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Sorption and desorption of per-fluoroalkyl substances (PFAS) on waste containment liner components

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ABSTRACT

This paper examines the sorption kinetics, isotherms and desorption behaviour of six per-fluoroalkyl substances (PFAS) from single- and multi-compound solutions with various landfill liner materials currently in use and those proposed for future lining systems. The compounds examined include perfluorooctanesulfonic acid, perfluorobutanesulfonic acid, pentafluoropropionic acid and trifluoromethanesulfonic acid. The impact of landfill leachate on the sorption properties of selected liner components, namely geotextiles, bentonite and a proposed bentonite modifier, was also investigated. No significant competitive effects on sorption were observed at typical environmental PFAS concentrations (1–80 nM). Biexponential and pseudo-second-order kinetics models sufficiently described the sorption process. Furthermore, the Freundlich isotherm model generally provided a better fit to the experimental data than the Langmuir model. The maximum PFAS sorption capacity for each material followed the order: ion exchange resin > activated carbon amended bentonite > clays > nonwoven polypropylene geotextile > woven polypropylene geotextile > bentonite > polyester nonwoven geotextile. Sorption generally increased with longer carbon-chain lengths, with sulfonate species exhibiting a stronger affinity than carboxylic acids. The desorption of PFAS from the liner constituents aligned with their sorption behaviour. The presence of matrix co-constituents in leachate reduced the sorptive affinity of most PFAS. The results suggest that incorporating activated carbon into geosynthetic clay liners may reduce the migration of long-chain PFAS but may be less effective for shorter-chain compounds. Adding additional sorptive materials to lining systems, such as ion exchange resins, may be necessary to effectively attenuate short and ultrashort PFAS compounds.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) constitute a broad category of over 15,000 ubiquitous synthetic organic compounds in which fluorine atoms in carbon chains partially or entirely replace hydrogen atoms (Buck et al., 2011; US EPA, 2023). Their terminal head groups and strong carbon-fluorine (C–F) bonds contribute to their hydrophobic and lipophobic nature and extreme environmental persistence (Du et al., 2014). PFAS are applied as surfactants in various industrial and consumer products, including firefighting foams, geotextiles, paints, semiconductors, carpets, and upholstery (Kannan, 2011; Glüge et al., 2020; Mikhael et al., 2024a). Owing to their global distribution, resistance to degradation, bioaccumulation and toxicity, certain PFAS, such as perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexanesulfonic acid (PFHxS) have been classified as persistent organic pollutants (POPs) under the Stockholm Convention (UNEP Decision SC-4/17, 2009, 2019, 2022).

Studies have reported extensive concentrations of PFAS in landfill leachates globally. Perfluorocarboxylic acids (PFCA) and perfluorosulfonic acids (PFSA) have been detected in landfill leachate at concentrations ranging from ng L⁻¹ to μ g L⁻¹ (Gallen et al., 2017; Hamid et al., 2018; Simmons, 2019; Bouazza, 2021). Research indicates a dominance of short and ultra-short compounds over longer-chain homologues (Gallen et al., 2017; Simmons, 2019; Wang et al., 2020), potentially reflecting either the shift in the industry towards shorter-chain PFAS since the early twentieth century (Glüge et al., 2020) or a preferential release mechanism from waste, owing to their higher aqueous solubilities and lower organic partitioning coefficients (Gallen

Abbreviations: CMC, critical micelle concentration; DI, deionised; DOC, dissolved organic carbon; GAC, granular activated carbon; GCL, geosynthetic clay liner; HPLC, high performance liquid chromatography; LC-MS/MS, liquid chromatography tandem mass spectrometry; LC-Q-TOF-MS/MS, liquid chromatographyquadrupole time-of-flight tandem mass spectrometry instrument; LOQ, limit of quantification; MDL, method detection limit; NOM, natural organic matter; PFASs, per- and poly-fluoroalkyl substances; PFBS, perfluorobutane sulfonate; PFCAs, perfluoroarboxylic acids; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFO, pseudo first-order; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid; PFPrA, pentafluoropropionic acid; PFSAs, perfluorosulfonic acids; pKa, acid dissociation constant; POPs, persistent organic pollutants; PSO, pseudo second order; SS, suspended solids; TFMS, trifluoromethanesulfonic acid.

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et al., 2017). Notably, systematic analyses of PFAS in landfill leachates did not commence globally until the 2010s; thus, the factors contributing to their presence and trends in landfill environments cannot yet be elucidated with certainty. Nonetheless, the international production and use of various PFAS in industry and consumer products have increased exponentially since the early 2000s (Lukić-Bilela et al., 2023), likely offsetting the reductions anticipated from phaseout initiatives.

Geosynthetic composite liners are often employed in municipal solid waste landfills to contain waste and prevent or reduce the migration of landfill leachate and contaminants to soils or groundwater (Bouazza, 2002; Gates et al., 2009; Bouazza et al., 2013; Hornsey et al., 2010; Rowe, 2020; Touze-Foltz et al., 2021). These lining systems typically consist of a geomembrane (GMB) overlying a compacted clay liner (CCL) or geosynthetic clay liner (GCL) and incorporate various nonwoven and woven geotextiles that provide separation, filtration, hydraulic retention and protection functions. The geomembrane is an advection and diffusion barrier when devoid of defects, while the underlying CCL or GCL acts as a low hydraulic conductivity barrier. When combined , they form a geocomposite liner (GMB + CCL or GCL) that minimises leachate and contaminant transport through the subsurface.

Geosynthetic composite liners, designed to prevent or mitigate contaminant release, are typically not engineered to address emerging contaminants such as PFAS (Bouazza, 2021; Gates et al., 2020). Research on contaminant transfer in these liners has focused primarily on heavy metals, volatile organic compounds, aromatic hydrocarbons, and phenolic compounds (Rowe et al., 2005; Lake and Rowe, 2005; Richards and Bouazza, 2007; Lange et al., 2009; Xie et al., 2018; Ahari et al., 2019; Wang et al., 2019). Studies have only recently begun to explore the impact of PFAS on the hydraulic performance of geosynthetics (Di Battista et al., 2020; Gates et al., 2020; Rowe and Barakat, 2021; Bouazza, 2021; Rowe et al., 2023) and their sorption behaviour with geotextiles (Mikhael et al., 2024b). However, further research is required to elucidate the interactions between PFAS and the various components of lining systems.

Sorption and desorption are critical processes that govern the fate and transport of PFAS in lining systems. The diverse characteristics of lining system constituents imply that these components may exhibit varying sorption capacities for PFAS, thereby impacting the distribution and transport of these compounds within geosynthetic lining systems. Numerous studies have investigated the sorption of PFAS homologues to various solid phases, such as sediments and soils (Higgins and Luthy, 2006; Yu and Hu, 2011; Du et al., 2014; Brusseau, 2018; Li et al., 2019; Alves et al., 2020; Ateia et al., 2020). These studies indicated that PFAS can sorb to negatively charged surfaces containing organic matter, despite electrostatic repulsion of the generally negative charge of PFAS compounds in environmental systems, owing to dominating physical and hydrophobic interactions (Higgins and Luthy, 2006).

Current literature suggests that the bentonite component of a GCL and geotextiles used in lining systems will not adequately attenuate PFAS (Bouazza, 2021; Mikhael et al., 2024b), likely due to insufficient organic matter for hydrophobic interactions and their negative surface charges in the environment. Thus, to improve PFAS attenuation, additive materials or sorptive layers could be incorporated into the lining system. Various sorbent media, including activated carbon and ion exchange resins, have been investigated for PFAS removal from contaminated water and leachate (Son et al., 2020; Liu et al., 2022). While activated carbon has been shown to sufficiently remove long-chain PFAS from aqueous solutions, it is less effective for sorbing short-chain congeners. Ion exchange resins have demonstrated superior performance, with greater sorptive capacities and the ability to remove short-chain PFAS more effectively (Murray et al., 2021). It is important to note that activated carbon and ion exchange resins have finite PFAS adsorption capacities, so their effectiveness declines as they near saturation.

Recent research indicated that the sorption of PFAS to materials in the environment was significantly impacted by solution-specific factors, including pH, salinity, ionic composition, the presence of natural organic matter, and the chain length of the compound in question (Higgins and Luthy, 2006; Chen et al., 2012). High concentrations of hydrophobic organic matter, long-chain PFAS, and inorganic anions can inhibit PFAS adsorption through competition for sites and pore blocking (Appleman et al., 2013; Dixit et al., 2019). This effect is likely more pronounced for short-chain compounds due to their lower hydrophobicity. Additionally, variations in solution pH and salinity can alter the properties of both the adsorbate and the sorbent, including surface charge and sediment organic matter structure (You et al., 2010). Thus, components in a leachate matrix can significantly impact the sorption process.

Although scientific literature provided some data on the sorption of a limited range of PFAS onto sorbents, knowledge of their sorption and desorption processes in individual liner system constituents remains limited. Additionally, studies investigating the partitioning of PFAS at typical concentrations reported in landfill leachates are scarce. Partitioning coefficients vary with concentration, with higher initial solute concentrations typically yielding a smaller percentage of the sorbed solute above the equilibrium concentration. Therefore, it is imperative that the initial concentration used in sorption tests sufficiently reflects the intended application for which this information may be used.

This study hypothesised that PFAS sorption and desorption will vary significantly across different liner system constituents and that leachate matrix components will influence sorptive capacities. Shorter-chain PFAS were expected to exhibit lower sorption due to reduced hydrophobicity and weaker interactions with liner components. Additionally, conventional liner components such as geotextiles and geosynthetic clay liners were considered unlikely to effectively sorb PFAS, particularly shorter-chain homologues. Based on these premises, the first objective of this study was to investigate the sorption and desorption behaviour of six environmentally significant PFAS in pure single- and multicompound solutions with various liner system constituents and proposed sorptive additives to evaluate their efficacy as sorbent phases in a landfill context. A second objective was to examine the impact of leachate matrix constituents on the sorption properties of selected liner components. Batch experiments were conducted using pure solutions to obtain sorption (kinetics and isotherm) and desorption data, and various kinetic and isotherm models were fitted to the data to determine sorption parameters. Additional batch sorption experiments were undertaken using a real landfill leachate matrix.

2. Materials and methods

2.1. Composite liner constituents

The sorption affinity and desorption capability of PFAS for various composite liner constituents were investigated. Eight materials comprising liner components commonly employed in modern composite lining systems (geosynthetic clay liners (GCL), compacted clay liners (CCL), and geotextiles) and potential sorptive additives were selected for this study. They included bentonite, activated carbon amended bentonite, woven and nonwoven polypropylene geotextiles which constitute geosynthetic clay liners, a nonwoven polyester geotextile typically used as a filter/separator or cushion material, two clays employed as compacted clay liners at two landfill sites, and an ion exchange resin used in a porous geocomposite material to promote encapsulation of PFAS. The selected properties of each component are presented in Tables SI–1.

2.2. Chemicals and reagents

Perfluorobutanesulfonic acid (PFBS, 97 % purity), perfluorooctanoic acid (PFOA, 95 % purity), perfluorohexanoic acid (PFHxA, 98 % purity), trifluoromethanesulfonic acid (TFMS, 98 % purity) and penta-fluoropropionic acid (PFPrA, 97 % purity) were obtained from Sigma-

Aldrich, Australia. Perfluorooctanesulfonic acid (PFOS, in methanol, 1000 µg/mL) was purchased from Novachem, Australia. The physicochemical properties of the target PFAS are detailed in Table 1. Internal PFAS standards (in methanol, 1 µg/mL) were acquired from Wellington Laboratories Inc., Canada. High Performance Liquid Chromatography (HPLC) grade methanol (\geq 99 %) and acetonitrile (\geq 99.9 %) were acquired from Sigma-Aldrich, Australia. Deionised (DI) water (>18 MΩ) was sourced from an in-house purification system from the Department of Civil Engineering, Monash University, Australia.

The leachate used in this study was obtained from an Australian landfill. Concentrations of the PFAS compounds in the raw landfill leachate investigated in this study are enumerated in Table 2. Other constituent concentrations in leachate are presented in Tables SI–2. Working solutions for single and multi-component experiments were prepared at 1 nM, 10 nM, 20 nM, 40 nM, and 80 nM (Tables SI–3) in 10:90 methanol-water. Where near-vertical isotherms were obtained for initial concentrations ranging from 1 to 80 nM, higher concentrations were employed (up to 7500 nM) to achieve a reduced slope of the curve, enabling more accurate sorption characterisation and estimation of maximum sorption capacity.

Notably, the aqueous PFAS concentrations in this study were well below their critical micelle concentrations (CMC) (refer to Table 1), where they may form hemi-micelles or micelles. This phase separation could potentially impact competitive or synergistic adsorption processes, thereby influencing the distribution of PFAS between solid and liquid phases (Du et al., 2014).

Target PFAS concentrations employed and analysed in this study were selected based on: a) typical constituents, concentrations and detection frequencies observed in landfills (Gallen et al., 2017; Simmons, 2019; Wang et al., 2020); b) their varied physicochemical properties, including ultrashort, short, and long chains, as well as sulfonates and carboxylates; and c) the detection and reporting limits as defined by the Natural Resources Defense Council's (NRDC) scientific guidelines (NRDC, 2019).

2.3. Single- and multi-component adsorption study

Batch sorption experiments were performed using 50 mL polypropylene centrifuge tubes. A 40mg/40 mL sorbent dose was selected for sorption tests, consistent with the Mikhael et al. (2024b) study. Sorption isotherm experiments were conducted initially using five concentrations ranging from 1 to 80 nM for the individual target PFAS. Where near-vertical isotherms were obtained for initial concentrations ranging from 1 to 80 nM, higher concentrations were employed (up to 7500 nM) to achieve a reduced curve slope. Sorbent (40 mg) was measured into triplicate sets of tubes, followed by the addition of 40 mL of single- or multi-component solution.

The samples were agitated on an orbital shaker (NB-101M, N-Biotek) at 150 rpm and 21 \pm 2 °C for 96 h, after which they were centrifuged (THR75004230CC, ThermoFisher Scientific). The supernatant was then decanted into a 2 mL vial for LC-MS analysis. PFAS adsorbed onto the sorbents were subsequently extracted using ultrasonic-assisted extraction. Sorbents were resuspended in 13.3 mL of methanol, agitated on an

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Table 2

Concentrations	of	the	PFAS	compounds	in	the	landfill	leachate	used	in	the
current study.											

Compound	Concentration	Concentration
	(µg/L)	(nM)
Perfluorooctanesulfonic acid (PFOS)	0.40	0.80
Perfluorooctanoic acid (PFOA)	0.87	2.10
Perfluorohexanoic acid (PFHxA)	9.71	30.92
Perfluorobutane sulfonic acid (PFBS)	12.21	40.69
Pentafluoropropionic acid (PFPrA)	8.38	51.09
Trifluoromethanesulfonic acid (TFMS)	4.15	27.65
Perfluoropentane sulfonic acid (PFPes)	2.34	6.68
Perfluorohexane sulfonic acid (PFHxS)	11.10	27.74
Perfluoroheptane sulfonic acid (PFHpS)	0.33	0.73
Perfluorodecane sulfonic acid (PFDS)	0.05	0.08
Perfluorobutanoic acid (PFBA)	22.62	105.68
Perfluoropentanoic acid (PFPeA)	6.19	21.27
Perfluoroheptanoic acid (PFHpA)	0.93	2.55
Perfluorononanoic acid (PFNA)	0.06	0.13
Perfluorodecanoic acid (PFDA)	0.05	0.10
Perfluoroundecanoic acid (PFUnDA)	0.05	0.09
Perfluorododecanoic acid (PFDoDA)	0.05	0.08
Perfluorotridecanoic acid (PFTrDA)	0.05	0.08
Perfluorotetradecanoic acid (PFTeDA)	0.42	0.59
Perfluorooctane sulfonamide (FOSA)	0.05	0.10
N-Methyl perfluorooctane sulfonamide (MeFOSA)	0.12	0.23
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	0.12	0.23
N-Methyl Perfluorooctane sulfonamidoethanol (MeFOSE)	0.12	0.22
N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)	0.12	0.21
N-Methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA)	0.05	0.09
N-Ethyl perfluorooctane sulfonamidoacetic acid (EtEOSAA)	0.05	0.09
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	0.05	0.15
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	0.57	1.33
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	0.05	0.09
10:2 Fluorotelomer sulfonic acid (10:2	0.05	0.08
FTS)	2100	0.00

orbital shaker, and heated in a 65 $^{\circ}$ C water bath (UB-405, Thermoline) for 25 min. The samples were centrifuged after sonication, and the supernatant was collected in a 50 mL polypropylene tube. This extraction procedure was performed three times, and the methanol extracts were analysed to determine the PFAS concentration in the solid phase.

In the single-component experiments, each tube contained only one of the target PFAS compounds at the specified concentrations, enabling the analysis of the sorption behaviour of individual PFAS in isolation. In contrast, the multi-component solutions comprised mixtures of all six target PFAS compounds at the same concentrations. This experimental design aimed to evaluate how the presence of multiple PFAS compounds in the solution influenced the sorption behaviour.

Kinetics experiments were conducted to ascertain sorption equilibrium time, with each test beginning at an initial concentration of 40 nM for individual PFAS. Three samples were collected at 0.5, 1, 2, 24, 72 and 96 h, with all other conditions remaining consistent with the batch

Table 1	1
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PFAS physical and chemical properties.

1 7 1 1						
PFAS Name	Acronym	Avg. Mol. Wt. (g/mol)	Molecular Formula	Classification	CMC (in water) (mg/L) ^a	pK _a ^a
Perfluorooctanesulfonic acid	PFOS	500.1	C ₈ F ₁₇ S _{O3} .	Long-chain	536-4573	<1
Perfluorooctanoic acid	PFOA	414.1	C ₇ F ₁₅ CO ₂ -	Long-chain	3777-4979	3.8
Perfluorohexanoic acid	PFHxA	314.1	C ₅ F ₁₁ CO ₂ -	Short-chain	24,949-27994	
						<1.6
Perfluorobutane sulfonic acid	PFBS	300.1	C ₄ F ₉ SO ₃ -	Short-chain		< 0.3
Pentafluoropropionic acid	PFPrA	164.0	C ₂ F ₅ CO ₂₋	Ultrashort chain		0.4
Trifluoromethanesulfonic acid	TFMS	150.1	CF ₃ SO ₃₋	Ultrashort chain		-14
Pentafluoropropionic acid Trifluoromethanesulfonic acid	PFPrA TFMS	164.0 150.1	C ₂ F ₅ CO ₂ . CF ₃ SO ₃ .	Ultrashort chain Ultrashort chain		0.4 -14

^a Values were obtained from Vierke et al. (2013), Bhhatarai et al. (2011), and Yu et al. (2009).

sorption tests. At each sampling interval, the tubes were centrifuged, and the aqueous supernatant was decanted into a 2 mL vial for LC-MS analysis. Experimental and method blanks were prepared and analysed concurrently with the batch sorption and kinetics tests.

2.4. Batch desorption experiments

Batch sorption samples from previous multi-component adsorption experiments conducted at an initial concentration of 80 nM were retained and reweighed. A 40 mL aliquot of DI water was added to each sample, and desorbed PFAS concentrations were determined. All replicates were shaken on an orbital shaker at 150 rpm and 21 ± 2 °C for 96 h. After shaking, the samples were centrifuged, and the supernatant was collected in a 2 mL vial for LC-MS analysis.

2.5. Investigating the impact of landfill leachate matrix constituents on the sorption of PFAS to liner materials

Batch experiments were performed in duplicate 5 mL high-density polyethylene (HDPE) bottles. 10 mg sorbent material (activated carbon amended bentonite, bentonite or polypropylene geotextile fibres) was added to the tube containing 3 mL of leachate or the multicomponent pure solution (PFAS dissolved in a water and methanol mixture) per replicate. PFAS concentrations employed in multi-solute system experiments were consistent with concentrations measured in the landfill leachate matrix investigated (See Table 2). To assess the effect of the landfill leachate matrix on PFAS adsorption, the experiments considered the composition of the leachate, the type of sorbent material, and the specific PFAS compounds. Each sample was shaken on an orbital shaker (NB-205, N-Biotek) at 150 rpm and 21 ± 2 °C for 96 h, after which the supernatant was decanted into a 2 mL vial for LC-MS analysis. The PFAS compounds were then extracted from the treated sorbents using ultrasonic-assisted extraction.

2.6. PFAS determination

Ultra-high-definition liquid chromatography-quadrupole time-offlight tandem mass spectrometry instrument (LC-Q-TOF-MS/MS, Agilent 6540) was employed to measure PFAS concentrations in both liquid and sorbent samples. Detailed instrumental parameters are provided in the supplementary information section (SI). Quantitative analysis of target PFAS compounds was conducted using a six-point calibration curve. Internal standard calibration was applied to measure PFAS levels in the solid phase, with the specific internal standards listed in Tables SI-4. All calibration curve correlation coefficients (R²) exceeded 0.99. The method detection limit (MDL), which represents the lowest concentration of a chemical reliably distinguishable from method blank results with 99 % confidence, was determined based on a signal-to-noise ratio of 3:1. The limit of quantification (LOQ), which denotes the minimum concentration required for precise detection and quantification, was established using a signal-to-noise ratio of 10:1. For all compounds analysed, the LOQ was 0.02 μ g/L.

2.7. Quality assurance and control

All single- and multi-component experiments were replicated in triplicate and leachate experiments in duplicate, with the mean concentration values utilised for subsequent data analysis. Teflon materials were not used in the experiments to avoid sample contamination. Reference control tubes containing either sorbent or solution were prepared to detect PFAS contamination in the sorbents or tubes and to evaluate sorption to tube walls. Instrumental blanks containing DI water were employed to ensure the cleanliness of the LC-MS instrument. A mass balance analysis was also conducted on all samples to identify possible contamination or loss of PFAS. stock solution varied from 82 % to 104 %. PFPrA was detected in geotextile laboratory blanks (where no PFAS were added), attributed to their potential use in geotextile manufacturing processes (Mikhael et al., 2024a). No other target analytes were found in laboratory blanks, indicating no contamination was introduced during sorption tests. The recovery of analytes for all samples varied between 69 % and 115 %.

2.8. Kinetic models and sorption isotherms

2.8.1. Adsorption kinetics

Experimental data were analysed using three different models: pseudo-first-order (PFO), pseudo-second-order (PSO), and biexponential. The PFO model assumes that the rate of sorption is directly proportional to the concentration of PFAS in solution and is represented by Eq. (1) (Lagergreen, 1907):

$$\mathbf{q}_{\mathrm{t}} = \mathbf{q}_{\mathrm{e}} \left(1 - \mathrm{e}^{-\mathrm{k} \mathrm{I} \mathrm{t}} \right) \tag{1}$$

Where k_1 (µg/g/h) is the PFO rate constant, and q_t and q_e (µg/g) represent the quantity of solute adsorbed per unit mass of adsorbent at time t (h) and at equilibrium, respectively.

The pseudo-second-order model posits that chemical processes govern the sorption rate and that the sorption capacity is related to the availability of active sites on the sorbent (Ho and McKay, 1998). This model can be expressed as Eq. (2):

$$q_{t} = \left(q_{e}^{2}k_{2}t\right) / \left(1 + q_{e}k_{2}t\right)$$
(2)

where $k_2 (\mu g/g/h)$ is the PSO rate constant.

The bi-exponential model can be expressed by Eq. (3) (Mikhael et al., 2024b).

$$F_{w} = F_{0} + F_{1}^{e-k1t} + F_{2}^{e-k2t}$$
(3)

where F_w represents the fraction of analyte remaining in the liquid phase at time t, F_0 is the fraction of analyte at the liquid-liquid interface, F_1 indicates the fraction of analyte adsorbed onto the liquid-solid interface at the independent sorption rate, k_1 and F_2 represents the fraction of analyte sorbed into the interior pore surface at the independent sorption rate, k_2 .

2.8.2. Adsorption isotherms

The main models employed in this study, which are commonly applied to characterise PFAS sorption onto various solids (Yu et al., 2009; Jiang et al., 2022; Le et al., 2022), are outlined below:

Freundlich model:
$$Q_e = K_f C_e^n$$
 (4)

Where Q_e denotes the mass of solute sorbed per unit mass of sorbent (µg/g), C_e is the mass of solute remaining in solution per litre (µg/L), K_f is the Freundlich constant related to sorption affinity ((µg/g)/(µg/L)ⁿ), and n represents the intensity of sorption.

Langmuir model:
$$Q_e = (Q_m K_L C_e)/(1+K_L C_e)$$
 (5)

Where Q_m is the maximum amount of sorbate that can be sorbed per unit of sorbent ($\mu g/g$), and K_L denotes the Langmuir adsorption energy (L/g).

2.8.3. Extracting statistical parameters

Experimental data and regression values were input into Microsoft Excel® for plotting and further analysis. The sum of squared residuals was computed, and kinetic and isotherm parameters were determined using the Solver add-in in Excel, utilising the Generalised Reduced Gradient (GRG) Nonlinear method. The coefficients of determination (R^2) values were optimised by adjusting the parameters within specified upper and lower limits, thereby minimising the squared differences.

3. Results and discussion

3.1. Single- and multi-component batch adsorption experiments

To assess and compare the efficacy of various lining constituents in containing PFAS from single- and multi-component solutions, their concentrations remaining in the solution were measured after 96 h. Aqueous-phase equilibrium concentrations (C_e , $\mu g/L$) for the sorbents investigated are illustrated in Tables SI–5. Tables SI–6 provides percentages of the initial congener concentration sorbed. Notably, sample blanks run in parallel with experiments indicated that geotextiles contributed to the total PFPrA concentrations measured in supernatants. Thus, PFPrA was excluded from the analysis for geotextile sorption experiments.

The averaged results indicate that the sorptive removal of PFOS and PFOA from both single- and multi-component solutions at an initial concentration of 80 nM varied in the order of ion exchange resin >activated carbon amended bentonite > Clay 1 > Clay 2 > polypropylene nonwoven geotextile > polypropylene woven geotextile > bentonite > polyester nonwoven geotextile. For PFHxA and PFBS, average sorptive removal varied in the order of ion exchange resin > activated carbonamended bentonite > polypropylene nonwoven geotextile > polypropylene woven geotextile > bentonite > polyester nonwoven geotextile > Clay 2 > Clay 1. No discernible decrease in TFMS and PFPrA concentrations was measured in any matrix for the sorbents assessed, except for the ion exchange resin, which exhibited near-complete removal of the compounds from the solution. Ion exchange resins have been reported to outperform other removal methods, such as activated carbon, particularly for short-chain PFAS (Dixit et al., 2020; Gagliano et al., 2020). The sorption mechanisms of short and ultra-short compounds onto ion exchange resins likely involve both anion exchange and physical interactions, such as van der Waals forces, which may be less influenced by the polarity of the substances (Woodard et al., 2017).

The removal rates for individual PFAS by activated carbon-amended bentonite, bentonite, polypropylene nonwoven and woven geotextiles and polyester nonwoven geotextile ranged between <0.2 % (PFPrA and TFMS at an initial concentration (C₀) of 80 nM for all sorbents) and >99.9 % (PFOS at C₀, = 80 nM for activated carbon amended bentonite) for the single solute system. In comparison, for the multi-solute system, sorptive removal ranged between <0.2 % (PFPrA and TFMS at $C_0=80$ nM for all sorbents) and 99.8 % (PFOS at $C_{02} = 80$ nM for activated carbon amended bentonite). The highest average percentage removal by sorbents at C_0 , = 80 nM, was observed for PFOS in both single (37.40 %) and multi-solute systems (32.25 %). Thus, no significant competitive effects on sorption were observed at the initial aqueous concentrations employed in this study, regardless of the chain length. Competitive sorption effects are typically observed at higher initial concentrations (1-50 mg/L) (Guelfo et al., 2020; Silva et al., 2021; Huang et al., 2022). Hence, the experiments conducted herein, at relatively low yet environmentally relevant input concentrations, were anticipated to demonstrate no measurable competitive sorption effects. This consideration aligns with previous batch experiments wherein minimal competitive sorption effects were observed for PFAS mixtures at μ g/L concentrations (Higgins and Luthy, 2006; Guelfo and Higgins, 2013). Siriwardena et al. (2019) also observed no significant competitive inhibition of PFAS sorption onto granular activated carbon in the presence of dissolved organic carbon at concentrations ranging from 0.1 to 1 mg/L. Thus, in a competitive multi-solute sorption scenario, it can be inferred that the sorption capacity of the examined liner constituents for PFAS would not be impacted by competitive sorption effects at low initial concentrations, given the abundance of available sorption sites.

Sorptive removal of PFAS from single- and multi-component solutions by sorbents varied significantly depending on the type of sorbent material and the specific PFAS homologue. The results indicate a generally higher sorptive affinity for long-chain congeners on liner constituents, with the specific functional group of PFAS influencing their sorption, as observed by Xiao et al. (2017), Niarchos et al. (2023) and Mikhael et al. (2024b). Mechanisms assumed responsible for PFAS retention in these sorbents may be attributed to physical retention within inner pores of the sorbent, hydrophobic and electrostatic attraction, and/or ion exchange, as described in Mikhael et al. (2024b) and discussed in Section 3.3 below. Compared to the longer-chain compounds, the relatively poor sorption of shorter-chain PFAS, particularly ultra-short homologous, continues to present challenges for their containment in geosynthetic composite lining systems, even with bentonite modified as described herein. Nonetheless, the modification proved useful in retaining long-chain PFAS at typical environmental concentrations.

3.2. Sorption kinetics

3.2.1. Equilibrium time for adsorption

The removal of target PFAS from pure solutions over 96 h was examined to evaluate the time-dependent sorption behaviour influenced by sorbents and determine sorption equilibrium. These investigations were limited to assessing the sorption kinetics of PFAS in multi-solute systems since no competitive effects on sorption were evident. Fig. 1 depicts the sorption kinetics of PFAS in multi-solute systems for various sorbents as plots of the fraction of the initial concentration sorbed versus time. Notably, the sorption of TFMS and PFPrA to sorbents, excluding the ion exchange resin, was negligible and thus not plotted.

It can be observed from Figs. 1 and 2 that sorption equilibrium (at which no significant changes in solution concentration occurred over time) was achieved after at least 2 h for all liner constituents, where almost all the sorption equilibrium concentrations were rapidly (within minutes) taken up by the sorbents irrespective of PFAS chain length. For all sorbents, all targeted compounds reached equilibrium after approximately 72 h. Thus, the sorption experiments were conducted for 96 h to ensure equilibrium was attained. Notably, no measurable sorption was observed for PFHxA to the nonwoven polyester geotextile after 96 h.

3.2.2. Modelling the kinetics of sorption

The biexponential, PFO and PSO model parameters are enumerated in Table 3, and biexponential adsorption model fittings, represented by solid lines, for sorption kinetics data, are illustrated in Figs. 1 and 2. Where measurable sorption was observed, the sorption kinetics for all PFAS congeners to liner components were well described by the biexponential adsorption model ($R^2 > 0.8028$) (see Table 3). The biexponential adsorption model infers rapid sorption onto the outer layer of the sorbent, followed by slower diffusional transport into its internal pore structure. This explanation aligns with previous studies regarding PFAS adsorption onto various materials such as geotextiles, soils and sediments (Higgins and Luthy, 2006; Du et al., 2014; Li et al., 2019; Mikhael et al., 2024b). Notably, biexponential slow sorption rate (k₂) values were significantly lower than the biexponential fast sorption rates (k_1) , indicating that diffusional transport was likely less significant in the overall sorption rate for the lining constituents. This suggests that PFAS rapidly transfer into the adsorbents, facilitated by increased easily accessible sites, with the potential for sorption through various mechanisms, as further explained in Section 3.3 below.

PFAS adsorption by bentonite and geotextiles was slower compared to other sorbents. Initially, the adsorption of PFAS by these materials increased rapidly within 2 h but subsequently levelled off gradually, reaching equilibrium at approximately 72 h. The sorption kinetics profiles indicated that, initially, PFAS took longer to penetrate the adsorbent-solution interface, suggesting weaker sorption to surface sites. Thereafter, PFAS molecules gradually diffused to deeper active sites within the adsorbent, such as surfaces of micropores typically present in polypropylene fibres and bentonite. Furthermore, the biexponential slow sorption rate (k_2) values generally increased with increasing chain length for the lining system constituents examined. The longer chain PFAS can be interpreted to diffuse more slowly into water

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filled pores due to their higher hydrophobicity, which restricts their access to these pores but also allows them to engage in stronger adsorption interactions. This behaviour suggests that longer-chain PFAS experience fast and slow sorption processes, depending on their ability to diffuse into the sorbent water filled pores and their interaction with the sorbent surface.

Both PFO and PSO models closely fit experimental data ($R^2 > 0.7561$), excluding the polyester geotextile, for which both models yielded a very poor fit due to its low adsorption capacity. Thus, no PFO or PSO constants were derived for the polyester geotextile. The PSO kinetics model generally showed a slightly better fit ($R^2 > 0.7958$) than the PFO model for all PFAS congeners to the sorbents for which a model could be fitted, indicating that the sorption rate is controlled by both physisorption (such as hydrophobic interaction), and chemisorption mechanisms possibly influenced by electrostatic attraction and/or ion

exchange. As shown in Table 3, the PSO model most effectively described the adsorption data for activated carbon amended bentonite, clay minerals and the ion exchange resin, with all R² values greater than 0.9511. Notably, the PSO sorption rate (k₂), which represents the overall sorption rate influenced by both fast and slower sorption processes, of PFAS onto activated carbon amended bentonite, Clay 2 and the ion exchange resin varied in the order of PFOS > PFOA > PFHxA > PFBS. In contrast, k₂ values of PFAS onto Clay 1 followed the order PFOS > PFOA > PFBS > PFHxA, indicating that sorption rates and, thus, the equilibrium constant increased with carbon chain length, influenced by the PFAS functional groups present. This could be attributed to a lower energy barrier for the adsorption of longer chain compounds by sorbents or the result of various mechanisms allowing PFAS molecules to reach the minimum Gibbs free energy, as described in Mikhael et al. (2024b). Furthermore, the bi-exponential model F₀ values decreased with



Fig. 1. a), b), c) and d). PFAS sorption onto liner materials at 0.001 kg/L, with an initial PFAS concentration of 40 nM. Error bars indicate the standard deviation for each time point, and lines represent the fitted biexponential adsorption model.



Fig. 1. (continued).

increasing carbon chain length. In contrast, F_1 and F_2 values increased for all sorbents, excluding the ion exchange resin, reaffirming that PFAS with longer carbon chains prefer to partition into the solid phase. This aligns with findings from previous studies, wherein longer carbon chains were associated with increased partitioning in geotextiles, sediments and soils (Higgins and Luthy, 2006; Li et al., 2019; Mikhael et al., 2024b).

For the PFAS concentration employed in kinetics studies (40 nM), the ion exchange resin exhibited F_0 values of less than 0.017, regardless of chain length. This indicates a high affinity for these molecules, attributed to an abundance of easily accessible sites that enable their sorption through hydrophobic and electrostatic interactions (Gagliano et al., 2020). For short- and ultra-short-chain PFAS, sorption is predominantly governed by electrostatic interactions, as their hydrophilicity restricts sorption via hydrophobic interactions compared to long-chain homologues. In ion exchange resins, electrostatic interactions of short and ultra-chain PFAS are facilitated by their ability to align their terminal head groups with the ion exchange active sites, enhancing their interaction with the positively charged resin. In contrast, sorption of long-chain compounds may involve electrostatic interactions with the charged sites of the ion exchange resin and hydrophobic forces between their nonpolar tails and the hydrophobic, non-functionalised surface of the resin.

The geosynthetic composite liner constituents displayed significantly different sorption affinities for PFAS as indicated by their q_e values, generally varying in the order of ion exchange resin > activated carbon amended bentonite > Clay 1 > Clay 2 > polypropylene nonwoven geotextile > polypropylene woven geotextile > bentonite. For example, the q_e values of PFOS on the ion exchange resin, activated carbon amended bentonite, Clay 1, Clay 2, polypropylene nonwoven geotextile, polypropylene woven geotextile and bentonite were 20.019, 19.979, 15.642, 13.312, 5.989, 5.741 and 5.492 μ g/g (dry weight) respectively.



Fig. 2. Sorption of ultra-short PFAS onto ion exchange resin at 0.001 kg/L, with an initial PFAS concentration of 40 nM. Error bars indicate the standard deviation for each time point, and lines represent the fitted biexponential adsorption model.

 Table 3

 Fitting parameters of employed kinetics models for the sorption of PFAS onto liner constituents.

Sorbent	Compound	Pseudo 1st	order		Pseudo 2nd order			Biexponential adsorption					
		q _e (μg∕g)	k1 (μg/g/ h)	R ²	q _e (μg∕g)	k ₂ (μg/g/ h)	R ²	F ₀	F_1	F_2	k_1	k ₂	R ²
AC-A bentonite	PFOS	19.865	9.529	0.9998	19.979	9.345	0.9998	0.003	0.957	0.040	8.224	0.880	>0.9999
	PFOA	16.493	8.341	>0.9999	16.541	7.986	>0.9999	0.000	0.984	0.016	10.839	0.305	>0.9999
	PFHxA	9.747	4.926	0.9986	9.714	6.592	0.9986	0.224	0.776	0.001	6.326	0.004	0.9938
	PFBS	9.511	2.513	0.9923	9.575	2.249	0.9992	0.133	0.792	0.075	4.518	0.000	0.9984
Bentonite	PFOS	5.099	0.800	0.9513	5.492	0.148	0.9784	0.709	0.185	0.107	1.115	0.030	0.9967
	PFOA	2.845	1.443	0.9699	2.936	0.862	0.9974	0.816	0.145	0.038	2.232	0.029	0.9893
	PFHxA	0.516	0.358	0.8151	0.573	0.800	0.8254	0.959	0.042	0.002	0.672	0.027	0.8661
	PFBS	0.978	0.321	0.7561	1.090	0.229	0.7958	0.900	0.030	0.069	1.055	0.024	0.8819
PP nonwoven GTX	PFOS	5.817	1.482	0.9608	5.989	0.447	0.9842	0.683	0.242	0.073	2.383	0.026	1.000
	PFOA	3.319	0.363	0.9305	3.537	0.108	0.9306	0.766	0.176	0.076	0.563	0.015	0.999
	PFHxA	1.480	0.300	0.8648	1.504	0.353	0.8789	0.878	0.117	0.018	0.600	0.014	1.000
	PFBS	0.840	0.423	0.8638	0.884	0.573	0.8650	0.862	0.058	0.087	0.876	0.004	1.000
PP woven GTX	PFOS	5.609	0.993	0.9704	5.741	0.289	0.9785	0.714	0.237	0.044	1.288	0.055	0.9757
	PFOA	3.216	0.386	0.9435	3.401	0.125	0.9348	0.790	0.191	0.038	0.524	0.016	0.9579
	PFHxA	1.331	0.030	0.9209	1.763	0.014	0.9237	0.876	0.021	0.105	1.191	0.015	0.9636
	PFBS	0.646	0.357	0.8386	0.716	0.400	0.8457	0.936	0.040	0.023	0.511	0.014	0.8544
PET nonwoven	PFOS	NA	NA	NA	NA	NA	NA	0.951	0.049	0.000	3.000	0.002	0.8647
GTX	PFOA	NA	NA	NA	NA	NA	NA	0.974	0.029	0.000	1.170	0.000	0.8028
	PFHxA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	PFBS	NA	NA	NA	NA	NA	NA	0.973	0.028	0.000	1.862	0.000	0.8662
Clay 1	PFOS	15.282	2.531	0.9944	15.642	3.000	0.9966	0.194	0.709	0.097	6.035	0.200	0.9862
	PFOA	5.783	4.358	0.9999	5.860	2.744	0.9999	0.647	0.339	0.013	4.873	0.181	0.9996
	PFHxA	1.111	1.184	0.9997	1.209	1.500	0.9997	0.912	0.091	0.000	2.214	0.029	0.9997
	PFBS	1.357	2.065	0.9999	1.404	2.569	>0.9999	0.882	0.095	0.023	3.380	0.100	>0.9999
Clay 2	PFOS	13.207	5.588	0.9998	13.312	3.592	0.9999	0.332	0.641	0.027	8.734	0.183	0.9996
	PFOA	5.035	4.920	0.9997	5.169	2.529	0.9999	0.676	0.280	0.044	7.516	0.038	0.9999
	PFHxA	0.785	1.000	0.9991	0.785	2.000	0.9991	0.938	0.062	0.000	8.695	0.006	0.9996
	PFBS	1.146	1.714	0.9999	1.193	1.429	0.9999	0.895	0.000	0.055	1.314	0.060	0.9982
Resin	PFOS	19.785	5.380	0.9997	20.019	2.186	0.9997	0.000	0.879	0.121	11.375	0.965	>0.9999
	PFOA	16.394	2.249	0.9990	16.799	0.290	0.9993	0.000	0.444	0.556	10.000	1.263	0.9991
	PFHxA	12.325	0.925	0.9921	12.633	0.169	0.9939	0.017	0.000	0.989	1.593	1.251	0.9987
	PFBS	12.166	0.441	0.9433	12.567	0.078	0.9511	0.000	0.016	1.100	0.851	0.851	0.9081
	PFPrA	6.644	0.840	0.9580	6.800	0.280	0.9602	0.000	0.128	0.883	1.181	1.179	0.9909
	TFMS	5.901	1.000	0.9669	6.047	0.389	0.9703	0.017	0.992	0.000	1.357	0.028	0.9983

Polypropylene geotextiles and bentonite demonstrated similar sorption capacities to the same PFAS, indicating that, in the absence of sufficient organic carbon and/or ion exchange mechanisms, their sorption onto solids is mainly analyte and solution-dependent.

3.3. Adsorption isotherms

Sorption isotherms of PFOS, PFOA, PFHxA, PFBS, PFPrA and TFMS (for which a model could be fitted) in multi-solute systems on geosynthetic liner constituents are illustrated in Figs. 3 and 4). Competitive effects on sorption extent were not evident, as demonstrated by similarities between C_e values in single- and multi-solute systems (refer to Tables SI–5). Thus, this sorption isotherm study was confined to multi-solute systems. For PFPrA and TFMS, no measurable sorption was observed for the constituents examined, excluding the ion exchange resin; therefore, isotherm constants were derived only for the resin.

The Langmuir and Freundlich equations were adopted to describe the experimental data, and related parameter estimates at initial PFAS concentrations ranging from 1 to 80 nM are summarised in Table 4. PFOS and PFOA were almost entirely sorbed by activated carbon amended bentonite and the ion exchange resin for initial concentrations ranging from 1 to 80 nM, and near-vertical isotherms were obtained. Similarly, PFBS, PFHxA, PFPrA and TFMS were almost entirely sorbed by the ion exchange resin for initial concentrations ranging from 1 to 80 nM. Due to inappropriate fits to the data at these concentrations inaccurate parameter estimates were obtained , as most surface sites Journal of Environmental Management 381 (2025) 125288

remained vacant at the maximum concentration applied. Thus, higher concentrations were employed (up to 7500 nM) to achieve a reduced curve slope, enabling more accurate sorption characterisation and maximum sorption capacity estimates.

Fig. 4 presents the Langmuir and Freundlich sorption isotherms for PFAS at initial concentrations ranging from 1 to 7500 nM on activated carbon-amended bentonite and the ion exchange resin. Related parameter estimates are listed in Table 5. Both models fit the experimental data well for activated carbon amended bentonite at initial PFOS and PFOA concentrations ranging from 1 to 7500 nM ($R^2 > 0.9487$). This can be attributed to the reduced percentage of solute uptake at higher initial concentrations due to the saturation of binding sites. Thus, more accurate sorption characterisation and estimation of maximum sorption capacity were possible. In contrast, even at the highest concentration of 7500 nM, the ion exchange resin sorbed almost all the solutes, implying





Fig. 3. Sorption data and extrapolated best-fit models for PFAS in multi-solute systems at initial concentrations ranging from 1 to 80 nM. Each data point represents the average of triplicate vials. The fitted Langmuir and Freundlich Isotherm models are depicted by dashed and solid lines, respectively.



■ PFOA ◆ PFHxA ▲ PFOS ● PFBS





that most surface sites were vacant. As shown in Tables 4 and 5, the Langmuir and Freundlich models produced poor fits for various PFAS compounds on the ion exchange resin at both concentration ranges. Furthermore, where parameter estimates could be derived, those from lower initial concentration ranges deviated significantly from those obtained at higher concentrations. This indicates that values of Langmuir and Freundlich parameters are highly dependent on initial aqueous concentration and highlight the importance of obtaining a saturated isotherm, particularly for accurate Langmuir maximum sorption capacity (Q_m) estimates.

The Freundlich and Langmuir models fit the experimental data well for polypropylene geotextiles (R^2 between 0.7479 and 0.9913). They are both suitable for describing the data, although the Freundlich model generally provided a marginally better fit for most compounds. For bentonite and clay minerals, the goodness-of-fit indices for the Freundlich and Langmuir models typically declined as the chain length decreased. The Freundlich model generally provided a better fit (R^2 > 0.6256) for PFOS, PFOA and PFHxA, while both models yielded poorer fits ($R^2 < 0.5945$) for PFBS due to low adsorption. Furthermore, no isotherm constants were derived for PFHxA and PFBS to Clay 1. Similarly, both models produced poor fits for the polyester woven geotextile due to its low adsorption capacity.

The Freundlich model assumes a heterogeneous surface with an exponential distribution of active sites and their corresponding energies (Freundlich, 1909). Sites with higher affinity are occupied first, and as more sites are filled, the adsorption energy decreases exponentially. Thus, the superior fit of the Freundlich model to the experimental data, in comparison to the Langmuir model, suggests that the adsorption process is multilayered. This type of sorption is characteristic of materials with a complex, heterogeneous surface structure, where variations in surface energy and pore size influence the capacity ,mechanism, and kinetics of PFAS adsorption.

Where appropriate model fits were obtained, the isotherm nonlinearity index (n) from the Freundlich model was generally less than 1 for







the constituents investigated. This reaffirmed that PFAS sorption was mainly concentration dependent. Additionally, the nonlinearity indices for each analyte on the same constituent generally showed minimal variation. For instance, the nonlinearity index of PFOA ranged from 0.234 to 0.469 for bentonite. Notably, at lower concentration ranges, the isotherms generally appeared linear. There is sufficient surface area for sorption at low concentrations, and the amount of solute adsorbed is directly proportional to its concentration in the liquid phase. As concentration increases, the isotherms become nonlinear due to the sorbent's finite capacity to adsorb a substance within a specific volume or mass. The nonlinearity of the isotherms depends on the concentration range, sorbing component, retention mechanisms, and characteristics of the phase system.

Activated carbon-amended bentonite and the ion-exchange resin exhibited the highest K_F values among the tested adsorbents. As shown in Tables 4 and 5, the adsorption capacities of PFOS, PFOA, PFHxA and PFBS on the materials generally decrease in the order of ion exchange resin > activated carbon amended bentonite > Clay 1 > Clay 2 >

bentonite > nonwoven polypropylene geotextile > woven polypropylene geotextile > polyester nonwoven geotextile, as indicated by K_F values. Given the low R^2 values obtained for some PFAS with ion exchange resin, clays and the polyester geotextile, the interpretation of K_F values to indicate sorption capacities should be treated with caution.

The Q_m value predicted by the Langmuir model was used to compare PFAS sorption across the investigated sorbents, owing to the model's good fit for most target compounds. The Q_m values, where applicable, for each analyte ranged from 14.682 to 2915.061 µg/g for activated carbon amended bentonite, 1.177–6.466 µg/g for bentonite, 2.665–10.716 µg/g for polypropylene geotextiles, 0.699–43.655 µg/g for clays, and 10,000.002–10,457.000 µg/g for the ion-exchange resin. These findings provide a comprehensive understanding of the sorption capacities of various sorbents for PFAS, with larger Q_m values signifying a favourable and strong affinity of PFAS for the adsorbents. Overall, the maximum sorption capacity of each adsorbent for PFAS, as indicated by Q_m values, followed the order: ion exchange resin > activated carbon amended bentonite > Clay 1 > Clay 2 > bentonite > nonwoven



PFOA + PFHxA • PFBS A PFOS

Fig. 3. (continued).

polypropylene geotextile > woven polypropylene geotextile.

The sorption of PFAS on bentonite corroborates the findings of previous studies (Ahmad et al., 2023; Khodabakhshloo et al., 2021; Zhou et al., 2010). For example, Khodabakhshloo et al. (2021) investigated the adsorption of PFOS from wastewater to bentonite, reporting a K_I value of 80 L/kg at initial concentrations ranging from 5000 to 300,000 μ g/L. In this study, the Langmuir isotherm model effectively described the adsorption process of PFOS on bentonite, with a K_I coefficient value of 137 L/kg. Notably, partitioning coefficients for PFAS are concentration-dependent, with higher initial solute concentrations above the equilibrium concentration yielding a lower percentage of the sorbed solute. This is because a higher analyte concentration remains in the liquid phase, resulting in lower partitioning coefficients. Therefore, it is imperative that the initial concentration used in sorption tests sufficiently reflects the intended application for which this information is utilised. The initial PFOS concentrations used in the Khodabakhshloo et al. (2021) study (5000–300,000 µg/L) were substantially higher than the concentrations applied in this study (0.2–40.01 μ g/L) and do not reflect typical PFOS levels encountered in the environment; thus, a direct comparison to the results of this study is not possible.

Although bentonite exhibits a fine particle size, with at least 65 % passing through a 75 µm sieve (Tables SI-1), suggesting a significant external surface area, its sorption capacity for PFAS, particularly short and ultra-short congeners, is limited by several key physicochemical factors. The net negative charge (permanent) layer charge of montmorrilonite crystallites influences the interlayer environment and controls the CEC of bentonite (53 mmol/kg) (Tables SI-1), but a residual net negative surface charge around particles also exists (Grim, 1968; Mitchell and Soga, 2005). The magnitude and extent of this negative surface charge potential emanating from the particles are influenced by solution pH, ionic strength and counter ion charge, as predicted by the Deryagin-Landau-Verwey-Overbeek (DLVO) theory (Lyklema et al., 1999). For most sodium smectite dispersions, the surface charge zeta potential, as measured by electrophoretic mobility, ranges from -25 to -35 mV (Delgado et al., 1985). Under the condition of our study, the negative zeta potential would be expected to cause electrostatic repulsion between the negatively charged PFAS molecules and the surface of bentonite, thereby hindering sorption, particularly for shorter PFAS congeners. Moreover, the sorption process was further limited by the absence of sufficient organic content, which reduces the potential for hydrophobic interactions. Notably, the external surface area of clay

minerals in bentonite likely correlates better for PFAS sorption than its total surface area, which typically ranges from 400 to 800 m²/g, as determined by liquid adsorption methods such as ethylene glycol retention (Correia et al., 2020). This is evidenced by the comparable sorptive capacity of bentonite for PFAS relative to kaolin and hematite, which generally possess significantly smaller total surface areas (Zhao et al., 2014). Taken together, these effects result in lower total sorption and complex sorption kinetics of PFAS as observed.

In contrast, the co-application of activated carbon with bentonite at a rate of approximately 20 % w/w significantly improved the sorptive capacity, demonstrating approximately 44,983 %, 72,502 %, 1211 % and 1147 % increases in maximum adsorption capacities for PFOS PFOA, PFHxA and PFBS, respectively. Adsorption of anionic PFAS onto activated carbon can be primarily attributed to organic-carbon partitioning (Du et al., 2014; Rahman et al., 2014) via physical retention mechanisms within inner pores of the solid-phase matrix, hydrophobic interactions between the carbon-fluorine chain and hydrophobic organic matter, electrostatic interactions involving the molecule head group with charged regions on the activated carbon surface, and/or ion exchange.

Clays 1 and 2 exhibited moderate sorption of PFAS, attributed mainly to hydrophobic partitioning into organic matter. However, the clay mineral component may also play a significant role in PFAS sorption. Clays carrying a net positive charge may exhibit enhanced sorption due to increased electrostatic interactions with the negatively charged PFAS, influenced by the pH-dependent positive charges on organic matter and clay minerals. Furthermore, the high cation exchange capacity (CEC) of Clay 1 may have promoted sorption through a cationbridge mechanism (Higgins and Luthy, 2006; You et al., 2010; Chen et al., 2012). Cations neutralise negative charges on sediment surfaces in this mechanism, reducing electrostatic repulsion between the sediment and anionic PFAS molecules. This enhances the electrostatic attraction between the negatively charged sediment surface and the anionic compound.

Polypropylene woven and nonwoven geotextile exhibited comparable sorptive capacities to bentonite, indicating that, in the absence of sufficient organic carbon and/or ion exchange mechanisms, sorption of PFAS onto solids is mainly solution and analyte-dependent. Sorption of PFAS onto polypropylene geotextiles is attributed to hydrophobic interactions with the carbon-fluorine chain, which causes the molecules to repel water molecules and adhere to interfaces or hydrophobic matter



PFOA A PFOS

Ion Exchange Resin Concentration of PFAS adsorbed onto the solid phase at 4000 3500 3000 equilibrium, C_s (μg/g) 2500 2000 1500 1000 500 o 20 0 5 10 15 Concentration of PFAS remaining in the liquid-phase at equilibrium, C_w (µg/L)

■ PFOA ◆ PFHxA ▲ PFOS ● PFBS ● PFPrA ■ TFMS

Fig. 4. Sorption data and extrapolated best-fit models for PFAS at initial concentrations of up to 7500 nM in multi-solute systems. Each data point represents the average of triplicate vials. The fitted Langmuir and Freundlich Isotherm models are depicted by dashed and solid lines, respectively.

due to their immiscibility with solvents. The rough and macroporous surface of polypropylene geotextile fibres likely enhances this sorption process (Mikhael et al., 2024b). In contrast, polyester nonwoven geotextiles exhibit a lower sorptive capacity for PFAS due to their smooth and non-porous structure, which inhibits the diffusion of molecules through the solid since there are no channels or pores available (Mikhael et al., 2023). The variation in sorption observed may also be due to polyester's reduced hydrophobicity compared to polypropylene, attributed to polar ester groups in polyester.

The ion exchange resin demonstrated the highest sorptive capacity, particularly for short and ultra-short chain PFAS. Additionally, the ion exchange resin effectively sorbs ultra-short chain compounds, which the other sorbents investigated in this study did not attenuate. The sorption mechanisms of PFAS onto ion exchange resins comprise ion exchange and physical sorption, such as hydrophobic interaction, that may be less dependent on substance polarity. The hydrophobic perfluorinated tail can bind to the hydrophobic backbone of the anion exchange resin or its cross-linkers. At the same time, the hydrophilic, charged PFAS head is drawn to the resin's anion exchange site via electrostatic attraction (Riegel et al., 2023).

Notably, marked differences in sorption capacities were observed among individual analytes, depending primarily on their perfluorocarbon chain length. The sorption amount decreased with decreasing chain length (hydrophobicity) for the compounds investigated in this study, as evidenced by the Q_{max} values tabulated in Table 4. PFOA and PFOS demonstrated significantly higher sorption to all sorbents than the other evaluated PFAS, owing to their longer carbon chain lengths, which enhanced sorption through increased hydrophobic interactions. Furthermore, a stronger affinity was observed for sulfonate species than carboxylic acids. This can be attributed to the greater hydrophobicity of PFSAs compared to PFCAs, owing to the larger sulfonate group (Higgins and Luthy, 2006). Additionally/alternatively, this trend can be attributed to the negative inductive effect (Verma et al., 2023), wherein the PFAS acid groups draw electrons from fluorine toward themselves,

Table 4

Constants for models of best fit for initial PFAS concentrations between 1 and 80 nM.

Sorbent Compound		Freundlich mod	el		Langmuir mo	Langmuir model			
		k _F	n	R ²	b _L	Sm	R^2		
AC-A bentonite	PFOS	NA	NA	NA	NA	NA	NA		
	PFOA	NA	NA	NA	NA	NA	NA		
	PFHxA	2.920	0.747	0.9230	0.220	20.000	0.8710		
	PFBS	5.685	0.365	0.9958	0.620	14.682	0.9334		
Bentonite	PFOS	1.509	0.361	0.7332	0.137	6.466	0.7940		
	PFOA	1.088	0.306	0.7472	0.202	3.547	0.8272		
	PFHxA	0.688	0.234	0.8492	0.442	1.525	0.8450		
	PFBS	0.208	0.469	0.5359	0.127	1.177	0.5443		
PP nonwoven GTX	PFOS	0.745	0.749	0.9783	0.102	10.716	0.8799		
	PFOA	0.277	0.981	0.9801	0.100	7.361	0.8002		
	PFHxA	0.251	0.740	0.9295	0.101	3.193	0.8776		
	PFBS	0.471	0.493	0.7479	0.155	2.665	0.8174		
PP woven GTX	PFOS	0.520	0.831	0.9913	0.100	9.596	0.8459		
	PFOA	0.174	1.082	0.9867	0.100	6.304	0.7538		
	PFHxA	0.215	0.775	0.9584	0.100	3.012	0.8965		
	PFBS	0.242	0.696	0.9332	0.100	2.736	0.9316		
PET nonwoven GTX	PFOS	NA	NA	NA	NA	NA	NA		
	PFOA	0.152	0.371	0.6897	NA	NA	NA		
	PFHxA	0.216	0.397	0.6701	NA	NA	NA		
	PFBS	NA	NA	NA	NA	NA	NA		
Clay 1	PFOS	5.074	0.629	0.9427	0.108	43.655	0.9619		
	PFOA	0.603	0.713	0.9556	0.102	7.486	0.8896		
	PFHxA	NA	NA	NA	NA	NA	NA		
	PFBS	NA	NA	NA	NA	NA	NA		
Clay 2	PFOS	4.375	0.512	0.9886	0.116	28.552	0.9722		
	PFOA	0.962	0.488	0.9488	0.101	6.360	0.8861		
	PFHxA	0.317	0.259	0.6256	0.835	0.699	0.8610		
	PFBS	0.028	0.431	0.5945	NA	NA	NA		
Resin	PFOS	NA	NA	NA	NA	NA	NA		
	PFOA	227.408	0.746	0.7858	0.800	606.893	0.7450		
	PFHxA	NA	NA	NA	NA	NA	NA		
	PFBS	NA	NA	NA	NA	NA	NA		
	PFPrA	20.838	0.467	0.5909	NA	NA	NA		
	TFMS	10.621	0.769	0.7231	0.800	21.951	0.7185		

Table 5

Constants for models of best fit for initial PFAS concentrations between 1 and 7500 nM.

Sorbent	Compound	Freundlich model			Langmuir model				
		k _F	n	R ²	b _L	Sm	R^2		
AC-A bentonite	PFOS	491.600	0.265	0.9714	0.100	2915.061	0.9487		
	PFOA	384.723	0.296	0.9921	0.083	2575.209	0.9998		
Resin	PFOS	1744.713	1.945	0.9998	0.404	10,457.000	0.9971		
	PFOA	5032.923	1.931	1.0000	0.559	10,000.002	0.9809		
	PFHxA	NA	NA	NA	NA	NA	NA		
	PFBS	NA	NA	NA	NA	NA	NA		
	PFPrA	227.818	1.900	0.9999	0.057	10,245.000	0.9870		
	TFMS	NA	NA	NA	NA	NA	NA		

owing to their electronegativity. Due to its higher electronegativity, the sulfonic acid group exhibits a more pronounced electron-withdrawing effect than the carbonic acid group. Thus, for a given PFAS chain length, the sulfonic acid group withdraws more electrons from fluorine than the carbonic acid group, causing the fluorine atoms to become more electron deficient and lowering the residual charge on each fluorine atom more effectively (Gupta, 2016; Zhang and Chen, 2018). This may lead to greater dipole-dipole and/or hydrophobic interactions.

3.4. Desorption experiments

Desorption experiments in water were conducted to evaluate the reversibility of the sorption process. Batch sorption samples from previous multi-component experiments at 80 nM were reweighed. A 40 mL aliquot of DI water was added to each sample, and desorbed PFAS concentrations were determined after agitating for 96 h.

The percentage of PFAS desorbed from liner constituents depended on the constituent type and PFAS characteristics. Desorbed percentages (see Table 6) for PFOS and PFOA in water followed the order: polyester geotextile > polypropylene geotextiles > bentonite > clays > ion exchange resin = activated carbon amended bentonite. For PFHxA, desorbed percentages followed the order Clay 1 > polypropylene geotextiles > polyester geotextile > bentonite > Clay 2 > ion exchange resin = activated carbon amended bentonite. For PFBS, desorbed percentages (where applicable) followed the order Clay 2 = polypropylene woven geotextile = bentonite > polypropylene nonwoven geotextile > polyester geotextile > polypropylene nonwoven geotextile > polyester geotextile > activated carbon amended bentonite > ion exchange resin. Desorption from the ion exchange resin was less than 1 % for both PFPrA and TFMS.

The concentrations of PFAS desorbed in water from the liner constituents were generally consistent with the sorption behaviour of these compounds, with the desorption of PFOS notably lower than the other compounds studied. Hence, the functional group and chain length are important parameters influencing the desorption potential of PFAS. The ion exchange resin exhibited the lowest desorption percentages for the target analytes, with less than 1 % desorbed, consistent with the results

Table 6

PFAS Concentration (C_d , $\mu g/L$) and percentage desorbed in 40 mL DI water.

Sorbent	PFAS C	ompound										
	PFOS		PFOA		PFHxA		PFBS		PFPrA		TFMS	
	C _d (ug/ L)	Desorbed (%)										
AC-A bentonite	0.0	0 %	0.0	0 %	0.0	0 %	2.2	16 %	< LOQ	NA	< LOQ	NA
Bentonite	0.4	7 %	0.3	11 %	0.3	23 %	0.9	100 %	< LOQ	NA	< LOQ	NA
Polypropylene woven geotextile	1.9	21 %	1.2	20 %	0.8	30 %	2.0	100 %	< LOQ	NA	< LOQ	NA
Polypropylene nonwoven geotextile	2.1	22 %	1.5	22 %	1.1	46 %	1.9	96 %	< LOQ	NA	< LOQ	NA
Polyester geotextile	0.3	29 %	0.2	46 %	0.2	24 %	0.3	63 %	< LOQ	NA	< LOQ	NA
Clay 1	0.1	0.4 %	0.1	1 %	0.1	65 %	< LOQ	NA	< LOQ	NA	< LOQ	NA
Clay 2 (Kooney)	0.0	0 %	0.0	0 %	0.1	17 %	0.1	100 %	< LOQ	NA	< LOQ	NA
Resin	0.0	0 %	0.0	0 %	0.0	0 %	0.2	1 %	0.2	1 %	0.1	1 %

from Liu et al. (2021), highlighting the strong adsorption of ultrashort, short and long chain PFAS onto the adsorbent. The extent of desorption from activated carbon amended bentonite was higher for short and ultra-short congeners, the weakest adsorbing compounds. In contrast, desorption percentages for PFOA and PFOS were negligible, indicating minimal dissociation of bound PFAS from binding sites. These results further suggest that PFOA and PFOS form strong interactions with activated carbon-amended bentonite.

3.5. PFAS adsorption from a landfill leachate matrix

Fig. 5 presents the aqueous-phase equilibrium concentrations of PFAS in landfill leachate and pure multi-compound systems (comprising PFAS dissolved in a 10:90 methanol-water mixture) for activated carbon amended bentonite, bentonite and polypropylene geotextile fibres. To enable comparison, initial concentrations employed in multi-solute system experiments were consistent with concentrations measured in the landfill leachate matrix investigated. Variations in PFAS removal percentages from the liquid phase were contingent on whether they were tested in pure solutions or leachate matrices. This experimental setup aimed to evaluate the sorption of PFAS in the context of a landfill leachate matrix, where various organic and inorganic components in the leachate could potentially influence PFAS adsorption. Leachate matrix constituents generally reduced the sorption affinity of most PFAS with the sorbents compared to pure solutions.

Tables SI-2 shows that the leachate composition included significant concentrations of various ions and organic compounds that may influence PFAS sorption. Key findings from the leachate composition analysis include a TOC concentration of 159 mg/L, with high concentrations of chloride (4690 mg/L), sodium (2290 mg/L), calcium (206 mg/L), and ammonia (4.66 mg/L). Additionally, trace metals such as arsenic (0.463 mg/L), iron (0.23 mg/L), and manganese (0.377 mg/L) were present. Matrix constituents were demonstrated (Fig. 5) to significantly inhibit sorption of PFBS and PFHxA onto activated carbon amended bentonite (mean C_w of 10.06 $\mu g/L$ in landfill leachate vs 2.09 $\mu g/L$ in pure solution tion) and bentonite (mean C_w of 10.43 µg/L in landfill leachate vs 9.28 μ g/L in pure solution). Competitive leachate constituents, particularly inorganic ions (e.g., chloride, sodium) and organic compounds, influence sorption dynamics by competing for available adsorption sites on the sorbent materials (Appleman et al., 2013; Dixit et al., 2020). Aqueous solutions containing higher concentrations of natural organic matter and inorganic anions have been shown to inhibit PFAS adsorption by competing for adsorption sites and blocking pores (Appleman et al., 2013; Dixit et al., 2019). This effect is likely more significant for

short-chain compounds due to their lower hydrophobicity. In contrast, the sorption of PFBS and PFHxA to polypropylene fibres was minimally impacted by matrix constituents (mean C_w of 10.63 µg/L in landfill leachate vs 10.40 µg/L in pure solution). Furthermore, the high concentrations of dissolved salts, reflected by an electrical conductivity of 13,800 µS/cm and total dissolved solids (TDS) of 8970 mg/L, also likely contributed to the competitive ionic environment.

PFOS and PFOA exhibited the smallest reductions in measured C_W values in the landfill leachate matrix compared to the multi-solute system for all materials investigated. These findings may indicate that PFOS and PFOA are more tightly bound, owing to the lower transport rate of long-chain PFAS due to their decreased solubility. However, these experiments conducted with relatively low PFOS and PFOA input concentrations are anticipated to demonstrate minimal competitive sorption effects. Furthermore, no discernible decrease in TFMS and PFPrA concentrations was measured in any matrix for the sorbents assessed, which was consistent with previous batch sorption experiments indicated that these fibres contributed to the total PFPrA concentrations in pure solutions and leachate matrices. Consequently, the final PFPrA aqueous concentrations were higher than the initial concentrations.

4. Implications and conclusions

The findings of this study offer valuable insights into the effectiveness of constituents of engineered lining systems for attenuating PFAS -at environmentally relevant concentrations- from landfill leachate. Landfills can pose as significant sources of PFAS contamination, which may ultimately lead to groundwater and surface water contamination if barrier systems are improperly designed and/or poorly managed. Understanding the efficacy of liner constituents in containing PFAS-laden leachates can enable the design and construction of the most appropriate geosynthetic composite liner system to contain PFAS and minimise their release into the environment.

Adsorption and desorption capacity can primarily assess sorbent effectiveness for removing PFAS in a liquid matrix. For example, considering the GCL component of geosynthetic composite lining systems, the low sorption capacity of bentonite for PFAS, as shown in this study, indicates that the bentonite component alone will not adequately attenuate these compounds. Thus, to prevent or slow the migration of PFAS through the GCL, attenuation capacity must be increased by employing additive materials, such as activated carbon, that will improve the sorptive capacity of the GCL constituents (Malusis et al.,



Activated carbon amended bentonite





Fig. 5. Average aqueous-phase concentration of target PFAS in landfill leachate and pure multi-compound systems.

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Fig. 5. (continued).

2009; Gates et al., 2020; Bouazza, 2021).

To place the results of this study in a practical light, we considered a hypothetical municipal solid waste landfill with a surface area of 10,000 m². Assuming a typical GCL thickness of 8 mm and that the GCL consists of two polypropylene woven and nonwoven geotextile layers encapsulating a 5 mm layer of bentonite, the total PFOS mass anticipated to be retained by the liner based on Q_m values and desorption percentages is 323 g. In contrast, if the bentonite component is replaced by this study's activated carbon amended bentonite, the total PFOS mass expected to be retained by the liner is 142,866 g. Notably, the sorption capacities derived from experiments employing pure solutions should not be anticipated to fully reflect the conditions present in landfill leachate. Therefore, directly comparing this study's results to a landfill scenario may not be entirely relevant. Nonetheless, such studies provide valuable data for assessing the relative effectiveness of alternative liner designs and components. They serve as a crucial step in evaluating potential methods to minimise PFAS transport from landfills, offering insights that can guide management as well as further research and refinement of landfill liner technologies.

Furthermore, the results of this study indicated that liner constituents, excluding the ion exchange resin, exhibit limitations in the removal and ongoing retention of short chain PFAS congeners. Thus, it may be necessary to incorporate additional materials, such as an ion exchange resin, into the lining system design to ensure short and ultra-short chain compounds are adequately retained.

CRediT authorship contribution statement

Elissar Mikhael: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Abdelmalek Bouazza: Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Will P. Gates: Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2025.125288.

Data availability

Data will be made available on request.

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