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Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: Influence of solution pH and [Ca^{2+}]

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Sorption of perfluorooctane sulfonate (PFOS) to oil and oil-derived black carbon (BC) from solutions varying in pH and [Ca^{2+}] was investigated. Oil is a strong sorbent for PFOS, together with the independence of oil–water distribution coefficient (K_{oil}) on solution parameters (pH values and [Ca^{2+}]), suggesting that hydrophobic interactions of the hydrophobic moieties of PFOS with oil played a dominant role. BC sorption for PFOS is not stronger or more nonlinear than other natural organic carbon from solution in the case of 0.5 mM [Ca^{2+}] and pH 5.05, indicating that specific adsorption sites on BC were probably not fit for PFOS. However, both sorption capacity and nonlinearity of PFOS increased obviously with decreasing solution pH and increasing [Ca^{2+}], resulting in the potential importance of BC at environmentally low PFOS level, from solution at high [Ca^{2+}] or low pH. The role of BC in PFOS sorption was significantly influenced by environmental conditions and solute aqueous concentrations.

1. Introduction

Perfluorooctane sulfonate (PFOS), an emerging contaminant, has received a great deal of attention in recent years for its endocrine disrupting effect and multiple toxicities such as hepatotoxicity, immunotoxicity as well as reproductive and developmental effects (Key et al., 1998; Beach et al., 2006). PFOS and its derivatives have been widely used as a coating material on paper, packaging, and textile products as they repel both water and oil (Kissa, 1994). Their ability to create stable foams and stability even at high temperature also allow them to be used as foams for combating hydrocarbon fuel fires, in particular, fires associated with fuel spills (Moody and Field, 2000; Brooke et al., 2004). Significant concentrations of fluorinated surfactants have been found in water near fire-fighting training sites as well as in emergency situations (Moody and Field, 1999). Recently, it was shown that New York State personnel who responded to the World Trade Center disaster had elevated levels of perfluorochemicals including PFOS in their plasma (Tao et al., 2008). It suggests that foams for extinguishing fires contribute significant amounts of PFOS to the environment and PFOS will often occur with fuel oil in water, thereby determining the extent to which oil will affect the transport and fate of PFOS in the environment is important. Quantifying the partitioning of PFOS between oil and water is inherently necessary to model the fate of PFOS. In addition, hydrocarbon fuel fires are often accompanied by the production of black carbon (BC) which has commonly been regarded as a strong and nonlinear adsorbent for nonionic organic contaminants (Fernandes and Brooks, 2003; Cornelissen et al., 2005). Nevertheless, current knowledge on the sorption of PFOS, as an anionic contaminant, on the oil-derived BC is scarce. Even though the aqueous phase is a major sink for PFOS (Nakata et al., 2006), sorption is still important in determining its ultimate fate and distribution because sedimentation was cited as one of only two major removal mechanisms on the global scale (Pervedouros et al., 2006). A detailed understanding of the transport and fate of fluorinated surfactants for foams must include elucidation of the sorptive interactions of these molecules with oil and BC.

Previous work (Higgins and Luthy, 2006; Johnson et al., 2007) found that both hydrophobic and electrostatic effects influenced the sorption of anionic fluorinated surfactants such as PFOS, and organic carbon content of the sorbent as well as solution pH and [Ca^{2+}] significantly influenced PFOS sorption. Recently it was observed that inorganic fraction and redox conditions in the sorbents were also parameters affecting PFOS sorption (Becker et al., 2008; Ferrey et al., 2009). Given the hydrophobicity of oil and the negative charges on BC surface (Qiu et al., 2008), it is suggested that oil is an important sorption phase for PFOS while BC sorption may be not stronger than other forms of natural organic carbon because of the electrostatic repulsion between anionic PFOS and BC.

The aim of this study was to examine sorption characteristics of PFOS on oil and BC as influenced by environmental factors

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including solution pH and [Ca^{2+}]. Meanwhile, using PFOS (an anionic organic contaminant) as the sorbate, our understanding of the BC sorption of this class of anionic contaminants should increase.

2. Materials and methods

2.1. Materials

PFOS ($\geqslant$98% purity) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Calcium chloride, sodium hydroxide, hydrochloric acid, and ammonium acetate were purchased from Kemiou Chemical Reagent Company (Tianjing, China). Methanol and acetonitrile were obtained from TEDIA, USA.

2.2. Sorbents

Diesel particulate standard referent material (SRM 2975) developed by the National Institute of Standards and Technology (NIST) was chosen as a model BC derived from diesel oil. This material was used as received from NIST.

Uncontaminated soil (organic carbon content of 0.91%) sampled from a paddyfield (Panjin, China) was sieved prior to air drying and homogenized, then contaminated with a crude oil from Liaohe oilfield in Panjin, China. Oil was added drop by drop in three different amounts to soil while being stirred intensively (Chen et al., 2008). Then, the samples were shaken on a rotation shaker for 7 d. Oil concentrations were determined as follows: subsamples were frozen-dried and Soxhlet-exacted with dichloromethane for 24 h. The resulting extracts were concentrated, solvent exchanged into hexane and cleaned up using activated silica gel columns as described previously (Reddy et al., 2002). Finally, extracts of 2-μL were injected into a 280 °C splitless injector and quantified by a gas chromatograph (GC, Shimadzu, Japan) equipped with a poly (dimethylsiloxane) capillary column (Rtx-1, 30 m, 0.25 mm i.d., 0.25 μm film) and a flame ionization detector (FID, 300 °C). The GC oven was temperature programmed from 40 °C (1 min hold) to 120 °C at 30 °C min^{-1} and then from 120 °C to 280 °C at 5 °C min^{-1} (30 min hold). A method detection limit of 0.010 g kg^{-1} was estimated according to procedures described by Glaser et al. (1981). Spike recoveries of oil were 83 ± 2.9% (n = 5). Laboratory blanks of uncontaminated soil were detected below the detection limit. It is calculated from the GC that the crude oil was composed of 74.7% normal alkanes and 25.3% unresolved complex mixture (UCM) containing branched alkanes and cycloalkanes, monoaromatics and polyaromatic hydrocarbons (PAHs).

2.3. Zeta potential

The zeta potential of BC at various pH values was measured using a Zetaplus potentionmeter (Brookhaven, USA). BC sample (~0.015 g) was equilibrated in 0.01 M KNO_3 solution for 24 h and the pH of suspension was adjusted by 0.4 M HCl or 0.4 M NaOH. The zeta potentials at various pH values were measured according to Qiu and Ling (2006). The potentials decreased monotonically with pH increasing. The pH_{IEP}, at which the surface charge on BC is zero, was measured to be 2.04. The BC surface has a net positive charge at solution pH <2.04, whereas the surface has a net negative charge at solution pH >2.04.

2.4. Sorption experiment

PFOS sorption on oil-contaminated soil and BC at various pH values as well as various [Ca^{2+}] was measured by the batch equilibration technique. All sorption experiments were conducted in 15 mL poly-styrene (PS) centrifuge tubes. Duplicate sets of tubes containing appropriate amounts of oil-contaminated soil or BC as the sorbent and 15 mL background solution were spiked with various amounts of PFOS stock solution to reach initial aqueous concentrations of 2–200 μg L^{-1}. The background $CaCl_2$ was 0.5 mM, which is within the range of previously reported sorption experiments for alkylbenzene sulfonate (LAS) surfactants with $CaCl_2$ varying from 0.1 to 3.0 mM (Westall et al., 1999). The sample equilibrium pH for oil-contaminated soil and BC were 7.10 and 4.03, respectively. For pH effect, subsequent experiments were conducted with sorbents (one oil-contaminated soil (C_{oil} = 8.70 g kg^{-1}) and BC) in which the pH of the solution was varied by adding various volumes of 0.4 M HCl or 0.4 M NaOH to the 0.5 mM $CaCl_2$ solutions prior to equilibration with the sorbents, with the pH of the slurry measured at the end of the experiment. To evaluate the effects of ionic strength on sorption, additional experiments were conducted with sorbents in which the $CaCl_2$ concentrations were varied from 0.5 to 50 mM. The tubes were then tumbled end-over end at 20 ± 1 °C for 4 weeks (preliminary tests indicated that equilibrium was reached before 4 weeks). After the attainment of sorption equilibrium, each 15 mL PS tube containing oil-contaminated soil as the sorbent was centrifuged and an aqueous supernatant removed. The combination of small particle size and low solid density of BC prevent effective settling by centrifugation. Hence, a polyaluminum chloride (PACl) stock solution of 1153 mg L^{-1} as Al was prepared as flocculant by dissolving PACl powder (Lijia Chemical Co., Dalian, China) in Milli-Q water (Millipore, Billerica, MA). PACl solution (10 μL) was added to each sorption tubes in which BC as a sorbent in order to facilitate the formation of flocculated aggregates of BC particles (for details, we refer to Nguyen et al. (2004)) prior to centrifugation and the supernatant was then carefully withdrawn with a syringe. The supernatant was diluted with methanol and then transferred to an autosampler vial for liquid chromatography–mass spectrometry (LC–MS, Shimadzu, Japan) analysis. A second set of duplicate tubes containing only the aqueous phase was performed and analyzed as controls.

Recoveries of controls from PS tubes were 96 ± 9.2% (n = 8), so the sorbed amounts were calculated via the aqueous loss method.

2.5. Chemical analysis

The aqueous samples in which PFOS concentrations were lower than 1 μg L^{-1} were concentrated with solid phase extraction (SPE). Presep-C Agri SPE columns were precleaned with 10 mL methanol and then 10 mL water prior to use. Samples (20 mL) were then loaded onto the columns. The SPE columns were finally eluted with 1 mL methanol for LC–MS analyses. Aqueous samples with PFOS concentration higher than 1 μg L^{-1} and methanol extracts (10-μL injection volume) were measured by LC–MS as previously reported (Saito et al., 2003). Briefly, the aqueous samples and extracts were separated on a Zorbax XDB C-18 column (Agilent Narrow-Bore 2.1 × 150 mm, 5 μm) with a flow rate of 0.2 mL min^{-1}. The gradient mobile phase was employed: the concentration of acetonitrile in 10 mM ammonium acetate started at 35%, then increased to 45% at 2% min^{-1} for 5 min, and was then maintained until 15 min. The column temperature was maintained at 40 °C. Mass spectra were obtained using a Shimadzu 2010 A ion spray MSD, employing a negative electrospray ionization mode. The drying N_2 gas flow rate was 1.5 L min^{-1}. The selected ion monitoring mode was employed for quantification of PFOS using the monitoring ion of 499 (m/z). The detection limit defined as the concentration corresponding to a signal three times the noise level of the background was 0.40 μg L^{-1}. The qualification limit was 1 μg L^{-1}. Spike recoveries of PFOS were 103 ± 8.7% (n = 4). Laboratory blanks containing water only were detected below the detection limit.