Effect of humic acid on the sorption of perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS) on boehmite

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HIGHLIGHTS

- The manuscript firstly reported the sorption mechanisms among PFCs, humic acid, and boehmite.
- A conceptual model was presented to delineate the different sorption behavior of PFOS and PFBS.
- The findings have revealed the crucial role of humic acid in affecting the fate of PFAAs in nature.

ARTICLE INFO

ABSTRACT

The sorption of PFOS and PFBS on boehmite was significantly retarded by the competitive sorption of humic acid (HA), implying that PFOS and PFBS are likely more mobile in water and groundwater systems enriched with HA. The sorption behavior of PFOS and PFBS on the HA-modified boehmite surface were also found to differ due to their different chain lengths. For a partially HA-modified boehmite surface, the isotherm study showed that PFOS had a much higher maximum sorption capacity than PFBS and that PFOS might possess additional surface interactions besides electrostatic interaction. For a HA-saturated boehmite, a linear sorption isotherm was found for PFOS while nearly no PFBS sorption was observed. This indicates that sorption behavior between PFOS and the sorbed HA on boehmite was dominated by hydrophobic interactions, instead of electrostatic interaction. In addition, a conceptual model combining hydrophobic and electrostatic interaction was established to explain the sorption behavior of PFOS and PFBS on HA-modified boehmite. Finally, the results revealed that the sorption of PFOS and PFBS on HA-modified boehmite is pH-dependent. The neutralization of negative sites on HA-modified boehmite reduced the electrostatic repulsion and enhanced the partitioning of PFBS on the sorbed HA.

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1. Introduction

Perfluoroalkyl acids (PFAAs) are a family of persistent organic pollutants (POPs) that have attracted global concern due to wide distribution in the environment. PFAAs are widely used in surface protectants, firefighting foam, cosmetics, lubricants, insecticides, and food packaging (Schultz et al., 2003). Perfluorooctane sulfonate (PFOS) is the most commonly found PFAAs in the environment due to the large production of PFOS-related compounds. Although the production of PFOS was phased out in 2003, it has been replaced by its four-carbon homology, perfluorobutanesulfonate (PFBS) (Sundstrom et al., 2012). Given their wide distribution and persistent nature, PFAAs have been detected in wastewater, surface water, groundwater, and even drinking water (Schultz et al., 2004; Plumlee et al., 2008; Mak et al., 2009; Post et al., 2009; Quinones and Snyder, 2009; Sun et al., 2011). Their fate and transport in the environment thus needs to be systematically investigated.

In groundwater, the fate and transport of PFAAs are reported to be strongly dependent on their interaction with surrounding minerals (Tang et al., 2010). The sorption behavior of PFAAs on sediments (Higgins and Luthy, 2006), Soils (Guelfo et al., 2011; Guelfo and Higgins, 2013), as well as specific minerals (goethite (Johnson et al., 2007), silica (Tang et al., 2010), alumina (Wang and Shih, 2011), and kaolinite (Xiao et al., 2011)), has been extensively studied. Furthermore, many of these studies have investigated the influence of pH, ionic strength, and Ca^{2+} on the uptake of PFAAs to explore the roles of different adsorption mechanisms (e.g. electrostatic and hydrophobic interaction).

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However, another important factor that may strongly influence the distribution of pollutants in groundwater is the presence of natural organic matter (NOM), because the binding of NOM with minerals can modify the mineral surface properties (Yoon et al., 2005; Kang and Xing, 2008). NOM is ubiquitous in groundwater systems and is formed primarily through the microbial and chemical transformation of plant and animal wastes. As a key component of both soil and sediment, NOM is known to have significant effects on the transport of pollutants (Aiken, 1985; Yoon et al., 2005). Surface modification by NOM can dramatically change the characteristics of mineral particles and, thus, substantially alter pollutant sorption capacity of minerals (Tipping, 1981; Davis, 1984; Feng et al., 2006). It was reported that the presence of NOM in solution can promote sorption of metal ions by minerals due to metal complexation with functional groups of adsorbed organic matter (Davis, 1984; Vermeer et al., 1999). Recently, a study of the influence of NOM on the sorption of phosphate and arsenate ions on goethite showed a strong competitive sorption of humic acid (HA) with these two anions for the surface sorption sites (Weng et al., 2008, 2009). Furthermore, the surface modification of minerals may affect the mechanism and transport efficiency of organic pollutants (Yoon et al., 2005). NOM is widely known to play a predominant role in the sorption of hydrophobic organic compounds (HOCs) (Yang and Xing, 2009). The presence of NOM in solution commonly enhances the sorption of HOCs on minerals (Jones and Tiller, 1999; Gunasekara and Xing, 2003; Wang et al., 2008) due to the strong interactions between NOM and HOCs (such as phenanthrene and anthracene). Yang and Xing (2009) reported the sorption of phenanthrene on TiO_2 and ZnO was significantly enhanced by hydrophobic and π-bonding interaction between HA and phenanthrene. However, to the best of our knowledge, the roles of the different sorption mechanisms of PFAAs on mineral surfaces under the influence of NOM have not been widely studied.

In this study, HA was used as the surrogate NOM compound (Weng et al., 2008, 2009; Yang and Xing, 2009), and boehmite was selected as the aluminum-rich mineral surface for sorption experiments, due to its thermodynamic stability under hydrous conditions and high surface area (Navrotsky, 2001). The influence of HA on the sorption behavior of PFOS and PFBS on boehmite was systemically studied to reveal (1) the effect of PFAA chain length on sorption capacities of the boehmite surface, (2) the conceptual model of PFAA sorption on the HA-modified boehmite, and (3) the role of solution pH in the sorption mechanisms of PFAAs and HA on boehmite.

2. Experimental section

2.1. Materials and material characterization

PFOS (potassium salt) and PFBS were purchased from Sigma-Aldrich Co. (St. Louis, MO). Optima grade methanol was purchased from Fisher Scientific (Pittsburgh, PA), and the ammonium acetate used to prepare the mobile phase in LC/MS/MS analysis was obtained from VWR International Ltd. (Poole, Dorset, UK). Humic acid was obtained from Fluka Co. (Buchs, Switzerland) and the carbon content was determined to be around 32% using a Total Organic Carbon (TOC) Analyzer (Shimadzu, Japan). Boehmite was purchased from Sasol Ltd. (Hamburg, Germany) and its mineral phase was confirmed by the XRD method (Supporting Information (SI) Fig. S1) using an X-ray powder diffractometer (D8 Advance, Bruker, Germany). The boehmite's PZC (pH_{pzc}) was determined to be pH 8.4, and the surface area and average particle size (d_{50}) of the as-received boehmite were measured to be $299.2 \pm 1.8 \, m^2 \, g^{-1}$ and 37.02 μm, respectively.

2.2. Sorption experiments

The boehmite concentration in all experiments was controlled at $5 \, g \, L^{-1}$. The HA and PFOS (or PFBS) concentrations in the working solutions were adjusted within the ranges of 2–$50 \, mg \, L^{-1}$ and 50–$1000 \, \mu g \, L^{-1}$, respectively. The pH (4.0–8.0) was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions. All sorption experiments were conducted in 50 mL polypropylene copolymer (PPCO) Nalgene centrifuge tubes (Rochester, NY) due to its good resistance to PFAA sorption (Wang and Shih, 2011). All solutions were placed on an orbital shaker (150 rpm, 25 °C) for 72 h to achieve equilibrium (SI Fig. S2). After the sorption experiments, the solution samples were centrifuged at 4000 rpm for 10 min and 10 mL of the supernatant solution was then transferred to the glass bottle for TOC analysis. The temperature used for the TOC combustion in this study was 680 °C, and the decomposition temperature of PFOS was around 450 °C (Wang et al., 2011). Thus, PFOS (or PFBuS) can be thermally degradation in the TOC analysis. The total TOC subtracting the TOC of PFAAs in the final solution was considered as the TOC of HA. Then, the equilibrium concentration of HA was calculated from the standard curve between HA concentration and TOC value. Finally, 1.5 mL of supernatant solution was diluted with 3.5 mL methanol (v/v = 3/7) and the mixture was filtered through a 0.2 μm Whatman inorganic membrane filter (Maidstone, UK) into small sample vials for the PFOS and PFBS analyses.

2.3. PFOS and PFBS determinations

The concentrations of PFOS and PFBS were determined using a Waters Acquity ultra-performance LC/MS/MS system (UPLC/MS/MS) equipped with a 50×2.1-mm Waters BEH C18 column (1.7-μm particle size) and tandem quadrupole mass spectrometers (Milford, MA). Two mobile phases with 2 mM ammonium acetate in methanol and ultrapure water/methanol (v/v = 95/5) mixture were used to achieve a combined flow rate of $0.4 \, mL \, min^{-1}$ in this study. The electrospray negative ionization model was used for the MS/MS operation due to the anionic properties of PFOS and PFBS, and the analyte ions of PFOS and PFBS were monitored using the multiple reaction monitoring (MRM) model. The monitored transitions of PFOS and PFBS were 499 > 80 and 299 > 80, respectively. The isotope labeled PFOS ($^{13}C8F_{17}SO_3Na$) standard purchased from Wellington Laboratories was used in the quality control and quality assurance of the sorption experiments. The results showed that the recoveries of isotope standard ($^{13}C8F_{17}SO_3Na$) for the used method were from 93% to 104%. Control experiments were conducted first before systematic experiments. Previous studies showed the recovery rate of PFOS in PPCO tubes were from 87% to 100% (Wang and Shih, 2011). Due to the conditions used in this manuscript is different, the recovery of PFOS and PFBS under different conditions were shown in Tables S1 and S2. Since the non-specific losses to vials were unavoidable, two controls were conducted together with three samples. If the recovery rates of controls were higher than 85%, the results of samples were considered as valid. Then the adsorption amounts of PFAA were calculated by the detected concentrations in controls subtracting the residue concentrations in the solution after equilibrium.

3. Results and discussion

3.1. HA initial concentration

Fig. 1 shows the influence of the HA initial concentrations on the sorption levels of HA and the two types of PFAAs (PFOS and PFBS) on boehmite. At HA initial concentrations of less than $30 \, mg \, L^{-1}$, the sorption of HA increased when the PFOS (or PFBS)