



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 Al³⁺ and Fe³⁺ 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.

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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, 3M 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 $[\text{Fe}^{3+}]$ and $[\text{Al}^{3+}]$ 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 ($\text{m}^2 \text{g}^{-1}$)
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 .

2.3. Aqueous solution composition

To evaluate the effects of cation on partition behavior of PFASs, experiments were conducted with different sludge in which the cation concentrations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) were varied from 1 to 100 mM. The 1 g of sludge was mixed with 50 mL of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration and shaken in an orbital shaker at 150 rpm for three days at room temperature. Triplicate experiments were conducted and blanks with the aqueous composition solution were run in duplicate along with the sorption samples. The sample pH was determined after centrifugation and the removal of the sludge sample.

2.4. Sample extraction

Aqueous samples were analyzed directly via LC/MS/MS. Each 50 mL polypropylene (PP) centrifuge tube containing a sludge-aqueous mixture was centrifuged and an aqueous aliquot was removed. This aliquot was diluted with methanol and transferred to an autosampler vial for analysis. For samples, a method modified from Powley et al. (2005) was performed to extract PFASs (Fig. S2). The sludge separated from the centrifuge was dried overnight and ground. The homogenized and 105 °C-dried sludge (0.5 g) was transferred to a 50 mL PP centrifuge tube and extracted 3 times for 10 min with basic methanol (1% NH_4OH) in a 60 °C sonication bath. Extracts were then combined and acidified with acetic acid (1% by volume) and concentrated under nitrogen purging to 10 mL. To remove potential matrix interferences, each sludge extract was passed through ENVI-Carb SPE Tube (1 g, 12 mL) for cleanup and followed by 2.5 mL methanol for cartridge rinsing. The collected methanol solution was evaporated under nitrogen purging to 5 mL. The extracts were diluted with water and transferred to a glass vial with polypropylene cap for analysis.

2.5. Sample analysis

Quantification of PFASs were performed using a Waters Acquity ultraperformance LC system, Waters BEH C_{18} column, $2.1 \times 50 \times 1.7$ (mm inside diameter \times mm length \times μm particle size) equipped with a Waters Acquity TQD, a tandem quadrupole mass spectrometer. Although the high-performance liquid chromatography coupled to quadrupole tandem mass spectrometer (LC/MS/MS) is the preferred instrumental method for quantifying PFASs, the presence of PFASs in various laboratory wares as well as the analytical instruments themselves cause significant difficulty in analyzing them. To overcome this, we substituted the Teflon tubes used for transferring the solvents and sample in UPLC system by polyetheretherketone (PEEK) tubes, and also utilized an in-line PFAS isolator column (Waters Corp., Milford, MA) to assist the analytical column to separate the background PFAS contaminants in mobile phase (Fig. S3). In this way, the background contaminants would be retained and eluted after the targeted sample.

To improve resolution and increase sensitivity of detection, a gradient mobile phase of 2 mM ammonium acetate in methanol and 2 mM ammonium acetate in water/methanol (95/5) was used. At a flow rate of 0.4 mL min^{-1} , the mobile-phase gradient was ramped from 25% to 85% methanol in 5 min, then to 100% methanol at 5–10 min, and finally ramped down to 25% methanol in 7 min. The MS/MS was operated in electrospray negative ionization mode due to the PFAS properties of easily losing the hydrogen ions. Analyte ions were monitored using the multiple reaction monitoring (MRM) mode. Primary and transition ions monitored for quantification were $363 > 319$ for PFHpA, $399 > 80$ for PFHxS. The IDL was 0.1 ppb for both PFHpA and PFHxS.

3. Results and discussion

3.1. Mass balance of PFAS sorption experiments

In sorption experiments, the targeted compounds may reside in sludge, aqueous solution, and on the surface of agitation container (PP tube). When the sorption equilibrium is achieved, the mass balance of tested PFAS can be represented as:

$$Cs_1Ms + Cw_1Vw = Cw_2Vw + Cs_2Ms + P \quad (1)$$

where Cw_1 is the initial concentration of PFAS in aqueous solution ($\mu\text{mol L}^{-1}$); Vw is the volume of aqueous solution (L); Cw_2 is the PFAS concentration in solution after the sorption experiment ($\mu\text{mol L}^{-1}$); Cs_1 is the initial PFAS concentration in sludge ($\mu\text{mol kg}^{-1}$); Cs_2 is the PFAS concentration in sludge after the sorption experiment ($\mu\text{mol kg}^{-1}$); Ms is the mass of sludge (kg); P is the amount of PFAS on the surface of PP tube.

To evaluate the mass balance of the targeted PFAS compound, the sludge samples without spiking PFASs were first extracted following the steps in Fig. S1 before sorption experiment. The extraction process was conducted with four replicates for each sample, and PFHpA and PFHxS were not detected in the sludge. To quantify the PFASs adsorbed on the PP tubes, blank experiments without sludge but with 5 ppb of PFHpA and PFHxS in aqueous solution were used. No distinct increase and decrease of PFHpA and PFHxS concentration in blank samples illustrate that PP tube has no significant effect on sorption experiment. So the mass balance can be defined by:

$$Cw_1Vw = Cw_2Vw + Cs_2Ms \quad (2)$$

which means that PFHpA or PFHxS was partitioned between the sludge and water. The PFAS may lose through extraction of sludge sample and spike experiment was prepared for all sludge samples to evaluate their recoveries through extraction. The recovery rate was consistently greater than 80%, which is comparable to 70–120% recovery rate reported by Powley et al. (2005) and 85% reported by Higgins and Luthy (2006).

3.2. Cations effect on sludge A

Fig. 1 shows the influence of cations concentrations on the sludge-water distribution coefficients for PFASs. The distribution coefficient between water and sludge, K_d (L kg^{-1}) was calculated by:

$$K_d = \frac{Cs}{Cw_2} \quad (3)$$

where Cs ($\mu\text{mol kg}^{-1}$) represents concentration of PFASs in sludge, Cw_2 ($\mu\text{mol L}^{-1}$) represents the PFAS concentration in solution after the sorption experiment.

When the concentrations of sodium and potassium ions increased from 1 to 100 mM, the distribution coefficients (K_d) of PFHpA or PFHxS on sludge had no significant changes. Higgins and Luthy (2006) reported that the sorption of PFOS onto the sediments did not change with NaCl concentration increase, which is consistent with current results. For calcium and magnesium ions, K_d values for PFHxS and PFHpA increased with the increase of calcium and magnesium concentrations from 1 to 30 mM but decreased with further increase from 30 to 100 mM. For the reason of enhancement, it was suggested that the negative charge of organic compounds in the sludge may be positively charged by sorbing $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ (Higgins and Luthy, 2006), which offer more positive sites for the anionic PFHxS and PFHpA molecules. However, when $[\text{Ca}^{2+}]$ or $[\text{Mg}^{2+}]$ concentration increased to higher than 30 mM, some organic contents in sludge would graduate released from solid phase to aqueous phase, which decrease the

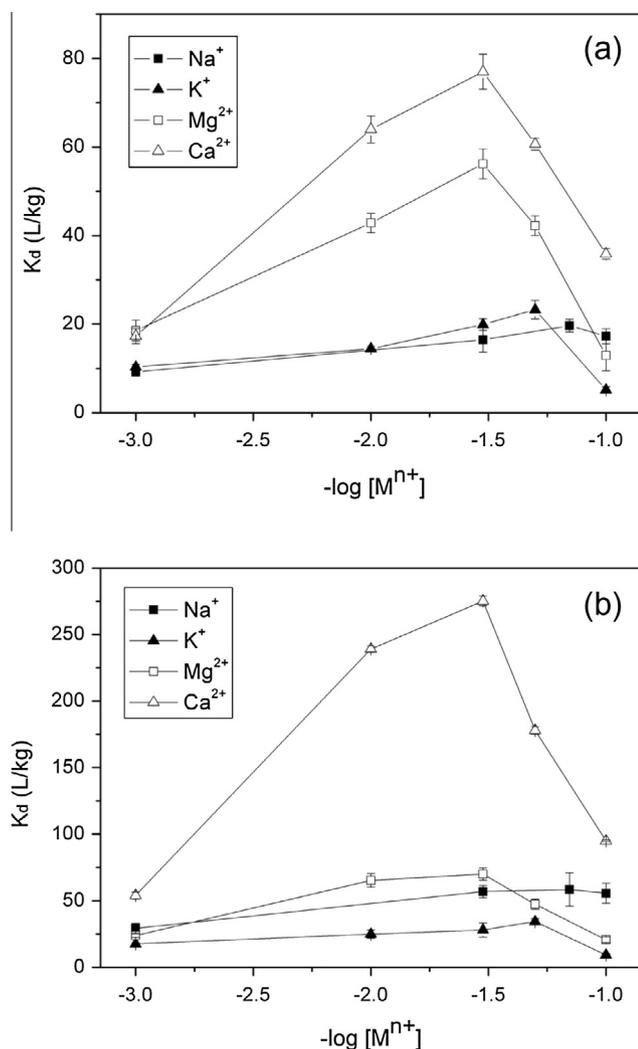


Fig. 1. Effects of different cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) on sorption of PFHpA (a) and PFHxS (b) on sludge A. Error bars represent standard deviations of triplicate samples.

sorbent amount. When comparing the K_d values of PFHpA and PFHxS on sludge with the same $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ concentration (Fig. 1), it is clear that K_d values in the presence of calcium ion were higher than those of magnesium ion. Similar observation was also found in our previous study on the adsorption of PFASs onto alumina, which showed that magnesium had less interaction with PFAS species (Wang and Shih, 2011). Kennedy et al. (2004) suggested that the higher covalent nature of magnesium relative to calcium may lead to stronger direct hydration and thus reduced its interactions with the PFAS species and sludge.

3.3. Cation effect on sludge B

To test the influences of cations on PFAS sorption by different type of sludge, dewatered sludge B from a WWTP adopting the chemically enhanced primary treatment process was used to conduct the sorption process again. Fig. 2 shows impact of cation on sludge B. The sorption amount of PFASs kept almost consistent from 1 to 100 mM in this study and suggests that sodium and potassium generally do not affect the sorption of PFHpA and PFHxS on WWTP sludge. The presence of $[\text{Ca}^{2+}]$ also shows a greater influence of the sorption amount of PFASs than the presence of $[\text{Mg}^{2+}]$ due to its higher covalent. Higgins and Luthy

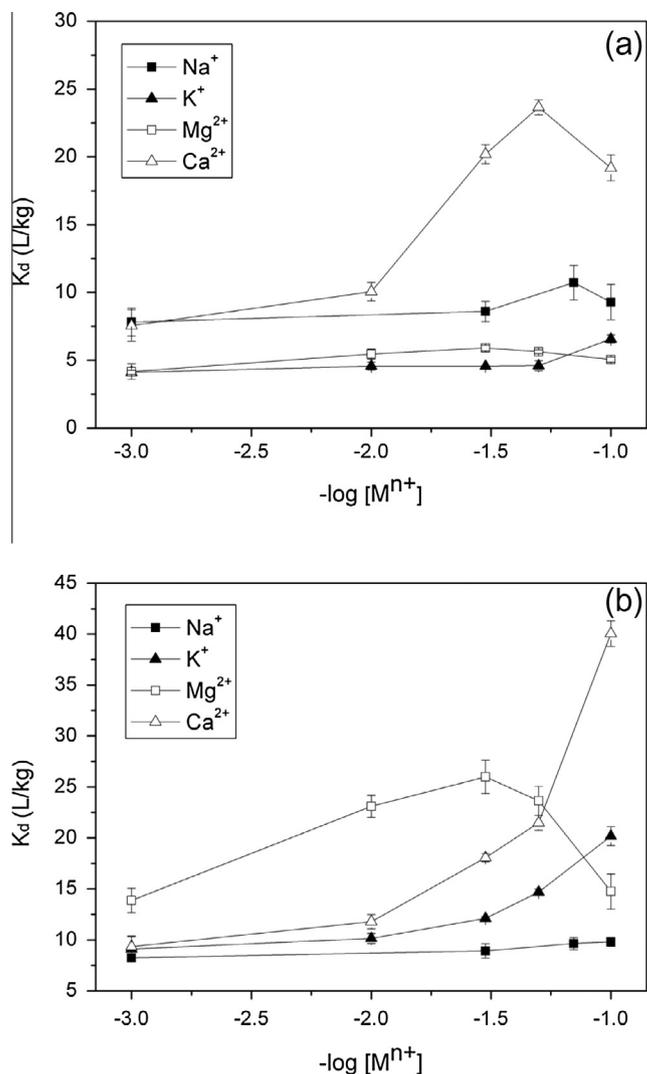


Fig. 2. Effects of different cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) on sorption of PFHpA (a) and PFHxS (b) on sludge B. Error bars represent standard deviations of triplicate samples.

(2006) observed that the sorption of a perfluorosulfonate was 1.7 times stronger than the perfluorocarboxylate analog on sludge, and they attributed the reason to the slightly larger size of the sulfonate functional group as compared to the carboxylate group. Thus, the stronger cation effect on PFHxS than PFHpA may likely attribute to the different functional groups of PFHxS and PFHpA.

When comparing the K_d values in Figs. 1 and 2, the PFAS sorption of sludge A is generally stronger than that of sludge B. Such observation showed the crucial role of sludge type on the sorption process. Higgins and Luthy (2006) demonstrated the sediment organic carbon was the dominant sediment parameter affecting the sorption of anionic PFAS surfactants. In this study, the organic carbon was 48.5% for sludge B and 41.5% for sludge A, respectively. Other sludge parameter like the surface area which was $0.6 \text{ m}^2 \text{ g}^{-1}$ for sludge A and $2.5 \text{ m}^2 \text{ g}^{-1}$ for sludge B. With lower surface area, sludge A is instead with a stronger sorption capacity than sludge B. These data strongly suggest that sorption to organic matter is the main sorption mechanism, which was supported by sorption data previously collected for PFOA (Westall et al., 1999). Furthermore, the higher sorption of PFASs on sludge A may be due to the different type of organic matters present in the sludge. Through a secondary activated sludge treatment process, sludge A may contains more biological organics than chemically enhanced

primary treatment sludge B. This result demonstrates even the quantity of organic matters in the sludge is the same; the type of organism in the sludge may have a great influence on the PFASs sorption.

Effect of PFAS sorption on sludge B in presence of aluminum and ferric ion were also studied (Fig. 3). The sorption amounts of PFHxS or PFHpA were significantly increased with the increase of these two types of cations. Besides the promotion effect of electrostatic attraction, the formation of aluminum hydroxide or ferric hydroxide colloids or precipitates may be another potential mechanism of sorption enhancement as PFASs can be sorbed and coagulated in such solutions (Wang and Shih, 2011; Wang et al., 2012).

3.4. TOC effect on sludge B

Since the organic matter in sludge is essential to its adsorption capacity, an experiment of removing 50% of the organic carbon content from the sludge B (sludge B1) by thermal treatment was carried out. As a result, the K_d of the sludge B1 was largely reduced. The K_d obtained for the sludge B ranged from 9.1 to 16.1 L kg⁻¹ for PFHpA and 9.1 to 20.1 L kg⁻¹ for PFHxS before thermal treatment, but the K_d values for sludge B1 with thermal treatment were decreased to 2.6 L kg⁻¹ for PFHpA and 4.7 L kg⁻¹ for PFHxS averagely (Fig. 4). Thermal treatment of sludge can change the surface structure of the sludge and of the organic matter and inorganic portion on the sludge, which lead to different partition coefficients. For sodium, the sorption amounts of PFASs decreased with the increasing sodium concentration and for calcium the sorption amount of PFASs increased with the increasing calcium concentration. The K_d values between monovalent and divalent cations are limited, but their differences between the perfluorosulfonates and perfluorocarboxylates of equal chain length were still clearly observed.

Ochoa-Herrera and Sierra-Alvarez (2008) evaluated the adsorption of PFOS onto different wastewater sludge and suggest that organic matter content must contribute to controlling sorption of PFOS. Higgins et al. (2005) confirmed that sorption to organic matter is more important for anionic PFAS surfactants than adsorption to mineral surfaces. Chiou et al. (1979) suggested that the transfer of nonionic chemicals from water to soil may be described in terms of a hypothesis of solute partitioning in the soil organic matter. In this study, the surface area of sludge B was 2.5 m² g⁻¹ before thermal treatment and 16.5 m² g⁻¹ of sludge B1 after thermal treatment. However, even the surface

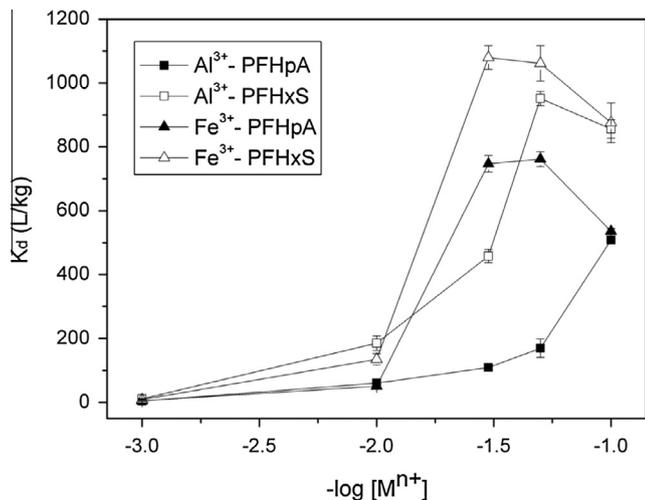


Fig. 3. Effects of Al^{3+} and Fe^{3+} on sorption of PFHpA and PFHxS on sludge B. Error bars represent standard deviations of triplicate samples.

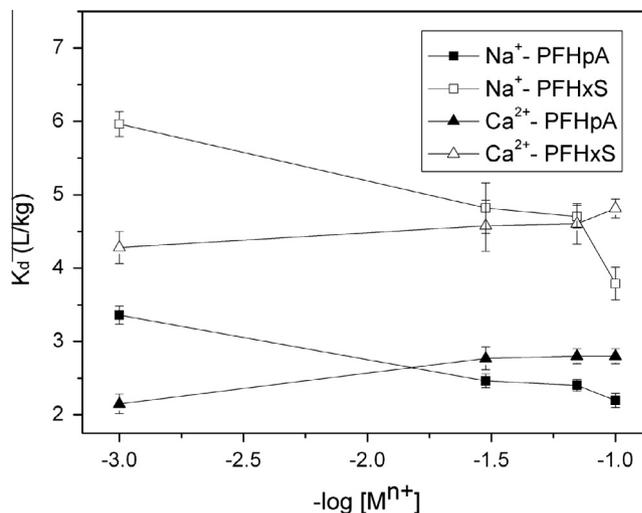


Fig. 4. Effects of Na^{+} and Ca^{2+} on sorption of PFHpA and PFHxS on sludge B1. Error bars represent standard deviations of triplicate samples.

area increase, the K_d value still decreased. These data strongly suggest that sorption to organic matter is more important for anionic PFASs than adsorption to mineral surfaces, this finding is also supported by sorption data previously collected for PFOA (DuPont Company, 2003). Same evidence also found in other organic compound. Lertpaitoonpan et al. (2009) found that organic content was the more dominant parameter on soil sorption of sulfamethazine. Xu and Li (2009) found that the K_d values of benzyl butyl phthalate were reduced by more than 70% when used H_2O_2 oxidation for removing the organic material from the sediments. These observations suggest organic matter content rather than minerals was the dominant sludge-parameter affecting the sorption of PFAS onto wastewater treatment sludge. Furthermore, our results also demonstrate that the types of organisms in the sludge and cations in solution strongly influence the partition behavior of PFASs in sludge.

The PFHpA and PFHxS recoveries in the sorption processes with different cations were shown in Table S1. It is clear that the losses of PFHpA or PFHxS were less than 15% even with different types of sludge. The results were even better than the spike experiments without cations.

4. Conclusions

For the effects of cations, divalent and trivalent ions showed stronger effects on PFHpA and PFHxS sorption by two kinds of sludge than monovalent ions. The promotion effects of the divalent cations were mainly caused by the potential bridging effects while that of the trivalent ions were the sorption and coagulation effects. The K_d value of PFHxS is generally higher than that of PFHpA due to the stronger sorption affinity of sulfonate group than carboxylate group toward sludge. Organic contents in sludge are crucial to the PFHpA and PFHxS sorption. Furthermore, the types of organisms in sludge are also found important for PFAS sorption.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.03.024>.

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