Proceedings of the 9ICEG
9th International Congress on Environmental Geotechnics
25-28 June, 2023 | Chania, Greece
© Authors: All rights reserved, 2023
https://doi.org/10.53243/ICEG2023-88

Sorption of Per- and Poly-Fluoroalkyl Substances on geotextile components of geosynthetic composite lining systems

E. Mikhael[1], A. Bouazza[2] and W. P. Gates[3]

[1]PhD student, Department of Civil Engineering, 23 College Walk, Monash University, Melbourne, Vic 3800, Australia, Email: elissar.mikhael@monash.edu

[2]Professor, Department of Civil Engineering, 23 College Walk, Monash University, Melbourne, Vic 3800, Australia, Email: malek.bouazza@monash.edu

[3]Associate Professor, Institute for Frontier Materials, Deakin University, Melbourne-Burwood Campus, 221 Burwood Highway, Melbourne, Vic 3125, Australia, Email: will.gates@deakin.edu.au

ABSTRACT

We present here an experimental investigation on the sorption kinetics of two perfluoroalkyl acids (PFAAs): namely, perfluorooctane sulfonic acid (PFOS) and perfluorobutane sulfonic acid (PFBS) to polypropylene nonwoven cover and woven carrier geotextiles commonly used in geosynthetic clay liners, as well as polyester nonwoven geotextiles typically used in modern geosynthetic composite lining systems for protection function purposes. In this study, the time required for the adsorption of each PFAA compound on geotextiles to reach equilibrium was 1-72h. The fraction of analyte remaining in the liquid phase at equilibrium followed the order: nonwoven polyester > woven polypropylene > nonwoven polypropylene for both PFOS and PFBS, suggesting that the structural and polymeric composition of the geotextile fibres strongly dictates the sorption. The PFAAs exhibited varying sorption affinities following the order: PFOS > PFBS. Thus, it can be inferred that PFAAs with longer carbon chains prefer partitioning to the solid phase. Furthermore, the biexponential adsorption model, which postulates sorption as a two-step mechanism controlled by diffusion, provided a better fit for polypropylene (PP) geotextiles than the pseudo-first order (PFO) and pseudo-second order (PSO) models. For the polyester (PET) geotextile, PFO, PSO, and biexponential adsorption models provided a similar fit, suggesting that PFAAs adsorption onto PET geotextiles was mainly through physical interactions. Since the PFO and PSO models do not explain the diffusion of solute into an adsorbent, it is inferred that the diffusion of molecules through the PET geotextile was minimal due to the absence of available channels and pores.

Keywords: Geotextiles, Perfluorooctane Sulfonic Acid, Perfluorobutane Sulfonic Acid, Sorption, Geosynthetic Composite Liner, GCLs

1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) constitute an extensive class of synthetically made chemicals that have been historically used in many industrial and consumer products, including textiles, non-stick cookware, and aqueous film forming foam (AFFF), for their surfactant properties and resistance to degradation (Kannan, 2011; Glüge et al., 2020). PFASs have been found in the environment, animals, and humans worldwide (US EPA, 2018). These compounds are toxic, bioaccumulative and resist biotic degradation (Glüge et al., 2020). Hence, increasing concerns for environmental and human health have led to the development of rigorous PFAS-related guidelines or regulations. For example, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), the two most commonly known and studied perfluoroalkyl acids (PFAAs) were added to the Stockholm Convention's annexes in 2009 and 2019, respectively, restricting their production and use (UNEP, 2009; 2019). As a result, PFOS, PFOA and related compounds have been substituted with shorter chain-length PFAAs and other fluorinated alternatives (Buck et al., 2011).
Consumer and industrial products disposed in landfills may leach PFAAs over time (Duarte et al., 2018). Hence, PFAAs have been detected ubiquitously in landfill leachates, with shorter-chain PFAAs

significantly contributing to the overall PFAS profiles (Gallen et al., 2017; Lang et al., 2017; Simmons, 2019; Wang et al., 2020; Solo-Gabriele et al., 2020). In modern waste containment facilities, geosynthetic composite liners play an important role to mitigate waste, leachate and contaminant releases into the surrounding environment (Bouazza et al., 2002, McWatters et al., 2016, Rowe and Jefferis, 2022). These lining systems typically incorporate a range of woven and nonwoven geotextiles for separation, filtration, and protection purposes, as well as indirectly contributing to sealing functions.

While geosynthetic composite liners are designed and constructed to prevent or limit waste and contaminant releases to the surrounding environment (Bouazza, 2002; Rowe, 2005, 2020; Gates et al., 2009; Hornsey et al., 2010; Touze-Foltz et al., 2021), most geosynthetic composite liners, have not been designed to retain or attenuate specific emerging contaminants such as PFASs (Gates et al., 2020; Bouazza, 2021). Knowledge of contaminant transfers in components of geosynthetic composite lining systems is currently limited mainly to metal substances, volatile organic compounds, aromatic hydrocarbons, and phenolic compounds (Lake and Rowe, 2005; Rowe et al., 2005; Richards and Bouazza, 2007; Lange et al., 2009; Xie et al., 2018; Wang et al., 2019; Ahari et al., 2019). Only recently have research efforts been directed towards addressing the possible effect of PFASs on geosynthetics engineering performance (Gates et al., 2020, Di Battista et al., 2020, Bouazza, 2021, Rowe and Barakat, 2021). However, there needs to be more information available in the current literature regarding interactions between PFASs and geotextiles or other geosynthetics. Thus, evaluating the potential of PFAA compound attenuation on geotextiles is paramount for designing modern lining systems.

This paper examines the partitioning behaviour of two environmentally significant PFAAs with varying perfluorocarbon chain lengths (C4 and C8) to polypropylene (PP) and polyester (PET) geotextile components of geosynthetic composite lining systems and fits sorption kinetics data to various kinetic models.

2 MATERIALS AND METHODS

2.1 Geotextiles

The geotextiles used in this study are commercially available and were produced by the same manufacturer. They are extensively used in lining systems of waste containment facilities and other engineering applications. They included two polypropylene (PP) woven and nonwoven geotextiles, referred to herein as GTX1 and GTX2, respectively, and one nonwoven polyester (PET) geotextile, referred to herein as GTX3. A summary of their description is given in Table 1.

Table 1. *Geotextiles description*

Geotextile	Description	Mass per unit area (g/m^2)*
GTX1	Woven PP	110
GTX2	Nonwoven PP	250
GTX3	Nonwoven PET	870

*average values as measured in our laboratory.

2.2 Chemicals and Reagents

Perfluorobutanesulfonic acid (PFBS, 97%) was purchased from Sigma-Aldrich, Australia; perfluorooctane sulfonic acid (PFOS, in methanol, 100ug/mL) was obtained from Novachem, Australia. The physicochemical properties of the PFASs analysed in this study are listed in Table 2. HPLC grade methanol (≥99.9%) and acetonitrile (≥99.9%) were purchased from Sigma-Aldrich, Australia.

Purity-corrected single compound stock solutions were prepared by dissolving a single PFAA in a 50/50 (v/v) methanol-water solution to set the aqueous concentrations to 100 nM. Working solutions were prepared by adjusting the PFAA concentrations to 40 nM, with the addition of DI water. In this study, a methanol-water solvent mix was employed to ensure a balanced compromise between the solubility needed to ensure PFAA compounds were sufficiently dissolved in solution and to minimise the effects of methanol on possible swelling of PP (Kutsuna et al., 2012; Okland, 2020; Kappert et al., 2019). Note that the liquid concentrations of PFAAs used in this study were considerably lower than their critical micelle concentration (CMC) values (Table 2), at which they may aggregate to form hemi-micelles and micelles. Such phase separation can promote either competitive or synergistic adsorption, thus,

impacting the partitioning of PFAAs between the solid and liquid phases (Du et al., 2014). Therefore, the impact of micelle-formation on adsorption is anticipated to be negligible.

Types and concentrations of PFAAs used in this study were selected based on typical constituent types and concentrations detected in Australian landfill leachates, as indicated in current literature (Gallen et al. 2017; Simmons 2019).

Table 2. *PFAS Physical and Chemical Properties*

PFAS Name	Acronym	Average Molecular Weight (g/mol)	Molecular Formula	Classification	CMC (in water) (mg/L) [a]	pK_a [a]
Perfluorobutane sulfonic acid	PFBS	300.1	$C_4F_9SO_3^-$	Short-chain	……	<0.3
Perfluorooctane sulfonic acid	PFOS	500.1	$C_8F_{17}SO_3^-$	Long chain	536-4573	<1

[a] Data obtained from Vierke et al. (2013), Bhhatarai et al. (2011), and Yu et al. (2009)

2.3 Batch adsorption kinetics experiments

The experiments were conducted in two stages: range-finding adsorption tests and adsorption kinetic tests. Preliminary range-finding sorption tests were carried out initially to ensure the retrieval of a sufficient concentration of test samples for analysis without falling below the limit of quantification (LOQ). The preliminary sorption experiments were carried out in 50 mL polycarbonate (PC) centrifuge tubes; three different geotextile masses (20, 40 and 80 mg) and 40 mL of PFAA working solutions at 80nM were added. The tubes were subsequently shaken on an orbital shaker (NB-101M, N-Biotek) at a speed of 150 rpm and a temperature of 21 ± 2°C for 72 h. The supernatant was transferred to a 2 mL sample vial for liquid chromatography-mass spectrometry (LC-MS) analysis. A set of instrumental and method blanks were prepared and analysed concomitantly with each experiment. Based on the abovementioned preliminary range-finding sorption tests, it was found that a 40mg sample mass was sufficient to ensure enough time points for subsequent kinetics experiments.

Kinetic studies were conducted to establish the time required to reach equilibrium; 40 mL PFAA working solutions at 40nM were added to triplicate sets of PC tubes containing 40 mg of geotextile cut into one piece. The tubes were subsequently shaken on an orbital shaker for 96 h. At the times of 0.5, 1, 2, 24, 72 and 96 hours, three samples were sacrificed. The aqueous sample was centrifuged (THR75004230CC, ThermoFisher Scientific), and the supernatant was transferred to a 2 mL sample vial for LC-MS analysis. A separate set of instrumental and method blanks were analysed for each time interval. Equilibrium times were determined based on sampling times, at which no change in solute concentration was observed after various measurements during the adsorption process.

2.4 PFAA analysis

Liquid chromatography-mass spectrometry (LC-MS) was used to determine the PFAA concentrations in aqueous samples. PFAA quantification was achieved using an external standard calibration curve of six points to determine PFAA concentrations in the liquid phase. All standard curve correlation coefficients (R) were > 0.999. The method detection limit (MDL), defined as the lowest concentration of an analyte that can be measured and reported with 99% confidence that the concentration is distinct from method blank results (NRDC, 2019), was determined from a signal-to-noise ratio of 3:1. The limit of quantification (LOQ), or the method reporting limit, defined as the minimum concentration at which the analyte can be reliably detected and quantified with statistical rigour (Armbruster et al., 2008), was determined from a signal-to-noise ratio of 10:1. The MDL and LOQ for the PFASs are listed in Table 3.

Table 3. *MDLs and LOQs for the PFAAs used in this study.*

Analyte	MDL		LOQ	
	µg/L	nM	µg/L	nM
PFOS	0.25	0.5	0.45	0.9
PFBS	0.06	0.2	0.15	0.5

2.5 Quality Assurance and Control

Before the start of the experiments, all tubes and HPLC vials were cleaned thoroughly using deionised (DI) water and HPLC-grade methanol to minimise PFAA loss and/or contamination. For the same purpose, no fluorinated materials were used in the experiments. Instrumental blanks consisting of DI water were used to monitor the cleanliness of the LC-MS instrument. Method blanks containing the methanol-water solution were used to monitor contamination and interferences from sample manipulations, laboratory equipment and the general laboratory environment. Reference control tubes were prepared without adding geotextiles and/or PFAA stock solution to test for the presence of PFAAs in geotextiles/tubes and to evaluate PFAA loss from sorption to tube walls. Target analytes were not detected in the laboratory blanks (nil addition of PFAAs), confirming that contamination was not introduced during adsorption experiments.

3 RESULTS AND DISCUSSION

The time required for the adsorption of each PFAA compound onto GTX1, GTX2 and GTX3 to reach equilibrium was between 1 and 72 hrs, as depicted in Figures 1 and 2. This period is consistent with equilibrium times obtained by Yu and Hu (2011) concerning the adsorption of PFAAs onto activated sludge and Deng et al. (2013) regarding the sorption of perfluorinated compounds on aminated rice husk. Figures 1 and 2 reveal that the sorption of PFOS and PFBS on GTX3 reached equilibrium at 1 h for both compounds. The time required for the adsorption of PFOS on GTX1 and GTX2 to reach equilibrium was 72 h, while the adsorption of PFBS on GTX1 and GTX2 reached equilibrium in approximately 24 h.

The fraction of analyte remaining in the liquid phase at equilibrium followed the order: GTX3 > GTX1 > GTX2 for both PFOS and PFBS, suggesting the structural and polymeric composition of the geotextile fibres strongly dictates the sorption. The presence of pores, available surface area and chemical configuration have been suggested to be the important features impacting the sorption of organic compounds by polymeric materials (Ateia et al., 2020). For porous material, the internal surface area due to the pores is typically much higher than the external surface area (Al-Maharma et al., 2020); hence porous geotextiles can be expected to exhibit higher specific surface areas than non-porous geotextiles. PP fibres contain random arrays of macropores, with sizes ranging from 0.96 µm to 13.8 µm, and the fibre surface is rough and textured, as shown in Figure 3a. Conversely, Figure 3b reveals the smooth and non-porous structure of PET fibres. Notably, the surface area also corresponds to the roughness of the sorbent exterior. Increasing total surface area has been shown to correlate positively with a sorbent's adsorption capacity (Petrovic et al., 2021). Hence, it is inferred that pores within PP geotextile fibres and the surface roughness increases pore and void spaces inside the fibres, resulting in increased available adsorption sites. As such, it is proposed that the presence of pores within the geotextile fibres plays an important role in the uptake of PFAAs by geotextiles.

An interesting observation was marginally greater sorption on the nonwoven PP geotextile compared to the woven PP geotextile. Although nonwoven geotextiles are similarly derived from synthetic polymers to woven geotextiles, they differ in morphological form. Woven geotextile fabrics are manufactured by tightly interlacing horizontal and vertical fibres together. Therefore, woven geotextiles are semi-impermeable, resembling plastic sheets. Nonwoven geotextiles are manufactured by entangling fibres through needle punching or other suitable methods. Therefore, unless broken, their fibres are loosely entangled without disturbing their active surface area. These characteristics increase the exposed surface area, enabling a higher surface capacity for adsorption (Yu et al., 2009; Du et al., 2014).

The overall observed variance in sorption for GTX 1&2 compared to GTX 3 may be attributed to the different sorption affinities of PFASs to polypropylene versus polyester geotextiles. Amphiphilic surfactants (such as PFASs) in aqueous solutions are known to sorb to polyester and polypropylene

fibres. Liu et al. (2010) observed that the adsorption affinity of amphiphilic silicone-based surfactants containing methylated siloxane hydrophobic groups attached to one or more hydrophilic groups was found to be strongly associated with the hydrophobicity of the polymer substrate. Moreover, various peer-reviewed studies have evaluated the possible mechanisms that dictate the adsorption of PFAAs to polymers, soils, and sediments (Brusseau, 2018; Gagliano et al., 2020; Higgins and Luthy, 2006). These studies suggest that the adsorption of anionic PFAAs is controlled primarily by hydrophobic interactions with the fluorinated tail, that drives PFAA molecules to repel water and to concentrate at an interface and/or be attracted to hydrophobic matter due to immiscibility with the solvent, and electrostatic interactions with the hydrophilic functional group (Chen et al., 2012; Zhao et al., 2014; Alves et al., 2020). Weak intermolecular interactions, such as van der Waals interactions or hydrogen bonding (Lath et al., 2019), are also important interactions.

PET is more hydrophilic than PP due to the presence of polar ester groups in the former. PP includes purely hydrocarbon groups and thus, is more hydrophobic. As such, PP geotextiles, being more hydrophobic than PET, likely exhibit a higher affinity for PFASs. Notably, at the solution pH values adopted in this study (~ 6.9 - 7.4), the two PFAAs were in their anionic form due to their low acid dissociation constant (pKa) values (shown in Table 2). Additionally, for the experimental conditions applied in this study, geotextiles may be expected to have a negatively charged surface (Lameiras et al., 2008). While sorption of anionic PFAAs may have been suppressed due to electrostatic repulsion, methanol employed for sample preparations in this study may have ameliorated this effect, owing to the preferential binding of methanol (dominated by hydrogen bonding) to the geotextile surface. The neutrally charged methanol molecules bound to the surface of the geotextile are presumed to have screened the repulsive forces between anionic PFAAs and geotextiles.

Pseudo-first order (PFO), pseudo-second order (PSO), and biexponential adsorption models were fitted to adsorption kinetics data of PFAAs onto GTX1, GTX2 and GTX3. The biexponential adsorption model, which postulates two-stage sorption controlled by diffusion (Eq. 1), provided a better fit for GTX1 and GTX2 than the PFO and PSO models. For GTX3, PFO, PSO, and biexponential adsorption models provided a similar fit, suggesting that PFAAs' adsorption onto PET geotextiles was mainly through physical interactions, likely based on weak Van der Waals and hydrophobic attraction forces (Agbovi and Wilson, 2021). Since the PFO and PSO models do not explain the diffusion of solute into an adsorbent, it is inferred that the diffusion of molecules through GTX3 was minimal due to the absence of available channels and pores.

$$F_w = F_0 + F_1 e^{-k1t} + F_2 e^{-k2t} \quad (1)$$

where F_w is the fraction of the remaining analyte in the liquid phase at time t, F_0 is the fraction of analyte that is partitioned at the liquid-liquid interface; F_1 denotes 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.

As shown in Figures 1 and 2, the bi-exponential model predictions align with the experimental data sets for GTX1 ($R^2 > 0.8642$), GTX2 ($R^2 > 0.9176$) and GTX3 ($R^2 > 0.866$). Parameter values that best fit the experimental data are summarised in Table 4. Sorption affinities of geotextiles for PFAAs followed the order: PFOS > PFBS. These results indicate that, with increasing carbon chain length, F_0 values decrease and F_1 and F_2 increase. Thus, it can be inferred that PFAAs with longer carbon chains prefer partitioning to the solid phase. This is consistent with previous findings, wherein increased partitioning of PFAAs to soils, and sediments was associated with longer carbon chain length (Higgins and Luthy, 2006; Li et al., 2019). The increasing trend in PFAA uptake with increasing chain length indicates that hydrophobic interactions were likely the dominant removal mechanism, particularly for PP geotextiles. Thus, retention of short-chain PFAAs by geotextiles is less likely than by long-chain homologues due to their lower hydrophobicity (Li et al., 2019).

As shown in Figures 1 and 2, the adsorption of PFAAs onto GTX1 and GTX2 can be classified into two stages: rapid adsorption at the initial stage, followed by a slow adsorption stage. The kinetic models infer rapid sorption of PFAA into the boundary layer of the geotextile, followed by gradual diffusional transport into the geotextile microstructure. Such an explanation corroborates previous studies concerning the adsorption of PFAAs onto various porous solids such as soils and sediments (Du et al., 2014; Higgins and Luthy, 2006; Li et al., 2019). In contrast, the sorption of PFAAs onto GTX3 occurred mainly via a one-step, surface sorption mechanism, where the increase in the number of available

sorption sites enabled the sorbent's interaction with the PFAA compound. For GTX3, it was observed that PFAA adsorption is a fast process requiring times less than 1 hour to reach saturation, likely due to the nonporous characteristics of the PET fibres that favour a rapid first step of adsorption onto the geotextile surface (Contreras–Mateus et al., 2022).

The fast (k_1) and slow (k_2) sorption rates of PFASs for geotextiles varied significantly. For GTX1 and GTX2, values higher than 0.00 for the parameters F_2 and k_2 imply that the fast step is followed by gradual sorption of PFAAs to geotextiles. The slow sorption rates (k_2) increased with increasing chain length, consistent with previous observations (Li et al., 2019). The longer-chain PFAAs are presumed to diffuse more gradually into the PP geotextile pores than the shorter-chain compounds. PFAAs exhibit surfactant properties attributed to their hydrophobic tail and hydrophilic head (ITRC, 2020). Longer-chain PFAAs are more effective as surfactants and therefore tend to self-assemble into interfacial films, potentially retarding PFAA migration and deposition into the sorbent (ITRC, 2020). In contrast, short-chain PFAAs can enter pores more easily than the longer-chain congeners as a factor of both their size and increased hydrophilic behaviour (Du et al.,2014). Hence, it can be inferred that increasing carbon chain length reduces the absorption rate by PP fibres due to increased hydrophobicity reducing pore accessibility. However, the results of the bi-exponential model infer that a second step for GTX3 is unlikely, wherein parameters F_2 and k_2 were less than 0.00. Hence, it is interpreted that intraparticle diffusion can be neglected for sorption on PET fibres. As such, for PET fibre surfaces, surface reactions control the kinetics of the sorption process, whereas both surface and pore reactions are important for PP fibres.

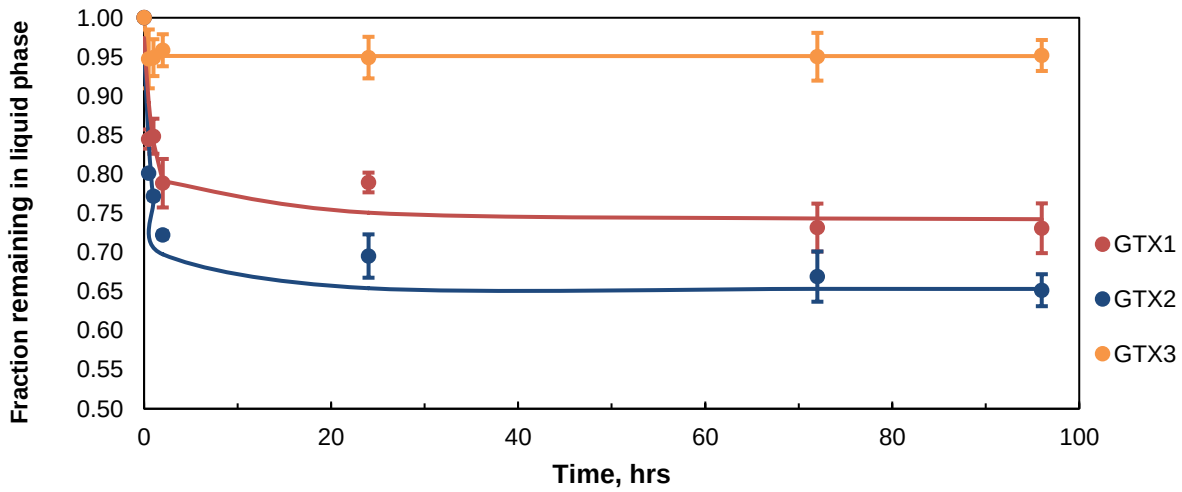


Figure 1. *Sorption kinetics of PFOS to geotextiles at 0.001 kg/L. The initial PFOS concentration was 40 nM. Error bars represent the standard deviation of uncertainty for each sampling time. The lines are the best-fitted biexponential adsorption model*

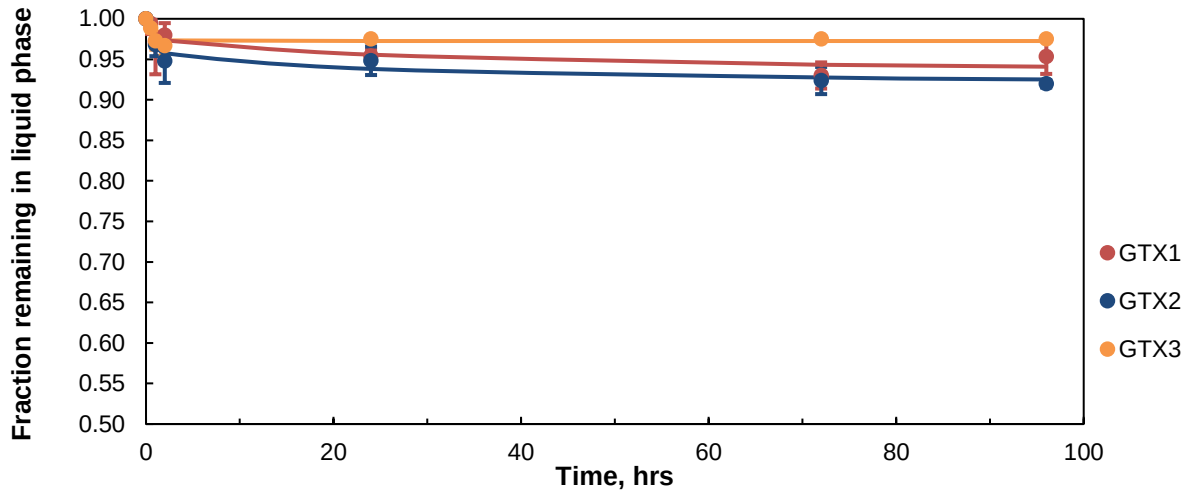


Figure 2. *Sorption of PFBS onto geotextiles at 0.001 kg/L. The initial PFBS concentration was 40 nM. Error bars represent the standard deviation of uncertainty for each sampling time. The lines are the best-fitted biexponential adsorption model*

Table 4. *Best-fit parameters of the biexponential adsorption model in capturing the sorption of PFAAs to geotextiles*

	PFOS						PFBS					
Geotextile	**F_0**	**F_1**	**F_2**	**k_1**	**k_2**	**R^2**	**F_0**	**F_1**	**F_2**	**k_1**	**k_2**	**R^2**
GTX1	0.742	0.211	0.022	0.990	0.037	0.909	0.938	0.030	0.033	0.990	0.026	0.864
GTX2	0.653	0.304	0.003	0.990	0.044	0.932	0.921	0.058	0.028	0.882	0.021	0.918
GTX3	0.948	0.045	0.000	3.010	0.002	0.867	0.972	0.029	0.000	1.814	0.000	0.866

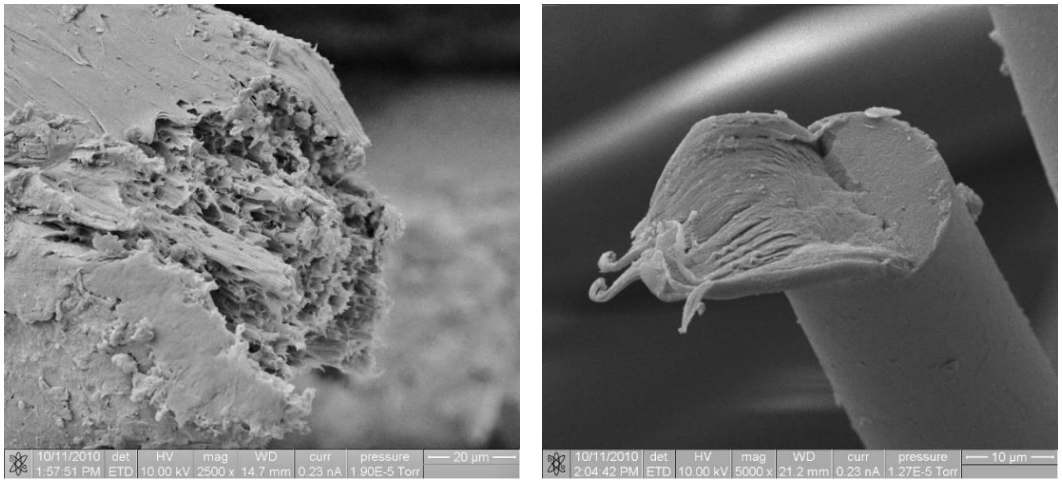


Figure 3. *a) SEM image of the PP fibre surface (scale bar 20μm) (left). b) SEM image of the PET fibre surface (scale bar 10μm) (right).*

4 CONCLUSIONS

This study investigated the sorption of long- and short-chain perfluoroalkyl substances (PFASs) on polypropylene nonwoven cover and woven carrier geotextiles commonly used in geosynthetic clay liners, as well as polyester nonwoven geotextiles typically used in modern geosynthetic composite lining

systems for protection function purposes. The above results indicate that geotextile fibres potentially play a role in the uptake of PFAAs by geosynthetic composite lining systems. The salient conclusions that can be drawn from this study are:

- Experimental adsorption equilibrium time for both PFBS and PFOS on all geotextile materials ranged from 1 to 72 hours. Generally faster equilibrium times were observed for PFBS than for PFOS, presumably related to molecular size. Greater sorption was observed on the nonwoven PP geotextile compared to the woven PP geotextile, owing to a larger exposed surface area in nonwoven PP GTX.
- The observed variance in sorption may be attributed to the different sorption affinities of PFASs to polypropylene versus polyester geotextiles. PP geotextiles, being more hydrophobic than PET, likely exhibit a higher affinity for PFASs.
- A rough and macroporous surface of the PP geotextile fibres plays an essential role in the sorption process
- Sorption of PFAAs onto geotextiles was attributed to hydrophobic interactions with the fluorinated tail, which drives PFAA molecules to repel water molecules and to adsorb on an interface and/or be attracted to hydrophobic matter due to immiscibility with the solvent. Thus, while the adsorption of short-chain PFAAs is faster, on geotextiles, their retention is less than long-chain homologues due to their lower hydrophobicity.
- The biexponential adsorption model, which postulates sorption as a two-step mechanism controlled by diffusion, provided a better fit for GTX1 and GTX2 than the PFO and PSO models. For GTX3, PFO, PSO, and biexponential adsorption models provided a similar fit, which suggests that diffusion of molecules through GTX3 was minimal due to the absence of available channels and pores.

5 ACKNOWLEDGEMENTS

This project was partly funded by the Australian Research Council's Linkage Project scheme (LP190101178) and the following industry partners: Geofabrics Australasia Pty. Ltd., Fabtech, TRI Australia, Solmax and Senversa. Their support is gratefully acknowledged. The SEM images used in this paper were obtained by Geofabrics Australasia Pty. Ltd.

REFERENCES

Agbovi, H., Wilson, L. (2021). 1 - Adsorption processes in biopolymer systems: fundamentals to practical applications, Natural Polymers-Based Green Adsorbents for Water Treatment, Elsevier, Pages 1-51, ISBN 9780128205419.

Al-Maharma, A.Y., Patil, S.P. and Markert, B. (2020). Effects of porosity on the mechanical properties of additively manufactured components: a critical review. Materials Research Express, 7(12), p.122001.

Alves, A.V., Tsianou, M. and Alexandridis, P. (2020). Fluorinated Surfactant Adsorption on Mineral Surfaces: Implications for PFAS Fate and Transport in the Environment. Surfaces, 3(4), pp.516–566.

Armbruster, D.A., Pry, T. (2008). Limit of blank, limit of detection and limit of quantitation. Clin Biochem Rev. 29 Suppl 1(Suppl 1):S49-S52.

Ateia, M., Maroli, A., Tharayil, N. and Karanfil, T. (2019). The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. Chemosphere, 220, pp.866–882.

Bhhatarai, B. and Gramatica, P. (2011). Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. Environmental Science & Technology, 45(19), pp.8120–8128.

Bouazza, A. (2002). Geosynthetic clay liners. Geotextiles and Geomembranes, 20(1), pp.3–17.

Bouazza, A. (2021). Interaction between PFASs and geosynthetic liners: Current status and the way forward. Geosynthetics International, 28(2), pp.214-223.

Brusseau, M.L. (2018). Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface. Science of The Total Environment, 613-614, pp.176–185.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. and van Leeuwen, S.P. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integrated Environmental Assessment and Management, 7(4), pp.513–541.

Chen, H., Zhang, C., Yu, Y. and Han, J. (2012). Sorption of perfluorooctane sulfonate (PFOS) on marine sediments. Marine Pollution Bulletin, 64(5), pp.902–906.

Contreras–Mateus, M., Sánchez, F.H., Cañas-Martínez, D.M., Nassar, N.N. and Chaves–Guerrero, A. (2022). Effect of asphaltene adsorption on the magnetic and magnetorheological properties of heavy crude oils and Fe3O4 nanoparticles systems. Fuel, 318, p.123684. doi:10.1016/j.fuel.2022.123684.

Deng, S., Niu, L., Bei, Y., Wang, B., Huang, J. and Yu, G. (2013). Adsorption of perfluorinated compounds on aminated rice husk prepared by atom transfer radical polymerization. Chemosphere, 91(2), pp.124–130.

Di Battista, V., Rowe, R.K., Patch, D. and Weber, K. (2020). PFOA and PFOS diffusion through LLDPE and LLDPE coextruded with EVOH at 22 °C, 35 °C, and 50 °C. Waste Management, 117, pp.93–103.

Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J. and Yu, G. (2014). Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. Journal of Hazardous Materials, 274, pp.443–454.

Duarte, A.C., Cachada, A. and Rocha-Santos, T. (2018). Soil pollution : from monitoring to remediation. London, United Kingdom: Academic Press, an imprint of Elsevier.

Gagliano, E., Sgroi, M., Falciglia, P.P., Vagliasindi, F.G.A. and Roccaro, P. (2020). Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. Water Research, 171, p.115381.

Gallen, C., Drage, D., Eaglesham, G., Grant, S., Bowman, M. and Mueller, J.F. (2017). Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. Journal of Hazardous Materials, 331, pp.132–141.

Gates, W.P., Bouazza, A. and Churchman, G.J. (2009). Bentonite Clay Keeps Pollutants at Bay. Elements, 5(2), pp.105–110.

Gates, W.P., MacLeod, A.J., Fehervari, A., Bouazza, A., Gibbs, D., Hackney, R., Callahan, D.L. and Watts, M. (2020). Interactions of Per- and Polyfluoralkyl Substances (PFAS) with Landfill Liners. Advances in Environmental and Engineering Research, 1(4).

Glüge, J., Scheringer, M., Cousins, I.T., DeWitt, J.C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C.A., Trier, X. and Wang, Z. (2020). An overview of the uses of per- and polyfluoroalkyl substances (PFAS). Environmental Science: Processes & Impacts.

Higgins, C.P. and Luthy, R.G. (2006). Sorption of Perfluorinated Surfactants on Sediments†. Environmental Science & Technology, 40(23), pp.7251–7256.

Hornsey, W. P., Scheirs, J., Gates, W. P., & Bouazza, A. (2010). The impact of mining solutions/liquors on geosynthetics. Geotextiles and Geomembranes, 28(2), pp. 191-198.

ITRC PFAS Team (2020). PFAS Fact sheets: Physical and Chemical Properties; Interstate Technology Regulatory Council: Washington, DC, USA.

Kannan, K. (2011). Perfluoroalkyl and polyfluoroalkyl substances: current and future perspectives. Environmental Chemistry, 8(4), pp.333.

Kappert, E.J., Raaijmakers, M.J.T., Tempelman, K., Cuperus, F.P., Ogieglo, W. and Benes, N.E. (2019). Swelling of 9 polymers commonly employed for solvent-resistant nanofiltration membranes: A comprehensive dataset. Journal of Membrane Science, 569, pp.177–199.

Kutsuna, S., Hori, H., Sonoda, T., Iwakami, T. and Wakisaka, A. (2012). Preferential solvation of perfluorooctanoic acid (PFOA) by methanol in methanol–water mixtures: A potential overestimation of the dissociation constant of PFOA using a Yasuda–Shedlovsky plot. Atmospheric Environment, 49, pp.411–414.

Lake, C. and Rowe, R. (2005). A comparative assessment of volatile organic compound (VOC) sorption to various types of potential GCL bentonites. Geotextiles and Geomembranes, 23(4), pp.323–347.

Lameiras, F.S., Souza, A.L. de, Melo, V.A.R. de, Nunes, E.H.M. and Braga, I.D. (2008). Measurement of the zeta potential of planar surfaces with a rotating disk. Materials Research, 11(2), pp.217–219.

Lang, J.R., Allred, B.M., Field, J.A., Levis, J.W. and Barlaz, M.A. (2017). National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. Environmental Science & Technology, 51(4), pp.2197–2205.

Lange, K., Rowe, R.K. and Jamieson, H. (2009). Diffusion of metals in geosynthetic clay liners. Geosynthetics International, 16(1), pp.11–27.

Lath, S., Knight, E.R., Navarro, D.A., Kookana, R.S. and McLaughlin, M.J. (2019). Sorption of PFOA onto different laboratory materials: Filter membranes and centrifuge tubes. Chemosphere, 222, pp.671–678.

Li, F., Fang, X., Zhou, Z., Liao, X., Zou, J., Yuan, B. and Sun, W. (2019). Adsorption of perfluorinated acids onto soils: Kinetics, isotherms, and influences of soil properties. Science of The Total Environment, 649, pp.504–514.

Liu, X., Song, J., Wu, D., Genzer, J., Theyson, T. and Rojas, O.J. (2010). Surface and Friction Behavior of a Silicone Surfactant Adsorbed on Model Textiles Substrates. Industrial & Engineering Chemistry Research, 49(18), pp.8550–8557.

McWatters, R. S., Rowe, R. K., Wilkins, D., Spedding, T., Jones, D., Wise, L., Mets, J., Terry, D., Hince, G., Gates, W.P., Di Battista, V., Shoaib, M., Bouazza, A., Snape, I. (2016). Geosynthetics in Antarctica: Performance of a

composite barrier system to contain hydrocarbon-contaminated soil after three years in the field. Geotextiles and Geomembranes, 44(5), pp. 673-685.

National Resource Defense Council. (2019). PFAS in Drinking Water: Scientific and Policy Assessment for Addressing Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water.

Okland, S (2020). Sorption of PFAS onto Synthetic Hydrous Iron Oxides. Department of Geoscience, University of Oslo, Master of Science Thesis.

Petrovic, B., Gorbounov, M. and Masoudi Soltani, S. (2021). Influence of surface modification on selective CO2 adsorption: A technical review on mechanisms and methods. Microporous and Mesoporous Materials, 312, p.110751.

Richards, S. and Bouazza, A. (2007). Phenol adsorption in organo-modified basaltic clay and bentonite. Applied Clay Science, 37(1-2), pp.133–142.

Rowe, R.K. (2020). Protecting the Environment with Geosynthetics: 53rd Karl Terzaghi Lecture. Journal of Geotechnical and Geoenvironmental Engineering, 146(9), p.04020081.

Rowe, R.K. and Barakat, F.B. (2021). Modelling the transport of PFOS from single lined municipal solid waste landfill. Computers and Geotechnics, 137, p.104280.

Rowe, R. K. and Jefferis, S. (2022). Protecting the environment from contamination with barrier systems: advances and challenges. Proceedings 20th International Conference on Soil Mechanics and Geotechnical Engineering, Sydney, Austral, pp.187-293,

Rowe, R.K., Mukunoki, T. and Sangam, H.P. (2005). Benzene, Toluene, Ethylbenzene, m & p -Xylene, o -Xylene diffusion and sorption for a geosynthetic clay liner at two temperatures. Journal of Geotechnical and Geoenvironmental Engineering, 131(10), pp.1211–1221.

Simmons, N. (2019). PFAS concentrations of landfill leachates in Victoria, Australia–implications for discharge of leachate to sewer. Proceedings 17th International Waste Management and Landfill Symposium, Sardinia, Italy, CISA.

Solo-Gabriele, H.M., Jones, A.S., Lindstrom, A.B. and Lang, J.R. (2020). Waste type, incineration, and aeration are associated with per- and polyfluoroalkyl levels in landfill leachates. Waste Management, 107, pp.191–200.

Touze-Foltz, N., Xie, H., & Stoltz, G. (2021). Performance issues of barrier systems for landfills: a review. Geotextiles and Geomembranes, 49(2), pp. 475-488.

UNEP Decision SC-4/17(2009). Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride SC-4/17, United Nations Environment Programme (UNEP), Secretariat of the Basel, Rotterdam and Stockholm Conventions, Geneva, Switzerland.

UNEP Decision SC-9/12 (2019). Listing of Perfluorooctanoic Acid (2019), its Salts and PFOA-Related Compounds UN Environment (UNEP), Secretariat of the Basel, Rotterdam and Stockholm Conventions, Geneva, Switzerland

US EPA (US Environmental Protection Agency) (2018), Human health toxicity values for perfluorobutane sulfonic acid (CASRN 375-73-5) and related compound potassium perfluorobutane sulfonate (CASRN 29420-49-3).

Vierke, L., Berger, U. and Cousins, I.T. (2013). Estimation of the Acid Dissociation Constant of Perfluoroalkyl Carboxylic Acids through an Experimental Investigation of their Water-to-Air Transport. Environmental Science & Technology, 47(19), pp.11032–11039.

Wang, F., Zhang, M., Sha, W., Wang, Y., Hao, H., Dou, Y. and Li, Y. (2020). Sorption Behavior and Mechanisms of Organic Contaminants to Nano and Microplastics. Molecules, 25(8), p.1827.

Xie, H., Wang, Q., Bouazza, A., & Feng, S. (2018). Analytical model for vapour-phase VOCs transport in four-layered landfill composite cover systems. Computers and Geotechnics, 101, pp.80-94.

Yu, J. and Hu, J. (2011). Adsorption of Perfluorinated Compounds onto Activated Carbon and Activated Sludge. Journal of Environmental Engineering, 137(10), pp.945–951.

Yu, Q., Zhang, R., Deng, S., Huang, J. and Yu, G. (2009). Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. Water Research, 43(4), pp.1150–1158.

Zhao, L., Bian, J., Zhang, Y., Zhu, L. and Liu, Z. (2014). Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. Chemosphere, 114, pp.51–58.