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Size effect of single-walled carbon nanotube on adsorption of perfluorooctanesulfonate

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HIGHLIGHTS

- PFOS adsorbed on SWCNTs with different diameters were studied with MD simulation.
- RDFs and non-bond energies were used to analyze the size effect in the adsorption.
- Size effect is highly dependent on the diameter of SWCNT.

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ABSTRACT

Perfluorooctanesulfonate (PFOS) is a typical persistent organic pollutant of more environmental concerns in the recent years. The adsorption of PFOS on the single-walled carbon nanotube (SWCNT) is studied with molecular dynamics (MD) simulation. The energy and conformational features are investigated via the statistical results from the MD trajectory. The size effect is observed from the adsorption of PFOS both on the inner and the outer surface. The non-bond interaction energy between PFOS and the inner surface of SWCNT is highly related to the diameter of nanotube. The conformation of PFOS is also changed by the sorbent surface. The PFOS molecule adsorbed on the outer surface is affected by the size of SWCNT more gently than that adsorbed in the nanotube. The aliphatic chain contributes most to the adsorption, as it locates more closely to the outer surface than the charged sulfuric group.

1. Introduction

Perfluorinated compounds (PFCs) are of great concern due to the high detection rates from variant places, besides the high persistence, bio-accumulation and toxicities (Giesy and Kannan, 2001). Within the PFC group, perfluorooctanesulfonate (PFOS) has been found in variant environmental compartments, such as soil, fresh and coastal water, sediment, even wildlife at the polar region (Giesy and Kannan, 2001; Martin et al., 2004; Skutlarek et al., 2006; Thompson et al., 2011). Owning to their wide distributions and high environmental risks, PFOS and perfluorooctane sulfonyl fluoride (PFOS-F) have been added into persistent organic pollutants (POPs) list of Stockholm Convention in 2009. However, the amphiphilicity of PFOS is very different from other well-known POPs which are of typical hydrophobicity. Therefore, PFOS shows high potential of adsorption both on organic and inorganic materials (Wang and Shih, 2011; Zhao et al., 2011).

Carbon nanotubes (CNTs) show high sorption capacities for PFOS, which have been applied in the water purification and the environmental trace analysis. Both of single-walled and multi-walled CNTs are more effective than other inorganic materials, such as active carbons, straw ash and chars in the adsorption of PFOS (Chen et al., 2011). One can conclude that single-walled carbon nanotube (SWCNT) showed higher capacity than the multi-walled due to the larger specific surface area. Besides the molecular structure of CNT, the functional groups on surface impact the sorption capacity to PFOS. The surface properties can affect the hydrophobicity of sorbent. Recently, oxidized multi-walled CNTs adsorbing PFCs has been studied. The severer oxidized had more active sites for water molecules, and therefore less surface area was accessible to PFOS or other PFCs (Li et al., 2011b). Ambient factors can affect the sorption of CNTs as well, including solvent effects, assistant approaches of sorption and so on. Recently, multi-walled CNTs have been applied to remove PFOS and PFOA in electronically assistant sorption (Li et al., 2011a). The electrochemical assistance can improve the sorption capacity of CNTs and accelerate extraction speed of PFCs from contaminated water.

The mechanism of CNTs adsorbing PFOS is very complicated, influenced by various factors. It is hard to describe the adsorption with a single model, although one can fit certain experimental results with some model to discuss the mechanism of adsorption

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(Pan and Xing, 2008). The strong affinity to different chemicals which are of variant hydrophobicity and polarity has been proved, such as hydrophobic interactions, π–π electron interactions and so on (Chen et al., 2007). The morphology of CNTs impacts the chemical and physical properties of the sorbent mostly, both of the single-walled and the multi-walled (Liu et al., 2010; Wang et al., 2010; Mazov et al., 2012). However, the size effect attributes differently to different adsorptions, which depends on the adsorbate. Besides the molecular morphology, the special adsorption site is another important factor in the adsorption, which may result in extra interactions such as hydrogen bonding (Fang and Chen, 2012). Multiple mechanisms act simultaneously, involving size effects, non-bond interactions, adsorption sites and condensations. Adsorption mechanisms of CNTs both to small molecules and macromolecules are still not clear at molecular level.

Molecular dynamics (MD) simulation can provide invaluable insight into the molecular-scale energy, structural, and dynamic information (Sanchez and Zhang, 2008). It also can be a powerful tool in studying adsorption mechanism of CNTs. The adsorption of single strained DNA on a SWCNT has been studied with MD simulation (Xiao et al., 2011). The results showed that the binding affinity of DNA was not predominantly influenced by the chirality but the curvature of SWCNT. Small molecules adsorbed in single nanotube and bundles were also simulated to demonstrate the adsorption mechanism of the SWCNT and the nanotube bundles (Vela and Huarte-Larranaga, 2011; Zolfaghari et al., 2011; Jalili et al., 2012). These studies based on MD simulation involved different kinds of adsorbates including biomolecules, gas molecules and solvents. The MD trajectory can provide valuable information at the atomic level such as atomic configurations and non-bond interactions to describe the adsorption mechanism of CNTs.

The surfactant-like properties make PFOS with amphiphilic structure different from other POPs. In this work, we studied the adsorption of PFOS on a series of SWCNTs with different sizes. A typical inner diameter of SWCNT is around 0.4–2 nm, therefore we built a series of nanotubes with diameters ranged from 0.7 to 1.6 nm. The MD simulation was employed to investigate the binding of PFOS to the surface of SWCNT. The conformational feature of PFOS molecule was also described with radical distribution functions to study the impact on of adsorption PFOS molecule in/out of SWCNTs with different diameters. And then the size effect was demonstrated with the comparison of the adsorptions of PFOS on SWCNTs with various sizes.

2. Experimental section

2.1. Molecular modeling

Adsorption of PFOS on SWCNT has been studied with MD simulation. All atom molecular models of PFOS and SWCNT have been constructed. There is no factitious constrain to the molecular models, so that the molecules are totally flexible.

PFOS composes of a perfluoroctyl chain and sulfonic acid group ($-SO_3H$). When the pH of the solution is around 7, PFOS tends to be anionic form with negative-charged group ($-SO_3^-$), as there is no hydrogen atom bonded to sulfuric atom in Fig. 1.

CNT is allotrope of carbon, with a hollow cylindrical structure. The structure of SWCNT is determined by their unique chiral numbers which are always noted as n and m. A series of zigzag type models of SWCNTs have been employed in this study, which have similar chirality: $n > 0$ and $m = 0$. All the nanotubes constructed are zigzag, so the diameter ranging from 0.7 to 1.5 nm is determined only by the n value.

As periodic boundary conditions (PBCs) are employed when building a unit cell for each MD simulation, the nanotube is infinite along axis direction. Consequently, the inner and outer spaces of SWCNT are separated completely. The adsorptions of PFOS in and out of SWCNTs were evaluated with corresponding models, respectively. For the outer space model, PFOS molecules were packed into the space randomly as well as water molecules (Fig. 1). For the model of PFOS out of SWCNT, each simulation cell contained 5 PFOS molecules. For the inner space model, only one PFOS was allocated in one SWCNT manually. Geometrical parameters of the unit cells are shown in Table 1.

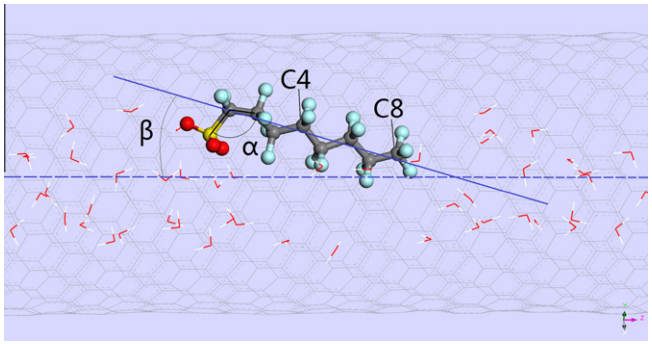

Fig. 1. PFOS in SWCNT (20, 0). Carbon is gray, fluorine is light blue, oxygen is red, and sulfur is yellow. The SWCNT and water molecules are shown in line form, and the hydrogen is white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this study, we focused on interactions between PFOS and CNTs, and therefore ignored either the functional groups on the CNT surface or the end effect CNTs. All nanotubes are assumed to have the same chirality and length, no dangling hydrogen on the surface, and no any additional chemical modification (e.g., oxidized carbon) as well.

2.2. Force field

MD simulations were employed in our study of PFOS adsorbed on SWCNTs. The Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) force field was applied to PFOS, SWCNTs and solvent molecules (Sun, 1998; Sun et al., 1998; Bunte and Sun, 2000; McQuaid et al., 2004; Grujicic et al., 2007). It is a general all-atom force field for atomistic simulation of organic and inorganic materials. It has been successfully used in studying CNTs systems to evaluate the mechanical, structural and physico-chemical properties by MD calculations (Grujicic et al., 2004; Guo et al., 2006; Mashapa and Ray, 2010; Coto et al., 2011). The functional form of the COMPASS force field has been described in the previous literatures (Sun, 1998; Sun et al., 1998; Bunte and Sun, 2000). The total potential energy (E_{pot}) contains 14 terms, describing bond stretching, angle bending, torsions, inversions, valence cross terms, and non-bond interactions. However, only non-bond energy ($E_{non\text{-}bond}$), composed of the van der Waals interaction and the electrostatic interaction, was investigated in the results because the summation of the two terms represents the non-bond interactions between PFOS and SWCNT. The others are also automatically calculated in the simulation but not included in these results.

$$E_{pot} = E_{valence} + E_{crossterm} + E_{non\text{-}bond}$$
$$E_{non\text{-}bond} = E_{vdW} + E_{Coulom} \quad (1)$$

where E_{vdW} is van der Waals interaction and E_{Coulom} is electrostatic interaction.

Atom based and Ewald summation methods were applied to calculate van der Waals and Coulombic energies, respectively. A

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