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Adsorption of acridine orange and methylene blue synthetic dyes and anthracene on single wall carbon nanotubes: A first principle approach

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ABSTRACT

Ab initio simulation based on the density-functional theory was used to evaluate the interaction between the pristine (5,5) and (8,0) Single Wall Carbon Nanotubes (SWCNT) and two synthetic dyes (Acridine Orange and Methylene Blue) as well as Anthracene molecule. The interaction between this molecules with pristine (5,5) and (8,0) SWCNT as well as one vacancy (5,5) and (8,0) SWCNT, was also investigated. Moreover, to appraise the effects on dyes + SWCNT interaction due to the SWCNT diameter, we compared the dyes + pristine SWCNT (5,5); (8,0) configurations with those of dyes + pristine SWCNT (16,0) and (25,0). The results showed that the main configurations exhibit an average binding energy 0.75 eV (or 72.36 kJ mol^{-1}), a characteristic of physical adsorption. Similarly, the SWCNT with one vacancy present lower binding energies than the SWCNT without vacancy, except the case of Methylene Blue + SWCNT. Furthermore, the dyes + SWCNT (5,5) present greater binding energies than dyes + SWCNT (8,0). Generally, significant changes in molecular structure and electronic character of SWCNT were not observed. Dyes + pristine SWCNT (5,5) and (8,0) present lower binding energies compare to respective dyes + pristine SWCNT (16,0) and (25,0). These results are very promising because they suggest that SWCNTs are suitable for real textile wastewater treatment.

1. Introduction

Many industries utilized synthetic dyes for coloring their products. Dyes are organic compounds, which can provide bright and firm color to other substances [1]. It has been estimated that about 10,000 different synthetic dyes and pigments exist and that over 7×10^5 tons of dyes are annually produced worldwide [2]. During manufacturing processes, between 10% and 60% of dyes are lost, thus generating enormous quantity of colored wastewater [3].

The dye-laden wastewater discharged from industry into the water bodies without appropriate treatment adversely affect the environment [4,5]. Synthetic dyes, for example, reduce sunlight penetration to aqueous flora, therefore, inhibiting photosynthesis process [6]. In the same way, a number of synthetic dyes are toxic to humans causing allergy, dermatitis, skin irritation or even carcinogenic [7]. Hence, treatment of wastewater contaminated with these dyes is an important environmental concern.

Adsorption has been found to be superior to other techniques for wastewater treatment, it is being considered as the most efficient method for the removal of synthetic dyes from aqueous solutions or effluents [7,8]. This technique is cheap because the treated water could be reutilized in the industrial processes and, subsequently, the adsorbent can be regenerated, stored in a dry place and reused [6]. Besides, the technique is highly efficient, easy to perform and insensitive to toxic substances [5,7].

From this perspective, different adsorbents have been used for removal of synthetic dyes from aqueous effluents [9–16]. Moreover, some recent studies [4–8] have reported the ability of Carbon Nanotubes (CNT) to act as nanoadsorbent material for wastewater treatment [6–8]. This CNT are attractive alternative for the removal of dye contaminants from aqueous effluents because they have small size as well as hollow and layered structures, large specific surface area, hydrophobic wall and easily modified surfaces [7]. CNTs have been found to be efficient adsorbents with capacities that exceed those of activated carbons [6,8]. Nevertheless, to the

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best of our knowledge, so far, no theoretical study focusing mainly on the interaction of CNT with these specific dyes is available.

Aiming to understand the dyes + SWCNTs interaction, we performed *ab initio* calculations based on density functional theory (DFT) [17,18] to evaluate physical and chemical properties.

The chosen synthetic dyes, Acridine Orange (AO) and Methylene Blue (MB), beyond the Anthracene (AN) molecule, have planar structures, which favor adsorption [19], and are fairly small molecules, which reduce the cost of computer simulation. Besides, these dyes are largely used for dyeing textiles in fabric industry [4]. These synthetic dyes have important differences among them, as regards their solubility in water and alcohol and their charge load [19]. Such differences are expected to influence their interactions with the SWCNT. Likewise, the SWCNT (5,5) and (8,0) show distinct characteristics, such as electronic character, for instance, the former is metallic while the latter is semiconductor [20]. All these differences allow a detailed analysis and comparison of how these features can interfere in the interaction of dyes – SWCNT. Lastly, in order to evaluate the effects on dyes adsorption due to SWCNT diameter, we compared the configurations dyes + pristine SWCNT (8,0), with dyes + pristine SWCNTs (16,0); (25,0).

2. Materials and methods

2.1. Theoretical calculations

The electronic and structural properties of AN molecule, AO and MB dyes interacting with pristine (5,5); (8,0); (16,0) and (25,0) SWCNT, in different configurations, were simulated using *ab initio* calculations based on density functional theory (DFT) [18] and implemented using the SIESTA code [21]. To this, twenty four different systems were studied: AN interacting with pristine SWCNT (5,5) and SWCNT(8,0); AO interacting with pristine SWCNT (5,5), (8,0); and MB interacting with pristine SWCNT (5,5), (8,0). Moreover, these molecules were placed to interact with one vacancy SWCNT (5,5), (8,0). In addition, as described in introduction, we also compared the configurations dyes + pristine SWCNT (8,0), with the dyes + pristine SWCNT (16,0); (25,0).

In order to solve self-consistently the Kohn–Sham equations, the SIESTA code uses a linear combination of pseudoatomic orbitals (LCAO) with numerical atomic basis sets, similar to that used by Sankey and Niklewski [22]. For the exchange and correlation functional, the local density approximation (LDA) was adopted, as established by the parameterisation scheme of Perdew–Zunger [23,24]. The core electrons are described by improved Troullier–Martins pseudopotentials [25] and a double-zeta plus polarization basis (DZP) [21] was used to expand the valence wave functions. The range of pseudoatomic orbitals is regulated by energy shifts, to all configurations, about 0.05 eV. To represent the orbital charge density, a cutoff of 200 Ry was adopted for the grid integration. The integrations over the first Brillouin zone were carried out with 12 Monkhorst–Pack k-points [26] along the tube axis. Total Energy minimization was performed using Feynman–Hellmann forces, including Pulay corrections to obtain the optimized atomic structures. The atoms positions were optimized using the conjugate gradient (CG) algorithm until the residual force acting on the each atom was less than 0.05 eV/Å [21].

We employed one-dimensional periodic boundary conditions along the tube axis and the supercell approximation to perform our calculations. Thus, for SWCNT (5,5), with and without vacancy, interacting with the AN molecule, we employed six unit cells corresponding to a supercell length of 14.76 Å. To AO and MB dyes we employed eighth unit cells corresponding to a supercell length of 22.16 Å. To SWCNT (8,0), (16,0) and (25,0), interacting with the AN molecule four unit cells corresponding to a supercell length of 17.00 Å were employed whereas to this same SWCNT interacting with AO and MB dyes, six unit cells corresponding to a supercell length of 25.52 Å were employed. The lateral separation was about 2–3 times the length of the supercell, to ensure that the images do not interact with each other.

The binding energies (E_b) between AN and dye molecules with SWCNT were calculated using the basis set superposition error (BSSE) [27]. This correction is necessary since the SIESTA code makes use of located basis wave functions. The use of these bases causes an error when it is intended to calculate the binding energy from a system that involves energy differences of the parts of this system. The following equation was used to correct this error:

$$E_b = -[E(SWCNT + X) - E(SWCNT + X_{ghost}) - E(SWCNT_{ghost} + X)]. \quad (1)$$

where $E(SWCNT + X)$ is the total energy of the SWCNT plus molecule X (*AN, AO or MB*). The subscript "ghost" corresponds to the additional basis wave functions centered at the position of the SWCNT or at molecule X, but without any atomic potential. The values for the minimum distances (d_b) between the dye molecules and an SWCNT were obtained from a plane tangent to the tube to the nearest atom of the dye molecules.

3. Results and discussions

3.1. Dyes and carbon nanotubes

The optimized structures of AN molecule and the dyes, AO and MB, as well as electronic levels and charge densities can be seen in Fig. 1.

The optimized structures show that all dyes exhibit a geometric planar configuration in accordance with the reference [19]. From energy levels, it can be seen that the HOMO–LUMO-differences (ΔH–L) of AN and AO-dye are greater than those of MB dyes, which play an important role in the stability of these molecules, and indicates a lower reactivity of the former dyes compare with the latter dyes.

An analysis from orbital charge density is very important to indicate the most significant sites of the dyes for subsequent interaction with the SWCNT, and to explain the dye-SWCNT interaction. In that way, from Fig. 1 one can be noted that AN molecule exhibit practically a homogeneous charge distribution, while AO dye presents mainly reactivity on the nitrogen atoms. Furthermore, MB dye exhibits a orbital charge density well distributed on nitrogen atoms and prevailing on the chlorine and sulfur atoms. A high charge concentration in some sites of dyes indicates a probability that these sites can undergo an electrophilic or nucleophilic attack.

It is known in the literature that the SWCNT (5,5) presents a metallic character while SWCNT (8,0) behaves like a semiconductor system, displaying a small difference of 0.6 eV between the valence and conduction bands [20,28]. The vacancy also plays an important role from the point of view of the reactivity of the nanotubes, so that the pristine SWCNT (5,5) and (8,0), exhibit a higher orbital charge density in the vacancy, this site being more reactive. This phenomenon occurs because there is a breaking of symmetry of the nanotubes [28]. Although, even with a vacancy, the electronic character of pristine SWCNT (5,5) and (8,0) remain unchanged. In addition, is noteworthy that both SWCNT (16,0) and (25,0) exhibit semiconductor character, with band gaps of about 0.45 eV and 0.26 eV, respectively. These results are in agreement with what has been reported, where the band gap decreases as the diameter of SWCNT increases [29].