliminated PFAS from the soil washing effluent in the presence of methanol or CD for each PFAS, reducing them below the detection limit (Figure 5). To further investigate the efficiency of these materials, experiments were also performed at higher PFAS concentrations (0.2 and 1 mg L⁻¹ of each PFAS) in artificially contaminated water in the presence of 5% methanol or 1 mg mL⁻¹ of HPCD. Activated carbon achieved complete PFAS adsorption, while the adsorptive efficiency of biochar decreased at higher PFAS concentrations. Notably, biochar capability decreased more prominently in the presence of HPCD (1 mg L⁻¹) (Figure 5b) compared to methanol (5% v/v) (Figure 5d), likely due to increased pollutant solubilization in the presence of HPCD. In addition, PFAS encapsulated by HPCD likely become less available to interact with adsorption sites.

The higher PFAS removal by activated carbon can be attributed to its improved properties (BET specific surface area = 790 m² g⁻¹, total pore volume = 0.83 cm³ g⁻¹) compared to biochar (232 m² g⁻¹ and 0.39 cm³ g⁻¹, respectively). Regarding biochar efficiency at elevated PFAS concentrations, PFAS adsorption varied according to their functional groups and chain lengths. PFOS, with its sulfonate functional group, exhibited higher adsorptive removal than PFOA, which contains a carboxylate group in agreement with (McCleaf et al., 2017). Moreover, PFAS sorption on biochar increased with greater fluorinated chain length, indicating

a predominant role of hydrophobic interactions in sorption processes as suggested earlier (Fabregat-Palau et al., 2022). Conversely, short-chain GenX posed greater challenges for removal using biochar, likely due to their lower affinity for adsorption sites and weaker interactions with the biochar surface. This study underscores the significant potential of the adsorption process, even in the presence of lower concentrations of methanol or HPCD, which offers flexibility to conduct experiments at varying L/S ratios.

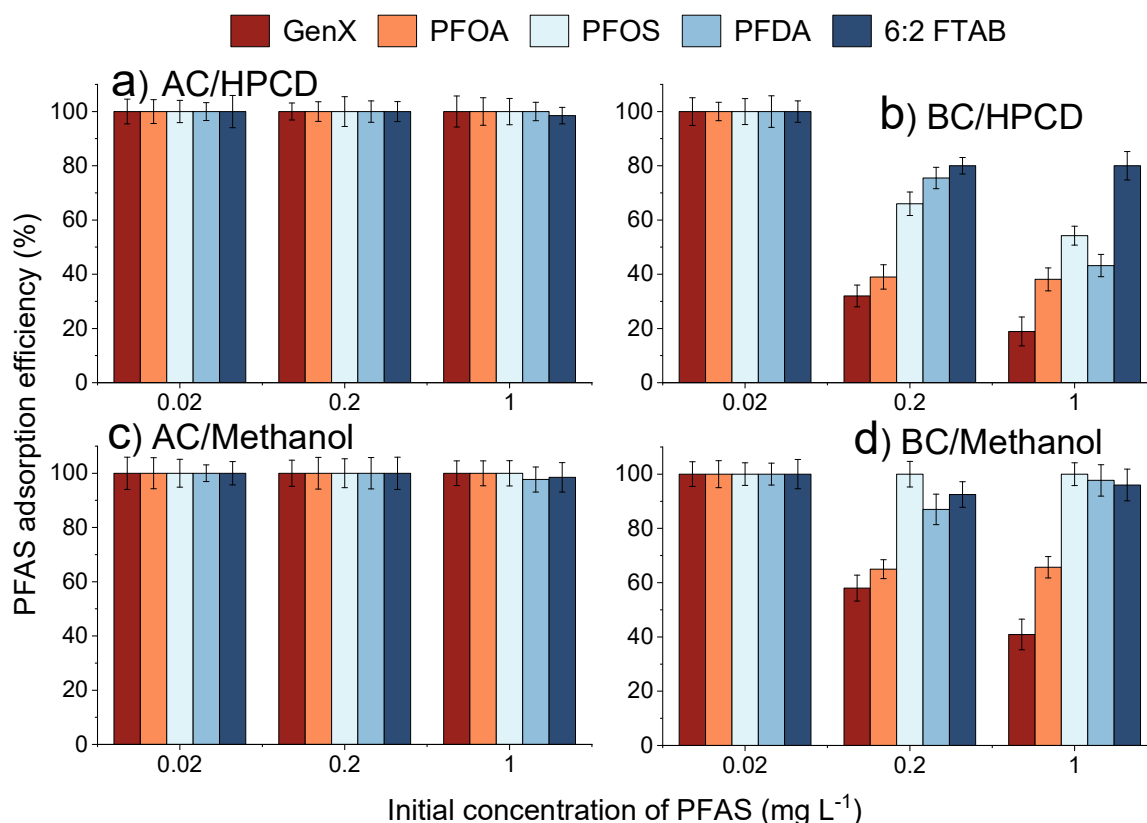


Figure 5: Batch adsorption of PFAS onto activated carbon (Figure 5a and 5c) or biochar (5b and 5d) in the presence of methanol (5% w/w) or HPCD solutions (1 mg mL⁻¹). Experimental conditions: 3 PFAS concentrations including 0.02 mg L⁻¹ (in soil washing effluent), 0.2 and 1 mg L⁻¹ in artificially contaminated water mixed with similar concentrations of methanol (5%) or HPCD (1 mg mL⁻¹); adsorbent dose: 1 g L⁻¹, reaction time: 24 h. Error bars are relative standard deviations of triplicates.

5. Conclusion

Poly- and perfluoroalkyl substances (PFAS) represent a significant environmental concern due to their persistence and widespread presence in various environmental matrices. This research investigates an optimized soil washing approach integrating subsequent treatment of wash effluents via adsorption onto carbonaceous adsorbents (activated carbon or biochar). Provided below are the key findings and their broader implications of this study.

- This study investigated the efficacy of different washing agents for PFAS removal from contaminated soils, aiming to contribute to the development of effective washing strategies. Highlighting the role of PFAS characteristics in dictating their removal by washing, the findings of this study underscore the importance of exploring alternative washing agents beyond traditional methods like water washing, especially considering the diverse characteristics of PFAS compounds. The study demonstrated that the inclusion of methanol or HPCD in washing solutions can significantly enhance the PFAS removal from contaminated soils. HPCD, as a green alternative, offered quick and efficient removal even at lower concentrations. Furthermore, column optimization experiments revealed the significance of solution concentration of washing agents and total washing reagent amount in determining the efficiency of PFAS removal. Our first-order mobilization model can well predict the transport and mobility behavior of PFAS in soil columns. These findings provide valuable insights into optimizing soil washing protocols for PFAS-contaminated soils in controlled settings, potentially reducing the volume of effluent requiring further treatment. However, it is crucial to validate the efficiency of these washing solutions in real-world scenarios. Given our observations are from only spiked soil, future research should investigate the use of these washing solutions in historically contaminated soils, as the age and history of contamination can significantly impact pollutant behavior and remediation efficiency. We also acknowledge that field soils are likely to exhibit more pronounced contaminant aging compared to the spiked soils in our study (Usman et al., 2022). Although studies observed comparable leaching of PFAS in AFFF-impacted soils aged for years

(Nguyen et al., 2022) and in a freshly-contaminated soil (Nguyen et al., 2022), further work is needed to explore the effects of soil aging of PFAS on soil washing in soils with varying properties.

- Subsequent treatment of soil washing effluents using activated carbon and biochar proved effective in adsorbing PFAS, reducing concentrations below detection limits of LC/MS. At higher PFAS concentrations in water, activated carbon demonstrated complete adsorption of PFAS, highlighting its potential as an efficient treatment option for PFAS-contaminated effluents. While biochar exhibited variable efficacy depending on PFAS characteristics, its cost-effectiveness and sustainability make it a promising alternative to activated carbon in certain applications. We also acknowledge that although simple and cost-effective, adsorption remains a pollutant separation-based process where PFAS are diverted from one phase to another (Usman et al., 2023). Further research should focus on integrating adsorption with PFAS degradation processes to achieve adsorbent regeneration for multiple treatment cycles and/or safe disposal. Development of technologies for PFAS destruction like advanced redox processes in separated soil wash will be highly rewarding to eliminate these pollutants (Uwayezu et al., 2024).
- Integrating the washing and adsorption and/or degradation processes within a single reactor system holds promise for long-term remediation sustainability. Future research should not only focus on scaling these techniques for field application in historically contaminated soils but also evaluate their cost-effectiveness, operational feasibility, and long-term environmental impact compounded with thorough eco-toxicity assessments.

Overall, this study highlights the importance of exploring alternative soil washing agents and treatment methods in PFAS remediation efforts. These findings contribute significantly to developing sustainable remediation practices by demonstrating the efficacy of alternative washing agents and efficient adsorbent materials.

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490

491 **Declaration of generative AI in scientific writing**

492 During the preparation of this work, the authors used chatGPT for the sole purpose of polishing
493 the language. After using this tool, the authors reviewed and edited the content as needed
494 and take full responsibility for the content of the publication.

495 **Credit Author Statement**

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