

ADSORPTION OF PER- AND POLYFLUOROALKYL SUBSTANCES BY FERRIHYDRITE IS NON-SPECIFIC AND GOVERNED BY SURFACE CHARGE

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1. Introduction

Accurate prediction of the binding of per- and polyfluoroalkyl substances (PFASs) in soil is essential for environmental risk assessment. However, information on PFAS binding to poorly crystalline iron (hydr)oxides is still essentially non-existent, despite that these phases are known to be important for contaminant and trace element soil retention¹⁻³ due to their large surface area^{7,8} and high reactivity. Here we reveal, for the first time to the best of our knowledge, the sorption behavior of 12 PFASs onto the poorly crystalline iron (hydr)oxide ferrihydrite (Fh). The specific objectives of the study were to 1) investigate pH-dependent Fh binding of PFASs in the absence and presence of phosphate (PO_4^{3-}) as a competing anion, 2) assess the role of Fh zeta potential on PFAS binding, and 3) derive sorption isotherms for selected PFASs onto Fh.

2. Materials and methods

2.1 Ferrihydrite synthesis

PFAS adsorption onto synthetic, poorly crystalline, 2-line ferrihydrite was investigated using the Fh synthesis method of Swedlund and Webster⁴ and Schwertmann and Cornell⁵ with minor modifications. Iron (hydr)oxide particles from such a suspension have previously been confirmed to be 2-line ferrihydrite using Fe K-edge EXAFS (extended X-ray absorption fine structure) spectroscopy⁶.

2.2 pH-dependent binding to ferrihydrite in the absence and presence of phosphate

Fh stock suspension was mixed with Milli-Q water and NaNO_3 in polypropylene (PP) tubes to obtain final concentrations of Fh and nitrate (NO_3^-) of 3.2 mM (based on Fe), and 10 mM, respectively. Different amounts of acid (HNO_3) or base (NaOH) were added to reach pH values between 4.0 and ~7.5 (after equilibration). Subsequently, 0 or 200 μM phosphate (PO_4^{3-} , as NaH_2PO_4) was added. Triplicate sets of vials were spiked with 20 μL of a stock mixture of $n = 12$ PFASs dissolved in MeOH, so that the initial aqueous concentration of each compound was approximately 0.60 nmol per mmol Fe as ferrihydrite. Suspensions were end-over-end shaken (45 rpm, 21 °C) for 24h before centrifugation at about 2000g. pH was measured in the supernatant of subsamples. Ferrihydrite zeta potential was measured at 21 °C using a Zetasizer Nano-ZS (Malvern) instrument.

2.3 Sorption isotherms

Varying volumes of either PFOA, PFOS or FOSA dissolved in MeOH were added to Fh suspensions (10 mM Fe) prior to equilibration for 24h using end-over-end shaking. After centrifugation, pH was measured in supernatants of sample aliquots (pH 4.4–4.6).

2.4 PFAS analysis

For quantification of aqueous PFAS concentrations, a mix of 8 mass-labelled internal standards was added to sample aliquots prior to gentle filtration (0.45 μm). PFAS analysis was conducted using ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS, Quantiva TSQ, Thermo-Fisher). The injected volume was separated on an Acquity UPLC BEH-C18 analytical column (1.7 μm , 50 mm, Waters, UK). PFAS sorption was calculated using the method of aqueous loss.

3. Results and discussion

3.1 pH-dependent binding in the absence and presence of phosphate

All the 12 investigated PFASs (i.e. PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, FOSA, 6:2 FTS, 8:2 FTS) showed a significant negative relationship ($p < 0.05$) between pH and sorption onto ferrihydrite (Fig. 1). This was most likely attributed to the pH-dependent charge of the ferrihydrite surface, i.e. the lower the pH value, the larger the positive surface net charge, and thus the larger the attraction between the ferrihydrite surface and the negatively charged PFAS anions. The crucial importance of ferrihydrite surface charge on sorption was thus clearly reflected also when PFAS binding was related to the zeta potential of the mineral's surface (Fig. 1). For all the 12 PFASs, there was a significant positive relationship ($p < 0.05$) between zeta potential and sorption. Moreover, there was a larger effect of pH and ferrihydrite zeta potential, respectively, on sorption of the longer-chained PFASs (e.g. PFOS, PFDA; Fig. 1) in comparison to that of the shorter-chained PFASs (e.g. PFBA, PFBS). In other words, sorption of long-chained PFASs was highly dependent on the presence of a strongly positive ferrihydrite surface, indicating limited van der Waals interactions between the long-chained perfluorocarbon backbone and the sorbent surface unless pH was low (<pH 5, i.e. sorbent charge strongly positive). At pH = 4.0 (i.e. surface zeta potential $\approx +30$ mV), binding of the long-chained PFASs ranged from 60% (PFOA) to 100% (PFDA, 8:2 FTS). Sorption of short-chained PFASs (i.e. PFBA, PFPeA, PFHxA, PFBS) was overall small (<50%), even when the pH value was low, i.e. even when the mineral surface possessed a large positive net charge.

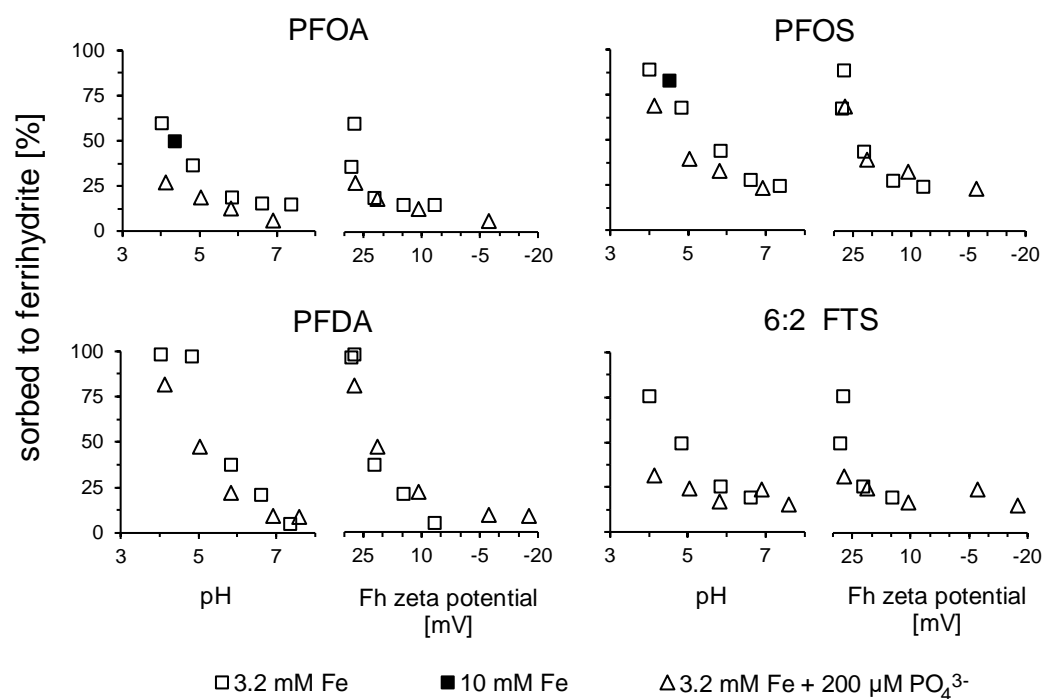


Figure 1. Effect of pH and zeta potential, respectively, on PFAS sorption onto ferrihydrite (3.2 mM Fe) in the absence and presence of 200 μM phosphate (PO_4^{3-}).

The PFAS sorption onto ferrihydrite decreased with the addition of phosphate (PO_4^{3-}) as compared to untreated samples, however, the effect was limited (Fig. 1). This shows that PFASs and phosphate do not compete for specific binding sites on the surface of ferrihydrite, thus, binding of PFASs to ferrihydrite is essentially of a non-specific nature. Instead, the decrease in PFAS sorption upon addition of phosphate anions may be explained by the decrease in positive charge present on the ferrihydrite surface due to phosphate co-adsorption. This was supported by ferrihydrite zeta potential measurements in the absence and presence of added phosphate (Fig. 1), showing that the surface charge of ferrihydrite, and not the availability of specific binding sites, is the governing sorbent parameter that determines the degree of PFAS sorption.

3.2 Sorption isotherms

PFOS and PFOA sorption isotherms onto ferrihydrite (Fig. 2) were consistent with monolayer adsorption, as both isotherms were well described by the Langmuir model ($C_{sorbed} = Q_{max} * C_{eq} / (K_{Langmuir} + C_{eq})$). The maximum ferrihydrite surface coverage Q_{max} was calculated to be 730 and 500 $\mu\text{g g}^{-1}$ Fe for PFOS and PFOA, respectively, or, assuming a specific surface area of ferrihydrite of 600 $\text{m}^2 \text{g}^{-1}$ (7,8), 1.20 and 0.80 $\mu\text{g m}^{-2}$ Fh, respectively. The sorption isotherm of FOSA onto ferrihydrite was relatively linear through an approximate aqueous equilibrium concentration of 160 ng mL^{-1} . The overall order of sorption affinity to ferrihydrite was as follows: PFOS > FOSA \approx PFOA. Thus, the presence of a negatively charged head group (SO_3^- (PFOS)) was generally observed to favor sorption as compared to the presence of an uncharged functional group (SO_2NH_2 (FOSA)). This may be attributed to the positive charge of the ferrihydrite surface at the given pH (4.5 ± 0.1) of the isotherm experiment. However, considering the highest point of the respective isotherms, adsorption of FOSA was significantly larger as compared to that of PFOS and PFOA (Fig. 2). A possible explanation for the high sorption of FOSA at high aqueous concentration may be that FOSA molecules self-aggregated (formed hemi-micelles)⁹ at the ferrihydrite–liquid interface, i.e. the critical aggregation concentration (CAC) may have been exceeded for FOSA.

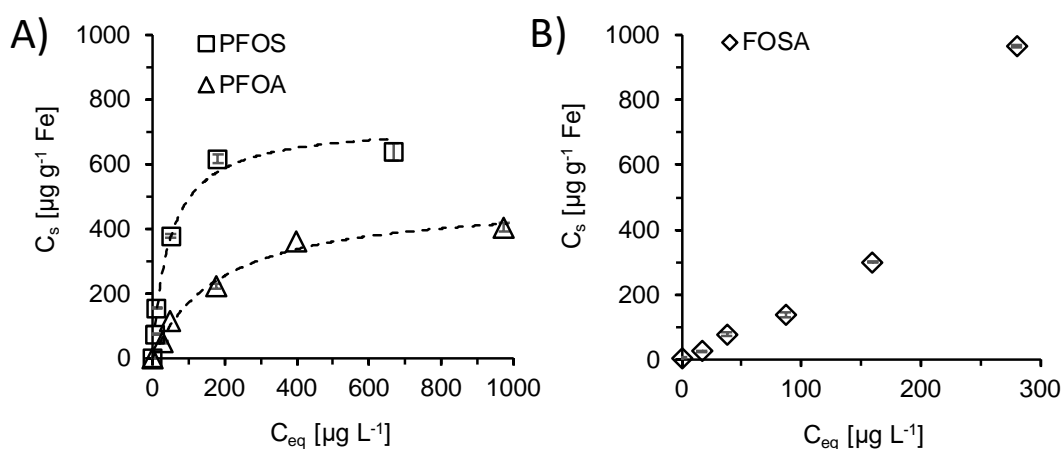


Figure 2. Sorption isotherms for A) PFOS and PFOA, and B) FOSA, onto ferrihydrite (10 mM Fe). pH 4.4–4.6. Dashed lines are the fitted Langmuir isotherms. Fitted Q_{max} and $K_{Langmuir}$ values for PFOS and PFOA: 730 and 500 $\mu\text{g g}^{-1}$ Fe, respectively, and 48 and 190 $\mu\text{g L}^{-1}$, respectively.

3.3 Conclusions

PFAS binding onto ferrihydrite is of non-specific nature, governed by ferrihydrite surface charge. Co-adsorbed phosphate decreases PFAS sorption onto ferrihydrite not by competing for specific binding sites, but by decreasing the positive surface net charge of the mineral. PFOS and PFOA sorption isotherms onto ferrihydrite were consistent with monolayer adsorption. A negatively charged head group (SO_3^- (PFOS)) favored sorption over an uncharged functional group (SO_2NH_2 , (FOSA)) when the ferrihydrite surface was positively charged.

The present study will contribute to improve environmental risk assessment of PFASs. In particular, the results will be essential for risk assessment in environments rich in secondary iron (hydr)oxides such as for example soil B horizons.

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