Applied Surface Science 403 (2017) 519–524

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Adsorption of triclosan on single wall carbon nanotubes: A first principle approach

S.M. Castro[a], A.B. Araújo[b], R.F.P. Nogueira[c], S. Guerini[a,*]

[a] Departamento de Física, Universidade Federal do Maranhão, 65080-805 SãoLuís, MA, Brazil
[b] Instituto Federal do Maranhão, Campus São Luis-Centro Histórico, 65010-500 SãoLuís, MA, Brazil
[c] Departamento de Química Analítica, Instituto de Química de Araraquara, UNESP e Univ Estadual Paulista, Araraquara, SP 14801-970, Brazil

ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form 16 January 2017
Accepted 21 January 2017
Available online 24 January 2017

Keywords:
Nanotube
Triclosan
DFT
Electronic properties

ABSTRACT

The interaction of triclosan on (8,0) and (5,5) single wall carbon nanotube (SWCNT) was investigated using density functional calculations. The results show that the adsorption of triclosan modifies the electronic properties of pristine (8,0) and (5,5) SWCNT and induced changes in the electronic properties are dependent on the triclosan adsorption site. It was observed through binding energy that triclosan molecule interacts mainly via chemical process in parallel configuration to (8,0) SWCNT, while interaction via physical process was observed with both (8,0) and (5,5) SWCNT. It is proposed that these SWCNTs are a potential filter device due to reasonable physical interaction with triclosan molecule. Furthermore, this type of filter could be reusable, therefore after the filtering, the SWCNTs could be separated from triclosan molecule.

1. Introduction

Endocrine disrupting compounds (EDCs) can mimic the biological activity of natural hormones in animals endocrine systems and impose a risk to animals and humans. Triclosan is a common antimicrobial found in personal care products, such as toothpastes, soaps, fabrics, and plastics [1,2]. Therefore, residual amounts are flushed into sewage streams and enters wastewater treatment plants resulting in contamination of surface water at $\mu g\,L^{-1}$ levels, and mg kg^{-1} in sediments [3–5]. Although triclosan presents low toxicity, studies have demonstrated that triclosan can form highly toxic dioxin type derivatives under solar irradiation when present in surface water [6]. The molecular structure of triclosan contains phenolic hydroxyl group, which is electrochemically active and can be oxidized under proper conditions, so it is very important to develop a rapid, sensitive, and efficient method to remove triclosan.

Various removal methods have been used in water treatment such as adsorption on carbon nanomaterials [7,8], membrane separation [9], electrochemical or photochemical processes [10,11]. Another possibility for the removal or detection of these toxic substances in the environment is to use carbon nanostructures, which are now considered as possible filters or sensors for toxic substances. The hydrophobic surface of carbon nanostructures favors a strong interaction between organic pollutants and these nanostructures. Carbon nanostructures such as carbon nanotubes [12] present unique electronic and structural properties such as porous structure, large surface area, and thermostability, which favors the removal of organic contaminants from various aqueous systems [13].

In particular, the strong dependence of electronic properties of single wall carbon nanotubes (SWCNTs) on their atomic structure, such as nanotube diameter and chirality, provides a versatile range of applications. For example, SWCNTs could be used as gas sensors, field emission sources, polymer composite fillers, protein immobilizers, filters, electronic components. Furthermore, studies indicate that SWCNTs have high adsorption capacities of heavy metals [14], phenols [15], and organic substances [16].

Zaib et al. investigated the adsorption of bisphenol A and 17β-estradiol onto SWCNTs and acid-treated SWCNTs at various temperatures by the use of several analytical techniques such as TEM, zeta potential measurements, and Raman spectra, confirmed the acidification of SWCNTs. SWCNTs and acid-treated SWCNTs proved to be ideal to adsorb bisphenol A and 17β-estradiol [17].

In other work, Pan et. al. studied carbon nanostructures through adsorption and desorption (kinetic) experiments. The kinetic models used to analyze experimental data and obtain kinetic parameters indicated that SWCNTs have high potential for water

* Corresponding author.
E-mail address: silvete@gmail.com (S. Guerini).

http://dx.doi.org/10.1016/j.apsusc.2017.01.215
0169-4332/

treatment and purification, due to its high adsorption capacity, high adsorption rate, and strong retention of adsorbates [18].

In this study, the effects on the electronic properties of (8,0) and (5,5) SWCNT when interacting with triclosan molecule using ab initio simulations were investigated. SWCNT (8,0) and (5,5) show different electronic characteristics, the former is semiconductor while the latter is metallic. Currently the research by computer simulation is particularly important because the computational study of nanostructured systems constitutes an essential tool for scientific practice, able to make predictions of physicochemical properties of these systems and ensuring a better predicting and understanding of experimental results. Triclosan molecule have planar structure, which contributes to adsorption, and its fairly small molecule reduces the cost of computer simulation. The calculations predict that triclosan molecule interacts with nanotubes and the calculated binding energies are typical of an physical integration in most configurations considered.

2. Method of calculation

The theoretical calculations are based on first-principle spin polarized density functional theory [19] using numerical atomic orbitals as basis sets. We used the Siesta code [20], which performed full self consistent calculations solving the Kohn–Sham equations [21]. Double zeta basis set with polarization function [22] was used in all calculations. For the exchange and the correlation terms, local density approximation with the parameterization of Perdew and Wang [23] was used. The interaction between ionic cores and valence electrons is described by norm conserving pseudopotentials [24] in Kleinamn–Bylander form [25]. A cuttoff of 150 Ry for the grid integration was used to represent the charge density. The Brillouin zone is sampled with twenty three k-points special along the Γ–X directions used Monkhorst–Pack method [26].

The calculations were performed using a (8,0) and (5,5) SWCNT, which are known in the literature by presents a behaves semiconductor and metallic character [27–29]. Periodic boundary conditions and a supercell approximation were used with a lateral approximation of 20 Å between nanotube center are ensure that the SWNT plus the molecule do not interact with the periodic images.

Table 1
Binding energies (E_b), distance of binding (D_b), gap energy (E_g), and charge transfer (CT) calculated for different adsorption sites of (8,0) SWCNT, as shown in Fig. 1. The minus and plus sign in the charge transfer values indicates that triclosan molecule receives or donates electronic charge, respectively.

Configuration	E_b (eV)	D_b (Å)	E_g (eV)	CT (e^-)
(a)	1.73	2.98	0.52	+0.05
(b)	0.65	2.46	0.60	−0.14
(c)	0.28	2.11	0.60	−0.12
(d)	0.10	3.40	0.60	+0.02
(e)	0.47	3.42	0.57	−0.01

The supercells that were used have 128 C atoms to (8,0) SWCNT and 180 C atoms to (5,5) SWCNT, respectively. On the other hand, the (8,0) SWCNT have a diameter of 6.37 Å and the (5,5) SWCNT has a diameter of the 6.78 Å which implies that the two nanotubes have a very close curvature. The structural optimizations were performed using a conjugated gradient procedure, and the atomic positions of the structure are relaxed until all the force components are smaller than 0.04 eV/Å.

The binding energies E_b between nanotubes and triclosan molecule were calculated using the basis set superposition error (BSSE) [30]. This correction is done through the counterpoise method using "ghost" atoms, as the following equation:

$$E_b = -\{E_T[SWCNT + t] - E_T[SWCNT + t_{ghost}] - E_T[SWCNT_{ghost} + t]\} \quad (1)$$

where $E_T[SWCNT + t]$ is the total energy for the system with SWCNT nanotube plus triclosan molecule in different configurations. The subscript "ghost" corresponds to additional basis wave functions centered at the position of the triclosan molecule or the nanotube, but without any atomic potential.

3. Results and discussion

The interaction between the (8,0) and (5,5) SWCNT and triclosan molecule were analyzed different in configurations, such as the triclosan molecule parallel to the axis of the nanotube (Fig. 1(a)), H atoms of triclosan molecule interacting with nanotube (Fig. 1(b)),

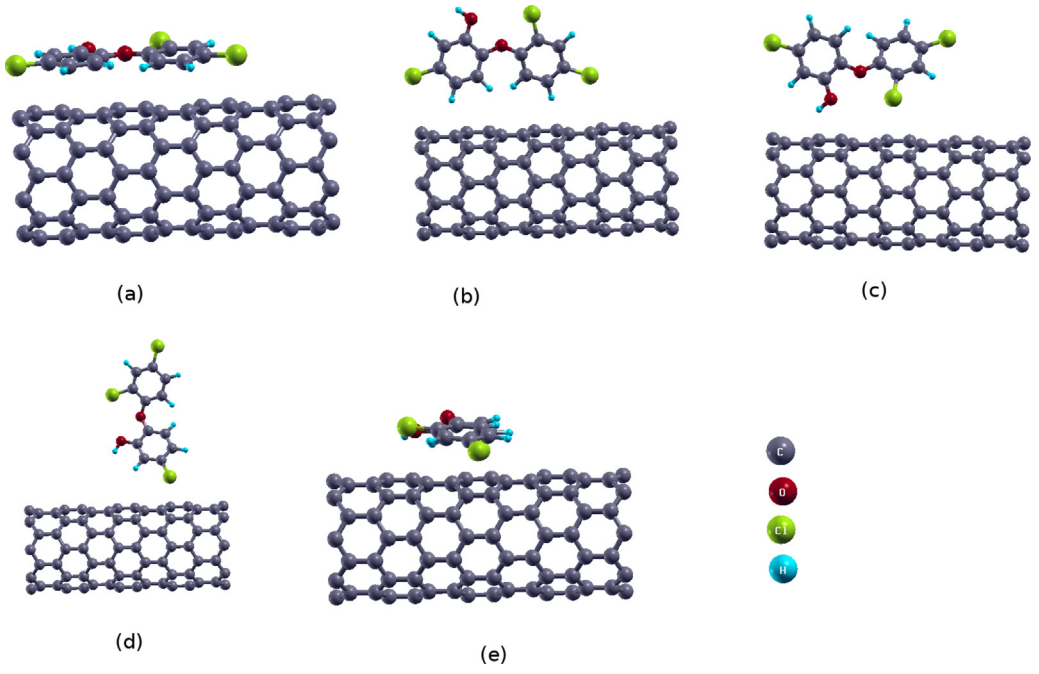

Fig. 1. Schematic view of all configurations considered for triclosan interaction with (8,0) SWCNT to references.