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Remediation of phenol-contaminated water by pristine and functionalized SWCNTs: Ab initio van der Waals DFT investigation

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ABSTRACT

Despite known toxic properties of phenol and its derivatives, their man-caused release into nature continues. Their importance as building blocks in polymers, pesticides, pharmaceuticals and other industrial chemicals remains a barrier for reducing their introduction into ecosystems. Hence, a considerable effort has been devoted to these organic contaminates removal from water sources. In the present work, we have employed functionalized (5, 5) carbon nanotubes (f-CNTs) for adsorption and remidiation of phenol pollutant from water. Several binding sites (including hydroxyl and phenyl groups) were considered due to their ability in π-π stacking and H-bonding interactions with phenol. The adsorption modes and energies of both water and phenol to these sites are evaluated using a general dispersion-corrected density functional (DFT-D3) method. We showed that both water and phenol molecules are weakly bound (weak physisorption) to the outer surface of pristine CNT while they can be adsorbed stronger on the functionalized CNTs. It was found that phenol bound stronger to the CNT-OH than water molecule which was due to the existence of simultaneous π-π stacking and H-bonding in the system. Also, we have prepared a brief report about the solvent effect in the adsorption nature of the more stable systems.The results show that the absorption energy sequence for the absorbing/carbon nanotube complexes in the aqueous phase is similar to the calculated absorption energy for in the gas phase, but adsorption decreased in the aqueous phase. We have also provided a succinct report about the reactivity, energy gap and polarity of the considered systems for all systems. For comparison, we evaluated the adsorption behavior for zigzag OH-CNT (8, 0).The calculation reveal that difference of the binding energy of phenol and water molecules on a zigzag is alike to the armchair CNT system. The phenol adsorption properties onto CNT-OH system in periodic and cluster SWCNT have compared and we were found that the results predicted by the CNT saturated with hydrogen can be comparable to periodic SWCNT. Furthermore, our *first-principles* calculations demonstrated the importance of dispersion corrections based on weak intermolecular interactions in designing absorbents. Our study offers molecular level understanding of the interactions between water/phenol molecule and CNTs surface and may be informative for toxicity agent adsorption and remediation from environment.

1. Introduction

Phenol and its derivatives are among the main pollutants of natural water sources. Extreme disposal to phenol may cause health effects on the brain, digestive system, eyes, heart, kidney, liver, lungs, skin and it can arise genetic damage [1]. Those mainly originate from the decomposition of pesticides, coke ovens, petroleum manufacture, paint stripping operations, etc. [2] Despite their toxicity even at p.p.b. levels, current technologies fail to remove them satisfactorily [3]. Several research studies have been focused on the removal of phenol from drinking water. These processes are based on the principles of precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange, etc. [4] Furthermore, adsorption properties of common adsorbents such as resins [5], zeolite [6], and activated carbon [7] have been evaluated for their removal. These absorbers have some disadvantages apart from their benefits. For example the adsorption efficiency of activated carbon was high but the high costs and the low amount of generation restrict its use [8]. Also the short time needed to achieve equilibrium also suggests that CNTs have very high adsorption efficiency and a potential in removal of organic

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pollution from water for example 20 h for equilibrium adsorption of phenol from water needed by activated carbon, in contrast, Peng et al. apperceived that less time (40 min) was taken for CNTs to adsorb dichlorobenzene [9]. Nanomaterials with unique mechanical and physical properties such as carbon nanotubes (CNTs) have been suggested as effective materials for removal of organic pollutants. It should be noted that the pristine CNTs after synthesis have a considerable fraction of impurities, to get rid of it can used method of chemical, physical, and a combination of both. The third kind of purification can lead to high yield and high-quality CNT products [10]. Both the outer side and inner sides of the nanotube wall can exhibite adsorbing properties, which is the reason for cylindrical hollow structure, large surface area, high aspect ratios, hydrophobic wall [1]. One example of a CNTs used for removal of organic pollutants from the environment is that of Young and Long for dioxin adsorption [11]. As another example, Fagan [12] studied single-walled CNTs (SWCNTs) interacting with TCDD by using ab initio method and showed that dioxin interacts with a pure carbon nanotube however it depends on the geometry of the molecule approximation, increasing if the tube is defective.

Jia et al. were reported that SWCNTs demonstrated higher adsorption capacity for pollution than MWCNTs because the total pore volume and specific surface area of SWCNTs were 91.9% and 114.3% higher than that for MWCNTs, respectively. This could be explained by the reality that a SWCNT has no multiple atomic layers structure similar a MWCNT, which needs more energy for the diffusion of adsorbate and thus, leads to slower adsorption velocity [8].

The major mechanisms by which CNTs adsorb organic compounds differ depending on the properties of the compound of interest (e.g., polar vs. nonpolar). The prediction of adsorption of organics on CNTs may not be straightforward, and several possible interactions between organics and CNTs have been proposed. Hydrophobic interactions, π-π stacking interactions, van der Waals forces, electrostatic interactions, and hydrogen bonding interactions might act individually or simultaneously. (12) Phenolic pollutants comprise one or more aromatic rings. Similarly, SWNTs have extended aromatic π-systems along their surface, which can provide π-π interaction binding sites for phenolic compounds. The π-π interaction is long-range, relatively weak, and includes van der Waals (vdW) forces [13]. Some studies have shown that pristine CNTs can bind molecules such as NO_2, NH_3 and, O_2 through vdW interactions in small concentrations. However, they fail to bind polar molecules like H_2O and CO and non-polarizable H_2 molecules [13].

An ideal adsorbent should be easily dispersible in water to have an effective surface area for contaminant removal. However, pristine CNTs suffer due to their hydrophobicity characteristics [14]. Surface functionalization is one strategy to improve their properties as suitable agents for water contaminant separation. Furthermore, functionalization with aromatic organic molecules and various functional groups such as hydroxyl groups can prepare new binding sites for organic pollutants [3,4]. Functionalization in covalent method depends on the chemical bonds between carbon atoms of CNTs, chemical reactions and conjugation of hydrophilic organic molecules on the surface of CNTs [15]. According to the location of the functional groups, the strategies to covalently functionalize CNTs can be classified into two main categories: defect functionalization and sidewall functionalization. The covalent functionalization of CNTs is more robust and better controllable as compared to functionalization based on non-covalent methods [16]. Functional groups commonly placed on the surface of as-prepared CNTs are carboxyl, carbonyl, and hydroxyl groups [17,18]. Carbon nanotubes are functionalized with hydroxyl and carboxylic groups by treatment with boiling nitric acid or other oxidants contain [19]. Synthesis of hydroxylated MWCNTs (MWCNT-OH) MWCNTs were firstly refluxed with 0.3 M $KMnO4$ [19]. Researchers are showed that the aryldiazonium salts can react efficiently with individual SDS-coated SWNTs in water to form aryl functionalized SWNTs [20]. Tour et al. reported that the electrochemical reduction or thermal treatment of aryl diazonium compounds with SWCNTs results in the radical involving arylation of SWCNTs [21]. They disclosed that even without electrochemical reduction, the arylation can proceed selectively with metallic SWCNTs. Briefly, the arylization of the nanotubes is done in three ways electrochemical, solvent-free and self- catalyzed [22]. The functional group content on the internal and external surfaces of CNTs can be controlled by appropriate surface treatment techniques [18]. For instance, Peng et al. [9] have successfully removed 1, 2-dichlorobenzene (1,2-DCB) from water with a 40-min equilibrium time by carbonyl-type oxygenated groups on the CNT surface. Paola et al. [23] have illustrated that modified CNT has a growth in adsorption capacity of phenol on CNT surface in comparison with the pristine CNTs. Peng and co-workers [9] have studied the adsorption of a variety of simple aromatic compounds such as phenol on a semiconducting SWCNTs using DFT calculations within the local-density approximation (LDA). They found that all selected derivatives are physisorbed mostly through the π-π interaction between the aromatic ring and those of the CNT surface. They proposed that these benzene derivatives are appropriate for non-covalent functionalization and molecule immobilization on nanotube surfaces.

On the other hand, the nanotubes composed of other chemical compositions have also been investigated. Among these boron nitride (BN) is the first candidate to replace carbon [24]. Hernandez et al. were done first principles total energy calculations to investigate the adsorption of phenol on boron nitride (BN) sheets. Their Results indicate that the binding energies of phenol is chemisorption [25].

Anota et al. were also performed DFT studies to investigate structural and electronic properties of the (5,5) BNNTs with surfaces and ends functionalized by thiol (SH) and hydroxyl (OH) groups. According to the work function the best option to construct a device is with the BNNT-OH system [26]. Perez et al. have been performed density functional theory calculations with PBE method to investigate two-dimensional hexagonal boron nitride structures functionalization with organic molecules. Results of the adsorption energies showed chemisorption in all selected configurations of cases [27].

Nonetheless, theoretical investigations based on reliable computational methods seem mandatory to explore the interactions between phenol contaminant and functionalized CNTs which comprehensive studies about this treatment are still scarce in research literature. To this end the ability of CNT as well as f-CNT in phenol and H_2O adsorption were investigated by carrying out dispersion corrected DFT calculations. The main purpose of this study is to calculate the binding energy of adsorbed molecules interacting with outer surface of CNT/f-CNTs considering different adsorption orientations. We found that CNT-OH system has the most adsorption capability and showed the highest binding energy in phenol adsorption. This functionalized CNT demonstrated about two-times stronger adsorption strength in phenol adsorption in comparison with water adsorption as competing entity. Our DFT findings are anticipated to be intuitive in providing a comprehensive outline in respect to interactions of phenolic contaminants with CNTs/f-CNTs and also can be useful as a starting point in addressing the fundamental issues that may arise about the key aspects of aromatics pollutants remediation techniques using nanostructures at nanoscale. More detailed information about the computational approaches employed in the present study and also the calculated results are exhaustively provided in the following sections.

2. Computational details

Density functional theory based calculations were carried out using the all-electron quantum chemistry software ORCA [28] version 3.0.3. We utilized generalized-gradient approximation (GGA) within the revised Perdew-Burke-Ernzerhof (revPBE) [29,30] functional for the exchange-correlation part which has been demonstrated to give reasonable results for the systems under consideration. Benchmark calculations also were performed using the DFT calculation at the