Adsorption of perfluorinated acids onto soils: Kinetics, isotherms, and influences of soil properties

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HIGHLIGHTS

- The sorption kinetics can be well described by a biexponential adsorption model.
- The sorption isotherms are well represented by Freundlich and/or Virial equations.
- The content of protein rather than TOC affects the adsorption of PFAs onto soils.
- AEC and iron oxides are also dominant soil properties affecting the adsorption.

GRAPHICAL ABSTRACT
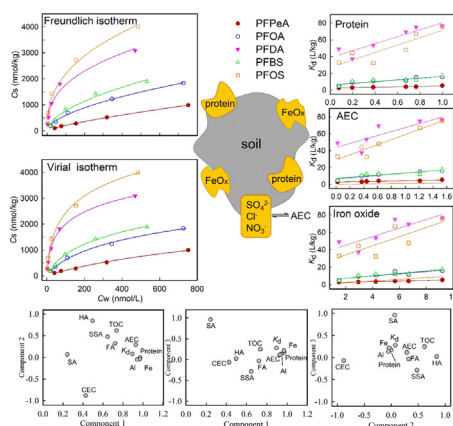
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ABSTRACT

The adsorption of perfluorinated acids (PFAs) onto soils with different physicochemical properties was investigated in this study. The adsorption kinetics for all PFAs onto the soil with the highest contents of total organic carbon (TOC) and iron oxide were well described by a biexponential adsorption model, indicating that two types of binding sites characterized by a fast and a slow sorption rates were involved in the adsorption, and the time required for achieving adsorption equilibrium was <48 h for all PFAs. The adsorption isotherms were well represented by both of Freundlich equation ($R^2 = 0.9547$–0.9977) and/or Virial equation ($R^2 = 0.8720$–0.9995). The interfacial capacitances derived from the Virial isotherm were substantially low (in the range of 33.7 to 851 $\mu F/m^2$) for all soils, but were not analyte-independent for all PFAs onto the same soil. The linear regression between distribution coefficient (K_d) and individual soil property as well as principle component analysis were conducted for determining the dominant soil physicochemical properties affecting the adsorption of PFAs onto soil in the present study. The results indicated that the content of protein rather than of total organic carbon (TOC) was the dominant property, and then followed by anion exchange capacity (AEC) and the content of iron oxides. For the other properties, the influences of fulvic acid (FA) and aluminum oxides were PFA-dependent, while there were no effects of saccharide, humic acid (HA), specific surface area (SSA) and cation exchange capacities (CEC) on the adsorption.

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1. Introduction

Perfluorinated acids (PFAs) have been manufactured and widely used in a variety of industrial and commercial applications for about 60 years because of their unique physiochemical properties (Kissa, 2001). However, once released into the natural environment and ecosystems, PFAs are not readily decomposable through physical, chemical, and biological mechanisms due to the strong carbon fluorine bonds (Kissa, 2001; Wei et al., 2017; Xiao et al., 2017). Therefore, PFAs have attracted increasing public and scientific attentions considering their high bioaccumulation potential, extreme persistence and toxic properties, such as endocrine-disrupting activity, carcinogenesis, neurotoxicity, and reproductive toxicity etc. (Chang et al., 2016; Jian et al., 2017; Karnjanapiboonwong et al., 2018; Rappazzo et al., 2017). For instance, perfluorooctanesulfonyl fluoride, perfluorooctanesulfonic acid (PFOS) and its salts have been added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May 2009 (UNEP, 2009).

PFAs have been extensively detected in soils (Dalahmeh et al., 2018; Filipovic et al., 2015; Lu et al., 2018; Xiao et al., 2015) and groundwater (Filipovic et al., 2015; Hongkachok et al., 2018; Lu et al., 2018; Xiao et al., 2015), even at high pollution levels. Given the important role of solid matrices in influencing the environmental fate of hydrophobic organic contaminants (Higgins and Luthy, 2006), a better understanding of the fate and transport of PFAs in the soil-groundwater systems requires the elucidation of the partitioning patterns of these compounds between solid and water phases. However, PFAs are expected to behave differently from traditional non-ionisable organic pollutants due to their hydrophobic and hydrophilic functionalities (Li, Y. et al., 2018). Although a substantial body of studies have focused on illustrating the adsorption behaviors onto various solids, most of them were conducted only for the typical representatives of PFAs, perfluorooctanoic acid (PFOA) and/or PFOS (Ahrens et al., 2011; Chen et al., 2012; Jeon et al., 2011; Johnson et al., 2007; Miao et al., 2017; Wang et al., 2012; Wang and Shih, 2011; Wei et al., 2017; Yang et al., 2013; You et al., 2010; Yu et al., 2012; Zhang et al., 2014; Zhou et al., 2010a, 2010b). In addition, a few studies were carried out for the sorption of PFA-homologues with different perfluorocarbon chain length onto some solid phases, such as sediment (Higgins and Luthy, 2006) and clay minerals (Zhao et al., 2014a), but there was no report for systematical analysis of their adsorption behaviors onto soil. Meanwhile, these studies concluded that organic carbon content was the dominant solid phase parameter affecting the adsorption, which is used as the indicator for the current environmental assessment on the fate and transport of PFAs (Li, Y. et al., 2018). However, another study conducted on sewage sludge indicated that the content of protein rather than organic carbon was the dominant sludge parameter affecting the adsorption (Zhang et al., 2013). Therefore, it is vital to evaluate the effects of some specific components of organic carbon, such as protein, saccharide, fulvic acid (FA), and humic acid (HA), on the adsorption of PFAs onto soil, and determine the correlations between distribution coefficients of PFAs and solid properties.

The objectives of this study were to comprehensively investigate the adsorption behavior of PFAs with the perfluorocarbon chain from C4 to C9 onto six selected soils with distinctively physicochemical properties. The influences of the total organic carbon (TOC) as well as its some specific components, such as protein, saccharide, FA and HA, on the adsorption of PFAs onto soil were studied. Meanwhile, the effects of the other soil properties including the contents of iron oxide, aluminum oxide, anion exchange capacity (AEC), cation exchange capacity (CEC), and specific surface area (SSA) were also evaluated in the present study. Beside linear regression analysis, principle component analysis was also performed between distribution coefficients and soil properties in order to identify the dominant solid parameters affecting the adsorption.

2. Materials and methods

2.1. Standards and chemicals

Perfluoropentanoic acid (PFPeA, 97%), perfluorooctanoic acid (PFOA, 96%), Perfluorodecanoic acid (PFDA, 98%), and perfluorooctanesulfonic acid potassium salt (PFOS, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), while perfluorobutanesulfonic acid (PFBS) was obtained from Aldrich (Milwaukee, WI, USA). Purity-corrected equimolar stock solution containing PFPeA, PFOA, PFDA, PFBS, and PFOS was then prepared in a 50/50 (v/v) methanol-water solution, and the PFAs concentrations were set to be 20 μM, 40 μM, 80 μM, 200 μM, and 400 μM, respectively. Internal standards, perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA, in methanol, 50 ± 2.5 μg/mL, >99% linear, >99% 1,2,3,4-$^{13}C_4$) and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]-octanesulfonate (MPFOS, in methanol, 50 ± 2.5 μg/mL, >99% linear, >99% 1,2,3,4-$^{13}C_4$), were acquired from Wellington Laboratories (Ontario, Canada).

HPLC grade methanol (≥99.9%) and acetonitrile (≥99.9%) were purchased from Sigma-Aldrich, while HPLC grade ammonium acetate (≥99.0%) and bulk Envi-Carb graphitized carbon sorbent (100 m^2/g, 120/400 mesh) were acquired from Fluka and Supelco (Bellefonate, PA, USA), respectively. All the other inorganic compounds were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), unless other specifics were mentioned. Milli-Q water (Milli-Q® Reference, Merck Millipore, Germany) was used in this study.

2.2. Soil collection, preparation and properties

The surficial soils (0–20 cm) were collected in polyethylene (PE) self-locked packages from farmland and road greenbelt in Xiamen, China, and six soils used for this study were selected to reflect a variety of geochemical parameters (Table 1) potentially influencing the adsorption of PFAs. All soils were air-dried at room temperature and crushed using a mortar and pestle, and then sieved with a 2-mm stainless steel mesh. The concentrations of the 5 PFAs in each of the six soils were analyzed according to Li et al. (2010, 2011), which ranged from <0.10 ng/g to 40.1 ng/g. The pretreated soils were stored at −20 °C and γ-irradiated to reduce biological activity prior to the adsorption experiments.

The soil moisture content was measured gravimetrically by oven-drying the sample at 105 °C for 24 h. Soil pH was determined according to US EPA Method 9045D (USEPA, 2004). The pH of zero point charge of soils were determined using potentiometric titration method (Sakurai et al., 1988). Total organic carbon (TOC) was measured by using a Shimadzu TOC-V$_{cpn}$ analyzer (Shimadzu, Tokyo, Japan) with solid sample module (SSM-5000A). Soil saccharide was extracted and prepared according to the procedures reported by Martens and Frankenberger (1990) and then determined by the phenol sulfuric acid method (DuBois et al., 1956). Soil protein was extracted and prepared according to Ogunseitan (1993) and then measured by the Lowry-Folin method (Lowry et al., 1951). Anion exchange capacity (AEC) and cation exchange capacity (CEC) were determined according to the procedures reported by Gillman and Sumpter (1986). Dithionite-citrate-bicarbonate (DCB) extractable iron and aluminum oxides were determined according to Jackson et al. (1986). Soil texture (sand, silt, and clay) was determined by pipette method (Gee and Bauder, 1986). Fulvic acid (HA) and humic acid (FA) were extracted by using 0.1 M Na$_4$P$_2$O$_7$ and 0.1 M NaOH at pH 13 as describe by Aguer et al. (2002). Soil specific surface area (SSA) was determined by a surface area analyzer (Gemini Y, Micromeritics, USA). The soil properties are summarized in Table 1.

2.3. Bach adsorption experiments and sample preparation

Bach adsorption experiments were conducted in 50-mL polypropylene (PP) centrifuge tubes in triplicate. All tubes were kept in an orbital shaker at a speed of 150 rpm and at a temperature of 25 ± 2 °C. To