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

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16 **Abstract**

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

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

34

35

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

47 **1. Introduction**

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

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

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

82 Soil washing, a method historically used for contaminated soils, employs physical and/or
83 chemical separation to reduce waste volume and concentrate contaminants into a smaller
84 liquid phase for easier and flexible treatment (Bolan et al., 2021; Usman et al., 2022). Despite
85 its potential, very few studies explored the use of soil washing for PFAS-contaminated soils
86 (Grimison et al., 2023; Høisæter et al., 2021; Pang et al., 2022; Uwayezu et al., 2024). Existing
87 studies primarily use water as the main washing agent (Grimison et al., 2023; Høisæter et al.,
88 2021; Quinnan et al., 2022; Uwayezu et al., 2024) occasionally combined with gas/foam
89 fractionation (Pang et al., 2022) or soil fractionation for separate treatments of coarse and fine
90 soil fractions (Grimison et al., 2023; Quinnan et al., 2022). Given the diverse array of PFAS
91 compounds with varying characteristics (hydrophobic/hydrophilic, short-chained vs. long
92 chained, sulphonic vs. carboxylic heads etc.), exploring alternative washing agents is crucial
93 for PFAS removal from contaminated soils.

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

101 and biodegradability (Sikder et al., 2019). CDs are characterized by a distinct hydrophobic
102 non-polar interior cavity, which forms host-guest complexes with thousands of organic
103 molecules improving their solubility (Crini et al., 2018). This study used (2-Hydroxypropyl)- β -
104 cyclodextrin (HPCD), a hydroxyalkyl derivative CD, recognized for its improved water solubility
105 and higher pollutant desorption capacity compared to traditional CDs (α -, β - and γ -
106 cyclodextrins) (Sikder et al., 2019; Viglianti et al., 2006). These washing solutions have been
107 used to remove PFAS from the coarse and fine fractions of an agricultural soil spiked with five
108 different PFAS, including legacy PFAS (PFOA, PFOS) and their newer substitutes (GenX and
109 6:2 FTAB, respectively), along with PFDA as a long-chained PFAS. Soil washing experiments
110 were conducted in both batch and flow-through column settings, including open-loop and
111 closed-loop column setups. Subsequently, the soil washing effluent was treated using
112 activated carbon and biochar for PFAS adsorption. Activated carbon remains a highly effective
113 adsorbent for PFAS removal in contaminated water and wastewater (Gagliano et al., 2020;
114 Pauletto et al., 2022). Similarly, biochar has demonstrated viable potential as an alternative
115 adsorbent to activated carbon (Karunakaran et al., 2022). However, there exists limited
116 information regarding the efficacy of these carbonaceous adsorbents in the treatment of
117 effluents generated by soil washing processes. Notably, this study represents the first reported
118 application of biochar for the adsorption of PFAS from soil washing effluents.

119 **2. Experimental section**

120 **2.1. Chemicals and reagents**

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

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

130 **2.2. Target soil**

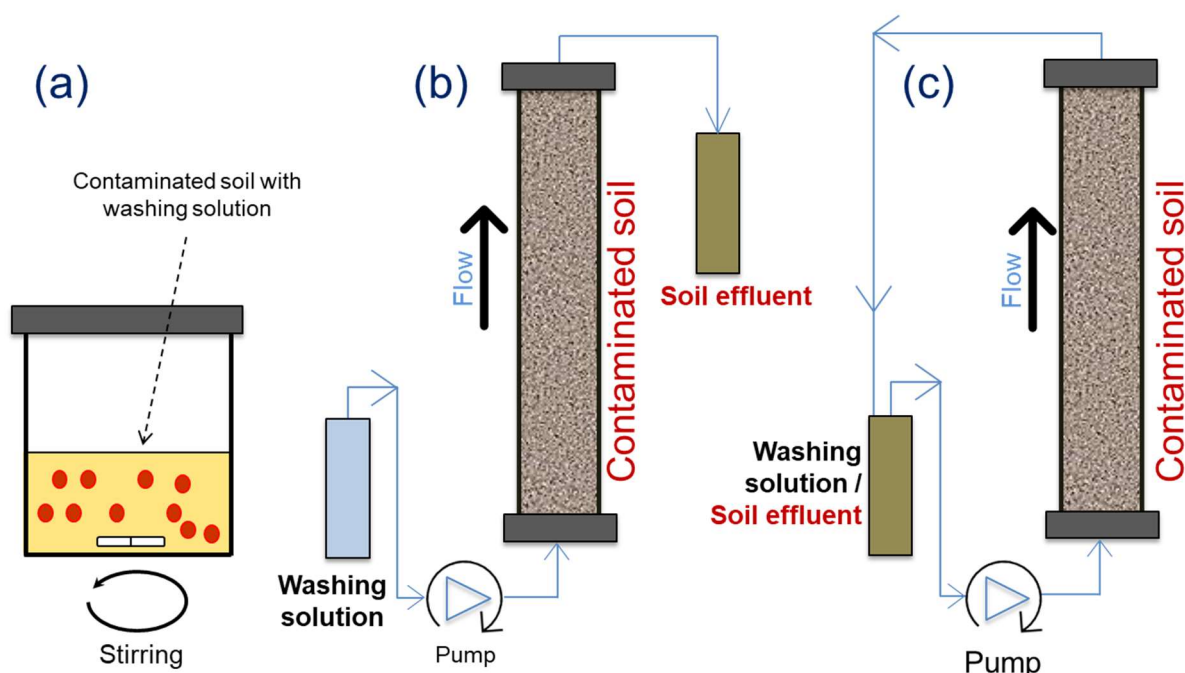
131 In this study, a non-contaminated agricultural soil was spiked with tested PFAS compounds
132 (GenX, PFOA, PFOS, PFDA and 6:2 FTAB). This soil was of silt loam type (20.5, 59.8 and
133 19.7 wt % of sand, silt and clay, respectively) with pH of 6.9. The major characteristics of this
134 soil are provided in Table S1 and a detailed description is provided in the context of our
135 previous study (Liu et al., 2023). Preliminary assays employing the same extraction and
136 analysis methods as described below revealed non-detectable PFAS concentrations in this
137 soil, i.e. below the instrument detection limit. This soil was sieved to achieve two particle size
138 fractions of 0–400 μm and 400–800 μm , which were then used in the subsequent experiments.
139 Both of these fractions were artificially contaminated by spiking with five different PFAS
140 compounds, namely PFOA, PFOS, PFDA, 6:2 FTAB, and GenX in methanol to obtain a
141 concentration of 200 $\mu\text{g kg}^{-1}$ for each PFAS (total PFAS concentration of 1000 $\mu\text{g kg}^{-1}$ dry
142 weight). This solution was allowed to evaporate under continuous mixing to ensure
143 homogeneous contaminant distribution. Spike-recovery tests of PFAS using methanol as the
144 extraction agent resulted in >99% recovery of the target PFAS.

145 **2.2. Soil washing**

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

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

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



162
163 **Figure 1:** Schematic illustration of the experimental setups utilized in this study: a) batch
164 conditions, b) open-loop column under water-saturated conditions, and c) closed-loop column
165 under water-saturated conditions. In open-loop experiments, the washing solution was
166 injected through the column until the entire influent solution had been introduced, followed by
167 completion of the outflow from the column (Figure 1b). Closed-loop columns maintained
168 similar conditions, with the effluent continuously collected and re-injected through the column
169 in a continuous loop for three cycles.

170
171 For column experiments, 10 g soil was packed into a glass column with an internal diameter
172 (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
173 g/cm^3 . The pore volume ($PV = 7.5$) was estimated by weight differences before and after the

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

188 **2.3. PFAS adsorption on carbonaceous adsorbents**

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

199

200 **2.4. PFAS quantifications and quality control**

201 The target PFAS (PFOA, PFOS, PFDA, 6:2 FTAB, and GenX) were analyzed using a liquid
202 chromatography-tandem mass spectrometry (LC-MS/MS) system with a limit of quantification
203 of 1 ppb as detailed previously (Liu et al., 2023). Background and instrumental contamination
204 of PFAS was removed by installing a PFAS delay column (PFAS analyses kit, Waters) that
205 effectively delayed instrumental contribution of PFAS from pump, solvent lines and solvents.
206 A continuous calibration verification sample was analyzed after every 30 samples with blank
207 runs after every 10 samples. A 10-point calibration was used for sample quantification ($R^2 >$
208 0.99). The detailed description of the analytical procedure has been provided in our previous
209 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		

212

213 3. Results and discussion

214 3.1. Batch washing of PFAS-contaminated soil

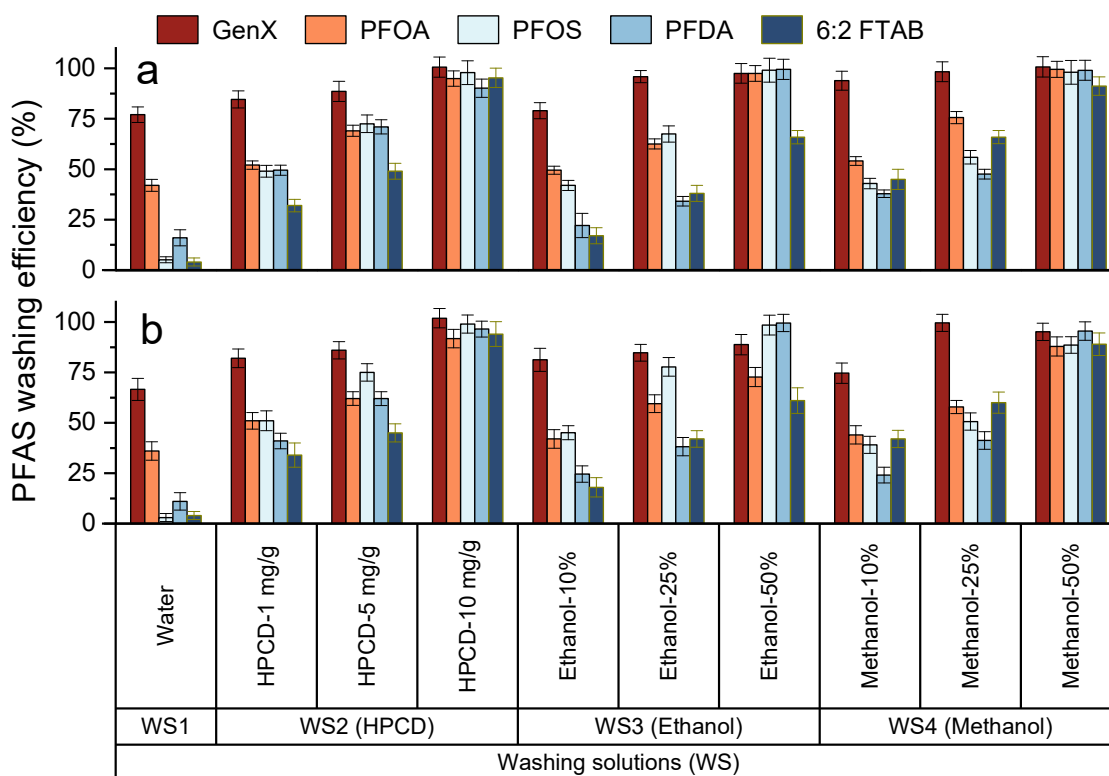
215 Figure 2 presents the recovery of 5 PFAS (GenX, PFOA, PFOS, PFDA, and 6:2 FTAB) after
216 washing both size fractions (0-400 μm and 400-800 μm) of agricultural soil spiked with the
217 PFAS mixture. The efficiency of different washing solutions including water, ethanol (1, 25,
218 and 50% v/v), methanol (1, 25, and 50% v/v) and HPCD (1, 5 and 10 mg g^{-1} w/w) was
219 compared. Water was able to remove about 65-75% of GenX and <45% of PFOA but showed
220 negligible efficiency against PFOS, PFDA and 6:2 FTAB. Higher washing efficiency of GenX
221 in water compared to other PFAS can be linked to its high water solubility and lower binding
222 affinity towards soil constituents (Heidari et al., 2021; Liu et al., 2023). Our recent column
223 study indicated lower binding capacity of GenX compared to PFOA in a pristine as well as
224 amended soil (Liu et al., 2023). Higher recovery of GenX with water, though beneficial in
225 context of soil washing, could threaten the groundwater resources due to its higher leaching
226 in groundwater in contaminated soils. This highlights the concerns over the safety and
227 environmental mobility of GenX as an alternative of PFOA. Moreover, 6:2 FTAB and long-
228 chained PFDA were the most resistant to soil washing using water which is consistent with
229 previous studies showing poorer soil washing efficiency for long-chain compounds, especially
230 $>\text{C}_8$ (Grimison et al., 2023) and with previous reports on PFAS desorption from aqueous film
231 forming foam (AFFF)-contaminated soils (Kabiri et al., 2021; Kabiri et al., 2022). The
232 resistance of longer chain PFAS to soil washing is linked to the increase in sorption with
233 increase in number of C-F_2 moieties, their low solubility in water and high hydrophobicity
234 (Grimison et al., 2023; Nguyen et al., 2020; Oliver et al., 2019; Uwayezu et al., 2024). In
235 addition to chain length, the results indicate that the type of functional groups (sulfonate and
236 carboxylic groups) also affected the efficiency of soil washing. The lower removal of PFOS
237 compared to PFOA, despite having the same carbon chain length, may be attributed to the
238 hydrophobic nature of PFOS and its greater retention in soil, possibly due to the CF_2 unit in
239 sulfonates (Uwayezu et al., 2024). Numerous soil immobilization and adsorption studies have

240 reported higher sorption of PFOS compared to PFOA (Knight et al., 2021; Rodrigo et al.,
241 2022).

242 The inefficiency of water against hydrophobic or long-chained PFAS indicates the need for an
243 additional washing solution. The inclusion of all the tested washing agents, even at low
244 concentrations, improved the PFAS removal efficiency compared to water. Among them,
245 methanol (50%) and HPCD (10 mg g⁻¹) showed particularly higher washing efficiencies to
246 remove all the target PFAS ranging from 92-98%. An increase in the dose of methanol and
247 HPCD improved the PFAS recovery. For example, the removal of PFOS increased from 51%,
248 75%, and 99% using 1, 5 and 10 mg g⁻¹ HPCD. The optimum concentration of methanol and
249 HPCD were 50% (v/v) and 10 mg g⁻¹, respectively. The optimum concentration of methanol
250 (50%) is consistent with previous studies showing the optimum desorption of PFOS from soil
251 (Senevirathna et al., 2021) and granular activated carbon for the successful regeneration of
252 this adsorbent (Deng et al., 2015).

253 PFAS removal was slightly higher (4-6% higher) in coarse soil fractions (Figure 2a) than the
254 fine soil fractions (Figure 2b). This can be linked to the higher sorption capacity of clay in fine
255 soil fractions compared to the coarse fraction (Abou-Khalil et al., 2023; Mahinroosta et al.,
256 2020). This difference was remarkable in a recent and similar - but mobile - soil washing study
257 where washing efficiencies were greater for gravel and sand fractions, up to 98% and 96%
258 respectively, compared to fine (clay) soil fractions, maximum 62% removal efficiency (Quinnan
259 et al., 2022). Due to PFAS's strong sorption affinity for fine soil fractions, traditional soil
260 washing studies have proposed separating these fractions (Grimison et al., 2023; Hubert et
261 al., 2023; Quinnan et al., 2022). Despite the recognized role of clay particles in affecting the
262 mobility of PFAS (Abou-Khalil et al., 2023), our study clearly demonstrates the robust
263 effectiveness of the tested washing solutions in removing PFAS from coarse as well as fine
264 soil fractions. This suggests that PFAS elimination from the soil can be achieved without the
265 need to separate distinct soil fractions, as required in traditional soil washing strategies. It is
266 worth noting that though partitioning coefficients of PFAS can vary according to their chain
267 length (Ahrens et al., 2010), similar recoveries between different PFAS were observed in our

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

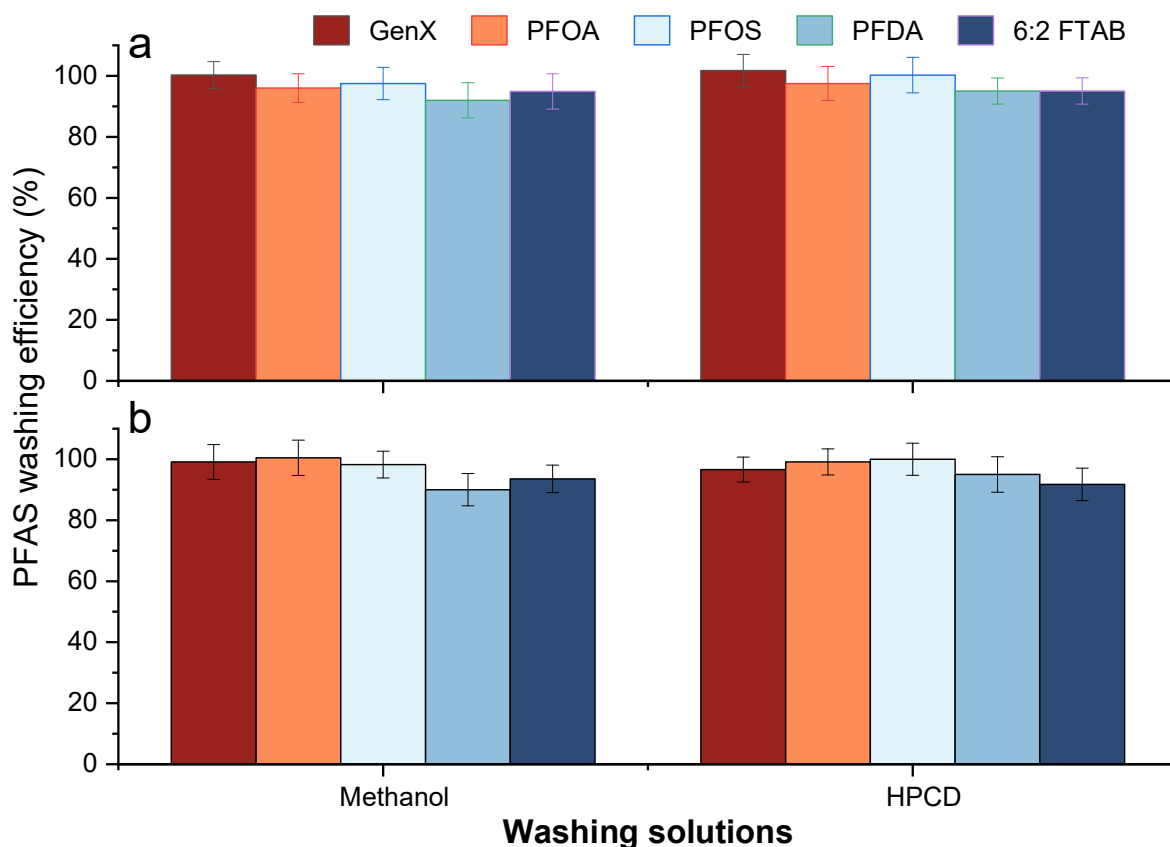


270
 271 **Figure 2:** Washing efficiency for 5 PFAS (GenX, PFOA, PFOS, PFDA and 6:2 FTAB) in two
 272 size fractions, including a) 400-800 μm and b) 0-400 μm, of an agricultural soil spiked with an
 273 initial concentration of 200 μg kg⁻¹ soil for each PFAS under batch conditions. Each bar and
 274 error bars are means and standard deviations of triplicates, respectively. Washing solutions
 275 include deionized water along with HPCD, ethanol and methanol at different concentrations
 276 (L/S ratio of 1).

277 3.2. Column washing of a PFAS-spiked soil

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

286 extended reaction time leading to improved treatment efficiency, a trend observed in previous
287 studies on the chemical oxidation or sorption of pollutants (Rybnikova et al., 2017). However,
288 in our case, both systems resulted in comparable treatment efficiency. The comparable
289 washing efficiency under both open and closed loop systems, even similar to the batch
290 systems, indicates the quick and efficient role of these washing solutions in removing PFAS.
291 It is important to note that in soil washing facilities, L:S ratios are typically higher compared to
292 our laboratory study (L/S ratio of 1), such as 5:1 (Quinnan et al., 2022), 18:1 (Grimison et al.,
293 2023) and 2-40:1 (Uwayezu et al., 2024). Therefore, the selection of appropriate washing
294 agents may also help decrease the volume of final effluent requiring treatment. It is, however,
295 important to acknowledge that our study utilized spiked soil samples. In these samples, the
296 PFAS have been in contact with the soil for a relatively short period compared to historically
297 contaminated sites. This recent contact may lead to higher desorption efficiencies compared
298 to aged contamination scenarios (Nguyen et al., 2022; Usman et al., 2022). Moreover, the role
299 of varying soil properties and experimental conditions (particularly flow rate which has been
300 0.1 mL min^{-1} in our study) should also be considered for a more comprehensive comparison
301 of the treatment efficiency.



302

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

313

314 3.3. Column optimization of the loading of washing solutions

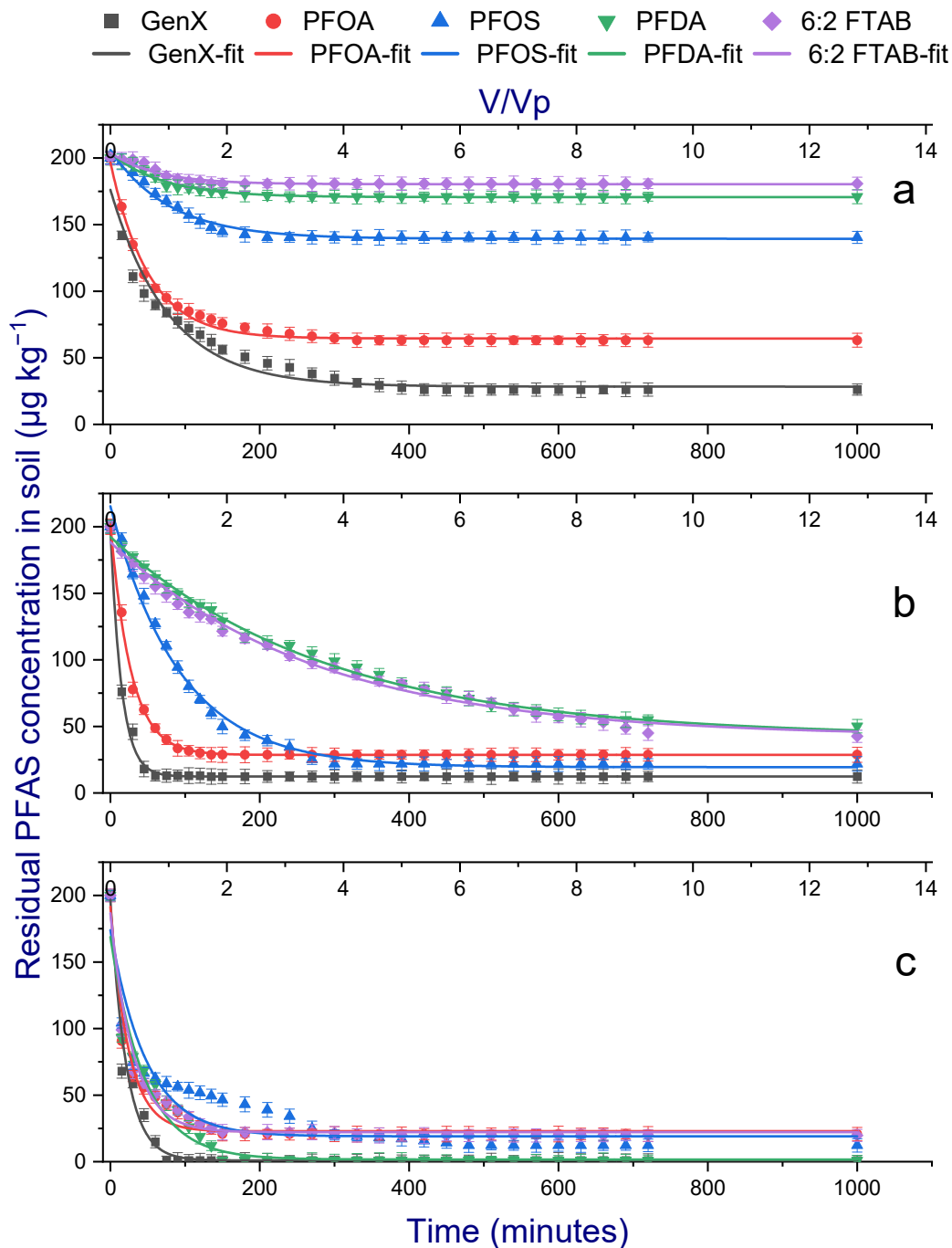
315 Although washing solutions containing 50% methanol or 10 mg g⁻¹ HPCD (equivalent to 10
 316 mg mL⁻¹ at L/S ratio of 1) effectively removed the target PFAS with minimal effluent volume,
 317 the discharge of effluents with high concentrations of solvents, particularly methanol at 50%,
 318 can raise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

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

322 To address these concerns, additional experiments were conducted at a higher L/S ratio of
323 10, while maintaining the total amount of methanol or HPCD constant. This involved increasing
324 the volume of the washing solution tenfold to lower the concentrations of methanol and HPCD
325 while maintaining a similar overall amount of washing agent. The objective was to assess
326 whether diluted solutions of methanol (10 mL of 5% solution instead of 1 mL of 50% methanol
327 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,
328 equaling 10 mg/g of soil in both cases) could effectively remove PFAS. Additionally, this
329 approach addresses whether a specific solution concentration is necessary or if the total
330 amount of washing reagents is the determining factor. For this, column experiments were
331 performed using coarse soil fractions (400-800 µm) under saturated open loop conditions. The
332 kinetic release of target PFAS was evaluated by taking samples at regular intervals. The
333 obtained results are illustrated in Figure 4 presenting the residual PFAS concentrations in the
334 soil after washing with respect to injection volume and the number of elution volumes per
335 column pore volume (V/V_p).

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

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



359

360 **Figure 4:** Evolution of PFAS concentration in contaminated soil columns over time (lower x-
 361 axis) and V/V_p , with the release of PFAS washing with three solutions including (a) water, (b)
 362 5% methanol, and (c) HPCD (1 mg mL^{-1}). The upper axis (V/V_p) represents the ratio of the
 363 injected solution volume to the pore volume. The initial concentration of each PFAS (GenX,
 364 PFOA, PFOS, PFDA, and 6:2 FTAB) was $200 \text{ } \mu\text{g kg}^{-1}$ of soil. Flow rate: 0.1 mL min^{-1} , $L/S =$
 365 10. The solid lines represent the fit of a one-phase decay exponential model to the data. Error
 366 bars are standard deviations of duplicates.

367

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

$$373 \quad C = (C_0 - p)e^{-kt} + p$$

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

383

384 **Table 2:** Fitting results of the one-phase exponential decay model adapted for soil washing
 385 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

386

387

388

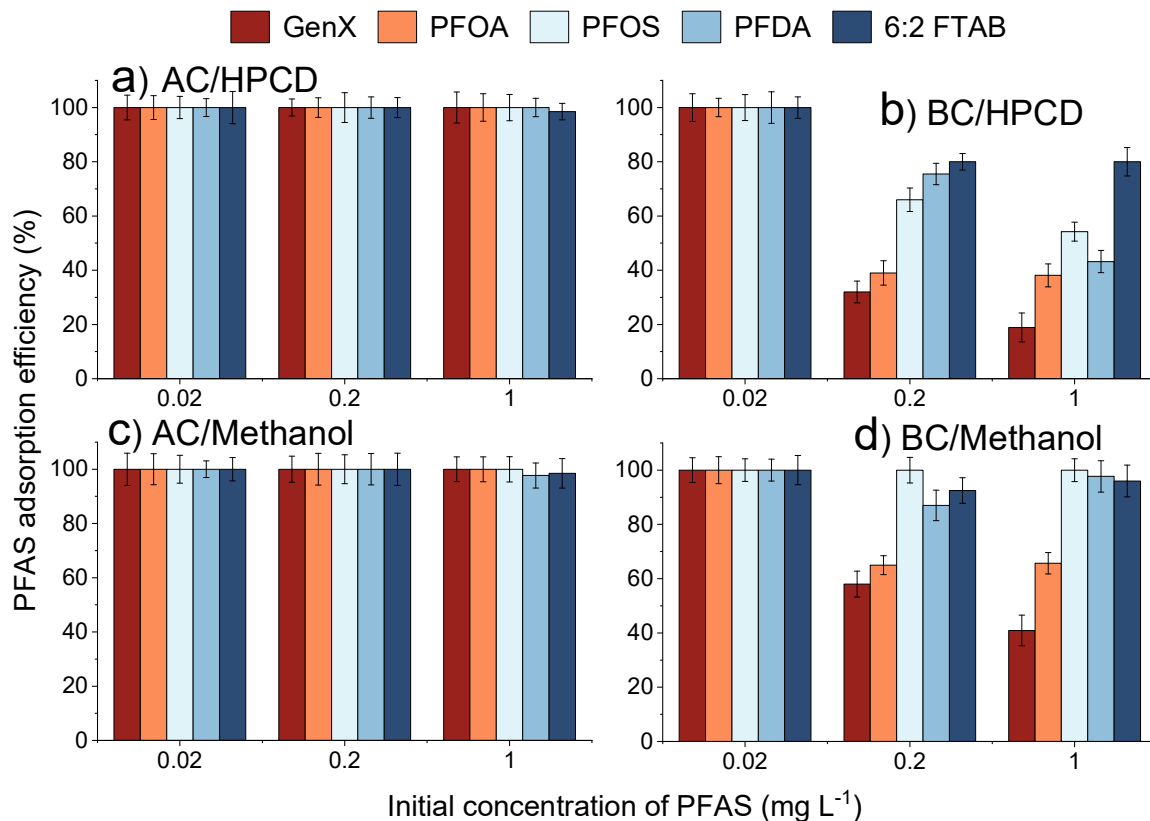
389 **3.4. Adsorption of PFAS from soil washing effluents using carbonaceous adsorbents**

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

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

410 The higher PFAS removal by activated carbon can be attributed to its improved properties
411 (BET specific surface area = 790 m² g⁻¹, total pore volume = 0.83 cm³ g⁻¹) compared to biochar
412 (232 m² g⁻¹ and 0.39 cm³ g⁻¹, respectively). Regarding biochar efficiency at elevated PFAS
413 concentrations, PFAS adsorption varied according to their functional groups and chain
414 lengths. PFOS, with its sulfonate functional group, exhibited higher adsorptive removal than
415 PFOA, which contains a carboxylate group in agreement with (McCleaf et al., 2017).
416 Moreover, PFAS sorption on biochar increased with greater fluorinated chain length, indicating

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



423

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

430

431 **5. Conclusion**

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

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

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

462 • Subsequent treatment of soil washing effluents using activated carbon and biochar
463 proved effective in adsorbing PFAS, reducing concentrations below detection limits of
464 LC/MS. At higher PFAS concentrations in water, activated carbon demonstrated
465 complete adsorption of PFAS, highlighting its potential as an efficient treatment option
466 for PFAS-contaminated effluents. While biochar exhibited variable efficacy depending
467 on PFAS characteristics, its cost-effectiveness and sustainability make it a promising
468 alternative to activated carbon in certain applications. We also acknowledge that
469 although simple and cost-effective, adsorption remains a pollutant separation-based
470 process where PFAS are diverted from one phase to another (Usman et al., 2023).
471 Further research should focus on integrating adsorption with PFAS degradation
472 processes to achieve adsorbent regeneration for multiple treatment cycles and/or safe
473 disposal. Development of technologies for PFAS destruction like advanced redox
474 processes in separated soil wash will be highly rewarding to eliminate these pollutants
475 (Uwayezu et al., 2024).

476 • Integrating the washing and adsorption and/or degradation processes within a single
477 reactor system holds promise for long-term remediation sustainability. Future research
478 should not only focus on scaling these techniques for field application in historically
479 contaminated soils but also evaluate their cost-effectiveness, operational feasibility,
480 and long-term environmental impact compounded with thorough eco-toxicity
481 assessments.

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

486

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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**

496 **M. Usman:** Conceptualization; Investigation; Data curation; Formal analysis; Writing - Original
497 draft preparation; Writing - Review & Editing. **A. Chaudhary:** Data curation; Writing - Review
498 & Editing. **K. Hanna:** Conceptualization; Funding acquisition; Supervision; Writing - Review &
499 Editing.

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