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TOPICAL COLLECTION ON PFAS ANALYTICS AND TREATMENT

Modified clays reduce leaching of per- and polyfluoroalkyl substances from AFFF-contaminated soils

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Abstract

Technologies applicable at a field scale to mitigate soil and groundwater pollution by per- and polyfluoroalkyl substances (PFAS) due to the release of aqueous film-forming foams are urgently needed. We demonstrate that modified bentonite clays as soil amendments can effectively reduce the leaching of PFAS from impacted soils. In batch experiments, the significant decrease (95%–99%) of leachable anionic PFAS, including perfluorooctane sulfonate, perfluorohexane sulfonate, and perfluorooctane carboxylate, was achieved in 1–4 days at a clay dosage as low as 0.5% w/w. A significant decline of leachable cationic and zwitterionic PFAS (70%–99%) was also observed. The clays performed the best in immobilizing PFAS anions, while granular activated carbon was effective in preventing PFAS cation leaching. Hardwood biochar had minor or negligible effects on any PFAS. The study provides strong evidence to support using modified clays as part of mitigation or remediation strategies to prevent PFAS from mobilizing on a field scale.

KEYWORDS

aqueous film-forming foams (AFFFs), groundwater remediation, modified clays, per- and polyfluoroalkyl substances (PFAS)

1 | INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) have been widely detected in environmental compartments, wildlife, and humans (Zhi & Liu, 2018). PFAS are chemically persistent (Houtz et al., 2013), some species are found bioaccumulative (Giesy & Kannan, 2001; Haug et al., 2010), and therefore this family of man-made chemicals poses considerable risks to humans and wildlife (Sunderland et al., 2019). The ubiquitous distribution of PFAS in the environment is due to their wide applications in various industries and products (Krafft & Riess, 2015), with a notable application of PFAS as primary components of aqueous film-forming foams (AFFFs) designed for fighting Class B fires (Pabon & Corpart, 2002). Repeated discharges of AFFFs have been linked to severe soil and groundwater contamination (Houtz et al., 2013; Martin et al., 2019). In many instances, PFAS are directly discharged into soils with little or no treatment, and thereby leaching from soils contributes to the PFAS load in groundwater and surface water. The elevated levels of PFAS are widely observed in the soil, water, sediment, and wildlife samples geographically relevant to the impacted sites, even when the discharges of AFFFs are discontinued for years (Barzen-Hanson et al., 2017; Nickerson et al., 2020).

Perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), and related analogs are the most detected and studied PFAS at AFFF-impacted sites. In recent years, increasing numbers of novel PFAS have been identified in AFFFs and impacted environmental samples (Backe et al., 2013; Barzen-Hanson et al., 2017; Mejia-Avendaño et al., 2016; Place & Field, 2012). The novel PFAS span various types of anionic, zwitterionic, and cationic fluorosurfactants, containing functional groups such as ammonium, amine oxide, sulfonamide, betaine, and many others. Most of the novel polyfluoroalkyl substances are considered as the "precursors" to perfluoroalkyl acids (PFAAs), since they have the potential to biologically or chemically degrade to perfluoroalkyl carboxylates (PFCAs) or sulfonates (PFSAs) (Haug et al., 2011; Houtz et al., 2013; Shaw et al., 2019). Previous investigations mainly focused on anionic PFAS, mainly PFCAs and PFSAs (USEPA, 2019), while the significant presence of the nonanionic compounds needs to be addressed as well. Particularly, cationic and zwitterionic PFAS can make up a significant fraction of the total PFAS load in impacted soils (Nickerson et al., 2020). Despite various challenges to study nonanionic PFAS, e.g., the incomplete understanding of their environmental behaviors, increasingly available chemical standards make it possible to address such a portion of nonanionic PFAS to developing soil remediation strategies (Mejia-Avendaño et al., 2017).

ncreasingly stringent PFAS regulations require treatment and remediation technologies to be cost-effective and applicable on a field scale. As source zone soils amass a significant amount of various types of PFAS, including precursors, remediation of the source zones will be critical and sustainable. Treating diluted groundwater plumes alone would be a never-ending treatment requirement with prohibitively high cost. So far, a broad array of treatment technologies, utilizing physical separation, photochemical degradation, advanced oxidation or reduction, sonolysis or thermal destruction, have been studied in laboratories for treating contaminated water (Ross et al., 2018). Technologies suitable for field scale installations are primarily granular activated carbon (GAC) adsorption, ion exchange, or membrane filtrations (e.g., reverse osmosis) (Appleman et al., 2014; Rahman et al., 2014). Far fewer technologies have been investigated for PFAS soil remediation. The predominant approach is through sorbent amendment, relying on the high affinity of the adsorbents for PFAS to keep the contaminants immobilized in the solid phase. The approach has been proven effective in reducing the leachability of hydrophobic organic pollutants such as PCBs, PAHs, and DDT in soils, as well as their bioaccumulation in invertebrates and fish (Deng et al., 2010; Ghosh et al., 2011; Hale et al., 2009; Hansen et al., 2010; McLeod et al., 2007; West et al., 2001; Woodard et al., 2017; Yu et al., 2009).

Article Impact Statement
The study demonstrated that modified bentonite clays effectively immobilize various PFAS in AFFF-contaminated soils to prevent leaching.

The soil amendments evaluated so far include activated carbon, compost soil, montmorillonite, modified palygorskite (MatCARE™), biochar, pulverized zeolite, chitosan, hydrotalcite, bentonite, and calcium chloride (Das et al., 2013; Hale et al., 2017; Kupryianchyk et al., 2016; Sörengård et al., 2019). Those studies mostly examined the efficacy of immobilizing anionic PFAAs. Activated carbon and modified palygorskite have shown higher efficiency in immobilizing PFOS than other materials. Besides modified palygorskite, modified smectites used in water treatment and soil remediation targeting PFAS have been reported (Du, 2016; Zhou et al., 2010; Zhou et al., 2013). The modified clays are made by embedding amine-based hydrocarbon surfactants (e.g., quaternary ammonium surfactants) in the exchange sites of expandable clays such as smectites. We have demonstrated that a commercially available modified clay can outperform granular activated carbon in removing long-chain (PFCAs with eight or more carbons; PFSAs with six or more carbons) anionic PFAS from contaminated groundwater (Yan et al., 2020; Yan et al., 2021). Mechanistically, we have shown that PFAS molecules diffuse into the interlayer space of modified clays and then interact with intercalant molecules (i.e., hydrocarbon surfactants with amine groups) through the ionic and van der Waals forces (Yan et al., 2020). At high PFAS loading, substantial uptake of PFAS is accompanied by clay expansion and structural rearrangement within the interlayer space of the clays. The fouling resistance of the modified bentonite is another advantage for their field applications; common groundwater organic co-contaminants (Yan et al., 2020) and natural organic matter at environmentally relevant concentrations little impacted removal efficiency.

Since a typical AFFF-impacted soil contains anionic PFAS of varying chain lengths, as well as cationic and zwitterionic PFAS, it is unclear whether the modified clay would perform equally well for PFAS other than PFOS or PFOA. Therefore, we initiated the study to evaluate how the newly developed modified clays may reduce the mobility or leachability of PFAS from AFFF-impacted soils. As no standard methods are available to assess

PFAS leachability, we modified a US EPA method and applied it to field-contaminated soils. The effect of clay dosage, leaching kinetics, potential microbial activities, and the effect of solution pH were investigated. A comparative assessment of the modified clays with commercial granular activated carbon (GAC) and biochar was also provided.

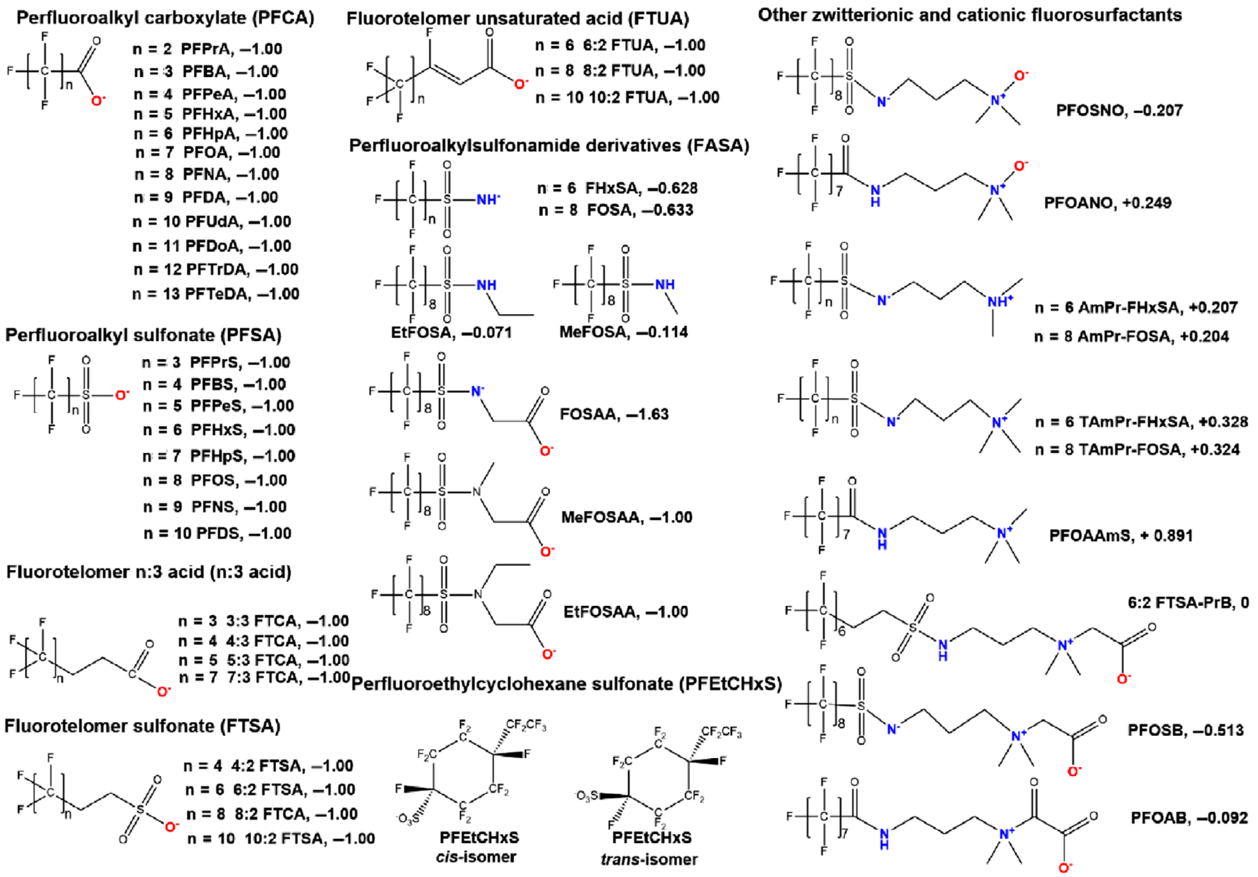
2 | MATERIALS AND METHODS

2.1 | Analytical standards and chemical reagents

Forty-nine standards of PFAS (see structures in Scheme 1) were quantitatively analyzed, including anionic, cationic, and zwitterionic compounds that have been detected in AFFF formulations or AFFF-impacted sites. In Scheme 1, ionizable groups and quaternary ammonium groups are marked out in red or blue colors. The charge status of each species was calculated for pH 7 using an online program SPARC (SPARC Performs Automated Reasoning in Chemistry) since no experimental values are available. Description of chemical standards, reagents, and experimental materials are provided in the Supplementary Materials (SM).

2.2 | Soil characterization

Four AFFF-contaminated soils were used in the study. Two soils (CAN1, CAN2) collected from one undisclosed Canadian site were donated by Environment and Climate Change, Canada. Two soils (US1 and US2) collected from a former US Air Force Base were provided by Minerals Technologies Inc. Soil characterization was performed by A&L Canada Laboratories Inc. using standard methods, and the details of the soil physical–chemical properties are provided in Table 1 as well as Table S1 and S2. Upon reception, the soils were air-dried for 48 h, and the fraction that passed through a 2-mm sieve was retained for the experiments. The moisture content of air-dried soils was determined gravimetrically after oven drying for 24 h at 105 °C. The results throughout the study are expressed as per gram of oven-dry soil weight where applicable.



SCHEME 1 The 49 PFAS that were targeted in the study and their overall charges at pH 7; a subset of the 49 PFAS was detected in four AFFF-impacted soils. The net charge of each molecule is the charge sum of all possible species of one specific PFAS compound at pH 7, as calculated via SPARC

TABLE 1 Properties of the four soils collected from two AFFF-impacted sites in the US and Canada

ID	Textural class	Sand (%)	Silt (%)	Clay (%)	Organic matter[a] (%)	CEC[b] (meq/100 g)	pH[c]	Total PFAS retained (ng/g)
CAN1	Loamy sand	89.2	0.8	10.0	0.4	32.6	8.0	59,783
CAN2	Loamy sand	83.2	4.8	12.0	0.6	6.8	6.0	3741
US1	Sand	91.2	0.8	8.0	0.3	7.3	7.9	1827
US2	Sand	93.2	0.8	6.0	0.4	7.4	7.9	2579

[a] Organic matter content was measured by weight loss on ignition at 360°C using an analytical balance.

[b] CEC was calculated as the sum of Ca^{2+}, Mg^{2+}, and Na^{+} concentrations from a Mehlich 3 extract.

[c] pH was determined by measuring 1:1 deionized water soil extract using pH electrode and mV meter.

2.3 | Adsorbent characterization

The modified clay FLUORO-SORB 100® (FS100) (bentonite modified with amine-based hydrocarbon intercalants) was provided by Minerals Technologies Inc. The particle size distribution of FS100 was determined using a laser diffraction particle size analyzer LA-950 (Figure S1, HPRIBA Ltd., Japan). X-ray diffraction (XRD) was conducted to demonstrate the structural difference between modified clay and nonmodified bentonite clay (Figure S2). Detailed sorbent characterization is provided in the SM. The capability of reducing PFAS leachability was also compared to a commercial granular activated carbon Filtrasorb 400 (Calgon Carbon Corporation, USA) and hardwood-based biochar (SKU-A 279, Charcoal House, USA). Both GAC and biochar were previously characterized, and the details can be found in two previous publications (Zhi & Liu, 2015, 2016).

2.4 | Soil leaching test

The soils were first subjected to solvent extraction using methanol-ammonium acetate extraction medium to reveal the full extent of PFAS contamination (Munoz et al., 2018) prior to leachability tests. As a standard leachability method for PFAS is not yet available, the US EPA method 1311 Toxicity Characteristic Leaching Procedure (TCLP) was modified for the present study to reduce adsorption loss of PFAS to vessel walls. Glassware was replaced by high-density polyethylene (HDPE) vessels, and all filtration steps were eliminated and substituted by high-speed centrifugations. Briefly, 5 g of air-dried sieved soil was weighed into each 60-ml HDPE bottle, and 50 ml of deionized water was added to reach a water-to-solid ratio of 10. The vessels were shaken on a horizontal shaker for 8 days at 150 rpm and 20°C in the dark. At each sampling time, a subsample was pipetted out and centrifuged at 20,000g for 10 min. The supernatant was taken out for further dilution with methanol and water (methanol: water = 80:20 v/v) and then stored at −20°C until chemical analysis.

Potential mass losses of PFAS due to adsorption by containers were evaluated for 60-ml HDPE bottles used in shaker tests. An aqueous solution (0.01 M NaCl) in HPDE bottles was spiked with eight PFAS authentic standards (PFOS, PFOA, PFDA, 6:2 FTSA, 8:2 FTSA, PFOAAmS, PFOAB and PFOSB) at 100 μg/L in triplicates and examined for concentration changes after 8-day equilibration under the same condition as leachability tests.

The role of leaching solution's pH was evaluated using soil CAN1 (see details in Table S3), as PFAS examined in the study could exhibit pH-dependent behaviors, the macro pKa values of all tested PFAS predicted by SPARC are listed in Table S24. Four extraction fluids with pH ranging from 4.0 to 8.0 were tested along with deionized water. Diluted 60/40 (w/w) sulfuric acid/nitric acid mixture and 0.01 N sodium hydroxide were used to adjust solution pH. Two grams of sieved CAN1 soil was mixed with 40 ml of an extraction fluid in HDPE bottles and kept agitated on a rotary mixer (30 ± 2 rpm) at 25°C for 3 days. As discussed in Section 2.2, the pH of leaching solutions was not observed to have any statistically significant impact on PFAS leachability. Therefore, later tests were performed using deionized water without pH adjustment, and solution pH was recorded at the end of each experiment (8 days).

2.5 | Assessment of adsorbent performance

The soil with the highest PFAS burden (Soil CAN1) was chosen to evaluate the effect of FS100 dosage, equilibration time, leaching kinetics, and potential microbial activities on PFAS leaching. FS100 dosages from 0.1% to 5% (w/w, clay/soil) were evaluated. Sodium azide (200 mg per 1-L leaching solution) was added to a subset to inhibit potential microbial activities. A comparative assessment was conducted at a dosage of 0.5% (w/w) for all the adsorbents (modified clay, GAC, and biochar) and all four soils. The same sampling procedures and preparation methods as described in Section 2.4 were used.

2.6 | Chemical analysis

All PFAS shown in Scheme 1 were quantified using authentic standards and internal standards, using the same method described in our previous study (Munoz et al., 2018). Quantitative analysis was performed by ultra-high-performance liquid chromatography coupled to a high-resolution accurate-mass Orbitrap mass spectrometry (UHPLC-HRMS). The separation was achieved by a Thermo Hypersil Gold C18 column (100 mm × 2.1 mm, 1.9 μm particle size). The Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was operated in Full Scan MS mode (mass scan range: m/z 150–1000) with a resolution setting of 70,000 FWHM at m/z 200. The instrumental analysis method was developed from the previous studies (Kaboré et al., 2018; Munoz et al., 2018; USEPA, 2019). Details on the instrumental analysis method are provided in the SM.

2.7 | Data analysis

The outcome of amending adsorbents was quantified by the reduction of PFAS aqueous concentration in soil leachate as compared to the nonamended soils using Equation (1):

$$\mathit{Concentration\ decrease}_{\mathrm{PFAS}}\,(\%) = 100\%(C_{\mathrm{NAm,PFAS}} - C_{\mathrm{Am,PFAS}})/C_{\mathrm{NAm,PFAS}}, \tag{1}$$

where $C_{NAm,PFAS}$ is the equilibrium aqueous concentration of a leached PFAS (or PFAS mixture) without an amended material and $C_{\mathrm{Am,PFAS}}$ is the equilibrium aqueous concentration with an amended adsorbent. Additionally, the leachable PFAS fraction relative to the total PFAS retained by soil was determined using Equation (2):

$$F_{\mathrm{Leaching\ PFAS}} = C_{\mathrm{Leaching\ PFAS}}\,(\mathrm{ng/g})/C_{\mathrm{PFAS\ retained\ by\ soil}}(ng/g), \tag{2}$$

where $C_{\mathrm{PFAS\ retained\ by\ soil}}$ was determined via the exhaustive soil solvent extraction with methanol and ammonium acetate, and $C_{\mathrm{Leaching\ PFAS}}$ was the mass of PFAS leached from each gram of soil, with or without the presence of an adsorbent amendment.

3 | RESULTS AND DISCUSSIONS

3.1 | PFAS detected in impacted soils

PFAS present in the AFFF-impacted soils (Figure 1) were determined by conducting multicycles of methanolic ammonium acetate soil extraction, an extraction medium found to greatly enhance the recovery of cationic and zwitterionic PFAS from soils (Munoz et al., 2018). Previously, the ASTM standard method (Method D7968-17a) using methanol-ammonia hydroxide was found to be ineffective for the recovery of certain nonanionic PFAS retained by soils (D'Agostino & Mabury, 2017; Mejia-Avendaño et al., 2017). Among 49 quantitatively monitored PFAS, 40 PFAS were detected in soil CAN1, 37 in CAN2, 32 in US1, and 25 in US2 (see Table S5). The summed concentration of quantifiable PFAS retained in four soils ranged from 1827 (Soil US1) to 59,783 ng/g (soil CAN1). PFOS was the most dominant PFAS detected in all soils, ranging from 868 to 44,441 ng/g and accounting for 33.7%–74.3% of total PFAS. Other abundant anionic PFAS were 8:2 FTSA (18–1109 ng/g), 6:2 FTSA (4.4–731 ng/g), PFHxS (12–483 ng/g), PFHxA (4.9–148 ng/g), and PFOA (14–108 ng/g). Polyfluoroalkyl compounds containing one or multiple ionizable groups that were detected at relatively high concentration included AmPr-FHxSA (zwitterion, 17–4111 ng/g), TAmPr-FHxSA (zwitterion, 109–3098 ng/g), FHxSA (anion, 91–545 ng/g), FOSA (anion, 81–366 ng/g), TAmPr-FOSA (zwitterion, 17–206 ng/g), and AmPr-FOSA (zwitterion, 1.2–145 ng/g). Their detection was expected, as studies have recently reported such nonanionic PFAS to make up a large fraction of fluorosurfactants in AFFF formulations (Adamson et al., 2020; Nickerson et al., 2020). The charge status of these compounds also varies widely, determined by one or multiple ionizable groups, as well as the permanently charged quaternary ammonium group (see Scheme 1). Our estimates using SPARC show that at pH 7 FHxSA and FOSA carry negative charges, while other major polyfluoroalkyl species

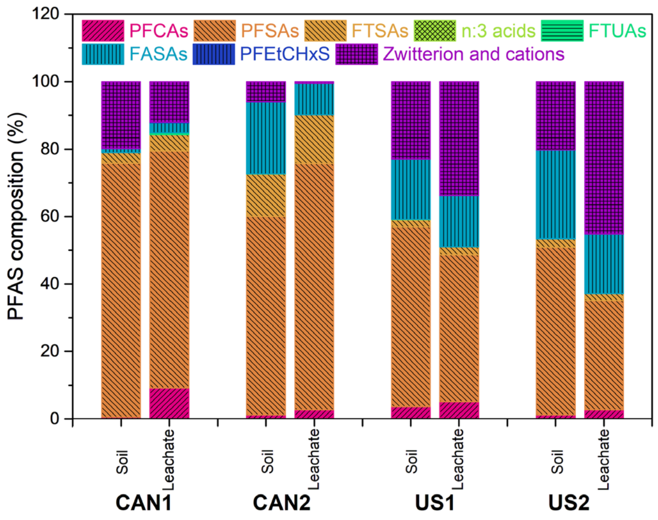


FIGURE 1 The PFAS compositions in four soils and their leachates (determined after a 7-day desorption test); because of low concentrations, n:3 acids and PFEtCHxS are not visible

carry net positive charges, the macro pKa values of all tested PFAS are listed in Table S24. Sorption and desorption behaviors of such polyfluoroalkyl compounds are highly dependent on chemical speciation and ambient pH; however, accurate pK_a values are not yet available, warranting further studies on the basic physicochemical properties of such compounds (Mejia-Avendaño et al., 2020).

3.2 | PFAS leaching profiles

The PFAS profiles in soil leachates were determined using the in-house modified TCLP procedures, where 8 days were found adequate for reaching equilibrium. More details on leaching kinetics can be found in Section 3.3. As shown in Figure 2 and Table S6, 31 types of PFAS were observed in the leachate of soil CAN1, 22 PFAS in the CAN2 leachate, 23 PFAS in the US1 leachate, and 22 PFAS in the US2 leachate. In a separate test, we found HDPE bottles retained little legacy anionic PFAS (less than 5%), but a significant amount of three zwitterionic and cationic PFAS (20%–45%) as shown in Figure S3. Therefore, the concentrations of some zwitterions and cations were likely underestimated in the leachate. The performance of amended materials (as discussed in Sections 3.3 and 3.4) was evaluated using Equation (1), which calculates the normalized difference between the PFAS leachate concentrations before and after the addition of soil amendment; therefore, the effect of adsorption is greatly minimized. In addition, as soils plus the amended materials are a more dominant sink than the HDPE containers, the adsorption on container walls has little influence on the assessment outcome (Higgins & Luthy, 2006).

In soil leachate, the predominant anions were PFOS, PFHxS, and 6:2 FTSA, but various types of polyfluoroalkyl zwitterions and cations were found to be readily leachable from soils, such as TAmPr-FHxSA, AmPr-FHxSA, TAmPr-

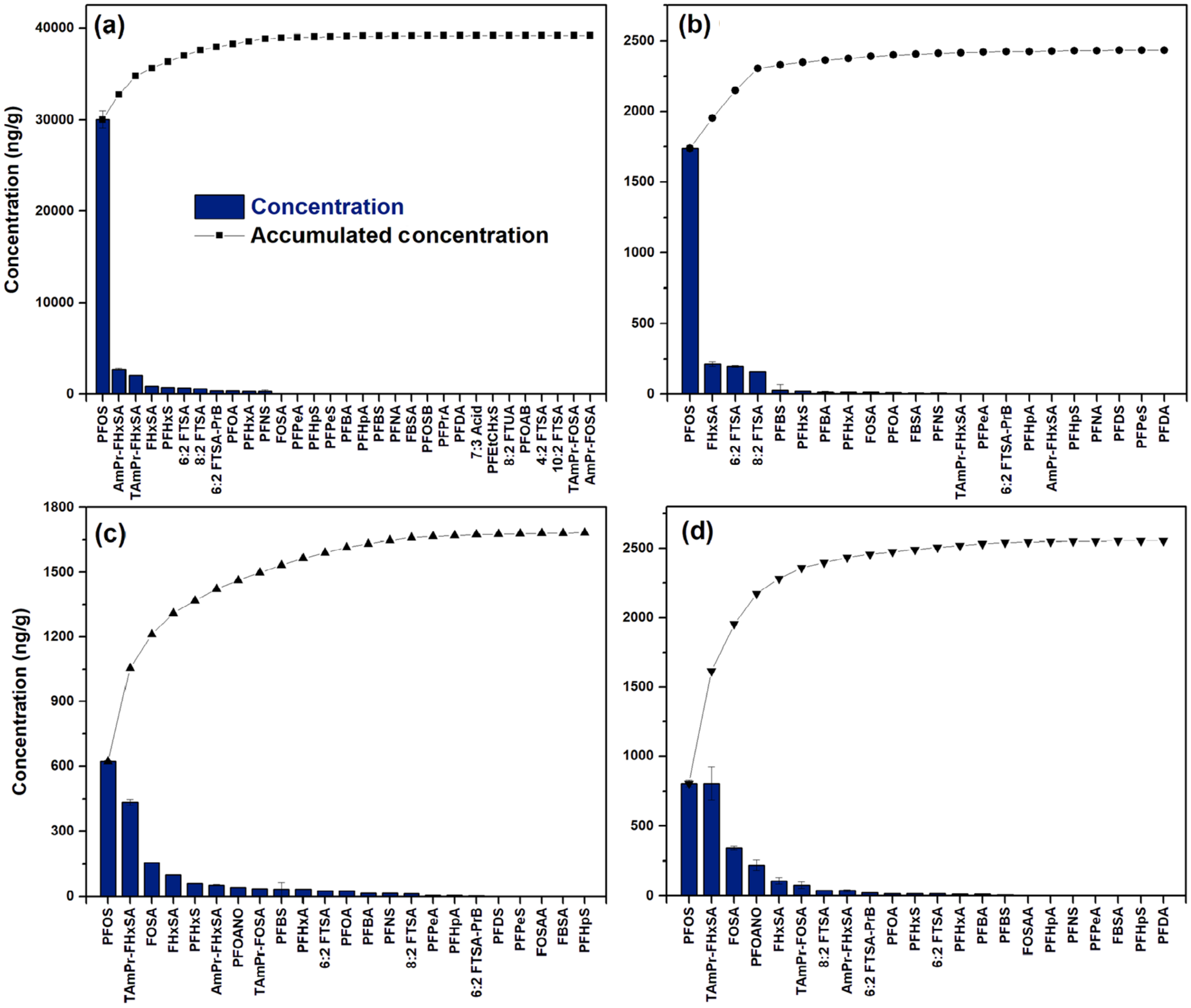


FIGURE 2 The PFAS profile in the leachate of each soil and contribution of each PFAS to the total PFAS concentrations. For the PFAS species, a total of 49 PFAS were monitored, and the ones below detection limits are not shown. (a) CAN1. (b) CAN2. (c) US1. (d) US2

FOSA, AmPr-FOSA, and PFOANO. Their general abundance roughly reflected their dominance in soils. The fractions of total leachable PFAS relative to total solvent extractable of CAN1, CAN2, US1, and US2 were 65.6%, 65.2%, 92.0%, and 98.9%, respectively. Notably, the fractions of PFAS by group in leachate significantly differ from those in soils, particularly for the zwitterionic and cationic PFAS. The percentage of zwitterions and cations in the leachates of CAN1 and CAN2 decreased from 19.8% and 6.0% to 12.1% and 0.4%, while increased from 22.9% and 20.2% to 33.7% and 45.2% in the cases of US1 and US2, respectively. The difference in PFAS leachability suggests that soil textural class may play a role and the sandy soils tend to leach out most of the PFAS (65%–99%) they retain. Whether such a trend can be generalized to other soils needs caution, as soil properties could greatly influence the desorption of nonanionic PFAS from soils (Nguyen et al., 2020; Schaefer et al., 2021; Xiao et al., 2019).

A few PFAS in leachate unexpectedly exceeded their levels in solvent extracts (see data in Tables S5 and S6), which was most likely caused by the transformation of select PFAS during storage. The transformation of polyfluorinated PFAS in aerobic soils has been well documented (Li et al., 2019; M. Liu et al., 2021; J. Liu & Mejia Avendaño, 2013). Solvent extraction of soil preceded the leaching test by 3 months, and biological activities in soils stored at room temperature might have caused changes in PFAS profiles. The increase in TAmPr-FHxSA and TAmPr-FOSA in US #1 and #2 soils could be due to the degradation of unidentified precursors, while many precursors can be degraded to form select PFCAs and PFSAs to increase their leachate concentrations as observed in CAN #1 soil. Note that biotransformation was likely in soils during the long-term storage but was not observed in the leaching experiments. Furthermore, soil heterogeneity could be another reason for the higher level of PFAS in leachate than soils. Nevertheless, the concentrations of dominant PFAS (e.g., PFOS, FOSA in all fours soils; AmPr-FHxSA and TAmPr-FHxSA in CAN #1 and #2) in soil leachates were lower than those of soil extract. The unintended transformation did not impact the outcome of the study.

The pH of the leaching fluid was evaluated using Soil CAN1, and the results are reported in Table S19. Based on the one-way analysis of variance at a level of 0.05, no significant impact was observed on either individual PFAS or the summed PFAS. The acid mixture or a base added to the leaching fluid also created higher ionic strength than deionized water. Though not directly evaluated, ionic strength at these low to moderate levels also did not appear to impact PFAS leaching. Previously, the sorption of several anionic PFAS (e.g., PFOS, PFOA) onto sediments exhibited a pH-dependent trend with weaker sorption observed at higher solution pH, attributed to the increasing electrostatic repulsion between the negative surface charge of sediment and the PFAS anions. However, since only one soil was evaluated in this study, assessment of the influence of pH on PFAS desorption or mobilization is needed in the future as part of the efforts to develop standardized leachability test methods.

3.3 | Effect of FS100 dosage on reducing PFAS leachability

Among four soils, Soil CAN1 with the highest PFAS load was used to determine experiment duration, the impact of FS100 dosage, and the role of microbial activities, with results shown in Figure 3 and Tables S7–S18. In the absence of an adsorbent amendment (0% in Figure 3a), the soil/water system reached equilibrium within 3–4 days in terms of total leachable PFAS, with a significant increase observed in the first 24 h (approximate 80% of the equilibrium concentration). In comparison, total PFAS concentration reached a plateau within 24 h in the presence of the FS100 amendment (0.1%–5% in Figure 3a). The control without sodium azide (0% No NaN_3 in Figure 3a) was set up to evaluate the effect of potential microbial activity because biotransformation of precursors would create additional anionic PFSAs or PFCAs. We did not observe any significant difference in total or individual PFAS concentration with and without the addition of sodium azide (0% amendment with NaN_3 vs. 0% amendment no NaN_3), which suggested there was little observable precursor degradation or microbial activities did not influence the outcome in this experiment. Previously, a C8 structural analog of TAmPr-FHxSA (i.e., TAmPr-FOSA) was found to undergo aerobic biotransformation in surface soil to form PFOS, but with a half-time greatly exceeding 180 days (Mejia-Avendaño et al., 2016). Similarly, FOSA can undergo biotransformation but also at a very slow rate (Avendaño & Liu, 2015). Given the relatively short observation window of the experiment, it is not unexpected that microbial biotransformation is negligible. We suspect that the soils used in the study were quite weathered before collection, and labile functional groups or PFAS probably had already been transformed in the field. Figure 3a also demonstrated that at equilibrium, about 70% of the reduction in total PFAS aqueous concentration in CAN1 leachate could be achieved with 0.1 wt% of FS100 as compared to no amendment, while 0.5 wt% of FS100 resulted in 90% removal in the aqueous phase (Figure 3a). Further increasing dosages to 1, 3, and 5 wt% could achieve 92%, 96%, and 98%, respectively, reduction of $\sum$PFAS after 8-day mixing.

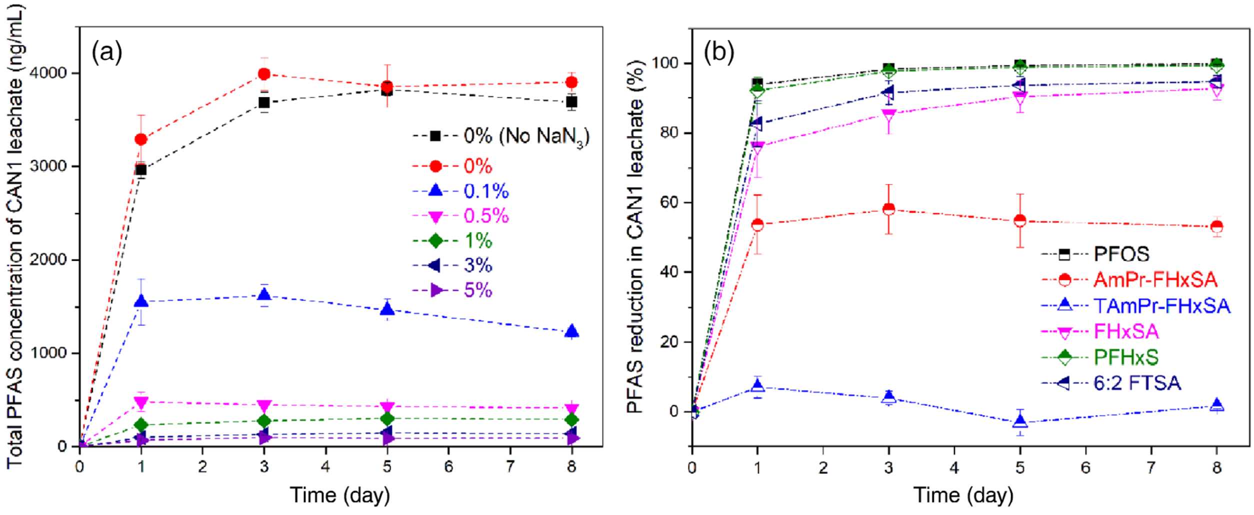


FIGURE 3 (a) The leaching kinetics of total PFAS from soil CAN1 with the addition of 0.1–5 wt% of FS100; (b) the leaching kinetics of the six dominant PFAS (PFOS, PFHxS, 6:2 FTSA, FHxSA, AmPr-FHxSA, and TAmPr-FHxSA) from soil CAN1 when 0.5% of FS100 was amended. The control without sodium azide (0% no NaN_3) was set to evaluate the effect of potential microbial activity because biotransformation of precursors would create additional anionic PFSAs or PFCAs

Figure 3b demonstrates the time course of the six dominant PFAS (PFOS, PFHxS, 6:2 FTSA, FHxSA, AmPr-FHxSA, and TAmPr-FHxSA) in the presence of a dosage of 0.5 wt% of FS100. Equilibration time shows some variability among different PFAS compounds and probably can be attributed to variable PFAS affinity for FS100 and their initial concentration. Still, 8 days were sufficient for the equilibrium to be established. At the low dosage of 0.5 wt%, FS100 can achieve ~99% removal for PFOS and PFHxS, ~90% removal for 6:2 FTSA and FHxSA, and ~55% removal for AmPr-FHxSA. However, TAmPr-FHxSA showed no decline over 8 days.

Figure 4a further shows the removal efficiency of six dominant PFAS in the CAN1 leachate at equilibrium, with the FS100 dose ranging from 0.1 to 5 wt%. Each PFAS species responded differently to increasing dosage. Very efficient removal of PFOS, PFHxS, 6:2 FTSA, and FHxSA can be achieved at a low dosage of 0.5 wt%. The further reduction of these four anionic PFAS at higher FS100 dosages was minor. However, for AmPr-FHxSA and TAmPr-FHxSA, the increasing trend in immobilization with an increasing weight percentage of the adsorbent appeared significant. TAmPr-FHxSA showed almost no removal at 0.1 wt% dosage, but about ~70% removal at 5 wt%. Figure 4b,c compare the PFAS leaching profiles from Soil CAN1 in the presence of 0.5 and 5 wt% FS100, respectively, and the contribution of each PFAS to ∑PFAS. Without FS100 (Figure 2a), 31 PFAS species were detected in the soil leachate, and ∑PFAS was as high as 3924 ng/ml. Amended with 0.5 wt% of FS100 (Figure 4b), 22 individual PFAS were identified in the leachate, with ∑PFAS declining to 413 ng/ml; when 5 wt% of FS100 was added (Figure 4c), only 13 types of PFAS were found in the amended CAN1 leachate with ∑PFAS of 91.4 ng/ml. Because of the highly effective removal of anions (e.g., PFOS and PFHxS), cationic TAmPr-FHxSA became the most dominant leachable PFAS in CAN1 soil leachate in the presence of FS100.

3.4 | Effect of PFAS speciation and charge

The equilibrium (8 days) solution pH in the presence of 0.5 and 5 wt% FS100 were determined to be 8.62 ± 0.06 and 8.61 ± 0.01, respectively, suggesting that the amount of clay adsorbents had little influence on solution pH. At such pH, the dominant species of strong (sulfonic) acids such as PFOS, PFHxS, and 6:2 FTSA were anions. FHxSA was also present largely as an anion with a net charge of −0.985 (calculated using SPARC for pH 8.61) because of the deprotonation of the sulfonamide group (Scheme 1). These anionic PFAS allow attractive charge–charge interactions with the positively charged quaternary ammonium group of the FS100 intercalant, enhancing their uptake by the clay adsorbent (Yan et al., 2020). Minor structural differences, yet very different removal efficiency (Figures 3b and 4a), can be observed between AmPr-FHxSA and TAmPr-FHxSA, showing the complex interactions zwitterions may engage in. At a pH of 8.61, both AmPr-FHxSA and TAmPr-FHxSA carry a negatively charged sulfonamide group [$-SO_2-N^{-}-$], which presumably forms attractive electrostatic interactions with the

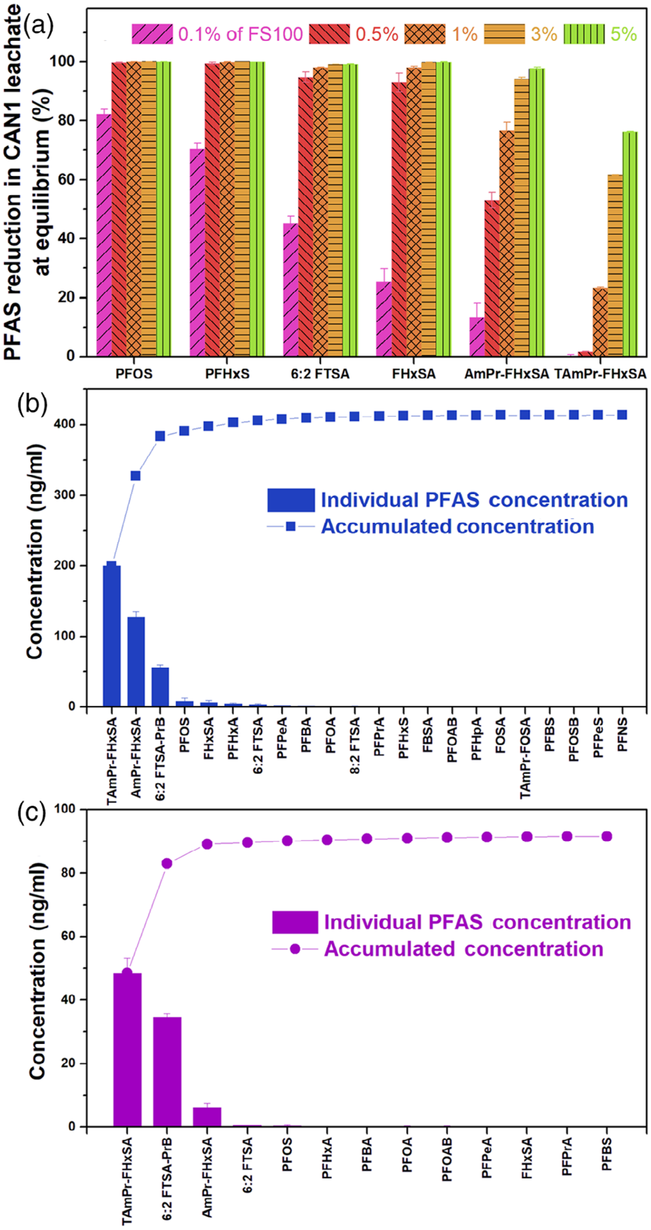


FIGURE 4 (a) Effect of FS100 dosage on the leachability of six dominant PFAS from soil CAN1 (measured after 8-day equilibration); PFAS that leached out from soil CAN1 with the addition of (b) 0.5 wt% and (c) 5.0% wt% of FS100

quaternary ammonium groups of intercalants of clay adsorbents. Furthermore, charge-dipole interactions can be formed between a positively charged head group of intercalant and perfluoroalkyl chain of both compounds, also facilitating the adsorption. However, TAmPr-FHxSA with a quaternary ammonium head group carries a more positive charge (+0.17 at pH 8.61) than AmPr-FHxSA (0 at pH 8.61) with an amine head group (Scheme 1). The relatively stronger electrostatic repulsion with the clay's intercalants might lead to the lower removal efficiency of TAmPr-FHxSA by FS100 than AmPr-FHxSA (Figures 3b and 4a). Therefore, the order by which FS100 exhibits removal efficiency for structurally similar compounds can be roughly ranked as: anionic PFAS> zwitterionic PFAS> cationic PFAS.

3.5 | Comparative assessment among FS100, GAC, and biochar

FS100, GAC, and biochar, all at 0.5 wt%, were compared for their ability to immobilizing PFAS in the field-contaminated soils (see details in Table S20-S23). The low dosage was purposefully chosen to reveal the difference between adsorbents. Results showed that the performance of amended adsorbents was closely related to PFAS type and PFAS concentration. As shown in Figure 5a, the extent of PFOS immobilization in four soils followed the order of FS100 > GAC > > Biochar. FS100 can achieve more than 99% of PFOS removal in all four soil leachates whose initial PFOS concentrations ranged from 62.1 to 3005 ng/ml. Meanwhile, GAC can also achieve an approximate 99% of PFOS reduction in soil CAN 2 and the two US soils when leachable PFOS (no soil amendment) was 62.1 to 174 ng/ml. For Soil CAN1 leachate with a leachable PFOS concentration of 3005 ng/ml, GAC could remove about 74.1% PFOS. In contrast, biochar showed almost no removal of PFOS in the soil slurry; PFOS decreased in the leachate ranging from −37.7% to 11.9%. The negative value probably resulted from sampling variability, compounded by the analytical variation. Previously, Kupryianchyk et al. (2016) also reported a small to no PFOS decrease in pore water concentration when two biochars made from either mixed wood and or paper mill waste were amended to PFAS-contaminated soil. The hardwood biochar was previously found to effectively remove anionic PFAS from a clean water matrix (Zhi & Liu, 2018); the complex matrix of soil-water slurry in this study might diminish biochar performance. Additionally, Hale et al. (2017) also observed the net increase of certain anionic PFAS (e.g., PFBS, PFHxS and PFNA) after adding soil amendment. Although our preliminary test of adding NaN_3 to FS100-amended soil did not show microbially catalyzed generation of anionic PFAS, the possibility cannot be completely ruled out for the biochar-amended soil. The challenges of working with the precursors need to be considered as a case-by-case scenario, depending on the types of AFFFs applied to the soil, and natural attenuation processes that the soil has experienced, as well as microbial activities present in a system.

As previously discussed, FHxSA as a sulfonamide is predicted to carry a negative charge (−0.985) at pH 7, so

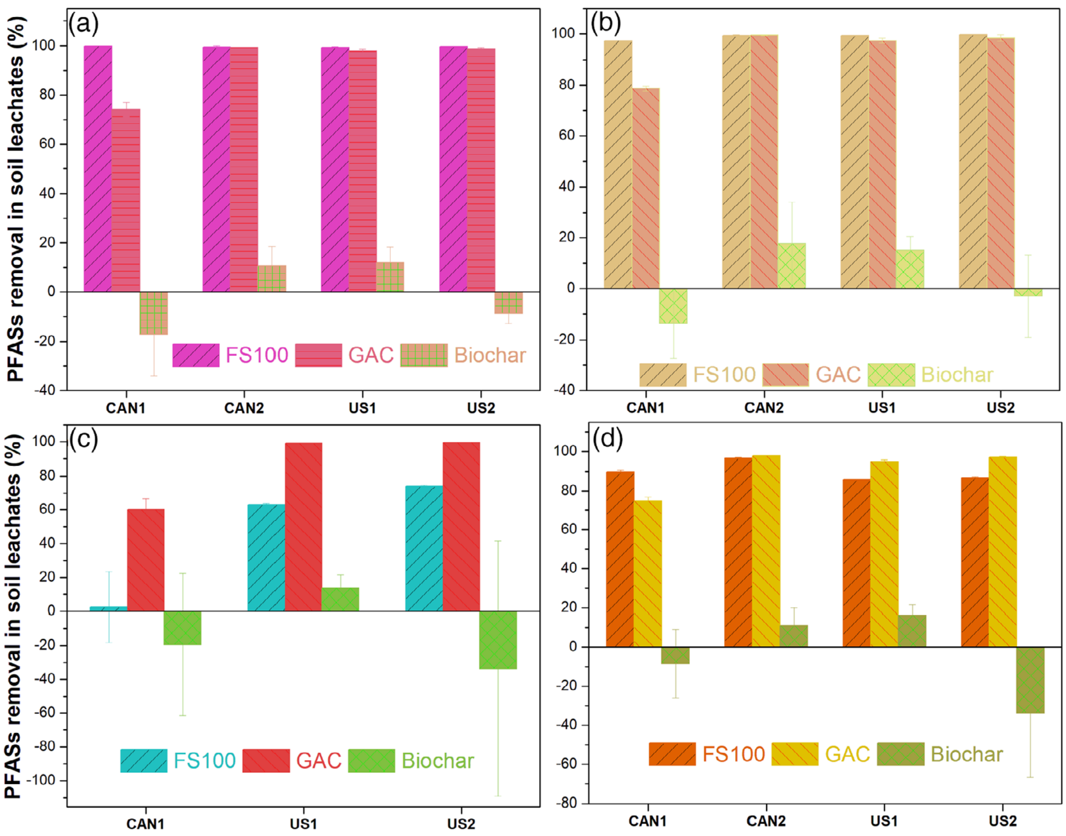


FIGURE 5 Comparison of performance of three adsorbents (Fluorosorb 100, granular activated carbon and wood biochar) in decreasing the leachability of (a) PFOS, (b) FHxSA, (c) TAmPr-FHxSA, and (d) total PFAS from four contaminated soils at the sorbent dosage of 0.5 wt% (n = 3)

at a pH of 8.61 it should behave as an anionic compound; the observed removal efficiency followed the same pattern as PFOS, confirming the anionic nature of FHxSA (Figure 5b). FS100 can achieve around 99% of FHxSA removal in all soil leachates when the leachable FHxSA concentrations ranged from 9.9 to 86.0 ng/ml. Meanwhile, GAC could reduce approximately 99% of FHxSA when starting leachable concentrations that ranged from 9.9 to 21.3 ng/ml. For the leachate of soil CAN1 with an initial FHxSA of 86.0 ng/mL, GAC achieved 78.7% of removal. Again, biochar could not lower FHxSA levels in soil leachates, with concentration changes ranging from −39.6% to 18.5%.

Figure 5c illustrated the decrease in leachability of TAmPr-FHxSA in 3 soil leachates (CAN1, US1, and US2) with the addition of 0.5% of FS100, GAC, or biochar; Soil CAN2 is excluded from the discussion due to the low leachable TAmPr-FHxSA level. When the initial TAmPr-FHxSA concentration in soil leachate was in the range of 43.5–80.7 ng/ml, GAC can achieve 99% removal, while FS100 can reach 63.0%–73.8%. When the TAmPr-FHxSA concentration was relatively high (i.e., 203 ng/ml in CAN1 leachate), GAC could achieve a 60.3% reduction while FS100 achieved 4.6%. Clearly, a dosage of higher than 0.5 wt% would be necessary for GAC or FS100 to substantially lower leaching of the cationic PFAS. In scenarios where anionic and cationic PFAS co-exist, applying a mixture of GAC and FS100 could be more effective than using one type of adsorbent alone. Biochar again showed almost no removal of TAmPr-FHxSA (from −44.4% to 13.8%). The experimental data for other individual PFAS in the presence of 0.5 wt% of FS100, GAC, or biochar are provided in the SM.

Figure 5d showed the removal of ∑PFAS by three adsorbents amended at 0.5 wt%, where the performance of each adsorbent can be in part explained by the relative abundance of anionic PFAS versus nonanionic ones. Soil CAN1's leachate was dominated by anionic compounds, with zwitterionic and cationic ones making up only a small fraction of ∑PFAS (~12%); FS100, which is highly effective for removing anionic PFAS, showed higher efficacy (89.7%) than GAC (74.8%), consistent with the pattern of PFOS (Figure 5a). For Soil CAN2, the cationic PFAS composition (1 ng/ml) is negligible in total leachable PFAS (246 ng/ml); both FS100 and GAC achieved similarly high removal (>96%). For the Soil US1 and

US2, the initial leaching concentrations were at a similar level (255 ng/ml for US2), or lower (168 ng/ml for US1) than that of CAN2, but zwitterionic and cationic PFAS made up higher fractions (34% and 45%, respectively, for US1 and US2). Hence, GAC (95.0% of immobilization for US1 and 97.2% for US2) performed better than FS100 (85.7% of immobilization for US1 and 86.7% for US2). Clearly, the type of leachable PFAS and initial leachate concentration are two critical factors strongly influencing the adsorbent performance. The biochar overall had little capacity to immobilize any PFAS, and therefore, the total PFAS removal efficiency of biochar in the soil leachates was very low, −28.9%–16.4%.

4 | CONCLUSIONS

Technologies applicable on a field scale offer hope for mitigating the impact of PFAS-impacted soils on adjacent water bodies; meanwhile, PFAS linked to severe soil pollution go beyond the legacy PFAAs. In this study, PFAS profiles in four AFFF-contaminated soils and their leachates demonstrated the significant presence of both anionic and nonanionic PFAS, while the presence and mobility of the latter have not been sufficiently discussed. Therefore, in comparing the performance of the new clay-based adsorbents (FS100) with other carbonaceous materials, we tested their ability to reduce the leachability of anionic versus other zwitterionic and cationic PFAS.

The study provides a comprehensive dataset for in situ PFAS stabilization. Although the field application rate can be more than 10 wt%, we found FS100 dosage as low as 0.5 wt% can reduce the leachability of anionic PFAS consistently by 90%–99%, and a higher dosage can also effectively lower the aqueous levels of nonanionic PFAS (70%–99%). Note that dosage rates evaluated through laboratory shaker tests by no means suggest a field application rate, which should be determined by taking into consideration site conditions, the lack of mixing, and other practical considerations. Nevertheless, our comparative assessment showed that the order of effectiveness generally followed the rank of FS100 > GAC> > biochar for immobilizing anionic PFAS and GAC > FS100> > biochar for cationic PFAS. Comprehensive characterization of soil properties, as well as thorough identification and quantification of PFAS, is essential to ensuring the right amendment or a combination of several adsorbents to be selected.

Our findings contribute to developing low-cost and easy-to-implement soil remediation technology for PFAS-contaminated soils and water and also reveal some knowledge gaps that create some uncertainty. Standardized methods for assessing PFAS leachability are not yet available, preventing a fair comparison of results across different studies and projects. Speciation behaviors of many dominant PFAS (e.g., AmPr-FHxSA, FHxSA) so far are solely dependent on predicted values, which could vary significantly from one software package to another platform to another; experimentally validated data are therefore urgently needed. Finally, investigations on how reliably the modified clays can retain PFAS in field conditions and resist weathering and dispose of spent adsorbents safely are warranted.

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CONFLICT OF INTEREST

The authors report no conflicts of interest.

AUTHOR CONTRIBUTIONS

Chenyang Wang: Data curation; investigation; methodology; writing - original draft. **Bei Yan:** Data curation; investigation; methodology; writing-review & editing. **Gabriel Munoz:** Investigation; methodology; writing-review & editing. **Sébastien Sauvé:** Supervision; writing-review & editing. **Jinxia Liu:** Conceptualization; supervision; funding acquisition; methodology; project administration; writing-review & editing.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in the supplementary materials of this article at http://doi.org/10.1002/aws2.1241

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

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