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Influence of cations on the partition behavior of perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge

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HIGHLIGHTS

- Na^+ and K^+ showed limit effect on PFHpA and PFHxS sorption by sludge.
- Divalent and trivalent ions affected sorption by bridging and coagulation.
- Organic contents and the types of organisms in sludge are crucial for sorption.

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ABSTRACT

The effects of different cations on the sorption behavior of PFHpA and PFHxS on two types of sludge were investigated in this study. The sodium and potassium ions did not significantly affect PFHpA and PFHxS sorption on different sludge. For calcium and magnesium, the sorption amount of PFAS increased with calcium and magnesium concentration increasing from 1 to 30 mM and then decreased with those increasing from 30 to 100 mM. The sorption level of PFHxS or PFHpA greatly increased with increasing Al^{3+} and Fe^{3+} cation concentrations due to the strong sorption and coagulation effects by the formation of aluminum hydroxide (or ferric hydroxide) colloids or precipitates. After the organics in sludge has been removed by thermal treatment, the PFAS sorption on sludge was greatly reduced. Such finding indicated that sorption to organic matter is more important for anionic PFASs than adsorption to mineral surfaces. However, due to the higher content of biological organics, a secondary activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge. It indicated that the organic types in sludge were also crucial to the sorption levels of PFASs by sludge.

1. Introduction

Perfluoroalkyl substances (PFASs) belong to one type of persistent organic pollutants (POPs) that have been used for nearly 60 years in a wide variety of consumer products and industrial applications. Their unique properties of repelling both water and oil made them widely used as surfactants and surface protectors in textile, carpets, coats, leather, paper, food containers, fabric, non-stick cooking wares, and upholstery, as well as performance chemicals in products such as fire-fighting foams, floor polishes, electroplating baths, shampoos, and insecticides (Giesy and Kannan, 2002). In addition, they have been detected in a wide range of organisms and environment, even in some remote regions, like the Arctic (Martin et al., 2004). Even if the production was to end today, levels would continue to increase in the environment for many years to come (Hansen et al., 2001). Researchers are finding serious health concerns about these compounds, including the increased risk of cancer (Key et al., 1997).

Although perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly found PFASs in the environment, other types of PFASs, such as perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS), also begin to attract more public concern on their releases and distribution. PFHpA is a breakdown product of stain and grease proof coatings on food packaging, couches, and carpets. PFHxS is used as a surfactant to make fluoropolymers and as the water and stain protective coatings for carpets, paper and textiles (3M Company, 1999), and it is the 6-carbon sister chemical of the better known 8-carbon PFOS. In 2000, 3 M decided to phase out all of its PFOS-based chemistry, including PFHxS due to its health concern. Although its production has been stopped, it was still detected in New York State waters, in the livers of birds in Japan and Korea, and in the blood of elderly

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residents of Washington State (Kannan et al., 2002; Olsen et al., 2004; Sinclair and Kannan, 2006). The blood levels of PFHxS were higher in children than in adults (Holzer et al., 2008) and its half-life was estimated in a range of 2.9–30.1 years (Olsen et al., 2005). Relatively much less research has been done on the toxicity of PFHxS and PFHpA, and their environmental fates and impacts have not been extensively investigated.

Many PFASs have been detected in a wide range in the organisms, water, sediment and wastewater treatment plants (Giesy and Kannan, 2001; Kannan et al., 2002; Higgins et al., 2005; Sinclair and Kannan, 2006). Some studies have shown the discharge of wastewater effluent is a significant source of PFASs to the environment (Higgins et al., 2005; Sinclair and Kannan, 2006; Loganathan et al., 2007) and some data indicate that PFASs, such as PFOS, may strongly sorb to sludge (Higgins et al., 2005; Zhou et al., 2010; Zhang et al., 2013; Arvaniti et al., 2014). These evidence shows that wastewater sludge can affect the fate and transport of PFAS in WWTP. Despite their detections in the wastewater treatment plants all over the world, the mechanism affecting the partitioning behavior of PFASs between the water and sludge is still unclear. The results of Higgins and Luthy demonstrated that the length of the fluorocarbon chain and the nature of the functional group influencing the sorption of PFASs on sediments (Higgins and Luthy, 2006).Ochoa-Herrera and Sierra-Alvarez (2008) evaluated the removal of PFASs by the sorption onto different types of sludge. The results indicate that different types of sludge could influence the degree of PFOS sorption onto wastewater treatment sludge. Yu et al. (2008) evaluated the ionic strength effect on the sorption of PFOS onto to molecularly imprinted polymer (MIP) and non-imprinted polymer (NIP), and it suggested that the increase of PFOS sorption at high salt concentration was attributed to the PFOS solubility, which decreased sharply in the seawater (Brooke et al., 2004).

Previous studies on PFAS sorption were mostly focusing on the behavior of PFOS. The sorption behavior of other PFASs, such as PFHpA and PFHxS, are rarely mentioned. Since PFHpA and PFHxS have been detected in a wide range in the environment (Martin et al., 2004; So et al., 2004; Powley et al., 2005), their sorption behavior on sludge are proposed to affect their fate and transport in wastewater system. Furthermore, due to the use of seawater for toilet flushing and the use of coagulant contains [Fe^{3+}] and [Al^{3+}] for wastewater treatment, high concentrations of metal ions may be present in the wastewater treatment processes. Higgins and Luthy (2006) have demonstrated that cation could affect the sediment–water distribution coefficients on the sorption of PFASs. However, the effects of different cations on the sorption of PFAS by sludge are not well documented. In case of this situation, different cations were selected to examine their effects on PFHpA and PFHxS sorption by wastewater sludge. In addition, Sludge from two WWTPs employing different wastewater treatment methods were selected to evaluate the function of different organic carbon content in the PFAS sorption by sludge. Sludge A was collected from a secondary WWTP in Hong Kong, which employs activated sludge treatment process and treats fresh wastewater. Sludge B was collected from a Hong Kong WWTP, which adopts the chemically enhanced primary treatment process and treats saline wastewater due to the use of seawater for toilet flushing in Hong Kong. Besides the type of wastewater, chemically enhanced primary treatment process often introduces additional cations, such as the iron or aluminum salts as coagulants, into the treatment wastewater and sludge. Previous studies also reported that the cation concentrations in aqueous solution would affect the property of organic compounds (Xi et al., 1997; Poulson et al., 1999), which may strongly influence the sorption behavior of PFHpA and PFHxS on wastewater sludge.

The objectives of this study are to observe the sorption behavior of PFHpA and PFHxS onto sludge materials, and to investigate the influence from solution composition. Two types of sludge corresponding to different types of wastewater treatment methods (secondary and chemically enhanced primary treatments) were collected for PFHpA and PFHxS sorption experiments. Also, a variety of common cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+}) ranging from concentrations of 1 mM to 100 mM in the aqueous solution were evaluated for their influence on the sorption behavior of PFHpA and PFHxS. Finally, sludge heat treatment was applied for removing part of the organic content in one of the tested sludge to observe the role and importance of sludge organics in the sorption of PFASs.

2. Materials and methods

2.1. Chemicals

Perfluoroheptanoic acid (PFHpA, 99%) and potassium salt of perfluorohexanesulfonate (PFHxS, 98%) were purchased from Sigma–Aldrich Co (St. Louis, MO). Sodium chloride, calcium chloride, potassium chloride, magnesium chloride, ferric chloride, aluminium chloride were purchased from BDH Ltd (Poole, Dorset, UK). Optima grade methanol and Optima grade water were purchased from Fisher Scientific (Pittsburgh, PA), and used for making 30% aqueous methanol in the process of sample preparation. The ammonium hydroxide (32%) and glacial acetic acid (99.8%) were obtained from Merck (Darmstadt, Hesse, Germany), and the methanol solution with 1% ammonium hydroxide and 1% glacial acetic acid was thus prepared from them. The ammonium acetate used for preparing the mobile phase in LC/MS/MS analysis was obtained from VWR International Ltd (Poole, Dorset). ENVI-Carb SPE tubes (1 g) used for sample cleanup were purchased from Supelco Inc. (Bellefonte, PA).

2.2. Sorbents

Sludge samples from two domestic WWTPs in Hong Kong with different treatment processes were selected to examine their specific sorbent behavior. All samples were collected in polypropylene (PP) bottles. Prior to sorption experiment, sludge samples were ball-milled for 24 h, dried at 105 °C overnight, and ground to be further homogenized by a solvent-rinsed blender. A portion of sludge B sample was further burned in the oven under 300 °C for 1 h to partially remove the organic matter (sludge B1). The sludge was ground after thermal treatment. PFAS sorption experiments were conducted on both the sludge and thermal treated sludge.

Some basic characteristics of sludge were provided in Table 1. The organic carbon content of the sludge samples were measured by a total organic carbon (TOC) analyzer (TOC-5000, Shimadzu, Japan) with a solid sample module (SSM-5000A, Shimadzu, Japan). Based on the size distributions measured by a particle size analyzer (Coulter Multisizer II, Beckman, Fullerton, CA), the particle size distribution in terms of their fractions of sand, silt and clay was estimated (Fig. S1). BET surface area was measured by a surface area analyzer (Coulter SA 3100, Beckman, Fullerton, CA).

Table 1
Characteristics of sludge samples used in the PFAS sorption study.

Sludge	Org C %	Sand (%)	Silt (%)	Clay (%)	BET surface area ($m^2\ g^{-1}$)
A	41.5	37.3	52.5	10.2	0.6
B	48.5	15.8	69.6	14.6	2.5
B1	24.6	4.7	63.9	31.4	16.5

Note: Org C% denotes organic carbon percentage (dry weight); BET surface area denotes Brunauer Emmett and Teller surface area (measured by N_2); Sand particles are with diameter larger than 62.5 μm; Silt particles range from 3.9 to 62.5 μm in diameter; Clay particles are with diameter smaller than 3.9 μm.