Science of the Total Environment 912 (2024) 168931

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Remediation of PFAS-impacted soils using magnetic activated carbon (MAC) and hydrothermal alkaline treatment (HALT)

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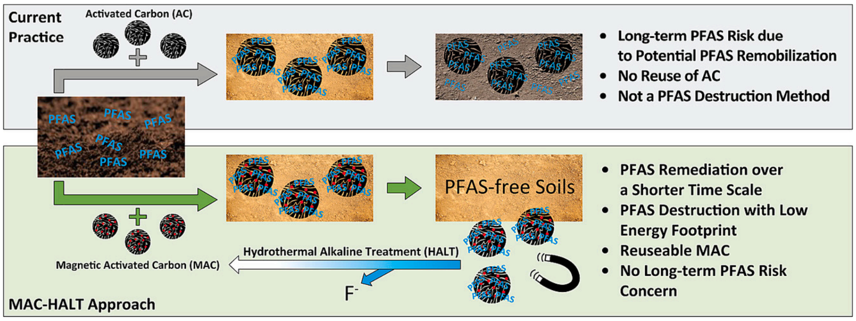
HIGHLIGHTS

- Magnetic activated carbon (MAC) sorbed PFAS from contaminated soils.
- Soil organic contents affected PFAS removal by MAC.
- Spent MAC can be magnetically separated from the treated soils.
- HALT technology destroyed and defluorinated PFAS adsorbed on MAC.
- HALT did not compromise the MAC sorption and magnetic properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jay Gan

Keywords:
Per- and polyfluoroalkyl substances (PFAS)
Magnetic activated carbon (MAC)
Hydrothermal alkaline treatment (HALT)
AFFF-impacted soils

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic pollutants that are bioaccumulative, toxic, and persistent. One long-term source for PFAS release is PFAS-contaminated soil. Addition of activated carbon (AC) to soil has shown the potential to immobilize PFAS and reduce PFAS bioavailability, but PFAS-loaded spent AC remaining in the treated soil could lead to remobilization. Here we report a novel approach to address this challenge. By applying magnetic activated carbon (MAC) to remediate PFAS-impacted soil, the PFAS-loaded MAC can be retrieved from the treated soil and sorbed PFAS in the spent MAC can be destroyed using hydrothermal alkaline treatment (HALT). Effective MAC recovery was observed when water/soil ratios (w/w) were either <0.07 or >1. Soil organic content and pH affected PFAS adsorption by the MAC added to soil. After three months of incubation with MAC, high PFAS removals [PFOS (87.6 %), PFOA (83.8 %), and 6:2 FTSA (81.5 %)] were observed for acidic environmental sandy soils with low organic content. In contrast, PFAS removal by MAC was poor for garden soils with high organic matter content. MAC was also used to remediate aqueous film-forming foam (AFFF)-impacted and PFAS-contaminated aged soils with varying PFAS removal performance. HALT technology was able to destroy and defluorinate PFAS adsorbed to the spent MAC. Additionally, the HALT-treated MAC retained its magnetic properties and PFOS sorption capacity, suggesting the potential reusability of HALT-treated MAC. Considering the low energy footprint of HALT compared to conventional PFAS thermal

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https://doi.org/10.1016/j.scitotenv.2023.168931
Received 24 August 2023; Received in revised form 24 November 2023; Accepted 25 November 2023

destruction techniques, the combination of MAC and HALT could be a promising treatment train for PFAS-contaminated soils.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic fluorinated chemicals that have been widely used in consumer products and industrial applications, including food-contact paper, textiles, pesticide formulations, coatings, and aqueous film-forming foams (AFFFs) (Buck et al., 2011; Wang et al., 2017). The unique properties of PFAS – chemically stable and present with both hydrophobic and lipophobic moieties – enable their wide application. Yet, the same properties also make PFAS persistent, bioaccumulative, and toxic, triggering serious public health concerns (Poothong et al., 2020; Post, 2021; Rand and Mabury, 2017; Ruan et al., 2019; Suja et al., 2009). PFAS have been detected at varying levels in natural and engineered environments, including groundwater, soil, sediments, landfill leachate, drinking water and wastewater treatment plants (Crone et al., 2019; Cui et al., 2020; Lenka et al., 2021; Liu et al., 2022; Lyu et al., 2022; Podder et al., 2021; Wang et al., 2017). PFAS-contaminated soils are long-term sources for PFAS exposure, as sorbed-PFAS can leach into and migrate through groundwater, be taken up by vegetation, or undergo further transport into downgradient soils and nearby waterbodies through run off (Brusseau et al., 2020; Guelfo and Higgins, 2013; Houtz et al., 2013; Lyu et al., 2022; Strynar et al., 2012; Wanzek et al., 2023). Thus, effective remediation technologies to treat PFAS-impacted soils and mitigate risks of human exposure are critically needed.

Remediation of PFAS-impacted soils remains challenging, and cost-effective remediation methods are not yet available. Current and emerging soil remediation technologies include soil washing or soil liquefaction, ball milling, thermal treatment, chemical oxidation and reduction, bioremediation and phytoremediation, and immobilization via sorbent amendments (Kang et al., 2023; Mahinroosta and Senevirathna, 2020; Shahsavari et al., 2021). Effectiveness of these technologies is limited, and several major challenges persist including difficulties in field scale-up, high cost, low removal efficiency, or incomplete destruction of PFAS. Among these technologies, soil amendment with activated carbon (AC) has been shown to effectively immobilize some PFAS (such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS)) from a firefighting training site at an airport in Norway (Kupryianchyk et al., 2016). However, because the AC-immobilized PFAS are not destroyed, they remain a long-term source that may be remobilized in the future. Ideally, the PFAS-loaded AC could be recovered from soil and further treated to ensure PFAS destruction.

Recent studies modified AC by adding magnetic materials (i.e., magnetic activated carbon (MAC)) to facilitate separation and recovery of the adsorbent material (Meng et al., 2019; Ren et al., 2021). Moreover, granular AC (GAC) composite with iron (II, III) oxide (Fe_3O_4; magnetite) has been found to enhance PFOA adsorption, attributed to concurrent electrostatic and hydrophobic adsorption mechanisms (Xu et al., 2020). However, a higher ratio of Fe_3O_4-to-AC could also result in decreased PFOS adsorption capacity (Meng et al., 2019). Use of MAC to remove several classes of contaminants has been documented, including heavy metals (Faulconer et al., 2012; Zhang et al., 2021), dyes (Moosavi et al., 2020), nitroaromatic explosives (Mohan et al., 2011), pharmaceuticals (Rocha et al., 2020; Saucier et al., 2017; Shan et al., 2016), polycyclic aromatic hydrocarbons (PAHs) (Inbaraj et al., 2021), and various other types of contaminants (Oliveira et al., 2002). However, many have focused on the application of MAC in aqueous matrices with incomplete experimental results on how the sorbed contaminants could be further handled or disposed efficiently. Previous applications of MAC for soil treatment include remediation of PAHs (Han et al., 2015a; Mirzaee and Sartaj, 2022) and control of soil phosphorous content (Lin et al., 2019). A growing body of research also exists regarding adsorption of PFAS within aqueous systems (Vu and Wu, 2022) and contaminated soils (Bolan et al., 2021). However, physical retrieval of sorbed PFAS using MAC in PFAS-impacted soil has not been reported. MAC (Meng et al., 2019) and another type of magnetized adsorbent (Yan et al., 2014) have been confirmed for adsorptive PFAS removal but were not shown to treat contaminated soil. Moreover, further treatment of adsorbent-immobilized PFAS has not been addressed.

Conventionally, the regeneration of GAC and destruction of adsorbed PFAS is concomitantly carried out at off-site centralized facilities by using high temperature thermal treatment processes. Unfortunately, such processes could potentially destroy magnetic properties of the embedded Fe_3O_4 (Cendrowski et al., 2017). Therefore, a milder treatment process is desirable to destroy PFAS and simultaneously regenerate MAC with magnetic properties retained. Recently, some of the present authors demonstrated effective destruction of PFAS adsorbed to GAC using a hydrothermal alkaline treatment (HALT) process, where the GAC is exposed to subcritical water (350 °C, 16.5 MPa) amended with NaOH (Soker et al., 2023). Stoichiometric defluorination was observed and tests showed that the HALT process did not negatively affect PFAS adsorption to the GAC, suggesting HALT may be a promising strategy for regeneration of adsorbents with a potentially lower energy footprint.

Here, we report the feasibility of using MAC in combination with HALT to remediate PFAS-contaminated soils. Initially, MAC is mixed with soil to adsorb PFAS and reduce soil-phase PFAS concentrations. Following the desired treatment time, magnets are used to separate PFAS-loaded MAC from the treated soils. Finally, the PFAS-loaded MAC is treated using HALT to destroy the adsorbed PFAS and potentially regenerate the MAC for reuse. Effects of water/soil ratios on magnetic separation of MAC from soil-MAC mixtures were also evaluated. The effectiveness of MAC for remediating PFAS-spiked and PFAS-contaminated soils with different properties, including varying texture, pH, and organic contents, was determined. Effective defluorination of PFOS adsorbed to spent MAC using HALT was also demonstrated using fluorine mass balance experiments.

2. Materials and methods

2.1. Chemicals and soil

2.1.1. Chemicals

Perfluorooctanesulfonic acid (PFOS, CAS# 1763-23-1) was purchased from TCI America (Portland, OR, USA). Perfluorooctanoic acid (PFOA, 95 % pure, CAS# 335–67-1) was purchased from Alfa Aesar (Lancashire, UK). 1H, 1H, 2H, 2H-Perfluorooctanesulfonic acid (6:2 FTSA, 98 % pure, CAS# 27619-97-2) was purchased from Synquest Laboratories (Alachua, FL, USA). Dichloromethane (DCM, HPLC grade, CAS# 75–09-2), methanol (MeOH, HPLC grade, CAS# 67-56-1), and ammonium hydroxide (NH_4OH, trace metal grade, 20 %, CAS# 1336-21-6) were purchased from Fisher Scientific (Pittsburgh, PA, USA). The activated charcoal DARCO® (100 mesh particle size, powder, CAS# 7440-44-0), iron chloride ($FeCl_3•6H_2O$, reagent grade, 97 % pure, CAS# 77-5-08-0), and the graphitized non-porous carbon powder Supelclean™ ENVI-Carb™ (CAS# 7782-42-5) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH, GR 97 % pure, CAS# 1310-73-2) was purchased from EM Science (Gibbstown, NJ, USA). Ferrous sulfate ($FeSO_4•7H_2O$, CAS# 7782-63-0) was purchased from J.T. Baker (Philipsburg, NJ, USA). Nitric acid (HNO_3, ACS reagent, 68–70 %, CAS# 7697-37-2) was purchased from Acros Organics (NJ, USA). Hydrogen peroxide (H_2O_2, ACS reagent, 30 %, CAS# 7722-84-1) was purchased from Macron (Center Valley, PA, USA).

2.1.2. Soil

Three clean soil types, designated as commercial sandy soil, environmental sandy soil, and Sunshine organic soil, were used in the PFAS-spiked experiments. Commercial sandy soil was prepared by mixing 95 % of sand (Pavestone, USA) and 5 % of perlite (Scotts Miracle-Gro®, USA). Environmental sandy soil (designated as C2 soil) was provided by Oregon State University. Sunshine organic soil (garden soil; Sphagnum peat moss, Scotts Miracle-Gro®, USA) was purchased at a local store in College Station, Texas. Soils that were aged with PFAS were used in separate experiments. An aged PFAS-contaminated garden soil was originally created by spiking a mixture of PFAS into the Sunshine organic soil for other research projects conducted in 2018 (hereafter referred as Sunshine PFAS-contaminated soil). Thus, the Sunshine PFAS-contaminated soil was aged at room temperature for >4 years before use in experiments detailed here. Another PFAS-contaminated soil was collected from an aqueous film-forming foam (AFFF)-impacted area at an Air Force base in San Antonio, TX (hereafter referred to as San Antonio AFFF-impacted soil).

2.2. Synthesis and characterization of magnetic activated carbon (MAC)

Magnetic activated carbon was prepared by a chemical coprecipitation method described previously with some modifications (Choi et al., 2016; Han et al., 2015b). Briefly, 7.32 g $FeSO_4\bullet7H_2O$ and 13.32 g $FeCl_3\bullet6H_2O$ were added into 500 mL of water that was preheated to 60 °C. Ten grams of PAC were added slowly into the solution with continuous mixing and sparging with N_2, followed by heating to 70 °C for 5 min. After cooling, NaOH (5 M) was added slowly to raise pH to 10. The solution was then mixed at 150 rpm for 24 h. The resulting MAC was then recovered from the mixture using a neodymium rectangular magnet bar (33 lbs. pulling force per magnet, 6 cm × 1 cm × 0.5 cm; DIYMAG) and washed 3 times with deionized (DI) water and 1 time with ethanol. The resulting material was then dried at 105 °C and used for experiments. The synthesized MAC along with the original PAC were characterized using X-ray diffraction (XRD) analysis (MiniFlex benchtop system, Rigaku, Japan) at the Baker Hughes Materials Laboratory at Texas A&M University.

2.3. Water/soil ratio impact on MAC recovery from soil-MAC mixtures

Experiments were conducted to determine the effects of water content on MAC recovery from soil-MAC mixtures. The magnetism of MAC was first confirmed using a neodymium rectangular magnet bar as described previously. A fixed weight ratio of 20:1 of commercial sandy soil to MAC was used for this experiment. Briefly, 4 g of clean sandy soil and 0.2 g of MAC were added to a series of glass test tubes and vigorously mixed before the addition of a known amount of water to create desired water/soil ratios (w/w) of 0, 0.357, 0.5, 1, and 2. Then, a neodymium rectangular magnet bar was used to separate MAC from the soil-MAC-water mixture. The test tube was held tilted ($30 \sim 60^o$) and rotated multiple times to facilitate the separation of MAC from the soil mixture, resulting in MAC being captured on the upper region of the tilted test tube while the soil settled to the bottom of the tube. The remaining soil was carefully scraped out using a spatula, and any soil particles adhering to the tube were removed with DI water. The recovered MAC and the soils were then dried in an oven at 105 °C and weighed after 18 h. Soil-free controls (1 mL DI water and 0.2 g MAC) were conducted for comparison. Recovery of MAC was calculated based on weight of recovered MAC per weight of MAC added.

2.4. Effectiveness of MAC to remediate PFAS-contaminated soil

Experiments were conducted to investigate the effectiveness of MAC to remove PFAS from PFAS-spiked soils and PFAS-contaminated aged soils. Three types of clean soils (commercial sandy soil, environmental sandy soil, and Sunshine organic soil) were used directly without drying. Briefly, 100 μL of 10 mg/L PFAS (PFOA, PFOS, or 6:2 FTSA) stock solutions (total mass 1 μg) were separately spiked into 50 mL Falcon Conical Tubes (Corning, USA) containing 10 g of clean soils. After PFAS spiking, the tube was vortexed to achieve initial concentration of 0.1 μg PFAS/g soil. Then, 0.5 g MAC was added into the PFAS-spiked soil and then vortexed again, achieving 5 % MAC (w/w) in the PFAS-spiked soil. The selected percentage of MAC amendment was based on the prior use of 2–4 % of carbonaceous materials that have shown effective performance for the removal of polychlorinated biphenyls and PAHs from sediments (Kupryianchyk et al., 2016; Zimmerman et al., 2005). The MAC-amended tubes were then incubated on a shaker at 150 rpm and 30 °C. Due to different densities of soils and MAC, the tubes were also rotated by hand twice weekly to avoid stratification and to ensure thorough mixing of MAC with PFAS-spiked soil. Two parallel sets of experiments using PFAS-impacted aged soils (San Antonio AFFF-impacted soil and Sunshine PFAS-contaminated soil) were also conducted using the same procedures, except that no external PFAS was amended before mixing with MAC. The MAC was recovered from the soils after one or three months of incubation. After separating MAC from the soils, residual concentrations of PFAS in the soils were extracted and analyzed by LC/MS. The PFAS in the recovered MAC samples was then defluorinated using HALT as described in Section 2.6.

2.5. PFAS extraction and analysis

The PFAS in the remaining soil samples (after separation of MAC) were extracted as described by Yang et al. (Yang et al., 2022). Briefly, 5 mL of 50:50 (v/v) DCM and MeOH solution with 1 % NH_4OH (v/v) was added to a 15 mL polypropylene Falcon conical tube containing a soil sample. After vortexing for 30 s, the tube was shaken (KS 260 basic, IKA®, USA) at 200 rpm at 37 °C for 1 h. The supernatant was then collected after centrifugation at 1500 rpm for 5 min (Sorvall™ Legend™ XTR, Thermo scientific, USA). The extraction process was repeated twice. Extracts were pooled, dried by purging with a gentle nitrogen gas stream, reconstituted in 1 mL of MeOH, and equilibrated with 50 mg of ENVI-Carb™ solid-phase extraction resin. Based on spike-recovery tests, the average recovery of this extraction process was 98.2 % for soil. Extracts were analyzed using LC-QqQ-MS as described previously (Yang et al., 2022). A Hypersil GOLD™ column (3 mm × 50 mm, 5 μm) (Thermo Scientific, USA) was used on a Vanquish ultra-high performance liquid chromatography (UHPLC) system (Thermo Scientific, USA); the sample injection volume was 10 μL. Quantification was achieved using an Altis™ triple-quadrupole mass spectrometer (Thermo Scientific, USA).

The collected MAC samples were extracted two to three times, depending on their initial PFAS content, using MeOH containing 100 mM ammonium acetate as described previously (Xiao et al., 2020). Depending on the mass of sample available, 50–150 mg MAC were extracted with 10–25 mL of the MeOH-ammonium acetate mixture. HALT experiments and MAC extracts were performed at a Colorado School of Mines and analyzed there using LC-QTOF-MS (X500R QTOF, Sciex, USA). A Sciex ExionLC™ high-pressure liquid chromatography (HPLC) system was used with a Gemini C18 analytical column and 1.0 mL injection volume. The QTOF-MS ran using electrospray ionization in ESI- mode with SWATH Data-Independent Acquisition, following analysis conditions described previously (Hao et al., 2021). Limit of quantification (LOQ) and limit of detection (LOD) values for the reported compounds are listed in Table S1 in the Supporting Information (SI).

2.6. PFAS defluorination from spent MAC using HALT

Two to five hundred mg of spent MAC were combined with 3 mL of 1 M NaOH and sealed in a stainless-steel mini-tube reactor (6 mL). The reactor was heated to 350 °C using a fluidized sand bath for the desired reaction time before quenching in room-temperature water. Following treatment, the MAC-NaOH slurry from the reactor was placed in a 50 mL centrifuge tube and centrifuged at 3000 rpm for 10 min to separate the MAC from the liquid. The supernatant was collected, after which MAC was rinsed with Milli-Q water to remove any residual hydroxide. MAC samples taken before and after treatment with HALT were subjected to extraction with 100 mM ammonium acetate in MeOH to recover any residual PFAS.

Fluorine mass balance experiments were conducted by initially adsorbing a known mass of PFOS to MAC before treatment (4.61 ± 0.06 mg PFOS/g MAC) and measuring fluoride release into the reactor liquid following HALT (350 °C, 1 M NaOH, 167 g/L PFOS-loaded MAC, 30–240 min). An Orion ion-selective electrode (Thermo Scientific, USA) was used to quantify fluoride, and PFOS was quantified using LC-QTOF-MS (X500R QTOF, Sciex, USA) to complete the mass balance by accounting for stoichiometric defluorination. MAC samples treated by HALT for 90 and 240 min were also analyzed through XRD to identify any changes in MAC composition that might occur following exposure to HALT reaction conditions.

Experiments to evaluate PFAS removal on MAC that was incubated with San Antonio AFFF-impacted soil were performed with 200 mg of recovered MAC (350 °C, 1 M NaOH, 67 g/L spent MAC, 240–600 min). Released fluoride was not measured because the low initial concentrations of adsorbed PFAS made fluoride quantification infeasible near the detection limit (0.02 ppm). PFAS destruction was calculated based on PFAS concentrations from the pre- and post-treatment MAC extracts.

3. Results and discussion

3.1. Soil and MAC characteristics, and water/soil ratio effect on magnetic separation

The characteristics of soils used in this study are listed in Table 1. Soil moisture contents ranged from 2.93 to 6.57 % (w/w of soil) and soil pH values ranged from 4.9 (environmental sandy soil) to 7.2 (San Antonio AFFF-impacted soil). The conductivity of San Antonio AFFF-impacted soil was 2350 μmho/cm, which was significantly higher than the other soils (50 and 579–693 μmho/cm), likely due to its higher content of calcium (7075 ppm) and potassium (386 ppm). Sunshine organic soil had the highest organic carbon content (56.93 %), followed by the San Antonio PFAS-impacted soil (9.94 %), Sunshine AFFF-contaminated soil (7.15 %), and environmental sandy soil (0.05 %). Textural analysis was not feasible for Sunshine organic soil. Based on size distribution, sand accounts for around 70– 79 % in all soil types except for the unknown Sunshine organic soil.

Table 1
Properties of soils used in this study.

Analysis	Environmental sandy soil	Sunshine organic soil	San Antonio AFFF-impacted soil	Sunshine PFAS-contaminated soil
Particle Size distribution	250–500 μm (70.19 %) Sandy	Unable to determine due to high organic content	Sand 79 % Silt 13 % Clay 8 % Loamy Sand	Sand 78 % Silt 14 % Clay 8 % Loamy Sand
Water content % (w/w)	2.93	5	5.49	6.57
pH	4.9	5.7	7.2	6.1
Conductivity (μmho/cm)	50	693	2350	579
Nitrate-N (ppm)[a]	3	119	25	134
Phosphorus (ppm)	21	9	52	25
Potassium (ppm)	4	22	386	96
Calcium (ppm)	48	1288	7075	3534
Magnesium (ppm)	12	91	190	241
Sulfur (ppm)	5	75	48	47
Sodium (ppm)	5	29	115	30
Organic matter (%)	0.05	56.93	9.94	7.15

[a] ppm = mg/kg.

Successful synthesis of MAC from PAC was confirmed by observing magnetite (Fe_3O_4) on the surface of MAC using XRD analysis (Fig. 1a). In addition to Fe_3O_4, a signal corresponding to goethite (α-FeOOH), a ferric oxyhydroxide with a weak magnetic property, was observed for both PAC and MAC samples.

Separation of MAC from MAC-sandy soil mixtures was achieved using a magnet. The recovered MAC from the mixture with different water/soil ratios appeared to have a high level of purity indicated by color-based visual observation. The effects of water/soil ratios (w/w) on magnetic separation of MAC from soil-water-MAC mixtures were observed (Fig. 1b). An average MAC recovery of 91 ± 4 % was observed for soil samples without water addition (i.e., water/soil = 0). When the water/soil ratios increased to 0.375 and 0.5, the average MAC recovery varied from 80 % to 120 %. The fluctuation of the recovery might be due to the challenge in separation of MAC that aggregates with soil particles in the presence of low water contents (forming paste-like slurry mixtures). However, such effects were minimized when the water/soil ratios increased to 1 and 2. These results suggested that satisfactory recovery of spent MAC would be possible when applying MAC to remediate contaminated dry soil and soils with water/soil ratios >1. Unfortunately, some portions of the original soil contents exhibited magnetic properties, suggesting that some soil may be separated along with the MAC (Fig. S1). For example, 2.4 ± 0.2 % (w/w) of the commercial sandy soil was attracted to the magnet in MAC-free controls, whereas only 1.1 ± 0.1 % (w/w) of the San Antonio AFFF-impacted soil was recovered in similar experiments. The magnetic soil particles were not distinguished from the recovered MAC as unknown physical interactions during the MAC recovery process are inherently unavoidable. Regardless, the total mass percentages that exhibit magnetic properties within the used soil types were small. Furthermore, considering the low density of the powder form the soils compared to the MAC, the soils with weak magnetic properties may not have been easily collected by the high-strength magnet. The magnetic strength difference between soil particles and the MAC may also provide a difference in magnet-assisted removal. Regardless of these potential factors, the detailed fraction of retrieved magnetic soil distinguishable from the MAC was not quantitatively evaluated due to technical limitations.

3.2. Removal of PFAS from PFAS-spiked clean soils using MAC

The amendment of MAC into PFAS-spiked clean soils achieved different PFAS removal efficiencies, depending on PFAS type and soil properties (Fig. 2). As shown in Fig. 2a and b, approximately 80–90 % of PFAS (PFOS, PFOA, or 6:2 FTSA) in PFAS-spiked environmental and commercial sandy soil were removed following treatment with MAC. Particularly, high PFAS removal was observed from environmental sandy soil. Considering the relatively low pH and low organic content of the environmental sandy soil, potentially reduced electrostatic interaction of the PFAS and increased hydrophobic attractions with MAC might have resulted in the high PFAS removal observed. The low water content within the environmental sandy soil (2.93 %), which might hinder PFAS transport between the environmental sandy soil and MAC, could be considered less significant than the impacts of low pH and organic content.

Effective PFAS removal from the PFAS-spiked clean soils was observed after one month of incubation, with marginal increases in removal after three months of incubation for commercial (36.3– 77.5 %) and environmental (73.4– 87.6 %) sandy soils (Fig. 2). Consequently, the adsorption of PFAS to MAC might have nearly reached equilibrium

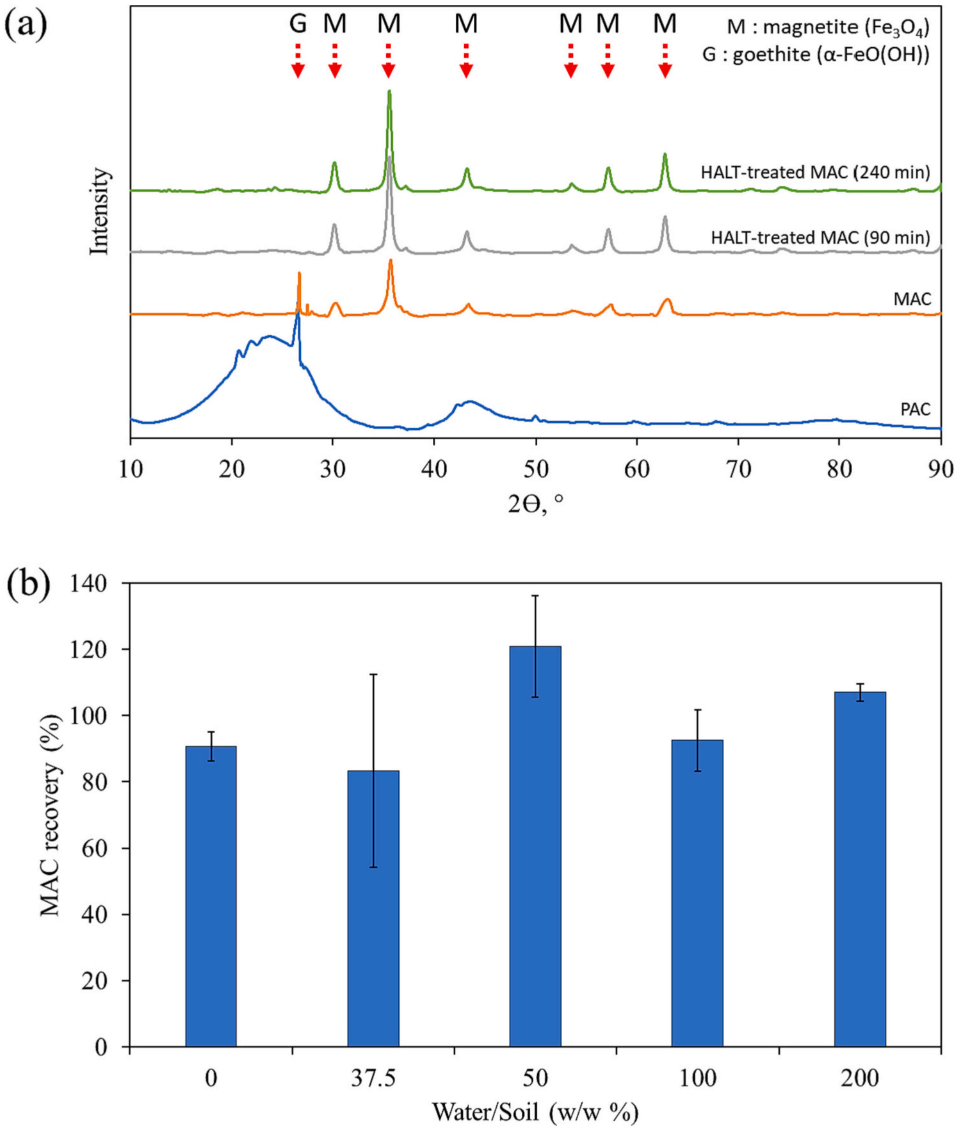


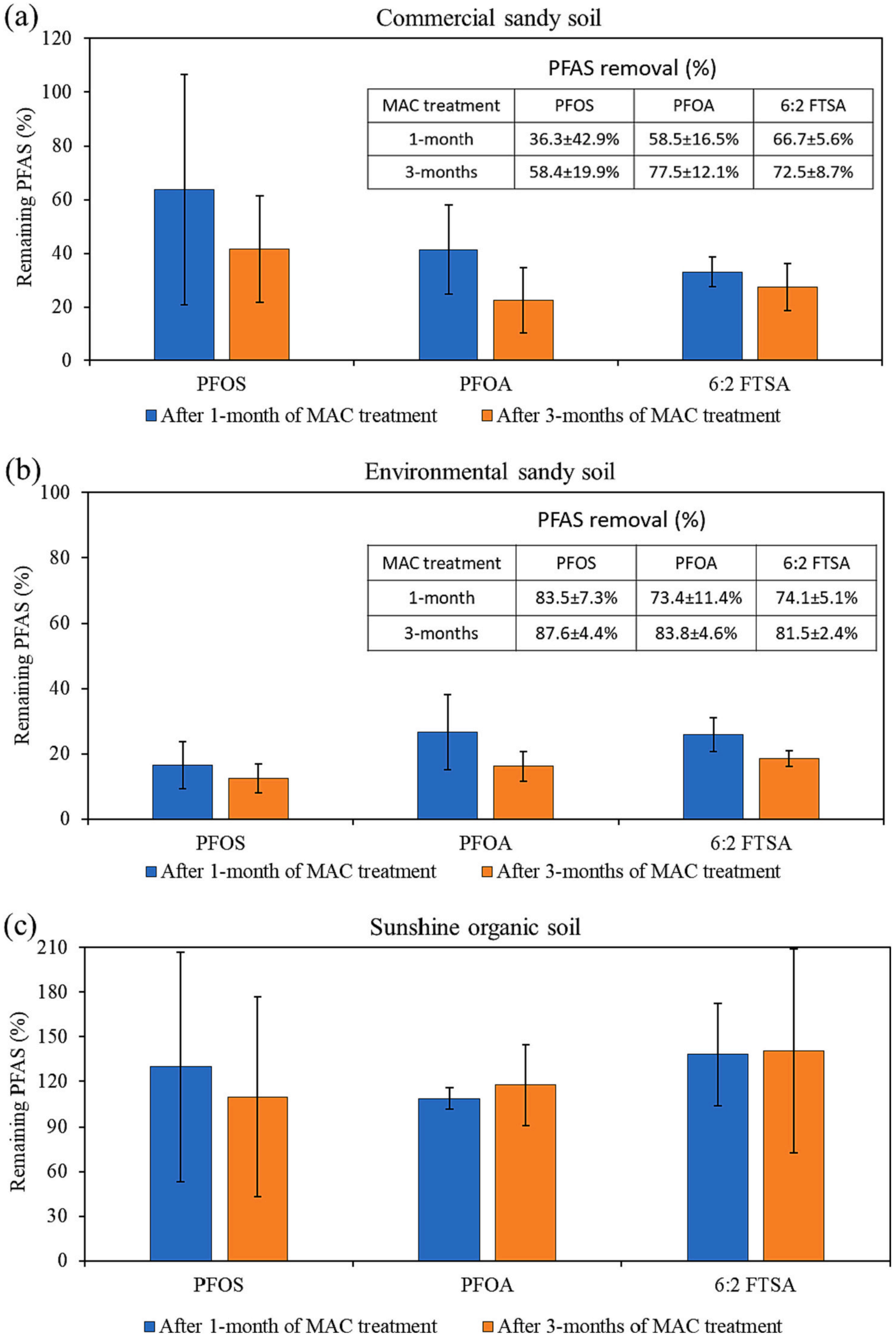
Fig. 1. (a) XRD analysis of PAC, MAC, and HALT-treated MACs (90 min and 240 min) with peak profiles of goethite (G) and magnetite (M). HALT reaction conditions: 350 °C, 1 M NaOH, 167 g/L of virgin MAC initially loaded with 4.61 ± 0.04 mg PFOS/g MAC; (b) Effects of water/soil ratios on MAC recovery from soils following treatment.

in soils within one month, especially for the environmental sandy soil. Based on these data, fresh MAC additions might be needed after 1 month of incubation to remove additional PFAS. Unlike the high removal observed in PFAS-spiked environmental and commercial sandy soils, treatment with MAC was ineffective (0 % PFAS removal with high variation) for the PFAS-spiked Sunshine organic soil (Fig. 2c). This is attributed to the very high organic carbon content compared to the environmental and commercial sandy soils (Table 1). High organic content has been known to negatively impact PFAS adsorption by AC through introduction of competition for adsorption sites and pore blockage depending on organic matter size (Saeidi et al., 2020; Yu et al., 2012).

3.3. PFAS removal from AFFF-impacted and PFAS-contaminated soils with MAC

Fig. 3 shows that MAC could also remove PFAS from AFFF-impacted and PFAS-contaminated, aged soils with different effectiveness. As shown in Fig. 3a, the San Antonio AFFF-impacted soil sample was contaminated with a wide range of PFAS including 6:2 FTSA, 8:2 fluorotelomer sulfonic acid (8:2 FTSA), perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), PFHxA, perfluorohexane sulfonic acid (PFHxS), PFOA, PFOS, perfluorodecanoic acid (PFDA), perfluoroheptanoic acid (PFHpA), perfluorononaoic acid (PFNA), perfluoropentanoic acid (PFPeA), perfluorotetradecanoic acid (PFTeDA), perfluorotridecanoic acid (PFTrDA), and perfluoroundecanoic acid (PFUdA). PFAS removal, ranging from 0 to 100 % for the detected compounds, was observed after 3 months of incubation with MAC. This could be due to the diverse PFAS types and concentrations in the San Antonio AFFF-impacted soil samples. Initial concentrations of PFAS in untreated soil were PFOS >200 μg/kg, 6:2 FTSA >85 μg/kg, 8:2 FTSA >120 μg/kg, and PFHxS >70 μg/kg on average. It was also possible that the MAC-adsorbed PFAS reached equilibrium with the soil-phase concentration within approximately one month. Under such a scenario, re-applications of MAC or increased initial amounts of MAC initially may be applied to enhance PFAS removal.

In the Sunshine PFAS-contaminated soil, poor PFAS removal after 3 months of MAC incubation was observed, ranging from 0 to 18 % (Fig. 3b). The low PFAS removal may be a result of high organic matter within the soil, yielding higher affinity of soil for PFAS and MAC pore



(a) PFAS removal (%)

MAC treatment	PFOS	PFOA	6:2 FTSA
1-month	36.3±42.9%	58.5±16.5%	66.7±5.6%
3-months	58.4±19.9%	77.5±12.1%	72.5±8.7%

(b) PFAS removal (%)

MAC treatment	PFOS	PFOA	6:2 FTSA
1-month	83.5±7.3%	73.4±11.4%	74.1±5.1%
3-months	87.6±4.4%	83.8±4.6%	81.5±2.4%

Fig. 2. Remaining PFOS, PFOA, and 6:2 FTSA percentages in the PFAS-spiked soils after one and three months of incubation. (a) commercial sandy soil; (b) environmental sandy soil; and (c) Sunshine organic soil.

blockage, as mentioned previously. This hypothesis is partially supported by the observation of improved PFAS removal within the Sunshine PFAS-contaminated soil compared to the PFAS-spiked Sunshine organic soil, which has about 8-fold higher organic matter content than the Sunshine PFAS-contaminated soil that was aged for >4 years. In the Sunshine PFAS-contaminated soil, removal of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoic acid (GenX) (54 %), PFOA (37 %), PFBA (73 %), and PFBS (62 %) was observed after 1 month of MAC treatment, with relatively little change after 3 months of treatment. However, the removal of 6:2 FTSA (~0 %), PFOS (25 %), and PFDA (2 %) remained poor. This observation could be explained by the relatively high PFAS concentrations (PFOA >1100 μg/kg, GenX >600 μg/kg, PFBA >290 μg/kg, PFBS >130 μg/kg) in the Sunshine PFAS-contaminated soils, leading to greater partitioning into MAC. Effective PFAS removal within AC-amended soils has been reported previously (Kupryianchyk et al., 2016). However, the evaluated soils were externally amended with excess water which can increase the mobility of the soil-sorbed PFAS compared to the present study. In addition, other studies evaluating GAC amendment to PFAS-contaminated soil have observed high PFAS retention (87– 99.9 %) based on leachate measurements (Barth et al., 2021; Zhang and Liang, 2022). The high PFAS removal could be also due to high mobility through the leachate within

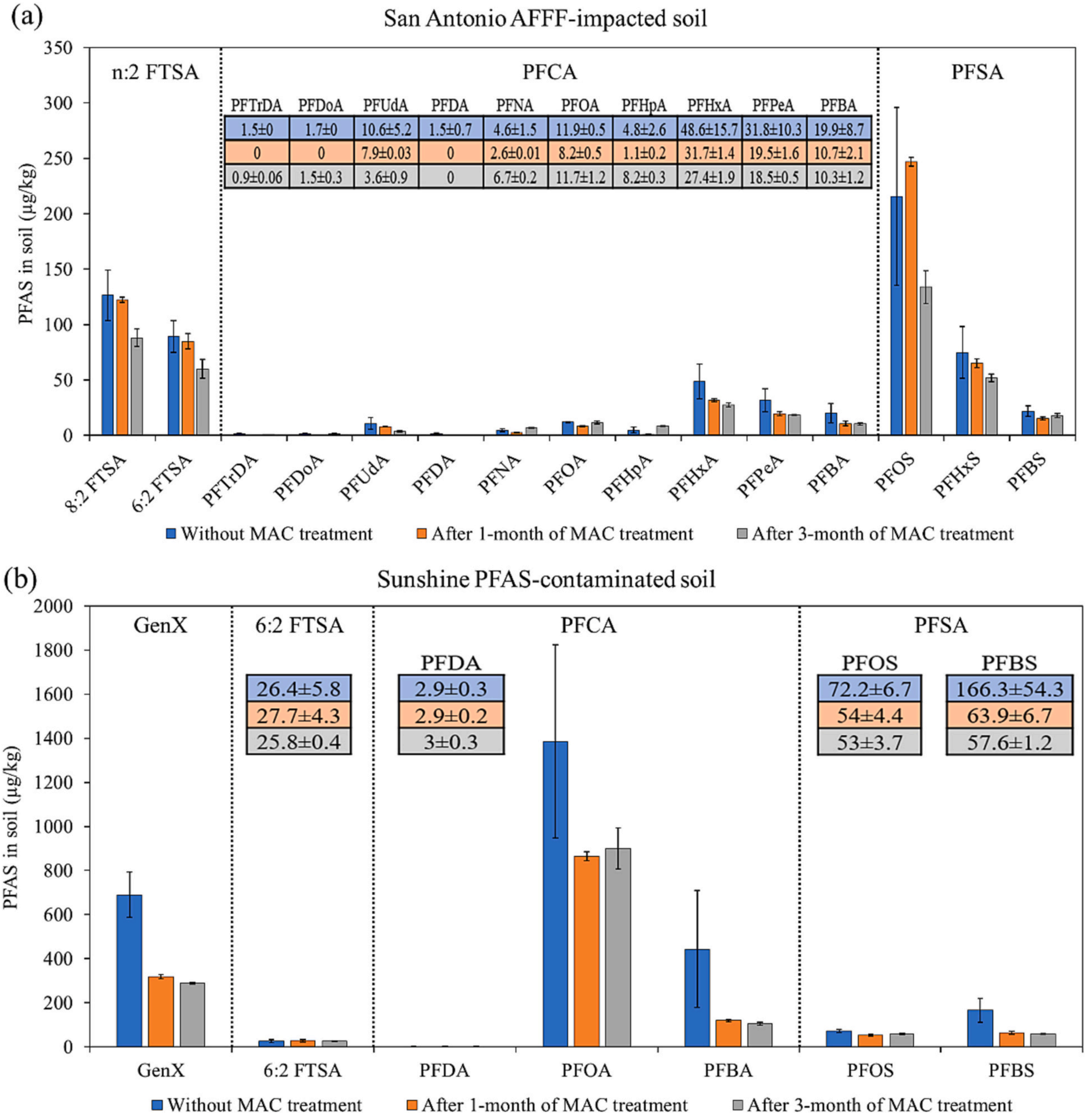


Fig. 3. PFAS concentration profiles from (a) San Antonio AFFF-impacted soil and (b) Sunshine PFAS-contaminated soil without MAC treatment, after 1 or 3 months of incubation.

contaminated soil. Accordingly, we believe further introduction of water could potentially enhance the effectiveness of MAC soil treatment. Furthermore, as previously discussed, PFAS removal in soils is strongly influenced by soil characteristics. As a result, only limited assessment regarding the superiority of MAC can be made without the information on the soils to which it is added. Further experiments should be conducted in various soil types to explore soil matrix effects on PFAS adsorption.

Several variables such as PFAS structure, inorganic ions, natural organic matter, dissolved organic matter, and pH have been shown to affect PFAS sorption to AC (Du et al., 2015; McCleaf et al., 2017; Saeidi et al., 2020; Wu et al., 2020; Yu et al., 2012). The effects of PFAS structure, particularly in terms of PFAS chain length, were observed in MAC-treated San Antonio AFFF-impacted soil. For example, removal of long-chain PFAS, such as 8:2 FTSA, 6:2 FTSA, and PFOS, appeared to increase throughout the 3-month treatment period, whereas short-chain PFAS reached their highest removal efficiencies within the first month of treatment (Fig. 3a). This could be attributed by the greater mobility of short-chain PFAS (Bolan et al., 2021).

Previous studies have reported that lower molecular weight natural organic matter decreases PFAS adsorption due to similarity in molecular size and the resulting competition for common adsorption sites (Yu et al., 2012). Organic matter with high molecular weights could also inhibit PFAS adsorption by blocking MAC pores, leaving adsorption sites unavailable (Saeidi et al., 2020). Additionally, pH might affect PFAS adsorption to the MAC. Previous studies have shown that at lower pH in aqueous phase, adsorption kinetics and total PFAS adsorption increase (Wu et al., 2020). High pH conditions could potentially induce electrostatic repulsion between anionic PFAS and ionizable functional groups on the AC surface that become negatively charged (Bei et al., 2014). In agreement with this mechanism, in this study, the environmental and Sunshine PFAS-contaminated soils that had low pH values of

4.9 and 6.1 respectively exhibited much higher PFAS removal than San Antonio AFFF-impacted soil (pH = 7.2). However, it is important to note that San Antonio AFFF-impacted soil had higher organic matter (9.94 %) than the lower pH soils, making it difficult to separate the contribution of organic content and pH to adsorption. Previous studies have shown that ions and ionic strength in solution also play an important role in PFAS sorption (Du et al., 2015; Wu et al., 2020). High concentrations of cations such as Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} in San Antonio AFFF-impacted soil and Sunshine organic soil might have also affected PFAS removal by MAC, further reducing PFAS removal in these soils.

3.4. Spent MAC treatment with HALT technology

A fluorine mass balance was tracked during application of HALT to PFOS pre-adsorbed onto MAC. Results showed that application of HALT (350 °C, 1 M NaOH) led to near-complete destruction of the adsorbed PFOS and stoichiometric generation of fluoride ion (Fig. 4). In the data shown, the extent of PFOS destruction reached 97.4 ± 0.2 %, and the extent of defluorination reached 101 ± 3 %. At the reaction times tested, residual PFOS was only quantified in MAC extracts, while aqueous PFOS concentrations were below the LOQ (Fig. S3). Moreover, no fluoro-organic intermediates were observed in extracts of the treated MAC. Instead, inorganic fluoride from the fluorine in PFOS is generated through HALT (Hao et al., 2021). Sulfonates are expected to also yield sulfate under HALT conditions (Fabes and Swaddle, 1975). These findings were consistent with previous experiments using PFOS adsorbed to GAC (Soker et al., 2023).

Rates of MAC-adsorbed PFOS degradation by HALT were found to be similar to those measured for PFOS dissolved in aqueous solution, demonstrating that the alkali reactants can readily access PFOS adsorbed within pores of MAC without significant mass transfer limitations. Based on the kinetics data presented in Fig. 4, the pseudo-first-order rate constant for PFOS destruction was estimated to be 0.0156 ± 0.0008 min^{-1}. This value compares to 0.015 ± 0.001 min^{-1} measured in homogeneous aqueous solution and 0.014 ± 0.001 min^{-1} measured for comparable GAC suspensions at the same HALT reaction conditions, 350 °C and 1 M NaOH (Soker et al., 2023). Thus, rates of PFOS destruction are similar in MAC suspensions, aqueous solutions, and GAC suspensions.

Further analysis showed that the magnetic properties of MAC were retained after application of HALT up to 240 min (Fig. S2). Although this was a qualitative test, it suggested that MAC may be re-usable as a magnetic adsorbent material following application of HALT. An experiment evaluating the reusability of HALT-treated MAC was conducted as described in the SI by comparing the PFOS adsorption capacities of virgin and HALT-treated MAC (Fig. S4). Results showed that the virgin MAC exhibited an adsorption capacity of 163 ± 8 mg PFOS/g MAC while the HALT-treated MAC (350 °C, 1 M NaOH, 240 min) adsorbed 200 ± 4 mg PFOS/g MAC, which were close to values reported previously under similar conditions (Meng et al., 2019). Although an increased adsorption capacity value was measured upon MAC being treated with HALT, the specific mechanism is unknown and the difference may result from sample variability; further experiments are needed to examine the effects of HALT on MAC adsorption capacities. Most importantly, treatment with HALT does not appear to diminish the adsorption behavior of MAC, suggesting potential for reuse of the adsorbent material. Moreover, future studies are suggested to evaluate repeated re-use of the MAC for adsorption following HALT treatment. Tests with GAC showed no significant change in specific surface area following repeated exposure to HALT reaction conditions, and adsorption of PFPeA and PFOS were not significantly affected by HALT (Soker et al., 2023). In addition, magnetite peaks observed through the XRD analysis of the HALT-treated MAC remained intact, suggesting that magnetic properties are retained during HALT (Fig. 1a). Under alkaline conditions, transformation of magnetite to goethite (He and Traina, 2007) was not observed here. Furthermore, no additional goethite peaks were observed. Rather, one peak corresponding to goethite observed for virgin MAC disappeared from the XRD pattern upon HALT treatment. The absence of this peak could suggest a potential reducing condition present within the HALT process that assists the reductive transformation of goethite iron (III) to the mixed iron (II/III) magnetite phase (Iwasaki et al., 2011; Usman et al., 2013).

Substantial degradation of PFAS on MAC derived from the AFFF-impacted soil was observed following 240 min reaction time. The data are shown in Table 2 and Fig. 5, which include PFAS compounds quantified on the MAC. Compared to the PFOS-loaded samples from the mass balance experiments (Fig. 4), destruction of PFOS was significantly lower for treatment of MAC recovered from the AFFF-impacted soil (81 % versus >97 % in the PFOS-loaded MAC) at the same treatment residence time and alkali dose. This could be due to incomplete separation of MAC from soil particles, leading to the presence of soil particles in the reactor, which may contain silica or other base-neutralizing compounds. Previous work demonstrated that silica-rich soils, which can act to partially neutralize the added NaOH base, reduce the net rate of perfluoroalkyl sulfonic acid (PFSA) destruction compared to aqueous reactions (Hao et al., 2022). Whereas several PFSAs were detected at relatively low concentrations following HALT, perfluoroalkyl carboxylic acids (PFCAs) were treated to values below the LOQ or LOD. The only

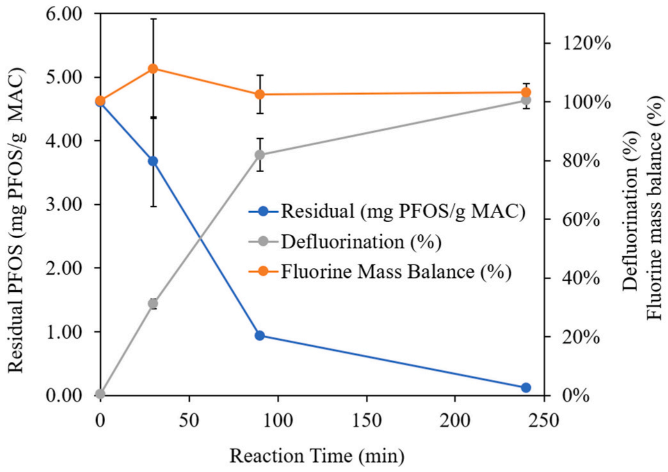


Fig. 4. Degradation and defluorination of a known mass of PFOS adsorbed on MAC prior to treatment. Reaction conditions: 350 °C, 1 M NaOH, 167 g/L of virgin MAC initially loaded with 4.61 ± 0.04 mg PFOS/g MAC.

Table 2
PFAS concentrations in untreated and HALT-treated MAC samples incubated with San Antonio AFFF-impacted soil for three months. Reaction conditions: 350 °C, 1 M NaOH, 240 min, 67 g/L MAC. LOQ = limit of quantification, ND = not detected.

Compound	Pre-treatment sample concentration (μg/g)	Post-treatment sample concentration (μg/g)
6:2 FTSA	0.138	LOQ
8:2 FTSA	0.123	ND
PFBA	0.026	ND
PFBS	0.036	LOQ
PFHxA	0.160	LOQ
PFHxS	0.081	0.009
PFOA	0.034	–[a]
PFOS	0.756	0.142
PFDA	0.005	0.001
PFHpA	0.010	ND
PFNA	0.009	ND
PFPeA	0.063	LOQ
PFTeDA	0.002	ND
PFTrDA	0.006	ND
PFUdA	0.017	ND

[a] PFOA contamination observed in post-treatment samples.

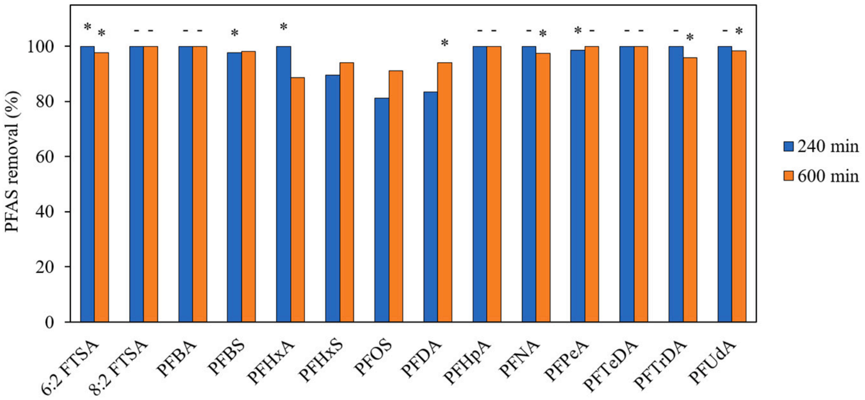


Fig. 5. Removal of PFAS adsorbed to MAC incubated with San Antonio AFFF-impacted soil following HALT. Reaction conditions: 350 °C, 1 M NaOH, 67 g/L MAC, 240 min (blue) and 600 min (orange). A "*" above the removal value indicates that the compound was treated to a value concentration below the LOQ and a "-" indicates a non-detectable concentration following treatment. The percentage removal for compounds detected below the LOQ represent a lower bound estimate for the actual removal percentage.

PFCA with a measurable post-treatment concentration, PFDA, had a similar concentration to controls with no added PFAS, suggesting that detection was the result of background sample contamination.

Another MAC sample previously incubated with AFFF-impacted soil for 7 days was treated, this time using a greater reaction residence time (350 °C, 1 M NaOH, 600 min, 67 g/L MAC). Data is shown in Table 3 and Fig. 5 alongside removal data from the 240 min reaction and demonstrates moderate improvements in destruction for certain compounds when reaction time is increased. Notably, PFOS removal increased to >90 % at the longer reaction time as compared to 81 % at 240 min. Treatment of PFHxS, a recalcitrant PFSA, also improved to >90 % at the longer reaction time. The PFCAs shown were either treated to concentrations below the LOQ or LOD, or present at levels similar to a PFAS-free control. The organic fluorine equivalent amount adsorbed to the 3-month spent MAC (49.2 nmol F/g MAC) was slightly higher than that in the 7-day spent MAC (42.6 nmol F/g MAC) based on the PFAS included in Tables 2 and 3, suggesting that PFAS reached equilibrium between contaminated soil and MAC fairly rapidly. Consequently, multiple applications of MAC could be used to accelerate remediation and achieve the desired treatment endpoint.

The potential to reduce large volumes of PFAS-contaminated matrices (e.g., soil with dilute adsorbed PFAS) into a smaller and more concentrated phase (e.g., spent MAC) for HALT treatment is highly favorable as it can be a more cost-effective treatment option for field applications. Furthermore, by treating PFAS sorbed to MAC instead of direct application of HALT to contaminated soils with base-neutralizing properties, NaOH consumption can be significantly reduced (Hao et al., 2022). Energy inputs for HALT are estimated between 130 and 350 kWh per m^3 of feed (Hao et al., 2021). Given the low heat capacity of activated carbon compared to water, hydrothermal treatment of MAC should be similar (Soker et al., 2023). Assuming PFAS from 1 m^3 of contaminated soil are concentrated onto ~0.05 m^3 of MAC (~20-fold reduction in feed volume), the total required energy input for HALT treatment will be reduced by a similar factor. Chemical inputs may be decreased by an even greater factor when considering the base-neutralizing behavior of soils, further reducing operating costs. Studies to investigate MAC re-application needed to achieve the desired treatment endpoint and the reusability of HALT-treated MAC can accelerate adoption and commercialization of this treatment train. Larger pilot-scale reactor system studies are also recommended to obtain data necessary for more accurate techno-economic assessment. Safety concerns related to elevated temperatures, pressure, and alkaline conditions required for HALT can also be addressed during scale-up demonstrations. In addition, the synthesis of MAC in large quantities and large-scale application and recovery following PFAS treatment are key obstacles to process scale-up.

Table 3

PFAS concentrations in untreated and HALT-treated MAC samples incubated with San Antonio AFFF-impacted soil for 7 days. Reaction conditions: 350 °C, 1 M NaOH, 600 min, 67 g/L MAC. LOQ = limit of quantification, ND = not detected.

Compound	Pre-treatment sample concentration (μg/g)	Post-treatment sample concentration (μg/g)
6:2 FTSA	0.102	LOQ
8:2 FTSA	0.103	ND
PFBA	0.046	ND
PFBS	0.031	0.001
PFHxA	0.101	0.010
PFHxS	0.072	0.004
PFOA	0.027	-[a]
PFOS	0.712	0.053
PFDA	0.004	LOQ
PFHpA	0.006	ND
PFNA	0.009	LOQ
PFPeA	0.034	ND
PFTeDA	0.003	ND
PFTrDA	0.006	LOQ
PFUdA	0.014	LOQ

[a] PFOA contamination observed in post-treatment samples.

4. Conclusion

This proof-of-concept study showed that a treatment train consisting of MAC and HALT could be a promising technique for the removal and destruction of PFAS in contaminated soils. Magnetic separation can be used to physically recover MAC from soils with water content <7 % (w/w ratio) (Table 1). Initially, controlled experiments showed that PFAS (i.e., 6:2 FTSA, PFOS, and PFOA) could be effectively removed (>80 %) from environmental sandy soil, which had low-organic content and low pH, after 1 month of incubation. Under low-organic content conditions, PFAS removal is enhanced because of reduced adsorption competition and MAC pore blockage. However, poor PFAS removal was observed in soils with high organic matter content such as Sunshine organic soil, which significantly decreased the MAC adsorption of 6:2 FTSA, PFOS, and PFOA. The effects of soil organic matter on PFAS removal by MAC were also evident in the San Antonio AFFF-impacted soil and Sunshine PFAS-contaminated soil. These results highlight organic content within soils as a key variable for PFAS adsorption by MAC.

Furthermore, HALT has been shown to repeatedly perform effectively towards PFAS destruction within PFAS-loaded MAC that were retrieved from actual field samples. Near complete destruction of all PFAS detected in samples was achieved. Importantly, magnetic properties and PFAS adsorption properties of the MAC were retained following HALT. This finding suggests that MAC may be reusable following HALT. Overall, HALT could be considered an economically feasible technique with a considerably low energy footprint compared to thermal PFAS destruction technologies like incineration.

CRediT authorship contribution statement

Chih-Hsuan Shih: Data curation, Methodology, Writing – original draft. **Jinha Kim:** Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Shih-Hung Yang:** Data curation, Methodology. **Ori Soker:** Data curation, Formal analysis, Writing – review & editing. **Timothy Strathmann:** Conceptualization, Funding acquisition, Investigation, Writing – review & editing. **Kung-Hui Chu:** Conceptualization, Formal analysis, Investigation, Project administration, Supervision, Visualization, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Strategic Environmental Research and Development Program (SERDP, ER22-3124 and ER18-1501). We thank Lefan Wang and Jooho Chung from Texas A&M University for assisting on water/soil ratio MAC recovery experiments and XRD analysis, respectively.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168931.

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