



Per- and polyfluoroalkyl substance (PFAS) removal from soil washing water by coagulation and flocculation

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ABSTRACT

Soil washing is currently attracting attention as a promising remediation strategy for land contaminated with per- and polyfluoroalkyl substances (PFAS). In the soil washing process, the contaminant is transferred from the soil into the liquid phase, producing a PFAS contaminated process water. One way to treat such process water is to use coagulation and flocculation; however, few studies are available on the performance of coagulation and flocculation for removing PFAS from such process water. This study evaluated 6 coagulants and flocculants (polyaluminium chloride (PACl), zirconium oxychloride octahydrate, cationic and anionic polyacrylamide, Polyclay 685 and Perfluor Ad®), for the treatment of a proxy PFAS contaminated washing water, spiked with PFAS concentrations found at typical Aqueous Film Forming Foam (AFFF) contaminated sites. PFAS removal efficiencies (at constant pH) varied greatly depending on the coagulants and flocculants, as well as the dosage used and the targeted PFAS. All tested coagulants and flocculants reduced the turbidity by >95%, depending on the dosage. Perfluor Ad®, a specially designed coagulant, showed the highest removal efficiency for all longer chain (>99%) and shorter chain PFAS (>68%). The cationic polyacrylamide polymer removed longer chain PFAS up to an average of 80%, whereas average shorter chain PFAS removal was lower (<30%). The two metal-based coagulants tested, PACl and zirconium, removed longer chain PFAS by up to an average of 61% and shorter chain PFAS up to 48%. Polyclay 685, a mixture of powdered activated carbon (PAC) and aluminium sulphate, removed longer chain PFAS by 90% and shorter chain PFAS on average by 76%, when very high dosages of the coagulant were used (2,000 mg/L). PFAS removal efficiencies correlated with chain length and headgroup. Shorter chain PFAS removal was dependent on electrostatic interaction with the precipitating flocs, whereas for longer chain PFAS, hydrophobic interactions between apolar functional groups and flocs created by the coagulant/flocculant, dissolved organic matter and suspended solids played a major role. The results of this study showed that by selecting the most efficient coagulant and aqueous conditions, a greater amount of PFAS can be removed from process waters in soil washing facilities, and thus included as part of various treatment trains.

1. Introduction

Due to their widespread use and persistence, per- and polyfluorinated alkyl substances (PFAS) are detected in many regions at alarming concentrations in soil (Hale et al., 2017), groundwater and drinking water (Teymoorian et al., 2023), landfill leachate and wastewater treatment sludge (Fredriksson et al., 2022). As contaminated soil is a common source of PFAS contamination to other environmental compartments, there is increasing interest in soil remediation options

(Bolan et al., 2021). One approach is soil washing, where the goal is to transfer PFAS from the soil to a washing water for further treatment, potentially allowing for reuse of the washed soil. The PFAS removal efficiency of this technology was recently demonstrated at field scale (Grimison et al., 2023; Quinnan et al., 2022). The process water from soil washing contains high concentrations of PFAS (up to 26 µg/L (Quinnan et al., 2022)) and consists of suspended fine soil particles that have high residual PFAS concentrations due to their strong sorption affinity (Hubert et al., 2023). Therefore, methods are needed to reduce

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aqueous PFAS concentrations, while at the same time separating the fine material from the water phase.

Coagulation and flocculation are commonly applied treatment approaches for process water, whereby coagulation is the destabilization of the surface charge of colloids to make flocs and flocculation is the aggregation of these flocs to larger particles (Crittenden et al., 2012). This can significantly improve further separation in subsequent treatment steps like sedimentation or granular filtration (Alexander et al., 2012). Coagulants and flocculants use various mechanisms such as charge neutralization, physical entrapment, sorption and complexation, which all depend on parameters like pH and dosage (Alexander et al., 2012). Conventional coagulants and flocculants used in water and wastewater treatment include inorganic multivalent metal species, like Fe^{3+} , Al^{3+} or Zr^{4+} , synthetic organic polymers like cationic and anionic polyacrylamides (Arp and Knutsen, 2020), and natural organic polymers such as chitosan (Crittenden et al., 2012). To improve the removal of dissolved compounds like organic micropollutants in the coagulation and flocculation stage, specifically designed sorbents can be added. Examples of this are addition of powdered activated carbon or ion exchange active compounds (Wan et al., 2011).

There is only a limited number of studies published that investigate the efficiency of coagulation and flocculation for the treatment of PFAS contaminated water (Bao et al., 2014; Deng et al., 2011; Pramanik et al., 2015; Xiao et al., 2013). These studies used surface water or synthetic surface water with relative low turbidity (<10 NTU) and spiked PFAS into the synthetic suspension at high concentrations (ranging from 0.1 mg/L to 1 mg/L). The study by Deng et al. (2011) looked at sorption differences for 4 perfluorocarboxylic acids (PFCA) with a carbon chain length ranging from C_4 to C_{12} and reported increased sorption to flocs with increasing perfluorinated chain length. All other previous studies focused only on PFOA and PFOS. The materials used in these previous studies were mostly aluminium and ferric based coagulants (Deng et al., 2011; Pramanik et al., 2015; Xiao et al., 2013). In addition, some of the studies tested powdered activated carbon (PAC) to increase PFAS sorption and removal (Deng et al., 2011; Pramanik et al., 2015).

In comparison to the studies above, soil washing process waters have higher turbidity (up to 100 NTU) and higher concentrations of suspended solids (Park et al., 2002). These aqueous media also contain a greater variety of PFAS (Hubert et al., 2023) that are found at lower concentrations. For example, Quinnan et al. (2022) used a pilot scale mobile washing treatment process to remediate PFAS contamination soil from an airbase in Fairbanks, Alaska. Before treatment PFAS concentrations (24 target PFAS) ranged from 316 ng/L to 25,900 ng/L. There is a clear knowledge gap related to the role of coagulants and flocculants in the treatment of process water from soil washing facilities.

To address this, the aim of this study was to evaluate the removal efficiency of 14 PFAS with a variety of chain lengths and head groups, from C_4 (PFBS) to C_{14} (PFTeDA), from a proxy soil washing water by coagulation and flocculation. Jar tests were carried out with 6 different coagulants and flocculants to investigate the role of material type and dosage on removal efficiency. The investigated materials included cationic and anionic polyacrylamides (Superfloc® HMW C-494 and FLOPAM™ AN 926 SH), two metal-based coagulants (polyaluminium chloride (PACl) and zirconium oxychloride octahydrate (zirconium)), Polyclay 685, a mixture of $\text{Al}_2(\text{SO}_4)_3$ and powdered activated carbon (PAC), as well as Perfluor Ad®, a specially designed coagulant for PFAS removal. Except Perfluor Ad®, the tested materials were chosen based on their common usage in water- and wastewater treatment applications (Crittenden et al., 2012; Uysal and Boyacioglu, 2021). Despite Perfluor Ad® being introduced to the market in 2015, there is a limited number of reviewed studies, and those that exist do not primarily address its application in treating soil wash water (Cornelsen et al., 2021). The results of this study will support the optimization of washing water treatment at soil washing facilities and possibly also at wastewater treatment facilities, by helping identify the correct coagulant or flocculant type to increase PFAS removal efficiency.

2. Materials and methods

2.1. Coagulation and flocculation materials and test conditions

The coagulant and flocculant dosages and experimental pH used in this study are presented in Table 1. The coagulants and flocculants were grouped for latter comparison to one and other based on their chemical properties and expected PFAS removal mechanisms. Recommendations for best working conditions and dosage ranges were provided by the distributors or used based on previous literature studies. The conditions were then verified and adjusted during pre-testing, based on the degree of turbidity removal (supplementary material S1). The dosages chosen were compared to other studies related to treatment of wastewater and waters with higher turbidity (Table 1). Pretests showed that coagulation with Perfluor Ad® will result in formation of very small flocs. To improve their sedimentation properties, zirconium was dosed in addition, since it showed better turbidity removal over a wider dose range, compared to PACl (Table S3).

2.2. Soil

To make the proxy soil wash water, an uncontaminated soil was collected and subsequently spiked with PFAS. The soil used in this study was collected from a road construction site close to Åsbygda, Norway ($60^\circ 13' 21.8'' \text{N}$ $10^\circ 22' 57.1'' \text{E}$) just below the topsoil layer. Before further processing, the soil was dried in an oven at 60°C for 72 hours. After that, the soil was sieved through a 0.063 mm meshed sieve to separate sand particles from the finer soil particles. The soil was then analysed for total organic carbon (TOC) and inorganic carbon (IC) content (in triplicate), and specific surface area (SSA, using N_2 - BET in duplicate). A detailed method description can be found in (Hubert et al., 2023). Measurements for DOC were carried out for individual samples by Eurofins Environment Testing Norway AS (Moss), following standard NS-EN 1484.

2.3. PFAS spiking procedure and analysis

For spiking, the following PFAS were purchased in salt and liquid form from SIGMA Aldrich, Germany: perfluorobutanoic acid (PFBA, purity: 98%), perfluoropentanoic acid (PFPeA, 97%), perfluorohexanoic acid (PFHxA, $\geq 98\%$), perfluoroheptanoic acid (PFHpA, $\geq 97\%$), perfluorooctanoic acid (PFOA, 95%), perfluorononanoic acid (PFNA, 97%) and perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUnDA, $\geq 97\%$), perfluorododecanoic acid (PFDoDA, 95%), perfluorotetradecanoic acid (PFTeDA, 96%), perfluorobutanesulfonic acid (PFBS, 97%), perfluorohexanesulfonic acid (PFHxS, $\geq 97\%$), perfluorooctanesulfonic acid (PFOS, 30–50%), and N-Ethyl-perfluorooctansulfonamid (EtFOSA, $\geq 98\%$). After sieving, the soil was spiked with these 14 PFAS. A detailed description of the soil spiking protocol can be found in the supplementary material (S2).

Water and soil samples were analysed for 13 target PFAS. The analytical procedure for PFAS was not able to detect PFBA and EtFOSA. PFHpS was found in substantial concentrations, even though it was not intentionally spiked into the soil. It is assumed to be an impurity from the other PFAS spiked. Information about all PFAS including CAS number, acronym, chemical structure, molecular weight, and the respective isotopically labelled internal standard used can be found in the supplementary material (S3). A detailed description of sample preparation for water and soil samples and target PFAS analysis can be found in the supplementary material (S4).

This study uses the same definition for “shorter chain” perfluorosulfonic acids (PFSA $\leq \text{C}_6$) and “shorter chain” PFCA ($\leq \text{C}_8$) as was used in our previous sorption study (Hubert et al., 2023) with one exception. PFHpS (C_7) is considered a “longer chain” PFAS given its removal patterns are similar to other longer PFSA. It should be emphasized that these classifications of “shorter chain” and “longer chain” differ from the OECD definitions of “short chain” and “long

Table 1
Coagulants and flocculants used in this study (Guida et al., 2007; Wong et al., 2006).

Grouping	Product name	Distributor	Material (Reference name)	Description	pH used	Dosage applied	Dosage ranges from Distributor or other studies
Inorganic metal-based coagulants	PAX-18	Kemira Chemicals (Norway)	Polyaluminium chloride (PACl)	Al ³⁺ : 9% [w/w] Basicity 42%	6.47±0.07	30.8 mg/L Al ³⁺ (1.14 mmol/L) to 369.9 mg/L (13.71 mmol/L)	24 - 71 mg/L Al ³⁺ (Guida et al., 2007)
	Aquator	Teta Vannrensing Ltd (Norway)	Zirconium (IV) oxychloride octahydrate (zirconium)	Zr ⁴⁺ : 27% [w/w]	6.18±0.05	1.35 mg/L (0.02 mmol/L) to 540 mg/L (5.92 mmol/L)	10 - 100 mg/L Zr ⁴⁺ (Uysal and Boyacioglu, 2021)
Cationic and anionic polyacrylamide flocculants	Superfloc® C-494 HMW	Kemira Chemicals (Norway)	Cationic polyacrylamide (C-494)	Molecular weight (MW): 8 M Daltons charge density (CD): 20%	6.28±0.07	0.05 to 15 mg/L	0.5 - 15 mg/L (Wong et al., 2006)
	FLOPAM™ AN 926 SH	Kemira Chemicals (Norway)	Anionic polyacrylamide (FLOPAM™)	MW: 12 to 14 M Daltons CD: 23%	6.59±0.03	0.05 to 15 mg/L	
Specially designed coagulants for contaminant and PFAS removal	Perfluor Ad®	Cornelsen Umwelttechnologie (Germany)	Cationic organic polymer (Perfluor Ad®)	fatty acid from plant origin with added cationic groups	5.97±0.04	25 to 200 mg/L Perfluor Ad® and 300 to 1,000 mg/L Zr ⁴⁺	25 - 200 mg/L for soil washing applications + additional coagulation aid
	Polyclay 685	Nordisk Vannteknikk AS (Norway), sample received from AF Decom AS	Powdered Activated carbon (PAC) /Aluminium sulfate (Polyclay 685)	AC >10%, AL ₂ (SO ₄) ₃ >10%, CaO <10%	6.48±0.03	17 to 4,000 mg/L	<150 mg/L Polyclay 685 for second treatment steps

chain" PFAS (Wang et al., 2021). The rationale for the definition used in this study is to describe the study's results more efficiently.

2.4. Jar test procedure

The PFAS removal efficiency of the selected coagulants and flocculants was investigated by using jar tests with constant pH (Table 1), but with varying coagulant or flocculant dosages, using a JLT 6 Flocculator (VELP Scientifica). To produce a proxy soil washing water, jars were filled with 500 ml of Milli-Q water; then NaCl₂ was added as an electrolyte to achieve a concentration of 0.01 M, in addition to 15 g of spiked sieved soil. This corresponds to a L:S ratio of 33:1 and is similar to that used in a previous PFAS soil washing field trial (L:S ratio 29.5±4.1) (Grimison et al., 2023). The prepared proxy soil washing water was mixed for 60 min to simulate the washing process in remediation facilities (Gautam et al., 2020). The mixing speed was set to 100 rpm to ensure that most solids stayed in suspension. The coagulant or flocculant was then added to the suspensions and the pH adjusted to the individual working pH (Table 1) using 1 M solutions of H₂SO₄ and NaOH. After

this, the suspensions were rapidly mixed at 300 rpm for one minute, followed by a slow mixing step at 25 rpm for 20 min. Afterwards, the stirrer was removed, and the suspensions were allowed to settle for 60 min. For PFAS analyses, analytical duplicates (each 50 mL) were taken using a polypropylene syringe around 2 cm below the water surface and filtered through a 0.45 µm Minisart® recycled cellulose filter. After this, 20 ml water samples were taken for turbidity measurement. Visual inspection was carried out for each jar noting the size of the flocs. Turbidity was measured with a TIR 210 (VWR, Norway), pH with an InoLab pH Level 2 pH metre (WTW), and electrical conductivity (measured in pretests) with a LF 538 Conductivity metre (WTW). Water samples were stored in 50 ml Falcon® tubes (VWR Norway), before analysis. Further information about the jar test procedure can be found in the supplementary material (S1)

2.5. Data analysis

Removal efficiencies (RE) were calculated for each duplicate sample following Eq. (1):

$$RE [\%] = \left(1 - \frac{C_{PFAS, treatment}}{C_{PFAS, no treatment}} \right) * 100\% \quad (1)$$

Where $C_{PFAS, no treatment}$ [ng/mL] is the concentration of PFAS measured in the jar tests without any treatment (no added coagulant or flocculant) and $C_{PFAS, treatment}$ [ng/mL] the measured concentration in the jar tests after treatment. In cases where PFAS concentrations were below the instrumental LOD, missing values were substituted with LOD/2. Removal efficiencies are presented as the arithmetic mean \pm standard error (SE) (supplementary material S5).

2.6. Quality assurance and quality control (QA/QC)

QA/QC protocols were implemented during all experimental and analytical steps. A detailed description is provided in the supplementary material (S6). Recovery rates for the membrane filtration step were PFAS dependent and in the range of 83 to 97% (Table S7). Instrumental LOD/LOQ and total relative recoveries for water (73 to 96%) and soil samples (52 to 95%) are also presented therein.

3. Results and discussion

3.1. Soil and proxy soil washing water characteristics

The sieved soil had low concentrations of TOC (0.76 ± 0.01 %) and IC (0.22 ± 0.01 %). After 1 hour of mixing in the jar test, the suspension pH was close to neutral (6.49 ± 0.04) and the electric conductivity was 2.16 ± 0.01 mS/m. The washing water DOC was 0.81 mg/L and the specific surface area was 1.96 ± 0.30 m²/g. After 1 hour of settling and without any added coagulant or flocculant, the turbidity was 38.4 ± 0.5 NTU. The PFAS concentrations in the spiked soil were between 970 ± 82.3 ng/g for PFOS and 33.4 ± 1.70 ng/g for PFDODA, resembling a highly PFAS contaminated soil, that is comparable to concentrations found at AFFF contaminated airport sites (Hale et al., 2017; Hubert et al., 2023). The PFAS concentrations detected were on average 28% below of those expected, based on calculated spiking levels. Analysed concentrations were used for the purposes of this study. More information can be found in the supplementary information S7.

After mixing the proxy soil washing water in the jar tests for 1 hour, PFAS with a chain length $\leq C_{10}$ desorbed by an average of 98% from the soil into the water phase. PFCA with $\geq C_{12}$ were below LOD in all water

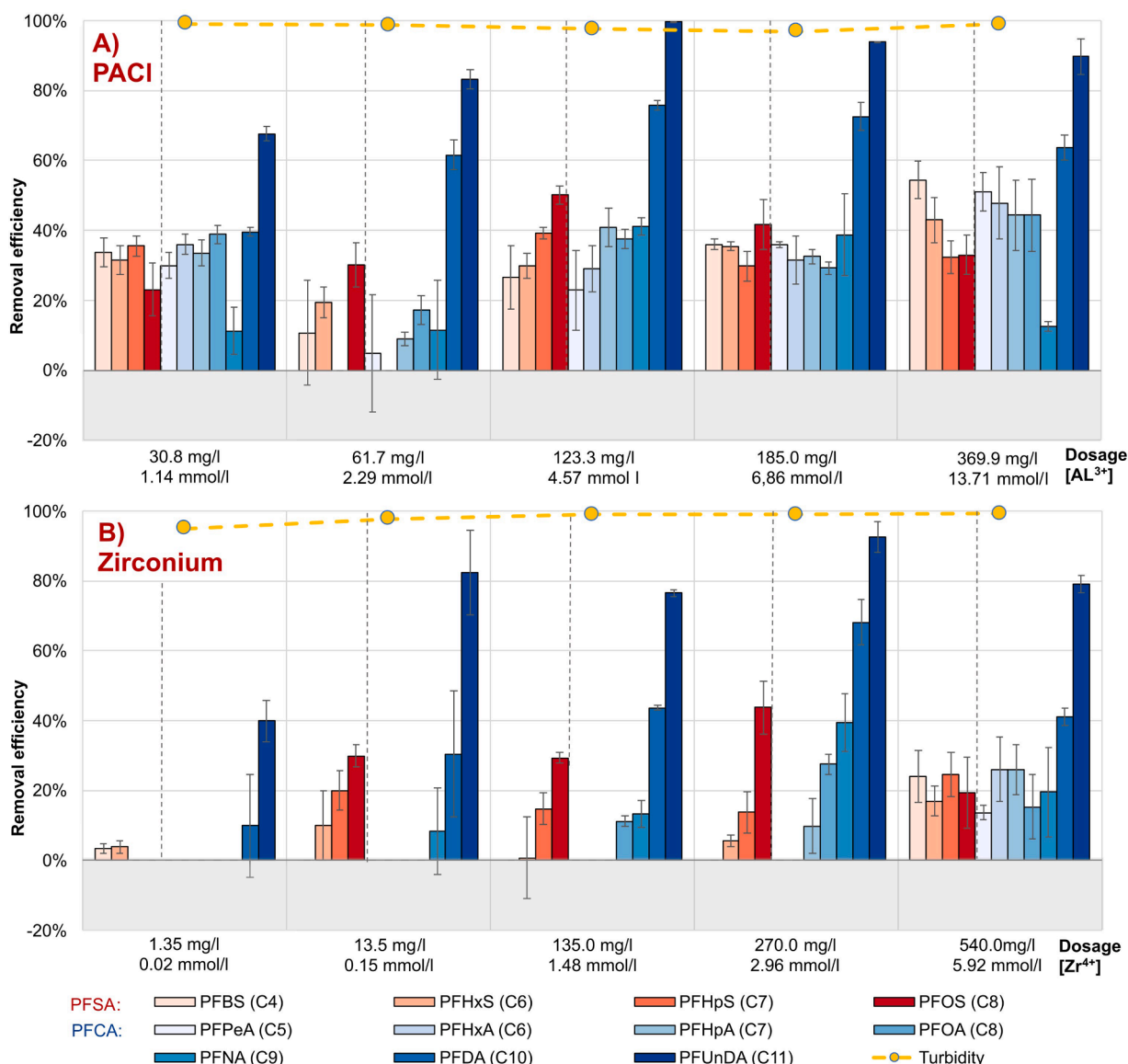


Fig. 1. PFAS removal efficiencies for different dosages of A) PACl [Al³⁺] at pH of 6.47 and B) Zirconium [Zr⁴⁺] at pH of 6.18.

samples due to their strong sorption to the soil. The PFAS concentrations in the water phase were in the range of 0.3 ± 0.03 ug/L for PFUnDA and 29.1 ± 1.9 ug/L for PFOS.

3.2. PFAS removal efficiency by coagulation and flocculation

3.2.1. Inorganic metal-based coagulants

Fig. 1 presents the removal efficiencies for each PFAS when PACl (PAX-18) and zirconium (Aquator) were used. PACl reduced the initial turbidity of 38.4 ± 0.5 NTU by more than 95% at all applied dosages. Zirconium reduced the turbidity by up to 99% when dosages ≥ 0.15 mmol/L were used. Depending on the solution pH, different aluminium and zirconium species are dominant. At pH 6.47 used here, the predominant species for all tested dosages of PACl would be amorphous aluminium $\text{Al}(\text{OH})_{3(s)}$ (Crittenden et al., 2012). For zirconium dosages above >0.02 mmol/L the neutral, amorphous $\text{Zr}(\text{OH})_{4(s)}$ species will prevail at the pH used in this study of 6.18 (Veyland et al., 1998). Under these conditions the amorphous form of the metal species forms by nucleation on the surface of particulates in solution. Consequently, these particles will become part of the floc structure, resulting in larger and more voluminous precipitate. This process, known as sweep flocculation, hereby effectively removes particles from the solution and will be the main removal mechanism under these conditions (Crittenden et al., 2012). For the lowest tested zirconium dosage (0.02 mmol/L), the main species observed, would be charged $\text{Zr}(\text{OH})_3^+$. When positively charged metal hydroxides are formed in solution, they will adsorb to negatively charged particles and destabilize them (charge neutralization). The positively charged surface serves as potential sorption sites for negatively charged solutes (Crittenden et al., 2012). Due to the prehydrolyzed state of PACl, positively charged mononuclear and polynuclear species can still be stable at neutral pH, which indicates that charge neutralization can occur even at the stated pH and dosages for PACl in this study (Yan et al., 2008). Hence for PACl in this study a charge neutralization effect cannot be ruled out.

In general, zirconium (Zr^{4+}) was less efficient than PACl (Al^{3+}) for both shorter and longer chain PFAS removal at similar concentrations (Fig. 1). Average removal efficiencies of shorter chain PFAS were up to 48% (13.71 mmol/L Al^{3+}) for PACl (Table S9) and 20% (5.82 mmol/L Zr^{4+}) for zirconium (Table S11). Longer chain PFAS were removed by an average of 61% (4.57 mmol/L Al^{3+}) and 52% (5.82 mmol/L Zr^{4+}), respectively. For PACl and zirconium the PFAS removal efficiency of shorter chain PFCA ($\leq C_8$) peaked at the highest coagulant dosage used. The removal efficiency of shorter chain PFAS ranged from 44% (PFOA) to 55% (PFBS) for PACl and was between 14% (PFPeA) and 26% (PFHxA) when zirconium was used. At lower zirconium dosages ranging from 0.02 to 2.96 mmol/L Zr^{4+} , the removal of shorter chain PFCA and PFSA was not observed and in some cases these substances were even released from the soil, leading to higher PFAS concentrations in the water phase ($C_{\text{PFAS, treatment}}$) compared to the jar tests with no treatment ($C_{\text{PFAS, no treatment}}$) (Table S11). This could be due to analytical uncertainty at very low dosages of coagulant, or possibly interactions in suspension with the predominant form of the zirconium, charged $\text{Zr}(\text{OH})_3^+$. Previous studies suggested that sorption of shorter chain PFAS is mainly driven by electrostatic interactions of ionic groups with charged surfaces (Campos-Pereira et al., 2020; Mei et al., 2021). At all pHs used in this study, all PFSA ($\text{pK}_a < 0.3$) and PFCA ($\text{pK}_a < 1.6$) will be deprotonated and thus negatively charged (Mei et al., 2021). Hence electrostatic interaction between positively charged metal hydroxides and PFAS are likely to be a main sorption mechanism for shorter chain PFAS. This is in line with Deng et al. (2011) who identified electrostatic interaction of shorter chain PFCA (PFBA, PFHxA) to PACl as the main PFAS removal mechanism during coagulation. This would also explain the higher removal efficiencies of the pre-hydrolysed PACl, where charged species are more abundant compared to zirconium. For both coagulants, shorter chain PFAS are removed the most at the coagulant dosage where the amount of charged hydrated cations, including Al^{3+} and Zr^{4+} in

solution, were the highest. This was further supported by the increase in the measured electric conductivity (Table S1).

Removal efficiencies for longer chain PFCA ($\geq C_9$) and PFSA ($\geq C_7$) increased up to a PACl dosage of 4.57 mmol/L Al^{3+} , ranging from 39% for PFHpS to $>99\%$ removal for PFUnDA. The PFAS $\geq C_{10}$ showed removal efficiencies above 75% at this coagulant dosage. For zirconium, longer chain PFAS removal efficiency peaked at dosage of 2.96 mmol/L Zr^{4+} , where at the same time turbidity reduction was comparably low (81%). In this case, removal varied from up to 14% for PFHpS and up to 94% for PFUnDA. This is in line with previous studies where higher coagulant dosages led to higher PFAS removal efficiencies for PFOA and PFOS at constant pH (Bao et al., 2014; Deng et al., 2011). At the highest tested dosage of zirconium (5.92 mmol/L) and PACl (13.71 mmol/L), longer chain PFAS removal was lower. It should be noted that at the highest dosage of PACl used (13.71 mmol/L) the flocs were visibly smaller and more voluminous compared to the lower dosages tested. Lower PFOA and PFOS removal efficiency with smaller floc size has previously been reported (Bao et al., 2014; Pramanik et al., 2015) and could explain the lower removal efficiencies for longer chain PFAS at the highest tested PACl dosage in this study. There was no visible change in the floc size for all tested dosages of zirconium but compared to PACl the flocs were overall smaller which could affect the removal efficiency. Compared to the longer PFDA and shorter PFOA, the removal efficiency for PFNA was lower at the lowest and the highest PACl coagulant dosages. This could not be explained by structural properties of PFNA and is assumed to be an analytical artefact.

For longer chain PFAS hydrophobic interactions between flocs and PFAS play a major role in PFAS removal, in addition to electrostatic interactions. The amorphous form of the coagulants, and charged hydroxide species, have a low reactive surface area for longer chain PFAS, unlike the suspended solids or the dissolved organic matter (DOM). Bao et al. (2014) reported that PFAS removal increased when fulvic acid (0 to 2 mg/L) was in solution and ferric chloride was used as a coagulant; the explanation suggested was that the negatively charged fulvic acid sorbed to the ferric hydroxides in solution, increasing hydrophobic interactions between flocs and PFAS. This can also be expected for PACl. Increased sorption of DOM to aluminium coagulants at higher coagulant dosages, which was observed by Duan and Gregory (2003) would lower electrostatic interactions with shorter chain PFAS due to local charge neutralization (Qi et al., 2022). This would explain the overall lower removal efficiencies of shorter chain PFAS at coagulants dosages when longer chain PFAS removal were high. As the coagulant dosage increases, the sorption of DOM to flocs will also increase, reaching a limit (in this study possibly at a PACl dosage of 4.57 mmol/L) that is dependent on the amount of DOM present in the water. This theory could be verified by incrementally adding more DOM to the solution, or by investigating soils with different TOC contents, which was out of the scope of this study.

It was previously reported that the more hydrophobic sulfonate headgroup exhibits increased sorption to flocs compared to carboxylate (Nguyen et al., 2020). In this study, the average removal efficiency for PFOS was slightly increased compared to PFNA when PACl ($<13\%$) (Table S10) and zirconium ($<9\%$) (Table S12) were used. For both coagulants, the average difference between shorter chain PFSA compared to PFCA with the same $-\text{CF}_2$ moiety was even lower ($\leq 9\%$). If hydrophobic interaction between PFAS and flocs would be dominant, there should be a clear difference between removal efficiency of shorter chain PFSA and PFCA, where in general electrostatic interactions prevail due to their overall shorter hydrophobic fluorinated tail. This is not the case in this study.

3.3.2. Cationic and anionic polyacrylamide flocculants

Both cationic C-494 (Superfloc® HMW C-494) and anionic FLO-PAM™ (FLOPAM™ AN 923) flocculants reduced the turbidity by 80% to $>99\%$ at all investigated dosages without changing the pH or the electric conductivity (Fig. 2, Table S2). Due to the charge of the cationic C-494

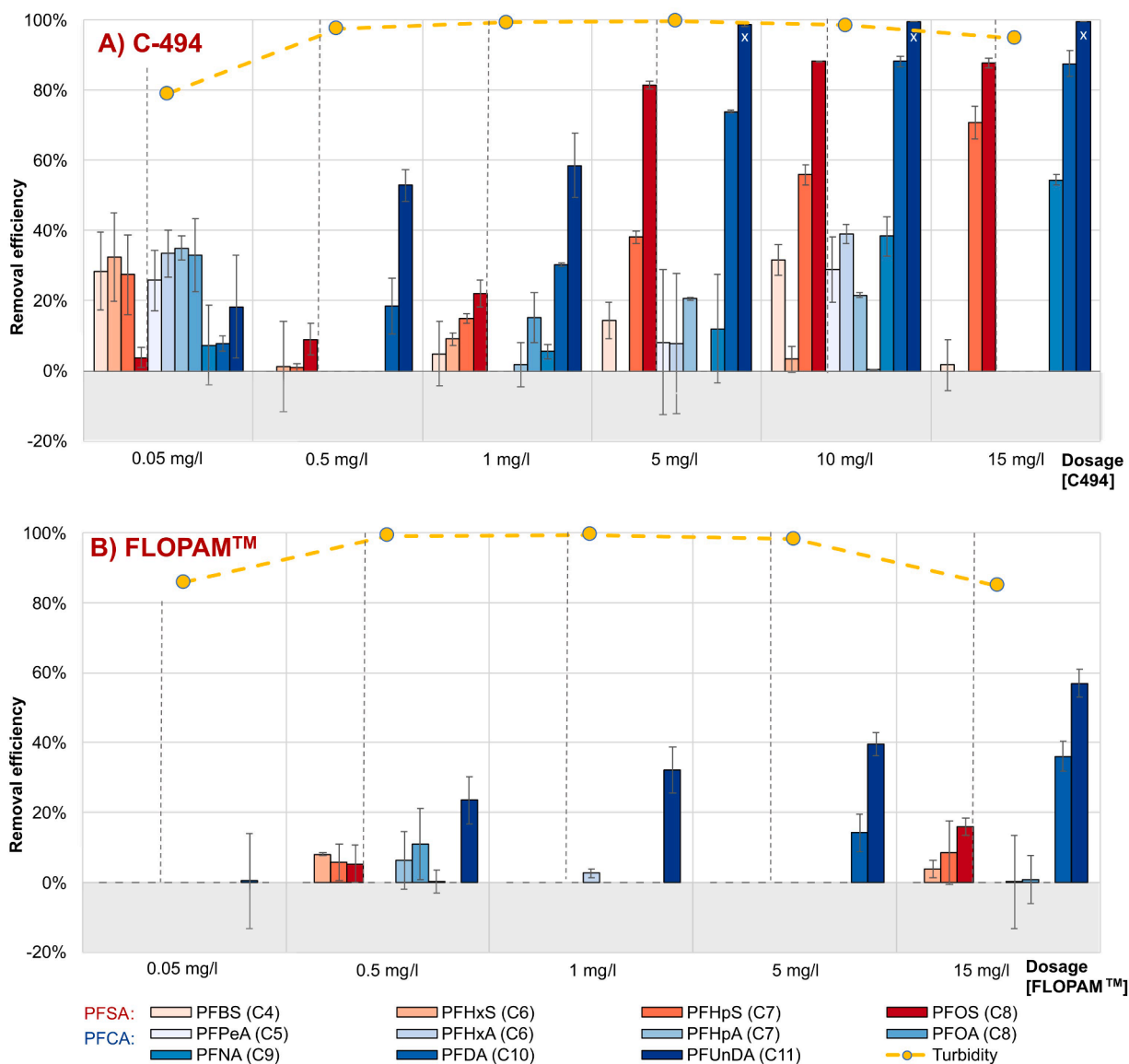


Fig. 2. PFAS removal efficiencies for different dosages of A) C-494 at pH of 6.39 and B) FLOPAM™ at pH of 6.28. White "x" in the bar indicates PFAS concentrations <LOD, with water concentrations assumed to be 0.5 the LOD.

polymer, which is introduced by a quaternary ammonium function with alkyl groups $[N-(CH_3)_4]$ and its high molecular weight, the coagulation and flocculation mechanisms with suspended solids are charge neutralization, sorption via electrostatic interactions, including hydrogen bonding and polymer bridging, where multiple polymer chains partly sorb and interconnect suspended particles or solutes (e.g., PFAS), resulting in flocs that can settle (Crittenden et al., 2012; Nasser and James, 2006). FLOPAM™ mainly consists of acid and amide groups, where the amide group adsorbs suspended solids through hydrogen bonding (to a lesser degree compared to cationic polymers), and the carboxylate group helps to crosslink sorbed polymer molecules via bridging to extend the polymer chain in solution (Nasser and James, 2006; Pillai, 2004).

In general, the two flocculants displayed very different properties related to PFAS removal. The cationic polymer C-494 performed better than the anionic FLOPAM™ for both shorter and longer chain PFAS in this study (Fig. 2). C-494 removed longer chain PFAS on average by 80%, whereas average shorter chain PFAS removal was lower (30%) (Table S13). FLOPAM™ removed longer chain PFAS on average by 19% (15 mg/L) and had nearly no effect on shorter chain PFAS removal

(Table S15).

When C-494 was used, PFAS removal efficiencies of shorter chain PFAS were highest at the lowest tested dosage of 0.05 mg/L where turbidity was comparably high (8.1 NTU), ranging from 25 to 35% (Fig. 2). At low polymer dosages, bridging between polymer molecules can be insufficient, which is indicated by the fact that relatively small flocs are formed and there is a higher residual turbidity (Table S2) (Crittenden et al., 2012). These insufficient aggregations are due to the partly charge neutralized suspended solids, which can leave positively charged groups available for interactions with PFAS. For higher dosages of C-494 the removal efficiency of shorter chain PFAS were lower compared to the lowest tested dosage (0.05 mg/L). But between 0.5 mg/L and 10 mg/L, the removal efficiency of shorter chain PFAS increased with increasing dosage, though still not reaching the removal efficiency at the lowest tested dosage (0.05 mg/L). In the dosage range of 0.5 to 10 mg/L, where turbidity removal was highest ($\geq 98\%$), most of the polymer will be sorbed to suspended particles eventually leading to local charge neutralization, lowering the number of positively charged groups which can electrostatically interact with shorter chain PFAS in solution. When too much polymer is added to the proxy soil washing

water (here this was at a dosage of 15 mg/L), polymer molecules will fully occupy the surfaces of the suspended solids and will sorb at multiple points to the same particle leading to charge restabilization and finally electrostatic repulsion (Crittenden et al., 2012), which could explain the lowest witnessed shorter chain PFAS reduction efficiency at decreasing turbidity removal (<95%). This is in contrast to the behavior of the two metal coagulants detailed above, where the highest dose of PACl and zirconium showed highest removal efficiency of shorter chain PFAS due to increased electrostatic interactions with flocs.

For FLOPAM™ the removal efficiency of shorter chain PFCA and PFSA were close to zero, or there was a small release of some of the shorter chain PFAS, for nearly all tested flocculant dosages (Table S15). Cation bridging was previously described as a binding mechanism for PFAS and soil minerals (Wang et al., 2022), but it seems that for FLOPAM™, possible cation bridges between PFAS and the polymer are less favourable than bridges between suspended solids, cations in solution and the flocculant. The release of shorter chain PFAS into solution at lower polymer dosages could be explained by electrostatic repulsion interaction between sorbed PFAS and the negatively charged FLOPAM™.

There was no clear difference in the average removal efficiency ($\leq 9\%$) of shorter chain PFCA and PFSA with the same fluorinated chain length for both flocculants (Tables S14 and S16), similar to the two metal coagulants tested.

Longer chain PFAS removal efficiency increased with increasing C-

494 dosages and peaked at the dosage of 15 mg/L with removal efficiencies of 54% for PFNA up to >99% for PFUnDA, while turbidity reduction slightly dropped to 95% (Fig. 2). Except for the lowest C-494 dosage, the removal efficiency of longer chain PFAS was higher compared to shorter chain PFAS, which can be explained by increased hydrophobic interactions with the flocs. These interactions are likely due to an increase in reactive floc surface for the more hydrophobic longer chain PFAS. Even though the system is dominated by positive charge at higher dosages of C-494, the system as well contains more organic polymer, which does contain hydrophobic functional groups (i. e. methyl groups (-CH₃)) in the alkyl groups, that provide the grounds for hydrophobic interactions, as a way of efficiently removing longer chain PFAS. These functional groups are at the same time lowering hydrophilic interactions (Singh and Kumar, 2006), which is in line with the overall lower shorter chain removal witnessed at the highest dosages.

Compared to the cationic C-494, the polymeric structure of FLOPAM™, mostly consisting of acid and amid groups, is less hydrophobic, which would explain the overall lower longer chain PFAS removal efficiencies. The electrostatic repulsion between the negatively charged flocculant and deprotonated PFAS could be another limiting factor for longer chain PFAS sorption. The importance of hydrophobic interactions for longer chain PFAS removal for C-494 (>1 mg/L) is supported by the 50% higher removal efficiency for longer chain PFSA versus PFCA with the same -CF₂ moiety (Table S14) compared to no notable difference for FLOPAM™ (Table S16).

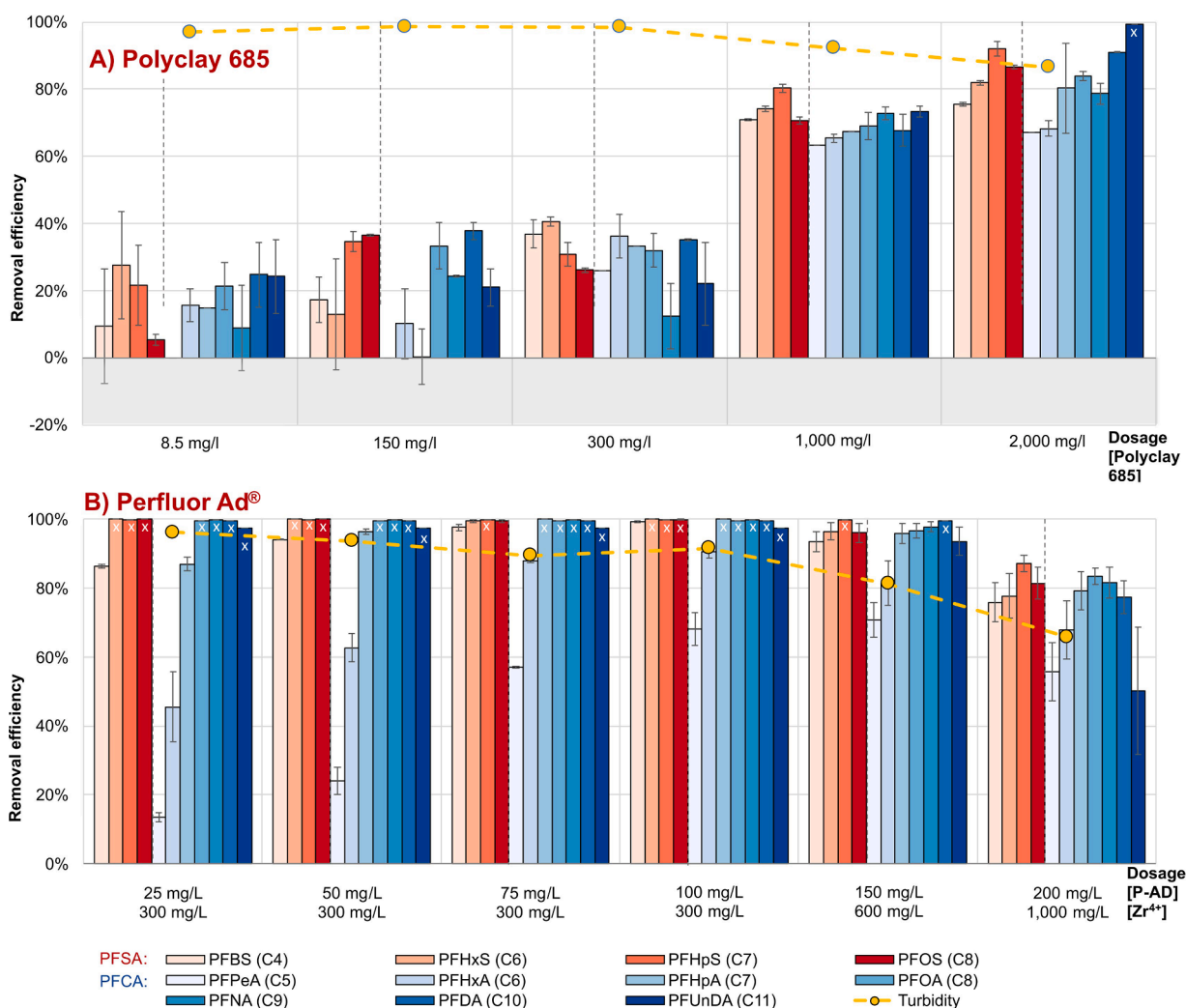


Fig. 3. PFAS removal efficiencies for different dosages of A) Polyclay 685 at pH of 6.48 and B) Perfluor Ad® at pH of 5.96. White "x" in the bar indicates PFAS concentrations <LOD, with water concentrations assumed to be 0.5 times the LOD.

3.3.3. Specially designed coagulants for contaminant and PFAS removal

Polyclay 685 and Perfluor Ad® differ from the other coagulants as they contain ingredients that were specifically used to sorb organic contaminants, such as activated carbon (AC) in Polyclay 685 (where the large surface area of the AC ingredient leads to increased sorption) and a designed fatty acid from a cellulose origin with added cationic groups in Perfluor Ad® (Cornelsen et al., 2021). These two coagulants were tested and compared (Fig. 3). Turbidity reduction for Polyclay 685 reached >97% for a dosage of ≤300 mg/L. Higher dosages led to a decrease in the turbidity reduction (<87% at 2,000 mg/L). Perfluor Ad® reduced the turbidity by >90% for dosages below 100 mg/L, but showed lower turbidity removal at higher dosages (200 mg/L, 66%) (Table S4).

Overall, Polyclay 685 and Perfluor Ad® showed the highest PFAS removal efficiencies compared to all tested coagulants and flocculants in this study. Polyclay 685, removed longer chain PFAS by 90% and shorter chain PFAS by up to 76%, when very high dosages of the coagulant are used (2,000 mg/L) (Table S17). Whereas 100 mg/L of Perfluor Ad® removed all longer chain PFAS by >99% and shorter chain PFAS by >68% (Table S19).

The removal efficiency of shorter and longer chain PFAS increased with increased dosage of Polyclay 685. For lower dosages of Polyclay 685 (8.5 to 300 mg/L), removal efficiencies of shorter and longer chain PFAS were below 40% (Fig. 3). Higher dosages of Polyclay 685 (1,000 and 2,000 mg/L) led to removal efficiencies of shorter chain PFAS between 60% and 80% (PFPeA and PFHxA, respectively) and for longer chain PFAS between 80% and >99% (PFHxS and PUnDA, respectively), indicating a chain length dependency. The removal efficiencies were in line with previously reported batch test data where powdered activated carbon (PAC) (25 mg/L) was used on PFAS contaminated groundwater (with lower turbidity) and sorption was dependent on chain length and headgroup, falling between 78% (PFHxA) up to 97% (PFOS) (Hansen et al., 2010). Higher dosages of Polyclay 685 compared to PAC were needed in this study, compared to Bao et al. (2014) and Hansen et al. (2010), to reach similar removal efficiencies (>90%). One reason could be the competition between PFAS and other soluble species for sorption sites and possible pore blocking (Krahn et al., 2023), due to the greater turbidity and suspended solid concentration found in this study.

For Perfluor Ad® the removal efficiency of shorter chain PFAS increased with dosage up to 100 mg/L and was between 68% for PFPeA and >99% for PFBS before efficiencies dropped at higher dosages (Fig. 3). The lower removal efficiencies of shorter chain PFAS with higher turbidity can be explained by possible charge reversal and electrostatic repulsion due to the cationic charge of Perfluor Ad® and zirconium, added as the coagulation aid. The exact structure of Perfluor Ad® is not publicly available. It is known to contain fatty acids from a cellulose origin with added cationic groups (Cornelsen et al., 2021). This implicates, that both hydrophobic and electrostatic interactions are likely to occur. Increased hydrophobic interactions led to the very high removal efficiency observed for longer chain PFAS of >95% for Perfluor Ad® dosages of 25 to 150 mg/L (Fig. 3). This was apparent as concentrations for most longer chain PFAS were below the LOD. For Polyclay 685 dosages ≤300 mg/L, the removal of shorter chain PFSA with the same -CF₂ moiety was on average 16% higher compared to PFCA (Table S18), indicating increased sorption of the sulfonated headgroup to the hydrophobic activated carbon surface, as expected (Son et al., 2020). For Perfluor Ad®, shorter chain PFSA showed even more substantial removal efficiencies between 20 and 70% compared to PFCA depending on the dosage (Table S20). This indicates that the surface of Perfluor Ad® is attractive for PFSA sorption. With increasing -CF₂ moieties in the PFAS, the increased removal efficiency for the sulfonated headgroup compared to the carboxylic group decreased for Perfluor Ad® and Polyclay 685 (≤6%), indicating the dominance of hydrophobic interactions with increasing chain-length compared to the influence of the headgroup.

4. Environmental and technical implications

The results of this study indicate that the correct selection of coagulant or flocculant can significantly increase PFAS removal efficiency in soil washing water. At soil washing facilities, the heterogeneous nature of the soils received means that coagulants or flocculants chosen should have a wide operating pH range. This is the case for Perfluor Ad® (depending on the used coagulation aid) and the polyacrylamides flocculants tested in this study. Though the metal hydroxides performed better than the organic polymers in terms of removing most PFAS (except some longer chain PFAS), organic polymers have the operational advantages of wider working pH ranges and lower dosages needed to achieve the best effect, and therefore produce lower volumes of sludge. C-494, a cationic acrylamide polymer, showed promising removal efficiencies for longer chain PFAS (e.g., PFOS) at relative low polymer dosages (unlike the anionic counterpart FLOPAM™, the weakest performing of the products tested). For PFAS contaminated sites where legacy, longer chain, anionic PFAS are the main group of contaminants, cationic acrylamide polymers could be an efficient choice. Perfluor Ad® showed the highest PFAS removal efficiencies in this study and could be considered as a relevant choice to add to existing soil or wastewater treatment processes managing PFAS contaminated sites.

PFAS contaminated water is often managed with treatment train solutions where different techniques are used in series to target different groups of PFAS, suspended solids and other co-contaminants. The results of this study can support this type of management as they suggest that coagulants can benefit from the presence of DOM or suspended solids in solution, which help to increase the removal efficiency for PFAS due to hydrophobic and electrostatic interactions. In treatment trains involving sorption or membrane techniques, such as using adsorbent filters containing GAC, ion-exchange resins or nanofiltration, suspended solids should be removed in pre-treatment steps to ensure the longevity of the sorbent or membrane using coagulants or flocculants. Furthermore, the presence of DOM in wastewater tends to decrease PFAS removal efficiency to sorbents, filters and membranes due to pore blockage or competitive sorption. The right choice of coagulant and flocculant, as indicated in this study, can be used to improve the lifetime and hence the cost effectiveness of the subsequent filtration step, both by reducing PFAS and DOM concentrations, as well as other soluble ions that may cause disturbances (Cornelsen et al., 2021). Hereby a two-step flocculation process as part of a pre-treatment step in a treatment train can be beneficial way to improve PFAS removal in soil washing water.

Environmental concerns have been raised regarding the use of polyacrylamide related to their long environmental persistency, potential for accumulation in the environment and toxicity (Arp and Knutsen, 2020; Groh et al., 2023). Therefore, effluent water leaving the soil washing facility needs to be monitored. For aluminium based coagulants the main concern for downstream water quality is the introduction of monomeric, reactive aluminium species. To ensure effective coagulation and flocculation, it is crucial to operate at specific pH and dosage conditions where the sweep flocculation process is predominant, resulting in low concentrations of residual reactive aluminium species (Kimura et al., 2013). Consequently, the implementation of permanent pH monitoring and automatic pH adjustment systems in soil washing facilities is crucial. It should be noted that studies regarding the risks on downstream water quality when zirconium is used are rare. Overall, zirconium is regarded to be non-toxic (Sonal and Mishra, 2021). Perfluor Ad®, based on its organic structure, is designed to be biodegradable under normal environmental conditions (Cornelsen et al., 2021). In general, it is important to ensure thorough turbidity reduction by an efficient sedimentation step, or optional additional filtration process. This prevents the introduction of unstable and degradable flocs into the environment where sorbed PFAS may be released. The use of coagulants and polymer will generate PFAS contaminated waste, which needs to be further treated. First, these sediments should be physically dewatered (e.g., by a filter press) to reduce volume. Given the high residual PFAS

concentrations in the material, the waste is considered hazardous waste. As potentially more sustainable and cost-effective options than disposing this sludge in hazardous waste-landfills, this flocculated sludge can be further treated by incineration or pyrolysis at 500 to 800°C to degrade PFAS (Sørmo et al., 2023) and minimize the waste volume for subsequent handling. When dealing with small waste quantities, landfilling with stabilization techniques in designated hazardous landfill sites that limit contaminant leaching is a viable choice. The economic impact of additional coagulation and flocculation application in soil washing facilities should be addressed by future research, a relevant aspect not covered in this study.

5. Conclusion

This study presented that the removal efficiencies in soil washing water greatly varied for different coagulation and flocculation agents, dosages used and targeted PFAS:

- For shorter chain PFAS the highest removal efficiency was in the following order: Perfluor Ad > Polyclay 685 > PACl > Zirconium > C-494 > FLOPAM™.
- For longer chain PFAS the highest removal efficiency was in the following order: Perfluor Ad® > Polyclay 685 > C-494 > PACl > Zirconium > FLOPAM™.
- Shorter chain PFAS removal was mostly dependent on electrostatic interactions introduced by the coagulants and flocculants.
- For longer chain PFAS, hydrophobic interactions with apolar functional groups introduced by the coagulant and flocculant as well as interaction with DOM and suspended solids incorporated into flocs play a major role in PFAS removal.
- The highest shorter and longer chain PFAS removal efficiency was not observed at the same coagulant or flocculant dosage, implying a two-step flocculation process would be needed to maximize removal of both groups.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2023.120888](https://doi.org/10.1016/j.watres.2023.120888).

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