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Adsorption of perfluoroalkyl acids by carbonaceous adsorbents: Effect of carbon surface chemistry

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ABSTRACT

Adsorption by carbonaceous sorbents is among the most feasible processes to remove perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) from drinking and ground waters. However, carbon surface chemistry, which has long been recognized essential for dictating performance of such sorbents, has never been considered for PFOS and PFOA adsorption. Thus, the role of surface chemistry was systematically investigated using sorbents with a wide range in precursor material, pore structure, and surface chemistry. Sorbent surface chemistry overwhelmed physical properties in controlling the extent of uptake. The adsorption affinity was positively correlated carbon surface basicity, suggesting that high acid neutralizing or anion exchange capacity was critical for substantial uptake of PFOS and PFOA. Carbon polarity or hydrophobicity had insignificant impact on the extent of adsorption. Synthetic polymer-based Ambersorb and activated carbon fibers were more effective than activated carbon made of natural materials in removing PFOS and PFOA from aqueous solutions.

1. Introduction

Perfluoroalkyl acids (PFAAs) and their derivatives have been used over half a century as high-performance surface-active agents in a variety of products (Kissa, 2001). However, their use and release have given rise to global distribution of PFAAs in various environmental compartments (Giesy and Kannan, 2001). Their presence in humans and wildlife poses great health and ecological risks (Ahrens, 2011; Houde et al., 2011). PFAAs in surface water are generally around low ng L^{-1} levels, but levels as high as mg L^{-1} close to point sources have been reported (Moody et al., 2003; Skutlarek et al., 2006). U.S. Environmental Protection Agency (EPA) has proposed provisional health advisory for two most prominent PFAA species: 0.2 μg L^{-1} for perfluorooctane sulfonic acid (PFOS) and 0.4 μg L^{-1} for perfluorooctanoic acid (PFOA) in drinking water (EPA, 2009). For protection of groundwater in the areas impacted by aqueous film-forming foams, which may contain PFAAs and other fluorinated surfactants, Environment Canada (2013) has proposed 50 μg L^{-1} for PFOS in its Federal Environmental Quality Guidelines. Current and upcoming regulations are among the major driving forces to investigate treatment technologies and options for PFAAs.

PFAAs are chemically and biologically stable and extremely persistent. They resist typical degradation processes in natural and engineered treatment systems (Liou et al., 2010; Sinclair and Kannan, 2006). Treatment technologies that can decompose PFAAs have been reported (Vecitis et al., 2009), but they are in early-stage development and infeasible for practical applications. Another primary concern is potential generation of degradation by-products of unknown toxicity due to incomplete reactions. In real-world treatment scenarios targeting PFAAs, adsorption by granular activated carbon (GAC) has been employed as the major process for wastewater (3M, 2004, Hartten, 2009) and drinking water treatment (Rahman et al., 2014), as well as groundwater remediation (Paterson et al., 2005). Uptake of PFAAs by activated carbon from aqueous solutions has also been investigated in laboratory-scale studies (Appleman et al., 2013; Deng et al., 2014; Ochoa-Herrera and Sierra-Alvarez, 2008; Senevirathna et al., 2010; Yu et al., 2009). However, varying performance observed in those studies and sorbent-specific parameters influencing PFAA adsorption by carbonaceous sorbents have not been explored.

PFOS and PFOA are amphiphilic molecules containing a perfluoroalkyl carbon chain and a hydrophilic head group. Because of low pK_a values, PFOS and PFOA predominantly exist as anions in environmentally relevant scenarios (pH of 5–8) (Goss, 2008; Rayne et al., 2009). Past studies on sorption by natural sorbents (e.g.,

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sediment, soil, iron oxide, clay and sand) have interpreted sorption of PFOS and PFOA mainly through hydrophobic effect and Coulombic effect (or electrostatic interactions) (Higgins and Luthy, 2006; Johnson et al., 2007). The hydrophobic effect appears to be the driving force for sorption by sediment and soil as shown by strong influence of sorbent organic carbon content. Electrostatic interactions are influenced by sorbent surface charge at a given pH, but none of the sorbent-specific parameters (e.g., anion exchange capacity or iron oxide content) has been found to correlate with the extent of PFAA sorption (Higgins and Luthy, 2006). Instead, the role of electrostatic interactions is exhibited through varying solution chemistry (e.g., solution pH, [Ca^{2+}] and ionic strength) (Higgins and Luthy, 2006; Tang et al., 2010). Other mechanisms such as repulsive forces between PFOS–PFOS molecules and hemi-micelle formation at sorbent–solution interface have been proposed (Tang et al., 2010; Yu et al., 2009).

Adsorption of organic contaminants by carbonaceous sorbents are influenced by many factors, and sorbent-specific factors including sorbent surface chemistry (e.g., elemental compositions, surface acidity and basicity, and point of zero charge) and physical properties (e.g., pore size distribution, pore volume and shape) are often examined and used for selecting proper sorbents for a specific application. Among the chemical factors, heteroatoms (e.g., O, H and N) that are interspersed within fullerene-like carbon network or carbon basal plane and in the form of various functional groups strongly influence surface chemistry. Speciation of these surface functionalities in particular oxygen-containing groups often controls the extent of uptake of organic contamination from aqueous solutions (Tascón, 2012). For instance, less hydrophobic activated carbon with higher oxygen and nitrogen contents (Li et al., 2002), or activated carbon with higher surface acidity imparted by surface oxygen groups have been reported less effectively in taking up organic contaminants such as trichloroethylene (Karanfil and Kilduff, 1999). For adsorption of non-fluorinated anionic surfactants, Pendleton et al. (2002) reported higher oxygen content of GAC lowered the adsorbed amount, though only three GAC was examined. Past studies also suggest the important role of physical interactions between sorbate molecules and activated carbon, in particular microporosity effect and size exclusion (Karanfil and Kilduff, 1999). Microporosity effect refers to the presence of high sorption energy sites within micropores (<20 Å, IUPAC definition) and these sites have pore sizes only slightly larger than sorbate molecules (Karanfil and Kilduff, 1999). Size exclusion refers to the phenomenon that the accessible adsorbent surface area (or pore volume) controls the access of a particular adsorbate to finer carbon pores. The importance of size exclusion is apparent when sorbates of different sizes co-exist. Previously, Yu et al. (2009) suggested the adsorption of PFOS and PFOA by activated carbon is also mainly due to hydrophobic effect and electrostatic interactions. However, no study has explored what sorbent-specific factors play a dominant role in determining the extent of PFAA adsorption by activated carbon or other types of carbonaceous sorbents, and how those factors affect relative significance of mechanisms of interactions. Understanding property–performance relationship is critical for selecting proper sorbents for removing target compounds (Li et al., 2002), and such knowledge can contribute to devising approaches to improve process efficiency or reduce competitive sorption (Karanfil and Kilduff, 1999); competitive sorption by dissolved organic matter is known to adversely affect PFAA uptake (Rahman et al., 2014).

Thus this study aimed to identify the most significant sorbent-specific factors for carbonaceous sorbents that control uptake of PFOS and PFOA. Ten sorbents with a wide range in raw materials and properties were evaluated in single-solute batch adsorption experiments. Main carbon characters controlling uptake of PFOS and PFOA were discussed on the basis of experimental observations and statistical analysis. Particularly, sorption of PFOS and PFOA by polymer-based carbonaceous sorbents has been reported for the first time.

2. Materials and methods

2.1. Chemicals

Perfluorooctanoic acid (PFOA, 96%) and sodium perfluorooctanesulfonate (Na–PFOS, ≥98.0%) were purchased from Sigma–Aldrich (Oakville, ON, Canada). Isotope-labeled sodium perfluoro-n-[1,2,3,4–$^{13}C_4$]-octanesulfonate (MPFOS) and perfluoro-n-[1,2–$^{13}C_2$] octanoic acid (MPFOA) were obtained from Wellington Laboratories (Guelph, ON, Canada) and DuPont USA (Wilmington, DE, USA), respectively. They were used as internal standards for chemical analysis of PFOS and PFOA. The information on other chemicals and reagents is included in the Electronic Supplementary Information (ESI).

2.2. Sorbents and adsorbent characterization

Ten carbonaceous sorbents (Table 1) were examined: bituminous coal-based GAC Filtrasorb 400 (F400) and powered activated carbon (PAC) BPL from Calgon Inc. (USA), wood-based GAC WVB 14×35 (WVB) and BioNuchar (BioNC) from Meadwestvaco Co. (USA), wood-based PAC AquaNuchar (AquaNC) from Meadwestvaco, coconut shell-based GAC AquaCarb 1240C (1240C) from Siemens Inc. (USA), and three activated carbon fibers (ACF15, ACF20 and ACF25) from Kynol Inc. (Japan). The ACFs are carbonaceous fibers made via pyrolysis of phenolic formaldehyde fibrous resin. The study also included Ambersorb 563 (Ambersorb, Supelco Inc. USA), which is a carbonaceous resin produced via controlled pyrolysis of a highly sulfonated styrene/divinylbenzene ion-exchange resin. Ionic functional groups on the resin are lost during carbonization process. The sorbents (except for Ambersorb) were first washed in deionized water under sonication for 3 h, and then dried at 103 °C for 24 h. Subsequently, all the granular sorbents (except for Ambersorb) were sieved and particles retained between sieves 0.85 and 1.00 mm were used for the study.

Nitrogen adsorption isotherms measured at 77 K with an Autosorb-1 analyzer (Quantachrome Co., USA) were used to determine physical characteristics. Specific surface area was computed by using a Multi-BET equation. Pore volume and distribution were generated by applying density-functional theory and Monte Carlo simulation (Lev et al., 1999; Ravikovitch et al., 1998). Point of zero charge (*PZC*), the pH at which the total net surface charge is zero, was measured by mass titration/pH equilibration method (Noh and Schwarz, 1990). Total surface acidity (NaOH uptake) and basicity (HCl uptake) were measured by titration using CO_2-free water and under nitrogen atmosphere (Boehm, 1966). Elemental compositions of the sorbents were analyzed using a PerkinElmer 2400 series elemental analyzer by a certified commercial laboratory.

2.3. Adsorption experiments

Uptake kinetics and equilibrium adsorption isotherms were determined using single-solute batch adsorption experiments. Prior to the experiments, plastic vessels made of different materials were tested for PFOS recovery, and polypropylene (PP) bottles showing negligible adsorption of PFOS at current experimental conditions were chosen as test vessels. Aqueous PFOS and PFOA concentrations (C_e) were measured using liquid chromatography tandem mass spectrometry (LC-MS/MS), and the corresponding