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Sorption of short- and long-chain perfluoroalkyl surfactants on sewage sludges

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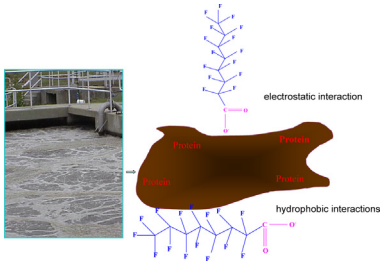
HIGHLIGHTS

- The equilibrium data were well represented by the Freundlich isotherm.
- Dominant sludge parameter affecting sorption was protein rather than carbohydrate.
- The enhanced sorption of PASs on sludge was found when solution pH decreased.
- For all PASs, enhanced adsorption occurred with increasing calcium concentration.
- Sorption on sludge increases with increasing alkyl chain length for PASs with C5–C15.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl surfactants (PASs) have attracted increasing concerns in recent years due to their global distribution, persistence, bioaccumulation and potential toxicity. Since sludge was a significant source of PASs to environment, the sorption of short (C2–C6) and long-chain (C7–C15) PASs on different sewage sludge was investigated in this study. The equilibrium data were well represented by the Freundlich isotherm and were generally nonlinear. In order to elucidate the sorption mechanism of PASs to sludge, effect of sludge property, solution chemistry and molecular structure were also investigated in details. The dominant sludge parameter influencing sorption of PASs was protein in extracellular polymeric substances. The sorption of PASs onto sludge increased as solution pH decreased. For all the PASs homologues, enhanced adsorption occurred with increasing calcium concentration in solution. For PASs with C5–C15, sorption on sludge increases with increasing alkyl chain length, while for PASs with C2–C5, the association of sludge decreases when the alkyl chain length increases. The perfluorinated sulfonic acid (PFSA) demonstrated substantially stronger sorption than perfluorinated carboxylic acid (PFCA) analog. Evidence for both hydrophobic and electrostatic interactions was found.

1. Introduction

Perfluoroalkyl surfactants (PASs) have emerged as global environmental contaminants [1,2]. Because the perfluorinated alkyl chain is both hydrophobic and oleophobic [3], PASs have been widely used in a variety of industrial and commercial applications for about 50 years as surfactants, emulsifiers, fire retardants and polymer additives [4]. The strong carbon–fluorine bonds make PASs resistant to physical and microbial degradation [1]. Therefore, PASs

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Table 1
Sludge characteristics.

Sludge	Water content (%)	pH	TOC (mg/g)[a]	Carbohydrate (mg/g)[a]	Protein (mg/g)[a]	CEC (mmol/g)[a]	AEC (mmol/g)[a]
S1	75.0	7.05	292.9	20.6	93.0	69.2	77.0
S2	73.3	6.51	317.0	10.0	90.6	31.7	139
S3	79.1	6.11	169.9	19.9	144.4	80.1	296
S4	78.1	6.39	338.9	21.7	132.6	85.3	398
S5	84.4	6.44	383.7	22.6	127.9	93.3	454
S6	73.0	7.43	126.0	14.6	88.9	105	298
S7	79.9	5.28	465.5	13.3	73.1	129	270
S8	87.5	6.47	486.6	35.7	192.3	168	338
S9	91.6	6.87	481.9	52.6	244.5	289	167
S10	77.1	6.54	328.9	13.4	86.3	70.9	405
S11	73.0	6.40	346.1	9.4	74.5	120	124
S12	64.1	7.54	253.6	2.8	47.7	89.6	46.2
S13	84.8	7.18	558.6	21.8	170.3	212	147

[a] Based on dry weight.

are globally distributed and found in remote rural locations [5,6]. There is growing interest in the environmental transport and fate of perfluorinated surfactants due to their widespread occurrence, persistence, and bioaccumulation.

PASs have been detected in surface waters downstream from the discharge of wastewater treatment plants (WWTPs), which indicates that a significant route of PASs to environment is *via* WWTPs [7,8]. PASs have been detected in sewage sludge from several wastewater treatment plants at ng g^{-1} concentrations [9,10], suggesting the partitioning of these compounds from the aqueous phase to the sludges during the treatment process. Given that most PASs are recalcitrant to microbial degradation [1] and that measurable concentrations are detected in sewage sludge [9], it is likely that sorption of PASs on sludge is a main removal mechanism during the wastewater treatment process. Therefore, investigation of sorption of PASs on sewage sludge is of great importance since their sorption behavior may affect the overall fate and dominant mass flow of PASs through WWTPs.

The sorption of PASs to sediments, sand and clay has been reported in some detail [11,12], only a few papers were published on the sorption behavior of these chemicals to sewage sludge [13,14]. Sewage sludge contains organic and mineral parts as well as living and dead biomass [15]. Sewage sludge also contains protein, and then the sorption behavior of PASs to sludge may not be the same as that to sediments.

The previous research on the transformation and removal of PAS *via* treatment plants has focused on long-chain PASs due to the lack of suitable methods for short-chain compounds. For example, Zhou et al. have reported sorption of the PASs with a carbon chain greater than four [13]. Since the development of analytical methods, the short-chain PASs, such as trifluoroacetic acid (TFA), were detected as the major PASs in wastewater [16]. For these reasons, it is important to carry out the research on the behavior of shorter-chain PASs in the environment as well as longer-chain ones.

The goal of this study is to elucidate the various sorbent-specific, solution-specific, and chemical structure-specific parameters that potentially affect sorption of short- and long-chain perfluorinated surfactants to sewage sludges. The sorption of PASs on thirteen characterized sludges was examined as a function of the characteristics of the sludges, the properties of the surfactant and the compositions of solutions as well.

2. Materials and methods

2.1. Perfuoroalkyl surfactants (PASs)

Trifluoroacetic acid (TFA, 99%) and perfluoroundecanoic acid (PFUnA, 95%) were purchased from Sigma–Aldrich (St. Louis, MO). Pentafluoropropionic acid (PFPrA, 97%), perfluorobutyric acid (PFBA, 99%), perfluoroheptanoic acid (PFHpA, 99%), perfluorodecanoic acid (PFDA, 98%), perfluorododecanoic acid (PFDoA, 95%), perfluoro-1-butanesulfonic acid potassium salt (PFBS, 98%) and perfluorooctanesulfonic acid (PFOS, ~40% in water) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Perfluoropentanoic acid (PFPeA, ≥94%), perfluorohexanoic acid (PFHxA, ≥97.0%), perfluorooctanoic acid (PFOA, ≥90%), perfluorononanoic acid (PFNA, ≥95.0%) and perfluorohexanesulfonic acid potassium salt (PFHxS, ≥98.0%) were purchased from Fluka (Buchs, Switzerland). Perfluorotetradecanoic acid (PFTA, 96%) was provided by Alfa Aesar (Ward Hill, MA). Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA, ≥98%, ≥99% 13C) and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate (MPFOS, ≥98%, ≥99% 13C) were acquired from Wellington Laboratories Inc. (Guelph, ON, Canada). The internal standard MPFOA was used for the quantification of the PFCAs (perfluorinated carboxylic acids), while MPFOS was used for the quantification of the PFSAs (perfluorinated sulfonic acids).

2.2. Sewage sludges

Thirteen sewage sludges were selected and used in this study. The sludges were collected from different wastewater treatment plants near Shanghai City, China in March and April 2009. Additional information regarding the WWTPs included in this study is available as Supporting Information (SI Table 1). All samples were stored in 1 L polypropylene bottles and then transported to laboratory on ice. All sludges were stored at −20 °C until the performance of sorption experiments. Their main characteristics are shown in Table 1. The sludge freezing process was fast in this study. This freezing/thawing treatment had little effect on the characteristics of sludge since that any transformation of sludge characteristics was only observed when the sludge is completely frozen at a relatively slow rate [17].

2.3. PASs analysis

Sample was centrifuged at 2450 × *g* for 15 min and the supernatant was removed. This aliquot was diluted by methanol and centrifuged at 17,800 × *g* for an additional 30 min, and then analyzed directly *via* liquid chromatography tandem mass spectrometry (LC/MS/MS) similar to that previously described [16]. Sludges were dried, extracted and analyzed by the method previously described [18].

2.4. Sludge property

Total organic carbon (TOC) was measured by a TOC analyzer (Shimadzu Company, V-CPN). Cation exchange capacity (CEC)