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Experimental and molecular dynamic simulation study of perfluorooctane sulfonate adsorption on soil and sediment components

Ruiming Zhang, Wei Yan, Chuanyong Jing[*]

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E–mail: zhangruim07@163.com

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ABSTRACT

Soil and sediment play a crucial role in the fate and transport of perfluorooctane sulfonate (PFOS) in the environment. However, the molecular mechanisms of major soil/sediment components on PFOS adsorption remain unclear. This study experimentally isolated three major components in soil/sediment: humin/kerogen, humic/fulvic acid (HA/FA), and inorganic component after removing organics, and explored their contributions to PFOS adsorption using batch adsorption experiments and molecular dynamic simulations. The results suggest that the humin/kerogen component dominated the PFOS adsorption due to its aliphatic features where hydrophobic effect and phase transfer are the primary adsorption mechanism. Compared with the humin/kerogen, the HA/FA component contributed less to the PFOS adsorption because of its hydrophilic and polar characteristics. The electrostatic repulsion between the polar groups of HA/FA and PFOS anions was attributable to the reduced PFOS adsorption. When the soil organic matter was extracted, the inorganic component also plays a non-negligible role because PFOS molecules might form surface complexes on SiO_2 surface. The findings obtained in this study illustrate the contribution of organic matters in soils and sediments to PFOS adsorption and provided new perspective to understanding the adsorption process of PFOS on micro-interface in the environment.

Introduction

Perfluorooctane sulfonate (PFOS), consisting of a sulfonate group and 8-carbon C–F tails (Appendix A Fig. S1), has been identified as an emerging contaminant of global concern (Nakayama et al., 2010; Zhang et al., 2013). Worldwide distribution and contamination of PFOS pose great threat not only to the environment, but also to the animal and human health (Beach et al., 2006; Betts, 2008; Nelson et al., 2010). PFOS can bind to peroxisome proliferator-activated receptors which are associated with carcinogenesis, affect growth and development, and even disrupt the hormone and immune systems (Betts, 2007). Hence, a long-term and high exposure to PFOS can lead to severe symptoms such as endocrine disruption and cancer (Betts, 2007), physical development delay (Gump et al., 2011), and neonatal mortality (Kannan et al., 2010; Luebker et al., 2005).

The fate and transport of PFOS in the environment greatly depend on its adsorption on soil and sediment (Chen et al., 2012;

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[*] *Corresponding author*. E-mail: cyjing@rcees.ac.cn (Chuanyong Jing).

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Higgins and Luthy, 2006; Johnson et al., 2007; Ochoa-Herrera and Sierra-Alvarez, 2008). Soil and sediment are complicated matrices and generally composed of multiple complex components, which could be operationally defined as humin/kerogen, humic/fulvic acid (HA/FA), and inorganic component after chemical treatment (Mikutta et al., 2005). These components may impact PFOS adsorption with different mechanisms. However, soil and sediment are usually deemed as a single entity to investigate PFOS adsorption using kinetics and isotherm experiments (Higgins and Luthy, 2006, 2007; You et al., 2010). The lack of molecular-level knowledge of PFOS interaction with different soil/sediment components may limit our understanding and prediction of the PFOS behavior in the environment.

Molecular dynamic (MD) simulation can provide molecular level morphological and structural details on the solid–aqueous interface and has been used to study the surface adsorption and transport of pollutants. For example, MD simulation was successfully applied to study the mechanism of benzene uptake in the interlayer of montmorillonite with alkyl-methylammonium as organic substances (Zhao and Burns, 2012, 2013). Their MD results well explained the molecular mechanisms of experimental observations that the uptake capacity of organic pollutants increased with the increasing total organic content in organoclays. In our study, MD simulation was applied, as a complimentary technique to experimental observations, to investigate the role of soil/sediment components on PFOS adsorption.

The objective of our work was to explore the molecular mechanisms of PFOS adsorption on soil/sediment components. The three major components, i.e., humin/kerogen, HA/FA, and inorganic component, were isolated using extraction methods and their effects were studied with PFOS adsorption experiments. MD simulations were employed to study the interaction between PFOS and surfaces at the molecular level. Our experimental and model simulation results should improve the understanding of the solid–aqueous partition mechanisms of PFOS on environmental matrices.

1. Materials and methods

1.1. Materials

Five soil samples and one sediment sample with a wide range of total organic carbon (TOC) content (1.0%–8.3%) were collected. The soil samples were collected on the surface horizon (0–20 cm) from Liaoning Province (SY, LN), Heilongjiang Province (HL) and Beijing (BJ1, BJ2) of China, respectively. The sediment (SE) was sampled from Qinghe River in Beijing. The samples were air-dried, sieved (<2 mm) and stored at room temperature. The sample properties are given in Appendix A Table S1. Two treatment methods with NaOH and H_2O_2 were carried on to remove HA/FA and organic substances including HA/FA and humin/kerogen, respectively (Liu et al., 2008; Shi et al., 2010).

For the NaOH treatment method, HA/FA was removed, and the remaining fractions were humin/kerogen substances and inorganic component. The soil/sediment and 0.5 mol/L NaOH were mixed at a solid/solution ratio of 1:50 for at least 8 times until the solution was colorless, and each time for 6 hr (Shi et al., 2010).

For the H_2O_2 treatment method, HA/FA and humin/kerogen substances were removed, and the remaining fractions in residual were mainly inorganic component such as SiO_2 and metal oxides (Mikutta et al., 2005). Samples were mixed with 10% H_2O_2 solution at a solid/solution ratio of 1:50 for at least 3 times, each time for 6 hr (Mikutta et al., 2005). After treatment, the TOC in the treated sample was measured, and the results are shown in Appendix A Table S1. Moreover, the TOC was consisted of 35.2%–75.9% HA/FA and 24.1%–64.8% humin/kerogen substances as shown in Appendix A Fig. S2.

1.2. Batch sorption

In kinetics experiments, an initial concentration of 200 μg/L PFOS solution in 0.01 mol/L NaCl was added to a 100 mL polypropylene bottle, adjusting with HCl and NaOH to keep the pH at 7.0 ± 0.1. At designated time intervals in a period of 7 days, a 1.5 mL sample was collected and centrifuged at 10,000 r/min for 20 min, and then PFOS in the supernatant was analyzed.

Adsorption isotherm experiments were carried out in 15 mL corning polypropylene tubes. Duplicate suspension samples contain 15 g/L of the raw/treated soil/sediment samples and 10–500 μg/L PFOS solution under the same experimental conditions to kinetics. After mixing on a rotator for 7 days, the suspension was centrifuged at 10,000 r/min for 20 min. Then, the supernatant was collected for PFOS analysis.

1.3. PFOS analysis

Dissolved PFOS concentrations were measured using an Agilent 1290 infinity liquid chromatography (Agilent Technologies, Palo Alto, CA, USA) coupled with an Agilent 6540 Ultra High Definition Q-TOF mass spectroscopy (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was performed on an XBridge™ C-18 column (2.1 × 100 mm, 3.5 μm; Waters Corp., Dublin, Ireland) with an injection of 10 μL samples. The mobile phase consisted of 10 mmol/L ammonium acetate and acetonitrile at a molar ratio of 30:70. The operation parameters were as follows: capillary voltage 3500 V in negative; nebulizer pressure 35 psig; drying gas 10 L/min; gas temperature 350 °C; sheath gas flow 11 L/min; sheath gas temperature 250 °C; nozzle voltage 1000 V in negative ion mode; and the fragmentor voltage 60 V. The data was processed with MassHunter software (Agilent Technologies). The detection and quantification limit of PFOS were 0.3 μg/L and 1.0 μg/L, respectively. The blanks without adsorbent showed that the total PFOS loss on the centrifuge tube wall was less than 3.6% of the initial concentration. Therefore, the uptake of PFOS by solids was calculated using the mass balance.

1.4. Model rationale

In MD simulation, simple organic molecules are often used to stand for complicated natural organic matter. For example, gallic acid, protocatechuic acid, 4-hydroxybenzoic acid (Giannakopoulos et al., 2006),tetramer undecanoid acid (Aquino et al., 2011), and benzoic acid (Sun et al., 2013) have been applied to simulate humic acid and dissolved organic matter.

The organic substances in soil/sediment are consisted of various components with different structures and functional groups. In these components, HA/FA and humin/kerogen are two general constituents. HA/FA contains much polar organic carbon with polar functional groups, whereas humin/kerogen are enriched in condensed structures and lead to higher sorption affinity to nonpolar solutes (Kang and Xing, 2005; Luo et al., 2008; Wang et al., 2011). Meanwhile, humin/kerogen are more aliphatic and less polar than HA/FA because humin/kerogen contains mainly aliphatic and aromatic carbon with