



Adsorption behavior of per- and polyfluoralkyl substances (PFASs) to 44 inorganic and organic sorbents and use of dyes as proxies for PFAS sorption



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ARTICLE INFO

Keywords:

PFAS
PFOS
Dye sorption
Stabilization
Proxy

ABSTRACT

Per- and polyfluoralkyl substances (PFASs) are a major concern in pollution of drinking water sources and aquatic environments. This study investigated the sorption behavior of 17 PFASs of varying chain lengths and functional groups to 44 conventional and novel inorganic and organic sorbents with potential in treatment of PFAS-contaminated water or soil. For the first time, a large number of sorbents were tested for a wide variety of PFASs in batch sorption experiments under controlled experimental set-up. Also, the sorption behavior of four different dyes (methylene blue, crystal violet, indigo carmine, rose bengal) was also determined, to assess whether dyes can be used as a proxy for PFAS sorption. Of the 44 sorbents tested, PFASs sorbed best (mean > 99.9 %) to activated carbons (granulated and pulverized ($n = 5$)). Sorption of PFASs to magnesium chloride-fortified biochar, *Moringa* seed, and pyrolytic carbon waste was 17- to 25-fold higher than to sand. Sorption generally increased with increasing perfluorocarbon chain length and based as follows on functional group: fluorotelomer sulfonic acids (FTSAs) < perfluoroalkyl carboxylates (PFCAs) < perfluoroalkane sulfonates (PFASs) < perfluorooctanesulfonamide (FOSA). Principal component analysis revealed that electrostatic sorption dominated for shorter-chained PFASs and that hydrophobic sorption dominated for longer-chained PFASs. All four dyes tested proved suitable as proxies for sorption of PFASs. In particular, methylene blue correlated best to short-chain PFASs (e.g., perfluorohexanoate (PFHxA)) and rose bengal to longer homologues (i.e., perfluorooctanesulfonate (PFOS)).

1. Introduction

Per- and polyfluoralkyl substances (PFASs) constitute an extensive group of > 4700 man-made organofluorine compounds [1]. Since the 1950s, PFASs have been used in numerous consumer and industrial products, e.g., firefighting foams, electronics, clothing, cookware, and lubricants, to enhance quality and performance with their water, dust, and oil repellency and high thermal stability [2–4]. However, the high persistence and widespread use of PFASs have resulted in their ubiquitous distribution in the environment [5,6]. Typical point sources of PFASs include fire training sites, landfills, and sewage treatment plants [7–10]. Public concerns about PFASs are increasing globally, particularly since multiple drinking water sources have been found to be polluted with PFASs [11–13].

A better understanding of PFAS sorption to materials could assist in development of stabilization remediation technologies for soils [14–18] and filter systems for drinking water [19,20] and wastewater [21]. Since PFASs have unique physicochemical properties that vary with chain length, functional group, and degree of fluorination, it is

important to test a variety of different sorbent materials, including natural media [18,22–25], engineered adsorbent materials such as zeolites and activated carbons [26], and completely novel materials such as quaternized cotton and crosslinked chitosan beads [27,28] and other cationic amine-engineered sorbents [29]. However, existing studies on PFAS sorption have been performed under a wide range of conditions (e.g., initial concentrations, pH, conductivity, liquid-solid ratio, ion composition, co-contaminants, solid phase carbon content, etc.). These are known to change PFAS partitioning behavior [30], making it impossible to compare sorbent performance. Hence, it is important to test the sorption behavior of a wide variety of PFASs to a wide range of sorbents under comparable conditions.

The conventional method for investigating the adsorption behavior of PFASs is time-consuming, complicated, and expensive, due to the need for a wide range of analytical standards and the use of advanced mass spectrometry for PFAS analysis (e.g., [31]). Because of analytical challenges, instrumental limitations and availability of PFAS standards, adsorption studies often only include a few well-recognized PFASs (e.g., perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid

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<https://doi.org/10.1016/j.jece.2020.103744>

Received 27 September 2019; Received in revised form 10 January 2020; Accepted 2 February 2020

Available online 03 February 2020

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(PFOA); see Tables S1 and S2 in Supporting Information (SI) for references). A user-friendly and cost-efficient approach to testing the sorption behavior of organic micropollutants is to use dyes as a proxy, since dye sorption can be easily analyzed using spectrophotometer measurements. Dyes have been used for evaluation of sorption efficiencies of novel filter materials [32–34], life spans of filter materials [35], environmental fate during soil infiltration [36,37], novel remediation methods such as electroremediation for micropollutants [38], photocatalytic degradation [39], and characterization of active carbons (i.e., assessing the methylene blue number) [40]. However, dyes have not been tested previously as a proxy for PFAS sorption behavior.

In this study, sorption of 17 PFASs and of four high-purity dyes to 44 different adsorbent materials (inorganic and organic) was investigated and compared in batch experiments. Specific objectives of the study were to (i) evaluate the sorption of PFASs and dyes to the 44 adsorbent materials, (ii) assess the influence of PFAS structure and chemical properties on sorption to the 44 materials, and (iii) evaluate whether the dyes can be used as a proxy to predict adsorption of PFASs to adsorbent materials. For the understanding of the two latter objectives, correlation tests and principle component analysis was conducted.

2. Materials and method

2.1. Analytical PFAS standards, dyes, and sorption materials

The target PFAS analytes were: C₃-C₁₁, C₁₃, C₁₅, C₁₇ perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTeDA, PFHxDA, PFOcDA), C₄, C₆, C₈ perfluoroalkane sulfonates (PFASs) (PFBS, PFHxS, PFOS), perfluorooctanesulfonamide (FOSA), and 6:2 and 8:2 fluorotelomer sulfonic acids (FTSAs). Nine isotopically labeled internal standards (ISs) were used: ¹³C₄-PFBA, ¹³C₂-PFHxA, ¹³C₄-PFOA, ¹³C₅-PFNA, ¹³C₂-PFDA, ¹³C₂-PFUnDA, ¹³C₂-PFDoDA, ¹⁸O₂-PFHxS, ¹³C₄-PFOS, and ¹³C₈-FOSA (purity > 99 %) (Wellington Laboratories, Guelph, ON). Abbreviation, supplier, and purity of the native and isotopically labeled PFAS standards are listed in Table S3 in SI. The high-purity dyes methylene blue (Merck, Sweden), crystal violet (Alfa Aesar, MA, USA), indigo carmine (Acros Organics, Belgium), and rose bengal (Alfa Aesar, MA, USA) were selected for testing, based on differences in molecular size, chromophores, and ionic charge. For details of supplier, structural and chemical formulae, dye class, molecular weight (MW), and water solubility (S_w), see Table S4 in SI.

In total, 44 relevant adsorbent materials were selected, covering organic sorbents such as activated carbon (AC) (5 replicas (*n*)), biochar (*n* = 5), sorbents with high organic content (*n* = 6), and organic waste products (*n* = 5), and inorganic sorbents such as soil minerals (*n* = 6), inorganic filter materials (*n* = 4), inorganic phosphorus filters (*n* = 5), and inorganic waste products (*n* = 2) (Table S5 in SI).

2.2. Batch experiments

The sorption behavior of the PFASs (*n* = 17) was evaluated for adsorbent materials (*n* = 44) and dyes (*n* = 4) in laboratory-scale batch experiments. Experiments were performed in duplicate for individual adsorbent materials (*n* = 44) fortified with: i) a standard PFAS mixture, ii) methylene blue, iii) crystal violet, iv) indigo carmine, or v) rose bengal. For the experiments assessing PFAS adsorption, the starting concentration was 0.1 µg mL⁻¹ for the individual compounds and the pH was adjusted to 7.5 ± 0.5 (Table S6 in SI) using 6 mM phosphate buffer solution, since PFAS adsorption behavior is pH-dependent (Higgins and Luthy, 2006). The starting concentration of the dyes was selected based on the sensitivity of the quantitative analysis (see Section 2.3.2 for instrument specifications) and was: 1100 µg mL⁻¹ for methylene blue (concentration was 3.4 µM mL⁻¹), 22 µg mL⁻¹ for crystal violet (0.042 µM mL⁻¹), 69 µg mL⁻¹ for indigo carmine (0.049

µM mL⁻¹), and 120 µg mL⁻¹ for rose bengal (0.118 µM mL⁻¹).

In the batch experiments, 40 mL of Millipore water, fortified with a PFAS mixture or a dye, was added to 50 mL polypropylene (PP) tubes (Corning®, nonpyrogenic) and 0.1 g ± 0.025 g of individual adsorbent material was added, resulting in a liquid:solid ratio (L/S) of 400. Positive control samples fortified with a PFAS standard mixture (*c* = 100 ng mL⁻¹ for the individual PFAS) (*n* = 3) and blanks (*n* = 3) without adsorbent containing 6 mM phosphate buffer solution in Millipore water were also prepared. All samples were shaken for 7 days (168 h) until assumed equilibrium [41] using a horizontal 1D-shaker (Gerhardt) at 100 rpm. Directly after shaking, the samples were centrifuged (Eppendorf Centrifuge 5810) for 15 min at 3000 rpm, and the supernatants were stored airtight at 5 °C and analyzed within 24 h.

2.3. Chemical analysis

2.3.1. PFAS analysis

For PFAS analysis, an aliquot of 700 µL from each batch experiment fortified with PFASs (*c*_{w,PFAS}) was transferred to an Eppendorf PP tube (Eppendorf, Germany) and fortified with 650 µL methanol (LiChrosolv, Merck, Germany) and 50 µL of internal standard (IS) mixture (0.05 µg mL⁻¹). The samples were then vortexed (VX-2500 Multi-Tube Vortexer, VWR, Sweden) for 10 min and centrifuged at 15000 rpm for 10 min (Eppendorf Centrifuge 5424 R). The samples were filtered through 0.45 µm recycled cellulose syringe filters (Sartorius) into 1.5 mL amber auto-injector glass vials (Eppendorf, Germany). The extracts were analyzed using a DIONEX UltiMate 3000 ultra-high performance liquid chromatography (UHPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (MS/MS) (TSQ QUANTIVA, Thermo SCIENTIFIC, Waltham, MA, USA). The PFASs were chromatographically separated on a BEH C18 column (1.7 µm, 50 mm, Waters Corporation, Manchester, UK) by using acetonitrile and Millipore water with 5 mM ammonium acetate eluent gradient during 12 min and a flow rate of 0.5 mL min⁻¹ in negative electrospray mode. A nine-point calibration curve, ranging between 0.00001–0.10 µg mL⁻¹, was used for quantification.

For all PFASs investigated, the blank concentrations were under the instrument detection limit (IDL) (*n* = 3), and hence limit of quantification (LOQ) was set to the lowest quantifiable calibration point (peak to noise ratio > 10). The LOQ ranged from 0.01 to 1.0 ng mL⁻¹ (Table S7 in SI). The average fit of the PFAS calibration curves was 0.990 ± 0.016 (Table S8 in SI). The relative recovery was, on average, 126 ± 29 %, where the shorter-chained PFASs had recoveries closer to 100 % (i.e. PFBA, PFHxA and PFHxS) while the longer-chained PFASs (i.e., PFDoDA, PFUnDA, and FOSA) suffered from ion enhancement (up to 185 % for PFDoDA) (Table S9 in SI). The average relative error based on relative difference between duplicate samples was 13 % (Table S10 in SI).

2.3.2. Dye analysis

The dyes from the batch experiments were analyzed for absorbance using a spectrophotometer (Hach DR 2800™, Hach Company, Loveland, CO, USA). The cuvettes were rinsed three times with ethanol before and between each reading. The absorbance was measured at a wavelength of 662 nm, 595 nm, 611 nm, and 564 nm for methylene blue, crystal violet, indigo carmine, and rose bengal, respectively. Calibration curves (4–5 point) were prepared for all individual dyes (Table S11 in SI) and used to calculate dye concentration (*c*_{w,dye}). The IDL of the spectrophotometer ranged between 4 and 0.001 [Abs] and the linear range was 3–0.005 [Abs]. Hence, the LOQ was set to 3–0.005 [Abs] for *c*_{w,dye} measurement. The average relative error based on relative difference between duplicate samples was 28 % (Table S12 in SI).

2.4. Data analysis

2.4.1. Data evaluation

The adsorption behavior of the PFASs and dyes was quantified by determining the solid-aqueous partitioning coefficient (K_d [L kg⁻¹]), which is their partitioning between the aqueous phase (c_w [μg mL⁻¹]) and the solid phase (adsorbent) (c_s [μg g⁻¹]):

$$K_d = \frac{c_s}{c_w} \quad (1)$$

c_s was calculated as:

$$c_s = \frac{c_{w,0} V_{w,i} - c_w V_{w,i}}{w_{s,i}} \quad (2)$$

where $c_{w,0}$ is the initial concentration (e.g., 0.1 μg mL⁻¹ for the PFAS experiment), $w_{s,i}$ [g] is the dry weight (dw) of each sample, and $V_{w,i}$ is the water volume of each sample.

2.4.2. Statistical analysis

Normality of distribution of the log K_d values was tested with 10 different normal distribution tests using a Matlab package [42]. Because of non-normality of the data, Spearman's rank correlation test was used for log K_d data. The significance level was set to 0.05 and was acquired from a Pearson moment correlation test. Principal component analysis (PCA) (using SIMCA V. 14 software) was applied to the normally distributed datasets to visualize the correlations between adsorption behavior (log K_d) of PFASs and dyes to the non-AC containing sorbents. PCA was not used for the highly adsorbing AC-containing sorbents, as they produced non-normally distributed data.

3. Results and discussion

3.1. Sorption of PFASs and dyes to adsorbent materials

The sorption (log K_d -values) of individual PFASs varied greatly depending on the adsorbent material and PFAS homologue (Fig. 1). However, regardless of individual PFASs, the five different AC sorbents tested (i.e., GAC ($n = 2$), PAC ($n = 2$) and Rembind®) had the highest log K_d values, ranging between 1.0 and 5.0 (mean 3.5 ± 0.79) for the PFCAs and between 2.9 and 5.2 (4.2 ± 0.55) for the PFSAs, FTSA, and FOSA. Strong sorption of PFASs to AC-based materials has been reported in previous studies on AC materials and on treatment of contaminated soil, drinking water, and sewage sludge [20,21,26].

Sorption of PFASs to the 39 non-AC based sorbents had an average log K_d of 0.50 ± 1.0 for the PFCAs and 0.14 ± 0.61 for the PFSAs, FTSA, and FOSA. The high variability can be explained by the large number of tested different sorbents ($n = 44$) and PFASs with very different physiochemical properties (particularly PFCAs). PFCAs showed the strongest median sorption to the pulverized pyrolytic carbon, magnesium chloride (MgCl₂)-treated biochar, and *Moringa* seed (mean log K_d 0.93 ± 0.29), with up to > 99 % sorption for the PFCAs with perfluorocarbon chain length > 10. For the PFSAs and FTSA, the strongest sorption was to Bentonite 3 (*Nanocor*®), MgCl₂-treated biochar, and *Moringa* seed (mean log K_d 0.87 ± 0.51). FOSA showed the strongest sorption to rubber granules and *Moringa* seed (mean log K_d 1.8). Very few previous studies have investigated sorption of PFASs to non-AC based sorbents for remediation purposes and most have focused only on PFOA or PFOS in laboratory batch experiments (see Tables S1 and S2 in SI). In the present study, MgCl₂-treated biochar was found to be the best non-AC sorbent for sorption of PFASs. The performance of biochar in sorption of PFASs has been assessed for both soil and wastewater treatment. For example, Dalahmeh et al. [43] observed good removal of PFASs with perfluorocarbon chain length > 5 in wastewater treatment, whereas biochar used as a stabilizer of PFAS-contaminated soil showed limited ability (approximately 80 %) to reduce leaching of PFASs compared with AC soil stabilizers (around 99 % reduction in

leaching) ([16,17]). A previous study has shown that the origin of the biochars, and ultimately their specific surface area, are crucial for the sorption efficiency of PFASs to biochars [44]. *Moringa* seed was the second best non-AC sorbent tested in the present study, with high sorption of PFASs. To our knowledge, *Moringa* seed has not been tested previously for use in PFAS stabilization, but is reported to show good sorption for other organic micropollutants [45,46]. A previous study on plant-based hemp (*Cannabis sativa*L.) protein powder showed > 98 % removal of PFASs with perfluorocarbon chain length > 6 from contaminated groundwater, which was explained by high sorption of PFASs to the plant proteins [47]. In the present study, sorption of PFASs was stronger to Bentonite 3 (*Nanocor*®) than to most other non-AC materials tested, including Bentonites 1, 2, 4, and 5, for reasons that remain unclear. Montmorillonite (bentonite) has been demonstrated to be a good sorbent for PFASs when modified with organic amendments [48,49], while retention of > 99.3 % of PFOS has been reported for soil amended with modified (unspecified) montmorillonite (10 % w/w amendment) [14]. As in the present study, in a previous investigation Polonite® showed much lower removal of PFASs from wastewater than AC combined with a Polonite® filter [21].

Similarly to the PFASs, the dyes generally showed stronger sorption to AC-based adsorbent materials (mean log K_d 2.7 ± 0.86) than to non-AC-based adsorbent materials (mean log K_d 1.0 ± 0.89) (Fig. 2). However, the dyes showed high variation in their individual sorption behavior, with indigo carmine having the strongest sorption to AC-based adsorbent materials (mean log K_d 3.8 ± 0.33) and rose bengal having the lowest (mean log K_d 1.7 ± 0.28). Rose bengal showed the highest sorption to other sorbents such as chitosan (log K_d 2.6) and pulverized carbon (log K_d 2.4). Crystal violet adsorbed particularly strongly to inorganic pulverized zeolite (log K_d 3.4) and diabase (log K_d 3.4), which was in the same log K_d -range as for the AC-based adsorbent materials (log K_d 3.1 ± 0.33). This is higher than previously reported for sorption of crystal violet to the zeolites MCM-22 (log K_d 1.6) and synthesized magnetic NaY (log K_d 1.7) [50]. Identification of adsorbent materials with particularly high sorption of dye is of great relevance, since dyes have been shown to be problematic pollutants of aquatic environments and remediation techniques such as wastewater treatment or stabilization are needed in many places world-wide with e.g., textile industries [51].

3.2. Impact of perfluorocarbon chain length and functional group on PFAS sorption to adsorbent materials

Sorption of PFASs showed great variation depending on perfluorocarbon chain length and functional group (Fig. 3). For the PFCAs, there was an increasing trend for log K_d with increasing perfluorocarbon chain length, with median log K_d ranging from -0.26 for PFBA (C₃) to 2.0 for PFOcDA (C₁₇) (Fig. 3). The trend was not significant for C₃-C₇ PFCAs ($p > 0.05$, ANOVA), but was significant for C₇-C₁₇ PFCAs ($p < 0.05$). The log K_d value increased, on average, by 0.22 log units per CF moiety for C₇ to C₁₇ PFCAs. This is slightly lower than previously reported, e.g., log K_d values increasing by 0.5-0.6 log units per CF moiety for sediment (Higgins and Luthy, 2006) and of sorption on soil organic matter (log K_{oc}) increasing by 0.83 log units per CF moiety [24]. The variation in log K_d values was greater for C₁₃, C₁₅, and C₁₇ PFCAs compared with C₇-C₁₀ PFCAs. This indicates that other or additional sorption mechanisms such as steric hindrance [24], micelle formation [20,52], and geometrical change [53] are influential for the longer-chain PFCAs. This corroborates previous findings that sorption of PFASs differs significantly from that of other micropollutants due to their unique physiochemical properties [21]. For the PFSAs and FTSA, the median log K_d values were within the range -0.1 to 0.3 and no significant trend of increasing adsorption as a function of increasing perfluorocarbon chain length was observed ($p > 0.05$). Comparing the homologues with similar perfluorocarbon chain length, median log K_d increased in the order FTSA < PFCAs < PFSAs < FOSA, which is in

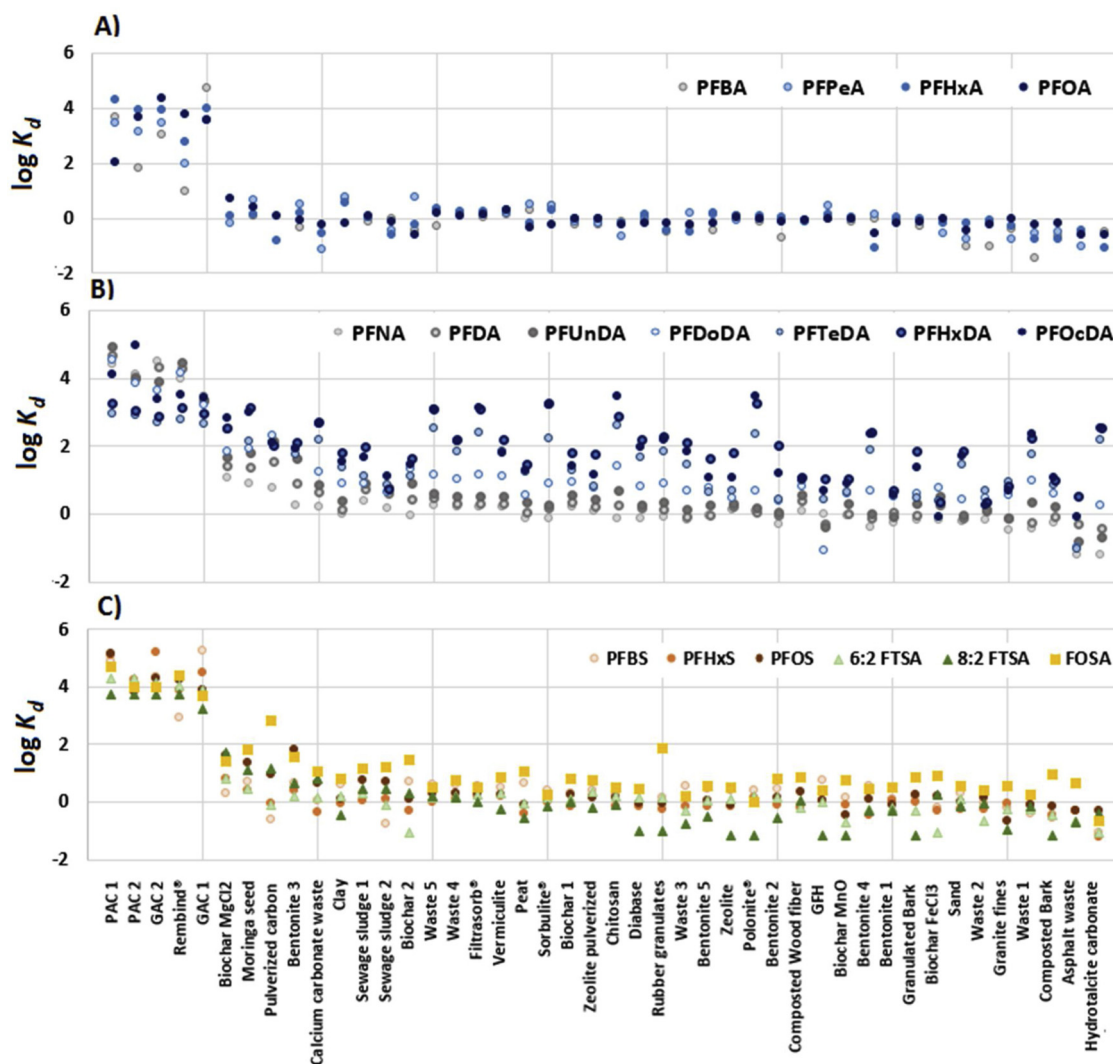


Fig. 1. Mean $\log K_d$ values [L kg^{-1}] ($n = 2$) for sorption of PFASs to different adsorbent materials ($n = 44$). A) Short-chain C_3 - C_7 PFCAs, B) long-chain C_8 - C_{17} PFCAs, and C) PFASs, FTSAs, and FOSA. The adsorbent materials are listed in order from highest to lowest mean $\log K_d$ of all PFASs (left to right on x-axis).

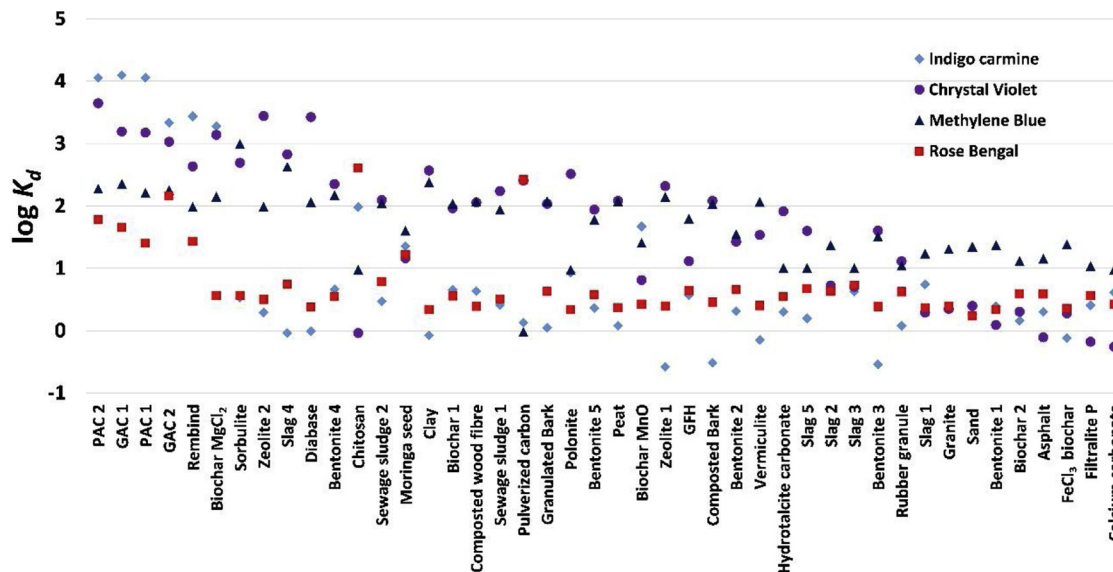


Fig. 2. Mean $\log K_d$ adsorption values [L kg^{-1}] ($n = 2$) of the dyes indigo carmine, crystal violet, methylene blue, and rose bengal to different adsorbent materials ($n = 44$). The adsorbent materials are ranked in order from highest to lowest mean $\log K_d$ (left to right on x-axis).

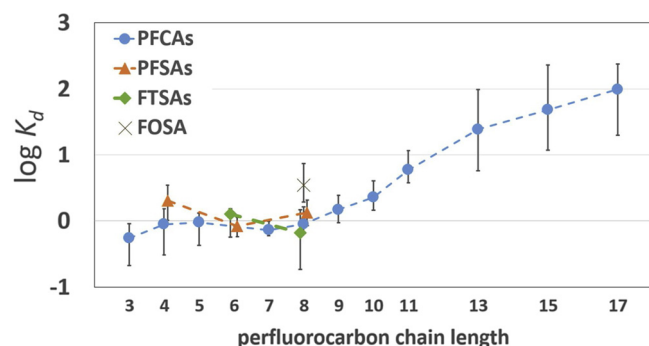


Fig. 3. Median $\log K_d$ values [L kg^{-1}] for all sorbent materials as a function of perfluorocarbon length for PFCAs, PFASs, FTSA, and FOSA. The bars represent the lower and upper interquartile ranges.

agreement with previous findings [18,23,24].

3.3. Correlation of sorption behavior of PFASs and dyes

Spearman's rank correlation showed that the PFASs displayed relatively similar sorption behavior, with an overall average correlation (Spearman's ρ value) between individual PFASs of 0.59 ± 0.07 (Fig. S1 in SI). The highest average correlation was found for PFOA (mean 0.65 ± 0.18), followed by PFNA (0.62), PFDoDA (0.62), PFHxS (0.61), and PFDA (0.60), whereas the shortest-chained PFAS (PFBA) showed the lowest correlation with other PFASs (0.43 ± 0.25). This can be explained by their relatively higher water solubility and low sorption potential to sorbents (e.g., [20]). A generally low correlation was also found for FOSA (mean 0.34 ± 0.19), which can be explained by the fact that FOSA was the only PFAS with a neutral functional group (sulfonamide) at the experimental pH, which has an impact on adsorption behavior (e.g. [23]). These results indicate that, when testing novel materials for PFAS stabilization purposes, it might be sufficient to test only selected PFASs considering their perfluorocarbon chain length (e.g., C_7 to C_{17} PFCAs) and functional group (e.g., sulfonamide).

The $\log K_d$ values of the PFASs and the dyes for all sorbents ($n = 44$) showed, on average, a correlation (ρ value) ranging from 0.28 ± 0.17 for methylene blue to 0.38 ± 0.12 for crystal violet (Table 1). A significant correlation was found for 16 out of 17 PFASs with crystal

violet, and for 12 out of 17 PFASs with rose bengal, whereas methylene blue (9 out of 17 PFASs) and indigo carmine (8 out of 17 PFASs) were less well correlated with the PFASs. A particularly good linear correlation in $\log K_d$ was found for cationic crystal violet with PFTeDA ($R^2 = 0.81$) and PFOcDA ($R^2 = 0.88$) when grouping all pyrolytic carbon materials with assumingly similar surface chemical properties (i.e., AC ($n = 5$) and biochars ($n = 5$)) and excluding carbon-based materials with different surface chemical composition (i.e., chitosan, granulated bark, *Moringa* seed, peat, rubber granules, composted bark, composted wood fiber, and sewage sludge ($n = 2$)) (Fig. S2 in SI). These two opposing relationships indicate that sorbent surface charge was important for sorption, even for the longest-chained PFASs (C_{13} and C_{17}).

When excluding the highly adsorbing AC-based sorbents ($n = 5$) from the correlation analysis, better normally distributed data were obtained (Table S11 in SI), but the correlation of the dyes with PFASs was generally lower ($n = 39$) (Table 1). The best correlation was between methylene blue and the short-chained PFCAs (i.e. PFBA ($\rho = 0.48$), PFPeA ($\rho = 0.41$), and PFHxA ($\rho = 0.39$)). Crystal violet showed significant correlations to PFBA ($\rho = 0.35$), PFNA ($\rho = 0.33$), and 6:2 FTSA ($\rho = 0.35$), and rose bengal showed a significant correlation to PFOS ($\rho = 0.39$) (Table 1, Fig. S1 in SI). Apart from the latter, no significant correlation was found with any of the PFASs ($p > 0.05$) and indigo carmine or rose bengal. The weak correlation for the non-AC based materials can be explained by the small variation in PFAS sorption (significant difference in PFAS sorption for 7 out of 38 materials compared with sand; t-test, $\alpha = 0.01$) (Fig. 1), and the larger variation in sorption of the dyes (Fig. 2). Consequently, the dyes could not capture the small variations in PFAS sorption. Overall, methylene blue, crystal violet, indigo carmine, and rose bengal showed a significant correlation for 16 out of 17 PFASs (except 8:2 FTSA) when all sorbents were included. On excluding the AC-based sorbents, a significant correlation was found for PFBA, PFPeA, PFHxA, PFNA, PFOS, and 6:2 FTSA. Thus we show for the first time that the selected dyes can be used as a proxy for PFAS sorption to different types of materials.

3.4. PCA analysis of sorption behavior of PFASs and dyes

A PCA on sorption ($\log K_d$) to the non-AC containing sorbents ($n = 39$) showed correlation of the dyes to PFASs (Fig. 4). Methylene blue was strongly correlated to the shorter-chained PFCAs, in particular PFBA, which is agreement with the Spearman correlation results

Table 1

Significant correlations (Spearman's rank coefficient ρ) between sorption of the four dyes tested and individual PFASs, for sorbents with and without activated carbon (AC).

	Spearman's ρ without AC ($n = 39$)				Spearman's ρ with AC ($n = 44$)			
	Indigo carmine	Crystal violet	Methylene blue	Rose bengal	Indigo carmine	Crystal violet	Methylene blue	Rose bengal
PFBA	−0.079	0.35*	0.48**	0.012	0.25	0.51***	0.59***	0.27
PFPeA	−0.087	0.24	0.41**	0.027	0.24	0.43**	0.54***	0.27
PFHxA	−0.13	0.27	0.39*	−0.021	0.21	0.47**	0.53***	0.24
PFOA	−0.038	0.25	0.13	0.12	0.28	0.44**	0.31*	0.36*
PFNA	0.027	0.33*	0.12	0.20	0.32*	0.5***	0.31*	0.42**
PFDA	−0.016	0.22	0.068	0.22	0.29	0.43**	0.27	0.44**
PFUnDA	0.019	0.15	0.028	0.24	0.32*	0.37*	0.24	0.45**
PFDoDA	0.081	0.067	−0.092	0.22	0.36*	0.32*	0.16	0.45**
PFTeDA	0.24	0.14	−0.21	0.13	0.47**	0.37*	0.082	0.38*
PFHxDA	0.24	0.17	−0.14	0.19	0.43**	0.35*	0.075	0.36*
PFOcDA	0.24	0.16	−0.19	0.19	0.47**	0.37*	0.074	0.41**
PFBS	−0.088	0.18	0.25	0.12	0.24	0.39**	0.42**	0.34*
PFHxS	0.11	0.27	0.18	0.14	0.38*	0.47**	0.36*	0.37*
PFOS	0.097	0.21	0.13	0.39*	0.37*	0.41**	0.32*	0.55***
6:2 FTSA	0.052	0.35*	0.20	0.037	0.22	0.43**	0.29	0.21
8:2 FTSA	0.17	−0.039	−0.081	0.22	0.08	−0.044	−0.051	0.16
FOSA	−0.28	0.078	0.14	0.13	0.11	0.32*	0.31*	0.37*
Average	0.033	0.17	0.038	0.14	0.30	0.38	0.28	0.36
std	0.14	0.10	0.20	0.099	0.11	0.12	0.17	0.097

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

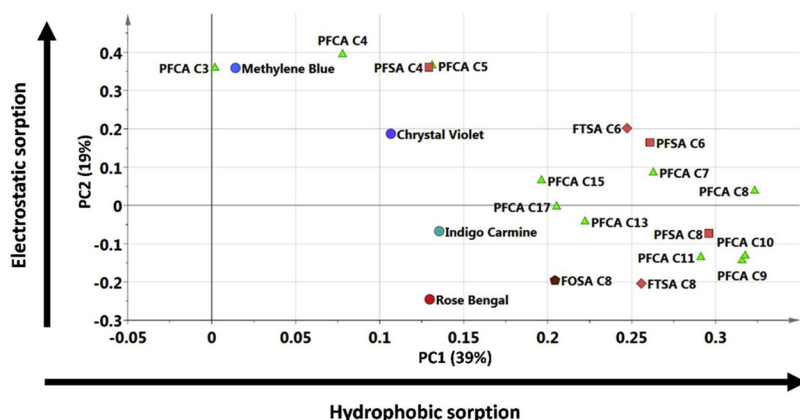


Fig. 4. PCA loading plot of PFASs, grouped as PFCAs (triangles), PFSA (squares), FTSAs (diamonds), and FOSA (pentagon), and of the dyes methylene blue, crystal violet, indigo carmine, and rose bengal (circles). The PFASs are shown with their corresponding perfluorocarbon chain length. The axes PC1 and PC2 are the principal components derived from the PCA.

(Table 1). Indigo carmine showed the best correlation with the majority of PFASs with perfluorocarbon chain length 6–17, followed by rose bengal and crystal violet. A noteworthy finding was that principal component 1 (PC1) showed a wide range (0.19–0.32) for PFASs with perfluorocarbon chain length 6–17, whereas PC1 for the dyes ranged between 0.01 and 0.13. This discrepancy indicates that the selected dyes did not model the majority of PFASs satisfactorily when the AC sorbents were excluded, confirming findings in Table 1. However, in general, the PCA results indicate that methylene blue best reflects sorption of the shorter-chained PFASs, whereas indigo carmine, rose bengal, and crystal violet are better in reflecting sorption of the longer-chained PFASs.

In the PCA, PFASs with perfluorocarbon chain length C₃–C₁₁ were aligned according to perfluorocarbon chain length for the PFCAs, PFSA, and FTSAs. On the other hand, C₁₃–C₁₇ PFCAs showed a relatively high correlation to PC3 in 3-dimensional PCA (Fig. S3 in SI). This again indicates that other reaction mechanisms are important for the very long-chained PFASs (see Section 3.2). The alignment of the C₃–C₁₁ PFCAs, PFSA, and FTSAs with their perfluorocarbon chain length may confirm that the hydrophobic and electrostatic interactions gradually change with each added CF₂ moiety in perfluorocarbon chain length, as reported in previous studies (summarized by [30]). Hence, the arbitrary PCA axis PC1 may represent the increase in hydrophobic interactions (i.e., with increasing perfluorocarbon chain length), while the arbitrary axis PC2 may represent the increase in electrostatic interactions with the polar functional groups. The better fit of PC1 (0.39) compared with PC2 (0.19) indicates that hydrophobic interactions are a more important binding mechanism than electrostatic interactions for the PFASs investigated here. For example, PFBA was mainly correlated to PC2 (PC1 = 0.001, PC2 = 0.40), which is in accordance with previous findings that electrostatic binding is dominant for PFBA and dependent on bridging divalent and trivalent cations [24]. This could explain why the dyes indigo carmine and rose bengal, which are negatively charged like the PFASs investigated, had a PC2 value of −0.07 and −2.5, respectively. On the other hand, e.g., PFOS is dominantly adsorbed by hydrophobic binding mechanisms (PC1 = 0.30, PC2 = −0.07). Hydrophobic sorption of PFOS and other long-chained PFASs has been reported as the dominant sorption mechanism in previous studies, where these PFASs showed a strong correlation to the hydrophobic organic content of the sorbent ([26,24,54]). Overall, the sorption of PFASs is mainly influenced by hydrophobic and electrostatic interactions (reviewed by [30]), and the results of this study are comparable to those of previous sorption studies investigating the influence of physiochemical properties of PFASs [21]. Although hydrophobic sorption was shown to be the dominant sorption mechanism, the impact of electrostatic interactions are not negligible (particularly for shorter chained PFASs) (Siriwardena et al., 2019). In particular, modification of the surface charge (i.e. hydrochloric acid treatment) (Siriwardena et al., 2019) and the design of charged polymer resins can increase the PFAS

sorption to sorbents [55]. The combination of hydrophobic and cationic sorption sites have shown to have an additive effect on PFAS sorption to different sorbents [28,56,57]. One novel finding was that the longest-chained PFCAs C₁₃–C₁₇ seem to be affected by other sorption mechanisms, e.g., steric hindrance.

4. Conclusions

Examination of the sorption behavior and mechanisms of PFASs to a wide variety of known and novel sorbents revealed that they sorbed most strongly to AC-based sorbents. Sorption strength was influenced by perfluorocarbon chain length, with shorter-chain PFASs showing generally weaker sorption than longer-chained PFASs. Sorption strength was also influenced by functional group, increasing in the order: FTSAs < PFCAs < PFSA < FOSA. Good understanding of PFAS binding mechanisms is important when selecting filters, e.g., in treatment of drinking water [20], wastewater [21], and soil [15–17]. Examination of the sorption behavior of dyes showed that they can be used as proxies for PFASs sorption when testing novel sorption materials, reducing the time requirement and cost, and enabling on-line measurement. However, due to the unique physiochemical properties of PFASs, it is important to test selected PFASs with representative perfluorocarbon chain length and functional groups in order to fully clarify PFAS sorption behavior.

CRedit authorship contribution statement

Mattias Söregård: Conceptualization, Methodology, Software, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Erik Östblom:** Methodology, Software, Formal analysis, Investigation, Writing - original draft. **Stephan Köhler:** Conceptualization, Methodology, Formal analysis, Writing - review & editing, Visualization. **Lutz Ahrens:** Funding acquisition, Conceptualization, Methodology, Writing - review & editing, Visualization, Supervision.

Declaration of Competing Interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Acknowledgement

This work was supported by the project PFAS-PURE from VINNOVA (2015-03561).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2020.103744>.

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