



Combination of separation and degradation methods after PFAS soil washing

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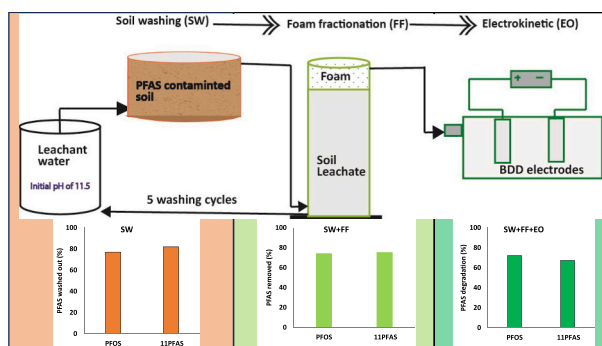
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HIGHLIGHTS

- A high initial pH and L/S ratio improve PFAS removal in sand soil via soil washing
- At the initial pH of 11.5 and L/S 10, the removal PFOS was 76 % and 95 % at L/S 40.
- Aeration effectively removed long-chain PFAS from leachate, reaching 99 % for PFOS.
- Reusing treated leachate after aeration in soil washing maintained efficiencies.
- Combining soil washing, aeration, and electrokinetic destroy PFAS from soil.

GRAPHICAL ABSTRACT



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ABSTRACT

The current study evaluated a three-stage treatment to remediate PFAS-contaminated soil. The treatment consisted of soil washing, foam fractionation (FF), and electrochemical oxidation (EO). The possibility of replacing the third stage, i.e., EO, with an adsorption process was also assessed. The contamination in the studied soils was dominated by perfluorooctane sulfonate (PFOS), with a concentration of 760 and 19 $\mu\text{g kg}^{-1}$ in soil I and in soil II, accounting for 97 % and 70 % of all detected per- and polyfluoroalkyl substances (PFAS). Before applying a pilot treatment of soil, soil washing was performed on a laboratory scale, to evaluate the effect of soil particle size, initial pH and a liquid-to-soil ratio (L/S) on the leachability of PFAS. A pilot washing system generated soil leachate that was subsequently treated using FF and EO (or adsorption) and then reused for soil washing. The results indicated that the leaching of PFAS occurred easier in 0.063–1 mm particles than in the soil particles having a size below 0.063 mm. Both alkaline conditions and a continual replacement of the leaching solution increased the leachability of PFAS. The analysis using one-way ANOVA showed no statistical difference in means of PFOS washed out in laboratory and pilot scales. This allowed estimating twenty washing cycles using 120 L water to reach 95 % PFOS removal in 60 kg soil. The aeration process removed 95–99 % PFOS in every washing cycle. The EO and adsorption processes achieved similar results removing up to 97 % PFOS in concentrated soil

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leachate. The current study demonstrated a multi-stage treatment as an effective and cost-efficient method to permanently clean up PFAS-contaminated soil.

1. Introduction

Nowadays, per- and polyfluoroalkyl substances (PFAS) are emerging as soil pollutants of critical concern. These substances are a class of toxic, bioaccumulative and persistent organic compounds that have been used in industrial and consumer products (Kissa, 2001; Kurwadkar et al., 2021). As a consequence, they are ubiquitously distributed almost everywhere causing threats to human health and the environment (Sunderland et al., 2019; Zeeshan et al., 2021). High PFAS contamination is found in the vicinity of sites historically used for firefighting training by applying aqueous film-forming foams (AFFF) (Langberg et al., 2021; Nickerson et al., 2021). Due to their persistent character, PFAS remain in the soil if no remediation options were undertaken (Goldenman et al., 2019). Occurrence of PFAS in soil results in long-term leaching of the pollutants to natural waters, which subsequently can pose health risks to living organisms such as immunotoxicity, hepatotoxicity, carcinogenicity and reproductive effects (Brusseau et al., 2020; DeWitt et al., 2012; Fenton et al., 2021). Hence, developing technologies for PFAS remediation in soil is urgently needed. Various techniques including biological treatment, in/ex-situ soil washing, heat-based treatments and stabilization were shown to be possible options for PFAS remediation in soil (Grimison et al., 2023; Høisæter et al., 2021; Leung et al., 2022; Mayakaduwege et al., 2022; Söregård et al., 2020, 2019; Stoiber et al., 2020). However, the techniques present significant challenges, including insufficient removal of some PFAS compounds, dislocating the contaminants elsewhere or generating other harmful byproducts.

Soil washing is a technique suitable to permanently remove PFAS from contaminated soil without creating any byproducts (Ross et al., 2018). This technology is also effective for the treatment of a wide range of environmental pollutants (e.g., petroleum hydrocarbons, polycyclic aromatic hydrocarbons and heavy metals) (Liu et al., 2022; Trellu et al., 2016). The washing of PFAS-contaminated soil was shown to be a proper option for large-scale application (Grimison et al., 2023; Høisæter et al., 2021; Quinnan et al., 2022; Senevirathna et al., 2021). The effectiveness of soil washing is affected by soil properties such as soil texture, mineral and organic matter content and chemical composition of washing solutions (Bolan et al., 2021; Li et al., 2019; Quinnan et al., 2022). Chemical additives increasing washing efficiency for PFAS include alkaline solutions, surfactants and organic compounds (e.g. oxalate) (Yanju Liu et al., 2020; Pan et al., 2009; Tang et al., 2017).

Due to its relative simplicity, soil washing can offer an economically feasible treatment of PFAS-contaminated soil, even when applied in situ (soil flushing) (Grimison et al., 2023; Høisæter et al., 2021; Quinnan et al., 2022). However, this method presents drawbacks such as requiring a high volume of water, which subsequently generates a substantial amount of PFAS-contaminated leachate that needs further treatment. Concentrating PFAS into a smaller volume of leachate could reduce the total amount of solution that needs to be treated.

Over the years, foam fractionation (FF) gained much attention as a viable option in wastewater treatment plants for the removal and concentration of contaminants that are not easily removed using traditional municipal treatment systems (Buckley et al., 2022; Burghoff, 2012; Lemlich, 1968). The FF separates hydrophobic solutes using air that generates bubbles in the solution. The bubbles provide a large surface area for contaminant adsorption (Lemlich, 1968). The contaminants thus rise with the bubbles through the solution forming a foam above the liquid which is referred to as foamate. The method presents several advantages, such as low capital and operation costs and low energy consumption, making it an industrially feasible treatment process (Wong et al., 2001). Currently, FF is becoming one of the focus of

research due to its simplicity and effectiveness for PFAS treatment. Several studies have demonstrated an efficient removal of PFAS in different environmental samples (Burns et al., 2021; McClellan et al., 2021; Smith et al., 2022; Wang et al., 2023). To be able to clean up PFAS-contaminated soil using FF, a pretreatment is needed to transfer PFAS into the liquid phase as the method is only suited for the removal of PFAS in the aqueous phase. Consequently, highly PFAS-concentrated waste is generated, mainly containing long-chain PFAS. Thus, further methods are needed to degrade PFAS present in the separated concentrate.

Advanced oxidation processes (AOP) (e.g., electrochemical, oxidation, activated persulfate oxidation), reduction processes (e.g., UV light combined with chemicals such as iodide (I^-), sulfite (SO_3^{2-}) or dithionite ($S_2O_4^{2-}$)) and ultrasound-based degradation are capable to breakdown PFAS (Ahmed et al., 2020; Nzeribe et al., 2019). Electrochemical oxidation (EO) is traditionally applied on a large scale for removing organic contaminants in drinking water and wastewater treatment facilities (Ben et al., 2018; Sanches et al., 2010). In regard to PFAS treatment, the EO method presents obvious advantages over other AOP methods such as being effective for the complete degradation of PFAS from solutions with complex matrix (Görmez et al., 2022; Sharma et al., 2022; Uwayezu et al., 2021). Boron-doped diamond (BDD) electrodes are extensively exploited by several researchers and treatment operators due to their effectiveness for PFAS degradation, stability and absence of hazardous by-products (Gomez-Ruiz et al., 2017; Nidheesh et al., 2019; Pierpaoli et al., 2020; Uwayezu et al., 2021). The EO using BDD electrodes is even effective in highly PFAS-containing solutions with high levels of other oxidizable substances, notably total organic carbon (TOC) and chlorides (Maldonado et al., 2021). However, in addition to being an expensive method, the EO only breaks down PFAS in solutions. Nevertheless, EO could be a suitable method to degrade PFAS in leachate after the pretreatment steps of transferring PFAS from soil into the aqueous phase through washing and concentrating to a smaller volume of leachate through FF.

Overall, the combination of soil washing, foam fractionation and electrochemical degradation could collectively offer a possible solution to remove and destroy PFAS in contaminated soil. To date, most available technologies for PFAS remediation in soil have focused on the use of soil washing, followed by a treatment of leachate using adsorption processes (with granular activated carbon or ion exchange resins) (Grimison et al., 2023; Høisæter et al., 2021; Quinnan et al., 2022). But the treatment is not complete until PFAS are fully destroyed or safely stored.

The aim of this study was to evaluate the operability of combining soil washing, foam fractionation and electrokinetic (or adsorption) methods for permanent removal of PFAS in an AFFF-contaminated sandy soil. The treatment stages were consecutively run one after another without adjusting conditions between them in order to provide a simple design that can practically be useful at larger scale.

2. Materials and methods

2.1. Materials

Two soil samples were collected at Umeå Airport, Sweden and will be named soil I and soil II hereafter. Soil I was sampled directly at the hotspot where activities (fire drills, fire engine flushing and armed forces exercise) that used PFAS containing AFFF took place. Soil II was sampled in the vicinity of the hotspot but no exercise with PFAS-extinguishing foam was carried out there. The soil samples were taken at approximately 0.5–1.5 m depth. Soil I was free of total organic carbon (TOC)

whereas soil II had 0.2 % of TOC. The current soils represented a large amount of PFAS-contaminated soil at the hotspot location, demanding an extensive cleanup effort.

Chemicals used in the experiments, including sodium sulfate (Na_2SO_4 , 99 %), sodium hydroxide (NaOH , >99 %) and hydrochloric acid (HCl , 37 %), were purchased from Merck (Germany).

2.2. Laboratory-scale washing experiments

Batch tests were performed to get insight into the effect of soil particle size on the leaching behavior of PFAS, batch leaching tests were conducted using fines (particle sizes below 0.063 mm) and sandy soil particles (between 0.063 and 1 mm). Prior to leaching tests, perforated plate test sieves of 0.063 and 1 mm size were used to separate the desired fractions of soil. Batch experiments were carried out in 500 mL PE bottles containing each soil fraction. Duplicate tests were performed with a 30 g sample of air-dried soil and deionized water to a liquid-to-solid (L/S) ratio of 10. Constant mixing of suspension was maintained using a rotary mixer during 24 h, a time that was chosen based on other studies (Campos-Pereira et al., 2023; Milinovic et al., 2015). Thereafter, the suspensions were centrifuged at 6000 rpm for 10 min followed by filtration through 0.45 μm nitrocellulose membrane filters. Supernatants were stored at 4 °C prior to the chemical analysis.

Column leaching experiments were performed at laboratory-scale using 50 g of PFAS-contaminated bulk soil that was sealed into a polyvinyl chloride column (50 mm \times 100 mm). Guidance on leaching procedures (Swedish Standard SS-ISO-EN ISO 18772:2014) (SIS (2014)) using pH-modified deionized water and unmodified soil conditions was followed. The sample was packed in the middle of the column and capped by filling the top and bottom with glass beads and with cellulose filter paper in contact with the soil to avoid material losses. The bed volume was 0.035 L. Deionized water, with or without adjusted pH, was continually flushed through the PFAS-contaminated soil and collected in a container. The pH effect on PFAS leaching was investigated by adjusting the leachant pH to pH 2.5, 6, 9.5 and 11.5. As the pH of the

solution was being measured using a pH meter, a 1 M diluted solution of either NaOH or HCl was added drop by drop into a bottle containing with deionized water until the desired pH level was achieved. Experiments were conducted in triplicate. A Watson Marlow pump (026.3001.00E model, supply Watson-Marlow Limited) was used to maintain an up-flow supply of leachant with a constant flow rate of 6 mL min^{-1} . Leachate samples of 100 mL were separately collected after 100, 400, 500 and 1000 mL had passed through the column, corresponding to L/S ratios of 2, 10, 20 and 40, respectively. The elutes were then stored at 4 °C prior to the chemical analysis.

2.3. Pilot experiment

The pilot experiment comprised three different stages connected in series (Fig. 1). The treatment was performed using soil I, which had the highest concentration of PFAS.

The first treatment stage was soil washing. A 60 kg soil that was packed in a rectangular polypropylene container (Width: 40 cm, Length: 60 cm, Height: 43 cm), with a bed volume of 25 L. A sand filter was placed on top and bottom of the container to maintain PFAS-contaminated soil in place in the center of the container. A geotextile fabric material (PFAS free material) was used to separate the soil and sand filter. Tap water, initially adjusted to pH 11.5 with dilute NaOH solutions, was used as a leachant. The water was continually pumped through the soil at a 300 mL min^{-1} flow rate using a peristaltic pump (Watson Marlow 520 Sn/R2 220 RPM). A total volume of 120 L per cycle was pumped through the soil, which corresponds to L/S 2.

The effluent from the soil washing process was collected in a polypropylene container. Subsequently, the collected leachate constituted the feed to the FF (stage II). Before continuing to the second stage, a 100 mL samples of the soil leachate were collected in a PP bottle and stored at 4 °C for PFAS analysis.

Stage II consisted of FF (Fig. 1). Unmodified PFAS-containing leachate collected from soil washing process was fed to a 50 L plexiglass fractionating column (19 cm \times 175 cm) using a peristaltic pump to

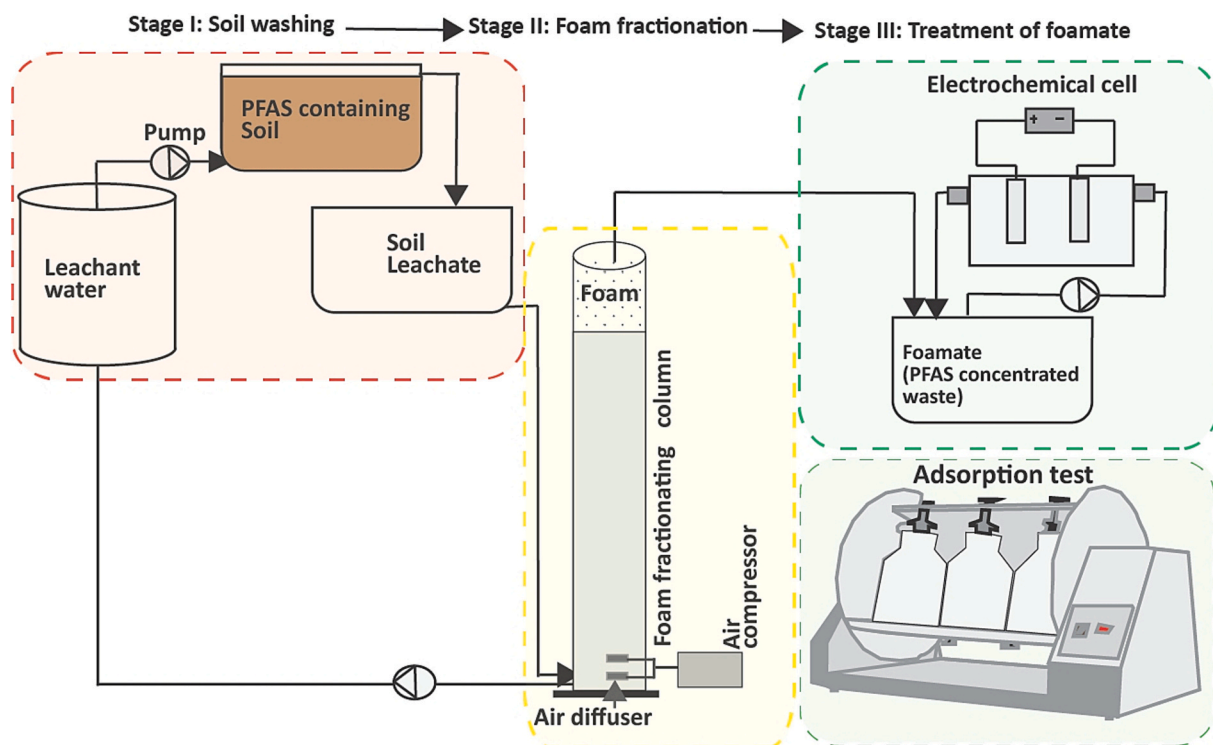


Fig. 1. Schematic of the pilot experimental setup of combining soil washing with foam fractionation and consequent destruction of PFAS by electrokinetics or removal by a sorbent.

a fixed level of 120 cm from the bottom (equivalent to approximately 35 L of leachate). The fractionating of PFAS in leachate was conducted in triplicate to treat the whole collected leachate. The FF was performed in enrichment mode, where the influent leachate entered the fractionating column at the bottom and the foam was collected above the liquid air interface. An airflow was dispersed at the bottom of the column using two stainless steel micro air bubble diffusers each having a 12 mm diameter, 25 mm length and a pore size of 5 μm . A rotameter (Series MR3000, 10–100 L min^{-1} , OEM Automatic AB, Sweden) was used to maintain a constant airflow of 50 L min^{-1} for 30 min. The foam was continuously built up and manually collected in a PP plastic container using a beaker. The foam was continuously built up and manually collected in a PP plastic container using a beaker. In each FF, treating about 35 L leachate, about 300 mL of foamate was collected. About 4 mL of pure foam (after bubble collapse) was collected and kept for further PFAS analysis, while the remaining was mixed with the foamate collected after all FF treatments, yielding about 900 mL foamate for each 105 L leachate treated. To assess the FF treatment's effectiveness, a 100 mL sample was taken from the leachate after FF and stored at 4 °C for PFAS analysis. The treated leachate, equivalent to 105 L, was subsequently reused for soil washing without pH adjustment. This soil washing and FF sequence were reiterated for 5 cycles, resulting in a cumulative L/S ratio of 10.

In the third stage of the treatment, EO was applied to degrade PFAS in the resulted foam from the second stage (FF). Prior to the treatment, the foam was left to rest, so the bubbles collapsed and the foam was back into a highly concentrated PFAS solution. The electrochemical cell comprised anodes and cathodes made of doped boron-doped diamond (BDD) coating on 2 niobium electrodes, with respective surface areas of 10 and 12 dm^2 . The two electrodes were spaced at 3 mm distance. A Peaktech- 1530 Laboratory switching mode power supply was used to apply 60 mA cm^{-2} for PFAS degradation in the foamate. A 5 L of PFAS-enriched foamate was continually recirculated through the electrochemical cell at 6 L min^{-1} . The foamate was initially modified with the addition of 1 g L^{-1} Na_2SO_4 , to adjust the solution conductivity to 2.5 S cm^{-1} , which has been applied elsewhere (Schaefer et al., 2015; Uwayezu et al., 2021). Samples were collected after 30, 60 and 120 min and stored at 4 °C for PFAS analysis.

EO was performed in parallel with adsorption (Fig. 1) to assess different options for PFAS treatment in waste generated from the FF process (stage II). Adsorption tests were carried out using polyethylenimine (PEI) and glycidyltrimethylammonium chloride (GTMAC) modified pine bark (PG-PB). The bio-adsorbent was developed as described by Ren et al., 2023. Briefly, 10 g of PEI was added to a mixture of 4 g pine bark and 40 mL water and stirred for 6 h. The product was cooled at room temperature and washed with deionized water to remove the excess of PEI. The product was then soaked into 40 mL of a 2 g L^{-1} NaOH solution and heated at 60 °C while stirring. A volume of 5 mL of GTMAC was added to the mixture and stirring was continued for 6 h. The final product (PG-PB) was then filtered and washed with deionized water to remove excess chemicals. The PG-PB was dried at 80 °C for 24 h and stored for further use. Adsorption experiments were carried out in 250 mL centrifuge bottles using 0.1, 0.4 and 0.8 g L^{-1} of the adsorbent and 200 mL of foamate. The suspensions were then shaken using a rotary mixer for 24 h at room temperature (21 °C). All experiments were run in triplicate. The supernatants were centrifuged at 2500 rpm for 10 min and filtered through 0.45 μm nitrocellulose membrane filters before PFAS analysis.

2.4. PFAS analysis

The analysis of PFAS in soil and solutions was performed by Eurofins Environment Testing Sweden AB, using Liquid Chromatography-tandem Mass Spectrometry (UPLC-MS/MS). The analysis of PFAS was done in compliance with DIN 38414-14 mod. Anal. Chem.2005,77,6353 mod and DIN 38407-42, UNEP Chemicals Branch 2015 mod; W-PFCLMS02

methods for soil and solutions respectively. Analyzed PFAS were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) and 6-2 fluorotelomer sulfonic (6:2 FTS).

2.5. Data treatment

The extent of washing of PFAS was determined from the ratio between the amount of PFAS removed from the soil and that in the original soil. A cumulative removal of PFAS in the soil washing on a pilot scale was determined using an expression shown in Eq. (1).

$$\%PFAS_{\text{washed out}} = \frac{\sum_{i=1}^n ([PFAS]_{\text{SL}} - \sum_{i=1}^n [PFAS]_{\text{TL}}) V_L}{m_s \times C_s} \times 100 \quad (1)$$

The $[PFAS]_{\text{SL}}$ represents concentration of PFAS in soil leachate ($\mu\text{g L}^{-1}$), $[PFAS]_{\text{TL}}$ is the concentration in the treated leachate after FF ($\mu\text{g L}^{-1}$), V_L stands for a volume of soil leachate (L), m_s represents the amount of treated soil (kg) and C_s the concentration of PFAS soil ($\mu\text{g kg}^{-1}$). The percentages of PFAS removal using FF, EO and adsorption methods were determined using expression in Eq. (2).

$$\%PFAS \text{ Removal} = \frac{[PFAS]_{i^*} - [PFAS]_{i^*}}{[PFAS]_{i^*}} \times 100 \quad (2)$$

where $[PFAS]_{i^*}$ and $[PFAS]_{i^*}$ are the mass concentrations ($\mu\text{g L}^{-1}$) of the initial and remaining PFAS, respectively.

The enrichment factors were calculated from ratios of PFAS concentration in foamate and untreated leachate as reported in a previous study (Meng et al., 2018).

A mass balance (MB) after soil washing-FF was done to track if PFAS was transferred into foamate or remained in treated soil and leachate. It was calculated using the expression in Eq. (3), which was adapted from Meng et al. (2018).

$$MB = \left(\frac{PFAS_{\text{treated soil}} + PFAS_{\text{treated leachate}} + PFAS_{\text{foamate}}}{PFAS_{\text{untreated soil}}} \right) * 100 \quad (3)$$

The $PFAS_{\text{treated soil}}$ represents the amount of PFAS remaining in soil, $PFAS_{\text{treated leachate}}$ stands for the amount of PFAS in treated leachate and $PFAS_{\text{foamate}}$ standing for the amount PFAS in the foamate.

A one-way ANOVA using Tukey pairwise comparison assuming equal variance was employed to examine whether the difference between the means of PFOS washed out at L/S ratios in the laboratory and pilot scale are statistically significant (95 % confidence interval). Minitab 19 was used for the statistical analysis. This was done to assess if the removal efficiencies on a pilot scale could be estimated using the results obtained from the laboratory scale.

3. Results and discussions

3.1. General characterization of the studied soils

The concentration of PFAS was 780 $\mu\text{g kg}^{-1}$ in soil I and in 27 $\mu\text{g kg}^{-1}$ soil II. Out of the eleven investigated PFAS, all were detected in soil I, whereas PFBS and PFDA were below the detection limit in soil II. PFAS compound with the highest detection was PFOS, which accounted for 97 % and 70 % of all analyzed PFAS in soil I and II, respectively. A large contribution of PFOS in the total analyzed PFAS was consistent with the activities employing the aqueous film-forming foams that took place on the site (Bergvall et al., 2019). The concentration of PFOS exceeded the Swedish Geotechnical Institute (SGI) guideline values of 3 and 20 $\mu\text{g kg}^{-1}$ for sensitive and less sensitive land use, respectively (Pettersson et al., 2015).

Particle soil analysis showed that the studied soils were predominated by particles with a size ranging between 0.063 and 1 mm, which represents the texture classification of sandy soil. These particles accounted for 88 % and 84 % in soil I and soil II, respectively. The second dominating particles ranged below 0.063 mm in size, representing silt-clay particles. The <0.063 mm size particles accounted for 9 % and 15 % in soil I and soil II, respectively. A detailed characterization of both soils including particle size distribution, pH, TOC, and elemental composition is found in Table S1. PFAS contaminated soils with characteristics similar to the current studied ones are widely found (Hale et al., 2017; Høisæter et al., 2021; Quinnan et al., 2022). PFAS was found in higher concentrations in the smaller particle size fraction, which can be linked to the high specific surface area, cation exchange capacity and low permeability of the clay-silt particles, making PFAS strongly retained on them (Y. Liu et al., 2020). In comparison to the bulk soils (unsieved), PFOS concentration was up to 2.0–2.5 times higher in the finer particles (<0.063 mm) and 1.0–1.5 times higher in 0.063–1 mm particles. PFAS concentration in the two soil particle size fractions and bulk soils is shown in Table S2.

3.2. Soil washing treatment on a small scale

Batch experiments were conducted to evaluate the release of PFAS from the two fractions, i.e., particles under 0.063 mm and particles within 0.063–1 mm soil.

The extent of PFAS washed out from the soils depended on different factors such as particle size, functional group of PFAS and carbon chain length of the compounds (Fig. 2).

The results indicated that soil washing was generally less effective for the fine particles under 0.063 mm. The PFAS removal efficiencies in

soil particles was consistent with the literature, stating that sorption coefficients of PFAS in soil is positively correlated with the clay content (Nguyen et al., 2020). A comparative analysis between two soils showed that the washing was more effective in soil II. For instance, the removal of \sum 11PFAS reached 37 ± 5.1 % in the fraction <0.063 mm and 50 ± 5.7 % for the fraction 0.063–1 mm (soil I), whereas the corresponding removals were significantly higher, i.e., 56 ± 0.9 % and 92 ± 6.9 %, respectively, in soil II. A plausible cause could be the presence of dissolved organic matter (DOC), which possibly comprised the TOC content in soil II. The soil washing process might have caused the leaching of DOC substances, which subsequently co-eluted with PFAS as was shown in previous studies (Jeon et al., 2011; Yang et al., 2013). This implies that the treatment of PFAS in soil via washing could be more appropriate for soil II after sieving since it exhibited significant differences in PFAS in finer and coarser particle size fractions. The overall removal via sieving-washing reached 47 ± 5.5 % in soil I and 85 ± 6.0 % in soil II.

The soil washing was more effective for the short-chain PFAS than the longer-chain. The removal efficiencies from the particles <0.063 mm in soil I were 100 ± 1.5 %, 100 ± 7.1 %, 82 ± 2.6 %, 83 ± 1.9 %, 73 ± 2.5 %, 50 ± 8.3 %, and 37 ± 6.1 % for PFBA (C4), PFPeA (C5), PFHxA (C6), PFHpA (C7), PFOA (C8), PFNA (C9) and PFDA (C10). The longer chain PFAS demonstrated a stronger retention in soil compared to the shorter chain PFAS, which is attributed to their low solubility in water and a relatively higher hydrophobicity (Du et al., 2014; Fabregat-Palau et al., 2022).

Furthermore, the results demonstrated that the functional groups (i.e., sulfonate and carboxylic group) influenced the efficiency of soil washing. The perfluorosulfonates (e.g., PFOS) were retained to a higher extent in soil than perfluorocarboxylates, having the same carbon chain length (e.g., PFOA). This behavior was consistent to their distribution to

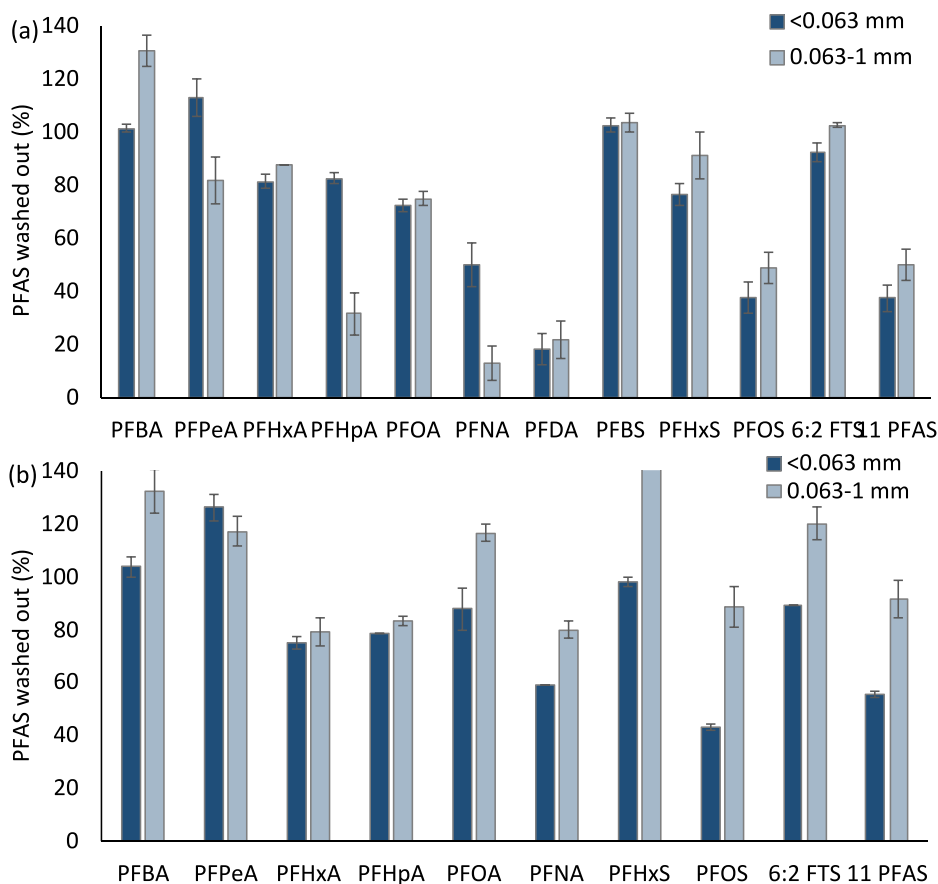


Fig. 2. PFAS removal through soil washing from two particle size fractions of soil I (a) and soil II (b). The solution pH was not modified. The error bars represent the minimum and maximum values (n = 2).

different components including suspended particulate matter, sediment and boehmite (Ahrens et al., 2010; Wang et al., 2012). The reason for this might be attributed to the perfluorocarbon tail. Even though the perfluorosulfonates and perfluorocarboxylates have the same number of carbon, the sulfonate has a larger number of carbons bonded to fluorine atoms ($\text{CF}_3\text{-(CF}_2\text{)}_n\text{-SO}_3^-$) as compared to the carboxylates ($\text{CF}_3\text{-(CF}_2\text{)}_n\text{-CO}_2^-$). The one CF_2 unit in the sulfonates increases their affinity for the solid phase (Higgins and Luthy, 2006).

The removal of PFOS in column experiments at different initial pH values is presented in Fig. 3. The extent of the removal of other PFAS is presented in Fig. S1. The leaching of PFOS was lower in acidic conditions and it gradually increased with increasing pH values. Acidic conditions increase the positive charges on the soil surface which binds anionic molecules of PFAS via electrostatic interactions (Kabiri et al., 2022; Y. Liu et al., 2020; Nguyen et al., 2020; Uwayezu et al., 2022). An increase in the pH value of the washing solution from 6 to 11.5 led to an increased leaching of PFOS by 50–70 % at L/S 10, explained by the electrostatic repulsion between the negatively charged soil surface and anionic molecules (Du et al., 2014).

The current results demonstrated that a continual replacement of leaching solution (i.e., increase in liquid-to-soil ratio) was another important factor that improved PFAS removal from soil. The removal of PFOS in soil I at pH = 11.5 increased by an average of 47 % after increasing the L/S from 2 to 10. This implied that the remediation of soils affected by firefighting training (dominated by PFOS contamination) would be practicable by increasing the pH of the washing solution and increasing the volume of the water passing through the soil. The current findings indicate that to meet SGI guideline values for PFOS in soil with less sensitive land use (to reach approximately 95 % PFOS removal in soil I), the treatment requires at least L/S 40 at pH = 11.5.

3.3. Pilot treatment of soil

3.3.1. Washing stage

A column washing test was upscaled to evaluate the operability of the soil washing method. The initial pH conditions that performed well on the lab-scale washing test were used (i.e., pH 11.5). Although alkaline conditions may disfavor further treatments such as FF, EO and adsorption (Y. Liu et al., 2020; Ren et al., 2023; Wang et al., 2023; Zhuo et al., 2012), a maximal soil washing efficiency was prioritized and pH 11.5 was used as an initial media condition. The concentration of detected PFAS in soil leachate in every washing cycle is shown in Table S3. To better illustrate the results, the removal efficiencies are shown for PFAS,

which had concentrations higher than $1 \mu\text{g kg}^{-1}$ in the original soil (Fig. 4). The results indicated that most PFAS were almost completely washed out after the third cycle except for PFOS. This result was similar to that observed on a laboratory scale (Fig. S1d). A high washing extent of PFAS (except PFOS) was expected to occur under the current conditions of pH and washing cycles, due to the nature of PFAS (short chain or perfluorocarboxylates PFAS) which prevents them from being retained in a sandy soil. The percentages above 100 % might have been caused by a combination of heterogeneities in soil samples and analytical errors, which underestimated the amount of PFAS in the untreated soil.

The means of PFOS washed out at L/S of 2 and 10 in the laboratory and pilot scales, determined using one way ANOVA are shown in Fig. 5a. The confidence intervals containing zero (reference dotted line at zero) indicate that the difference in means of paired L/S ratios was not statistically different (Fig. 5b). This implies that upscaling the treatment and reusing the treated leachate after foam fractionation did not affect the efficiencies of PFOS removal.

The ANOVA results permitted an estimation of 20 washing cycles (L/S of 40) to reach about 95 % PFOS removal in soil on a pilot scale, to attain Swedish Geotechnical Institute (SGI)-recommended guidelines for the less sensitive land use in Sweden. Although the initial pH value of the leachant was 11.5, it is worth mentioning that the pH was not kept constant during the treatment. This resulted in final pH values of the leachate ranging between 7.5 and 8.5 (Fig. S2), pH values which are very normal, and no further alteration of the soil due to extreme pH values would be expected. This decrease in pH is linked to the soil's buffering capacity.

3.3.2. Foam fractionation

Soil leachates obtained from the pilot soil washing were further treated using FF treatment. The removal efficiencies are shown in Fig. 6a. The results revealed a consistent removal of PFOS up to 95–99 % in every treatment cycle. The removal of other PFAS was 79 ± 5.0 % 6-2 FTS, 76 ± 5.4 % PFOA, 72 ± 6.2 % PFHxS, 63 ± 2.0 % PFHxA and 58 ± 1.6 % PFPeA. The current order of removal efficiencies indicated that the removal of PFAS was higher for the longer fluorocarbon chain PFAS. This behavior agreed with existing literature, which showed that the shorter chain PFAS exhibit a weak adsorption on the air-water interface due to high solubility in water and less surface activity (Brusseau, 2019; Meng et al., 2018). The perfluorosulfonates were also highly removed compared to the corresponding perfluorocarboxylates of the same carbon chain (i.e., PFOS versus PFOA or PFHxS versus PFHxA), which might be associated with the high surface active properties of the

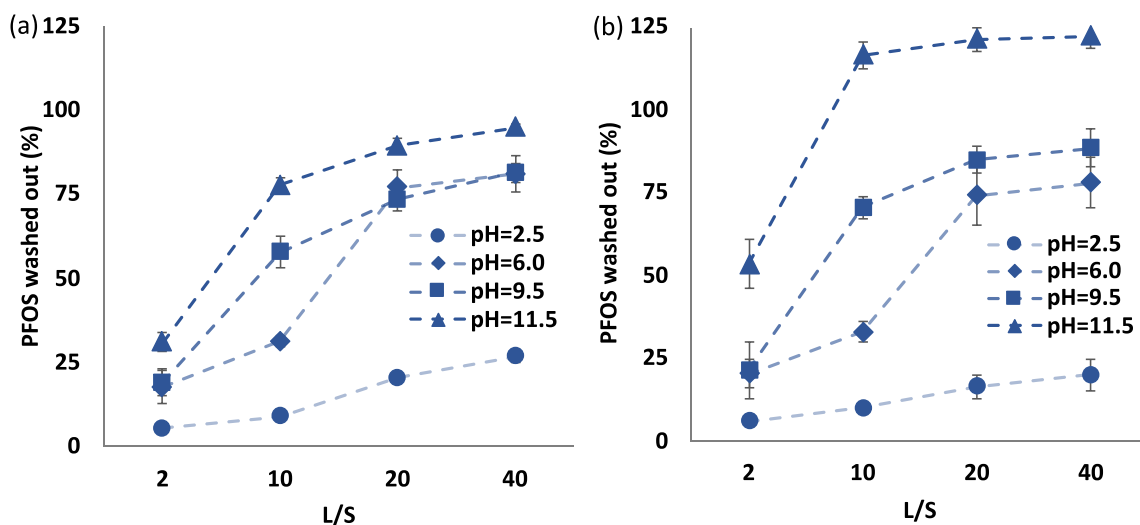


Fig. 3. Removal of PFAS in soil I (a) and II (b) through soil washing as a function of initial pH and liquid-to-soil ratio (L/S). The error bars represent the standard deviation, $n = 3$.

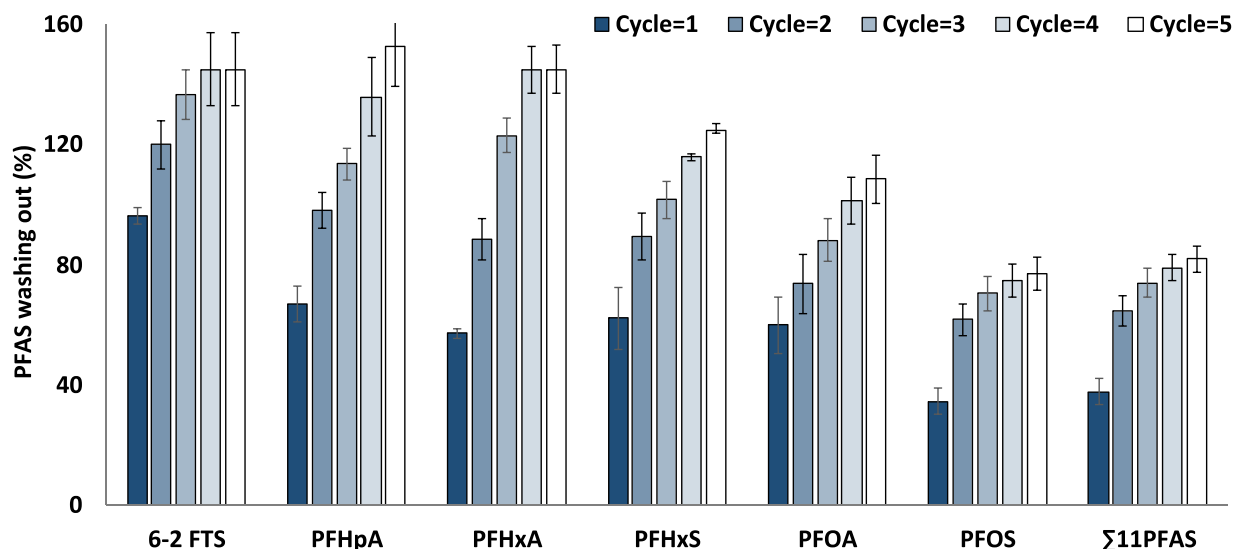


Fig. 4. Cumulative washing percentage on pilot scale for each washing cycle. The conditions were: 60 kg soil, 120 L washing solution in each cycle and initial pH value of 11.5. The error bars represent the standard deviations ($n = 3$).

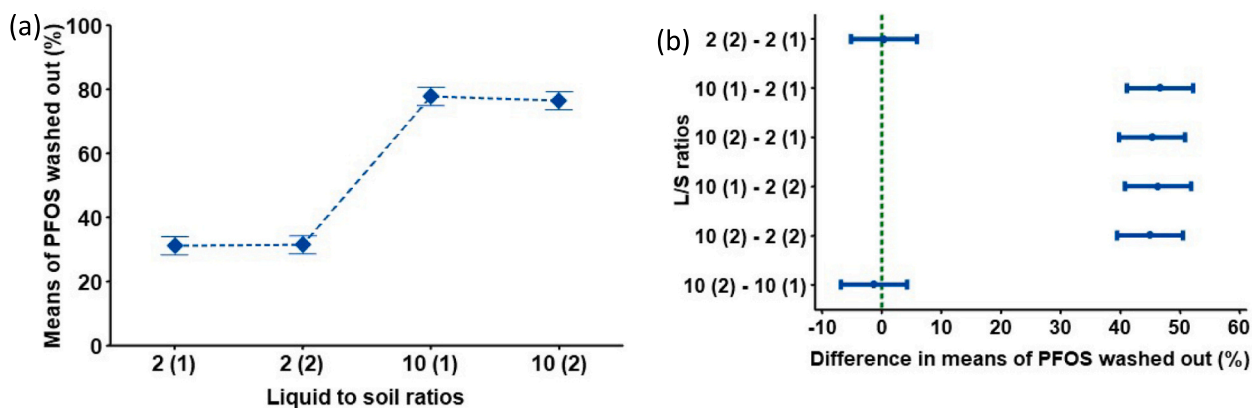


Fig. 5. Comparison for the means of PFOS washed out from soil in laboratory and pilot scales (a) and difference of means at different L/S ratios (b): 95 % confidence interval. The 2 (1) and 10 (1) stand for L/S = 2 and L/S = 10 on a smaller scale respectively whereas 2 (2) and 10 (2) stand for L/S = 2 and L/S = 10 on a pilot scale respectively.

perfluorosulfonates (Wang et al., 2023).

Since no study dedicated to investigating the competitive behavior between co-existing PFAS molecules on the water-bubble interface could be found in the literature, we compared our results to the competition between the molecules of PFAS onto different adsorbents (Deng et al., 2012; Du et al., 2015; Zhang et al., 2021). It was shown that the competitive adsorption decreased following the order of PFOS > PFOA > PFHxS > PFHxA > PFBS > PFBA (Deng et al., 2012; Du et al., 2015; Zhang et al., 2021). This order is consistent with the current PFAS removal on the water-bubble interface. Thus, it might be possible that the competition occurred during the sorption to the water-bubble interface, especially since the concentration of PFOS was higher. The current removal efficiency (i.e., 92 ± 2.2 % $\Sigma 11$ PFAS) under 50 L min^{-1} air flow and during 30 min was higher than the 66 % PFAS removal obtained at 20 L min^{-1} air flow and during 20 min and using a similar reactor design (Smith et al., 2022), implying that the airflow and treatment time are important factors that improve the removal efficiencies.

The removal efficiency of 92 ± 2.2 % $\Sigma 11$ PFAS meant that this fraction was concentrated in a small volume of waste (foamate). PFAS enrichment factors for each cycle are shown in Fig. 6b. The results evidenced a removal of PFAS from the leachates and their transfer into

the foam. The variability of the enrichment factors among treatment cycles is associated with the foam harvesting, i.e., the accidental collection of leachate with the foam diluted the foamate and caused a decrease in the enrichment factor. The average enrichment factor of 339 for the $\Sigma 11$ PFAS was significantly higher than previously reported factors of 2.9–3.7 obtained during FF treatment of landfill leachate (McCleaf et al., 2021; Robey et al., 2020), most likely due to the higher PFOS concentration in the current soil leachate. On the other hand, the current enrichment factor for PFOS (600) was considerably lower than the 8400 reported by Meng et al. (2018), work in which a non-ionic hydrocarbon surfactant was used to enhance the separation of PFOS. The assessment of the results indicated that only 3 % PFOS and 21–40 % of 6-2 FTS, PFOA, PFHxS, PFHxA and PFPeA remained in the leachate, allowing 99 % of the volume of the leachate recycled through soil washing. Interestingly, the amount of PFAS being returned to the soil significantly decreased as the washing sequence increased. Thus, the combination of soil washing and foam fractionation showed great potential to transfer PFAS from soil to the leachate and decrease in the volume of PFAS concentrated waste, which would be subjected to the further treatments. A mass balance (MB) determined as per Eq. (3) showed that 96 % of $\Sigma 11$ PFAS was contained between the treated soil, treated leachate and foamate (Fig. 6c). For individual compounds, the

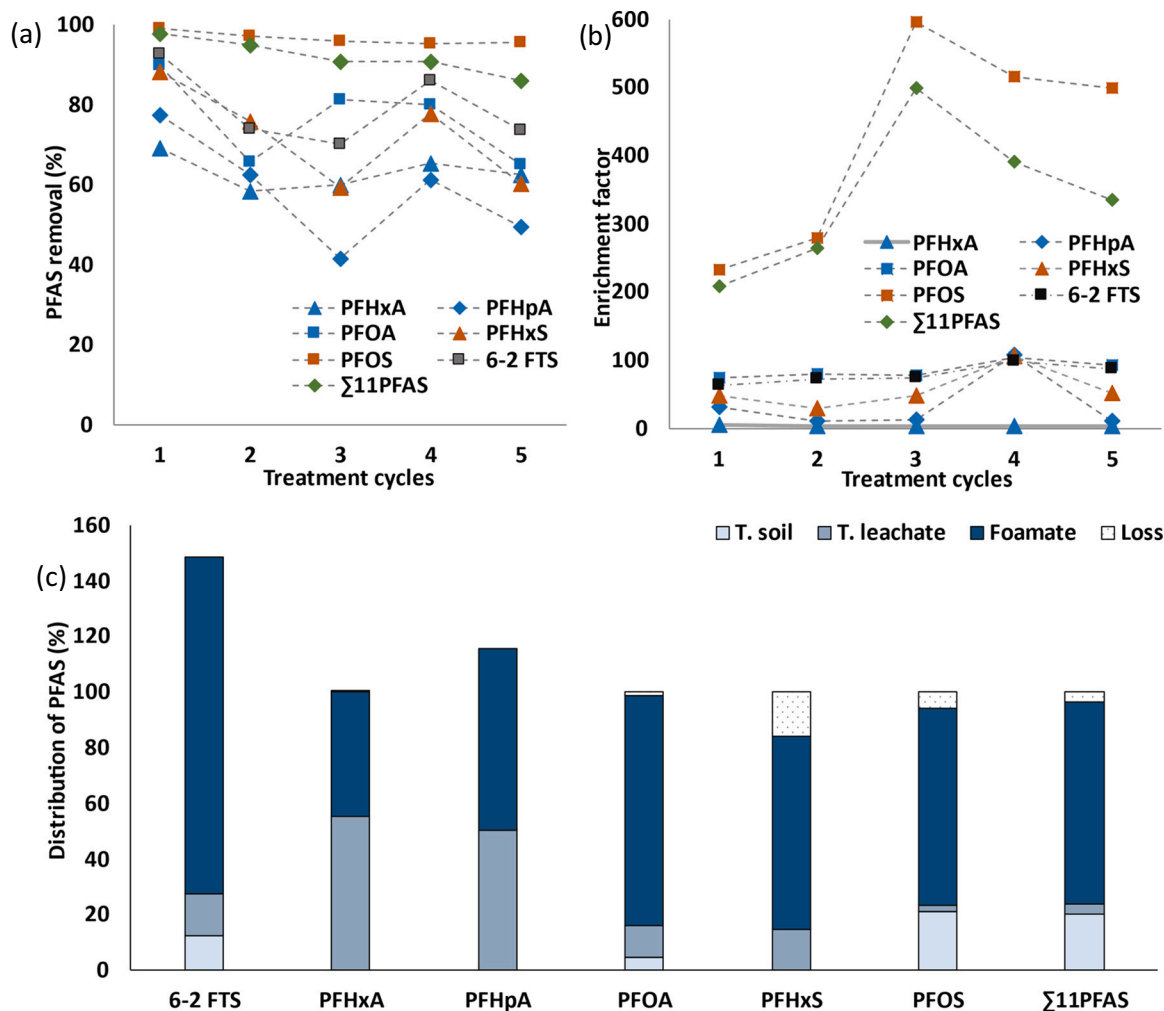


Fig. 6. PFAS removal in soil leachate using (a) FF, (b) enrichment factors and (c) the distribution of PFAS between treated soil, and leachate and foamate. The percentage above zero in (c) implied that there was no loss of PFAS.

MB was 94 % PFOS, 99 % PFOA, 84 % PFHxS and 148 % for 6-2 FTS. The distribution of PFAS between different phases was in line with the determined removal efficiencies in each phase, i.e., PFAS leached out from the soil and effectively removed by aeration were mainly concentrated in the foamate (e.g., PFOS, PFOA and 6-2 FTS), whereas PFAS that were easily removed from the soil and least removed using the FF process were mainly remaining in the treated leachate (PFHxA and PFHpA). Furthermore, the MB analysis revealed that 4 % of Σ11 PFAS was not recovered in any phase, which could be linked to the escape of PFAS (likely by air), which is commonly found during foam harvesting (McCleaf et al., 2021; Smith et al., 2022). Overall, as the intent was to add foam fractionation step to soil washing in order to concentrate PFAS into solutions, the MB indicated that after five consecutive treatment cycles, an amount of PFAS corresponding to 73 % of Σ11 PFAS (71 % PFOS) washed out from soil and effectively recovered into the foamate.

3.3.3. Treatment of PFAS in the foamate

The treatment of PFAS concentrated foamate was evaluated using a flow-through electrochemical cell for the degradation of PFAS. The concentration of the Σ11 PFAS in the foamate was $3283 \mu\text{g L}^{-1}$, out of which 88 % was PFOS. The second and third predominant PFAS were 6:2 FTS ($300 \mu\text{g L}^{-1}$) and PFOA ($38 \mu\text{g L}^{-1}$).

The electrochemical treatment of the foamate decreased concentration of the Σ11 PFAS to $2623 \mu\text{g L}^{-1}$ after 2 h (Fig. 7a), corresponding to 90 ± 4.0 % removal. The analysis of the results demonstrated that the concentration of PFOS dropped by 91 ± 2.0 % in the first 30 min and to

97 ± 1.0 % in 2 h. The current removal of PFOS was comparable with those reported during the electrochemical degradation of PFOS in landfill leachates or PFAS concentrated waste from regeneration of spent ion exchange resin (Anglada et al., 2010; Maldonado et al., 2021).

The concentration of long-chain PFAS such as 6-2 FTS, PFOA, PFNA and PFDA also decreased with an average removal of 70 %, 89 %, 94 % and 99 % respectively. However, a temporal increase was observed for the short-chain PFAS namely PFBA, PFPeA, PFHxA and PFHpA (Fig. 7b), likely attributed to the degradation of precursors and longer-chain PFAS (Anglada et al., 2010; Maldonado et al., 2021). The current decrease in the concentration of longer-chain PFAS and an increase in the concentration of shorter-chain PFAS followed the proposed mechanism for PFAS degradation via the electrochemical oxidation (Pierpaoli et al., 2021; Zhuo et al., 2012).

A complete removal of PFAS without generating byproducts can be achieved in complex solutions containing various amounts of PFAS and other substances (Anglada et al., 2010; Liang et al., 2022; Maldonado et al., 2021). This implies that optimizing the current electrochemical treatment process could lead to a complete removal of PFAS in the foamate. In fact, it was shown that current density and time are major parameters to optimize the electrochemical oxidation of PFAS (Uwayezu et al., 2021).

The removal of PFAS in the foamate through adsorption instead of electrochemical oxidation was assessed. The results showed that the amount of adsorbed PFAS increased with increasing the adsorbent dosage (Fig. 7c and d). The highest removal was found at a dosage of 0.8

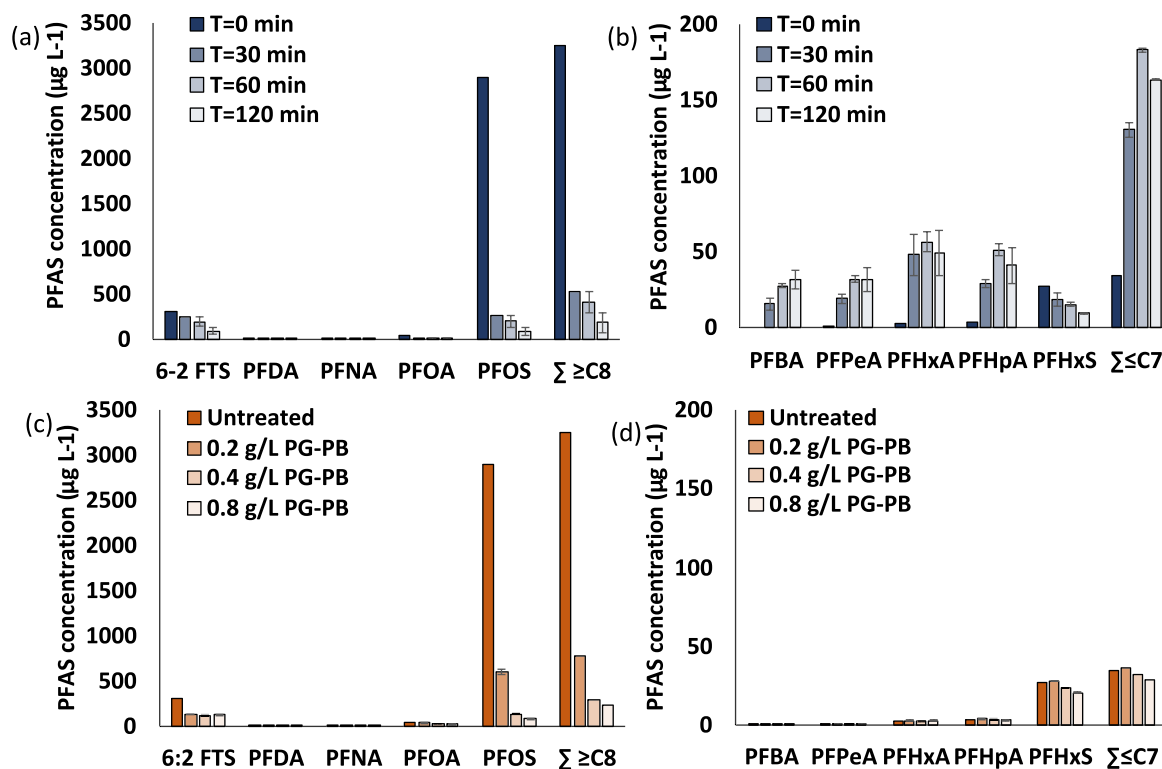


Fig. 7. PFAS removal in foamate using electrochemical degradation and adsorption: (a) degradation of longer chain and (b) degradation of shorter chain, (c) adsorption of longer chain and (d) adsorption of shorter chain PFAS. Current density 60 mA cm^{-1} flow rate 6 L min^{-1} and 24 h shaking time for adsorption experiments. The error bars represent the standard deviations ($n = 3$).

g L^{-1} obtaining $97.2 \pm 0.5 \%$ PFOS and $92 \pm 1.0 \%$ $\Sigma 11$ PFAS efficiencies. The adsorbent showed a higher adsorption for PFOS (Fig. 7c) than for any other measured PFAS compound. The long-chain PFAS were better removed by the PG-PB as compared to short-chain PFAS due to the strong hydrophobic interaction between the long-chain PFAS with the adsorbent (Ren et al., 2023). It was earlier demonstrated that the hydrophobic interaction between the adsorbed long-chain PFAS and free long-chain PFAS is strong enough to form bilayer or semi-micelles (Du et al., 2014) and increases the adsorption efficiency of the long-chain PFAS. However, as shown in Fig. 7d, the short-chain PFAS (PFBA, PFBS, PFPeA, PFHpA, and PFHxA) were not efficiently removed by the PG-PB, which resulted from the weak hydrophobic interactions caused by the low hydrophobic properties of these PFAS compounds (Ren et al., 2023). Furthermore, the long-chain PFAS compete with the short-chain PFAS for adsorption sites, making the removal of short-chain PFAS even harder in the presence of longer-chain PFAS (Maimaiti et al., 2018; Wang et al., 2019).

In general, the removal of PFAS in the foamate using electrochemical oxidation at 60 mA cm^{-1} and 2 h was nearly equal to the removal obtained when using adsorption at 0.8 g L^{-1} dosages (93–95 %) for the long chain PFAS (i.e., $\geq C8$). Under these conditions, the amount of short-chain PFAS ($\leq C7$) decreased by 20 % using the adsorption process whereas it drastically increased by 366 % using the electrochemical oxidation. However, extending the electrolysis time could also degrade the short chain PFAS (Uwayezu et al., 2021). Nevertheless, spent adsorbents would require further treatment (e.g., incineration), whereas degradation processes would represent the end of the contaminant life cycle. Incineration of the bio adsorbent at $1100 \text{ }^\circ\text{C}$ could produce ash without detectable PFAS as shown in a previous study (Sandblad, 2022), though it was not confirmed that PFAS would completely mineralize. For that reason, transformations into volatile by-products could not be dismissed after the thermal process.

4. Conclusion

The current study evaluated the operability of the remediation of PFAS-contaminated soil using a multi-step treatment system comprising soil washing, foam fractionation (FF) and electrochemical oxidation (EO) or adsorption. The technique was tested on sandy soil containing mainly PFOS. The results showed that up to 95 % of PFOS was removed at the initial pH of 11.5 and L/S 40. The other ten measured PFAS were easily washed out under the same conditions. The leaching behavior of PFOS on the small scale experiments was consistent and similar to that on the pilot scale with recirculated leachate. For soils with long-chain PFAS being the principal contaminants, the foam fractionation could offer a cost-efficient and effective way to reduce the final volume of leachate to be treated by applying more cost and energy-intensive destructive methods. However, a proper collection of foam is required to prevent the spread of PFAS into the surrounding environment.

By applying a three treatment steps consisting of soil washing, foam fractionation and electrochemical oxidation (SW-FF-EO), an overall destruction of 67 % $\Sigma 11$ PFAS that were detected in soil was achieved at $\text{pH} = 11.5$ and applying five washing and foam fractionation treatment cycles. This indicates a good potential of the technique for PFAS remediation in contaminated sandy soil, but optimization of the method is needed to increase its overall efficiency. The replacement of electrochemical oxidation by adsorption would lead to similar removal of PFAS in soil and generated solutions, however, the spent adsorbent would require further treatment. Once more, foamate escape was identified as one of the main mechanisms by which PFAS mass balance was unbalanced suggesting the importance of using well-designed facilities, capable of preventing PFAS from spreading during the treatment.

CRedit authorship contribution statement

Jean Noel Uwayezu: Conceptualization, investigation, methodology, writing– manuscript; Sarah Sonnenschein: Methodology; Ivan

Carabante: Conceptualization, planning, methodology, manuscript editing & supervision; Jurate Kumpiene: Conceptualization, planning, methodology, manuscript editing & Supervision; Tore Lejon: Methodology & manuscript editing; Patrick van Hees: Investigation & methodology; Patrik Karlsson: Investigation & methodology; Zhongfei Ren: Methodology & writing; Tiina Leiviskä: Conceptualization & planning.

Declaration of competing interest

The authors affirm that there are no recognized conflicting financial interests or personal affiliations that might have seemed to exert any influence on the work detailed in this paper.

Data availability

All relevant data and materials are included in the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.168137>.

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