THE ADSORPTION OF 17β-ESTRADIOL ON CARBON NANOSTRUCTURES[1]

ADSORÇÃO DO 17 β-ESTRADIOL EM NANOESTRUTURAS DE CARBONO

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ABSTRACT

The absence of proper treatment and disposal of chemical residues can realize substance, as endocrine disruptors, on the environment, affecting mainly water quality and causing irreversible damage to fauna, flora and humans. There is a growing number of publications highlighting the toxicity of these compounds, which affect the endocrine system of the animals exposed to it. The adsorption is a promising technique for removing pollutants from wastewater, in which the carbon nanostructures have been suggested as possible adsorbent materials. In this way, the aim of this study was to evaluate the interaction of carbon nanostructures with 17β-estradiol via computer simulations in order to explore the ability of the substance adsorption by these nanostructures. The results show that the interactions occur via physical adsorption, where greater stability were obtained with the 17β-estradiol interacting with the carbon nanotube, indicating the use of these systems as possible filters in wastewater.

Keywords: nanotechnology, endocrine interferent, *ab initio* simulation, density functional theory.

RESUMO

A falta de tratamento e destinação adequada de resíduos químicos faz com que substâncias como interferentes endócrinos cheguem ao meio ambiente afetando principalmente as águas, podendo causar danos irreversíveis à fauna, flora e seres humanos. Há um número crescente de publicações destacando a toxicidade destes compostos, que afetam o sistema endócrino de espécies animais expostas. A adsorção é uma técnica promissora para a remoção de poluentes de águas residuais, na qual as nanoestruturas de carbono vêm sendo sugeridas como possíveis materiais adsorventes. Sabendo disso, o objetivo deste estudo foi avaliar a interação das nanoestruturas de carbono com o 17β-estradiol via simulações computacionais a fim de explorar a capacidade de adsorção dessa substância por essas nanoestruturas. Os resultados mostram que as interações ocorrem via adsorção física, onde a maior estabilidade foi obtida com o 17β-estradiol interagindo com o nanotubo, indicando a utilização desses sistemas como possíveis filtros em águas residuais.

Palavras-chave: *nanotecnologia, interferente endócrino, simulação ab initio, teoria do funcional da densidade.*

INTRODUCTION

The conventional treatment process used for the purification of water does not remove low molecular weight molecules, as is the case of endocrine disruptors. These substances alter the natural functioning of the endocrine system of living things, including human beings (GHISHELLI; JARDIM, 2007). Among the consequences of the excessive exposure to these compounds, it can cause cancer, alterations in the reproductive system, infertility and the formation of congenital defects (BAIRD, 2002). There is a number of artificial and synthetic hormones present in wastewater from industrial and domestic origin, affecting directly the aquatic organisms, reaching even the human population (YING et al., 2002).

The 17β-estradiol is a steroid hormone, which is contained within the class of endocrine disruptors. This hormone is produced naturally by the body, and is the main responsible for the female characteristics. Its occurrence in the aquatic environment is through improper disposal of chemicals and pharmaceuticals containing this compound or in a natural way, since the 17β-estradiol is excreted by animals and humans (ZHANG; ZHOU, 2005). Studies have shown that the presence of this molecule in the water resulted in the production of vitellogenin in male fish (PURDOM et al., 1994), causing feminization. This hormonal change in male fish can result in sterilization and, consequently, in the reduction of species.

Among several techniques used for the removal and decontamination of wastewater pollutants, the adsorption technique stands out due to the low cost and the high efficiency. The ability of adsorption depends directly on the choice of suitable material, in which the ideal adsorbent is the one that has a greater surface area (ANDAL; BUVANESWARI, 2014; BERGMANN; MACHADO, 2015). The carbon nanostructures have this feature, and therefore are considered promising adsorbent materials for removal of wastewater contaminated with toxic substances (CHOWDHURY; BALASUBRAMANIAN, 2014).

Carbon is the most abundant element in the universe, and has the ability to form allotropes of different dimensionalities, known as carbon nanomaterials (CNT). Within this class of nanomaterials are the fullerene, graphene and nanotubes. The fullerene (C_{60}) has spheroidal structure, composed of 20 hexagons and 12 pentagons (KROTO et al., 1985). Yet, the graphene is a planar and two-dimensional hexagonal network, which has the structure to a honeycomb (RAO; MAITRA; MATTE, 2012), and is known as the basis of forming other types of allotropes. Carbon nanotubes can be understood as one or more graphene sheets rolled around its axis, forming a perfect cylinder (RAO; MAITRA; MATTE, 2012). These nanomaterials have numerous applications making them ideal in nanoengineering components (DRESSELHAUS; DRESSELHAUS; AVOURIS, 2001).

Assuming this, the objective of this work is to study the interaction of the CNT with 17β-estradiol through computer simulations, to analyze this interaction in different arrangements and to explore the ability of adsorption for further development of a filter.

MATERIAL AND METHODS

The simulations were done using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code (SOLER et al., 2002), in which the electronic and structural properties of the interactions were obtained by *ab initio* calculations, based on the density functional theory (DFT) (HOHENBERG; KOHN, 1964). To describe the exchange-correlation term the Local Density Approximation (LDA) (CEPERLEY; ALDER, 1980) was adopted, all calculations used double-zeta basis plus polarization function (DZP). The interaction between the electrons of the valence level the norm-conserving pseudopotentials of Troullier-Martins (TROULLIER; MARTINS, 1991) was used. We used the fullerene (C_{60}), graphene with 144 carbon atoms, and the single-walled carbon nanotube (SWNT) (8,0) with 128 carbon atoms for the CNT. Three different conformations were examined among the 17β-estradiol and the CNT, by varying the position of the molecule in relation to each nanostructure. Binding energies were calculated using basis set superposition error (BSSE) (BOYS; BERNARDI, 1970) using the following expression:

Binding energy = (E (CNT+ 17β-Estradiol) - E (CNT) - E (17β-Estradiol))

where: *E (CNT + 17β-Estradiol)* is the total energy of the system and *E (CNT)[E (17β-estradiol)]* is the total energy of the CNT [17β-estradiol] with the whole basis of 17β-estradiol[CNT] without the explicit presence of the atoms, respectively.

RESULTS AND DISCUSSION

CNT AND 17β-ESTRADIOL ISOLATED

Initially, the molecular and electronic structures of the isolated 17β-estradiol, fullerene (C_{60}), graphene and SWNT (8,0) were studied.
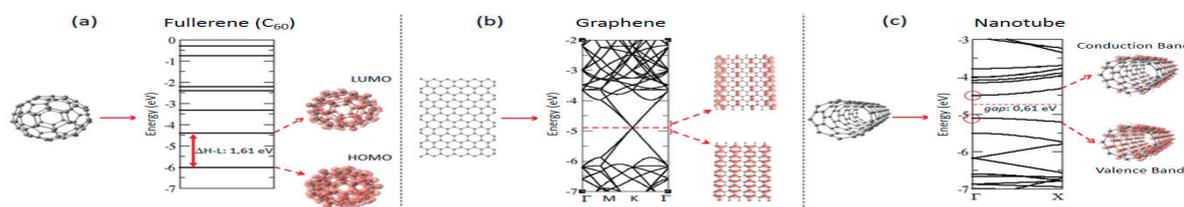
The optimized structure of the molecule of the 17β-estradiol, as well as the energy levels and their electronic structure can be seen in figure 1.

As can be seen in figure 1, the optimized molecule 17β-estradiol does not present a planar geometric configuration. The energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) is high (ΔH-L= 4 eV), providing greater stability. The concentration of charges for the molecule in the HOMO is present in benzene ring and also in the hydroxyl regions. For the LUMO, the charge are limited only to the area of the carbon ring. These results indicate the region of the molecule that is more favorable to perform approximations with other structures.

Figure 1 - Optimized structure, energy levels and charge density for the endocrine disruptors 17β-estradiol.
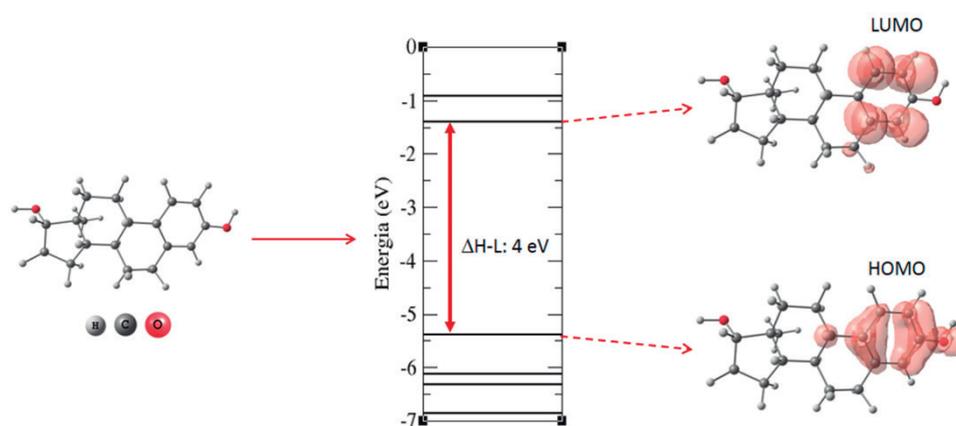
Source: author's construction.

For the CNTs studied, the optimized structures as well as their respective energy levels/bands and charge density of the molecules are shown in figure 2.

Figure 2 - Optimized structure, levels/bands of energy and charge density for:
(a) fullerene (C_{60}), (b) graphene, and (c) SWNT (8,0).

Source: author's construction.

The optimized structure of the C_{60} (Figure 2(a)) presented a difference HOMO-LUMO (ΔH-L) of 1.61 eV, this result is in agreement with the literature data (DRESSELHAUS et al., 2004; KROTO et al., 1985). In addition, it is possible to observe that there is a homogeneous distribution of charges across the surface in the region of LUMO and HOMO, indicating the apolar character of this molecule.

Observing the figure 2(b) it can be seen that optimized structure of the graphene presents an hexagonal planar structure for all its extension. The electronic band structure shows that the conduction band touches the valence band at the k-point of the Brillouin zone, characterizing the graphene as a zero band gap semiconductor, as provided for other results found in the literature (CASTRO NETO

et al., 2009; PHILIP WONG; AKINWANDE, 2011). The electronic charge density, in both analyzed regions, is delocalized all over the surface of the molecule, showing the possibility of approximations at any point.

The analysis of the SWNT (8,0) (Figure 2(c)) shows a value of 0.61 eV for the electronic band gap, which is in conformity with the data found in the literature (DRESSELHAUS et al., 2004). The analysis of the electronic charge plots for the conduction and valence bands show a uniform distribution throughout the nanostructure. This behavior is similar to that found for the fullerene and graphene CNTs.

CNT INTERACTING WITH 17β-ESTRADIOL

C_{60} + 17β-Estradiol

The optimized structures for interaction of the fullerene with 17β-estradiol and the plots of the electronic charge density for the most stable configuration can be seen in the figure 3. Interaction distances, binding energy and ΔH-L of the three arrangements are shown in table 1.

Figure 3 - Configurations optimized for the system C_{60} interacting with 17β-estradiol and (a)-(c) representation of the energy levels and plots of charge density for the most stable configuration of the system (configuration 1). The value of the isosurface plot was 0.001 e-/Bohr³.
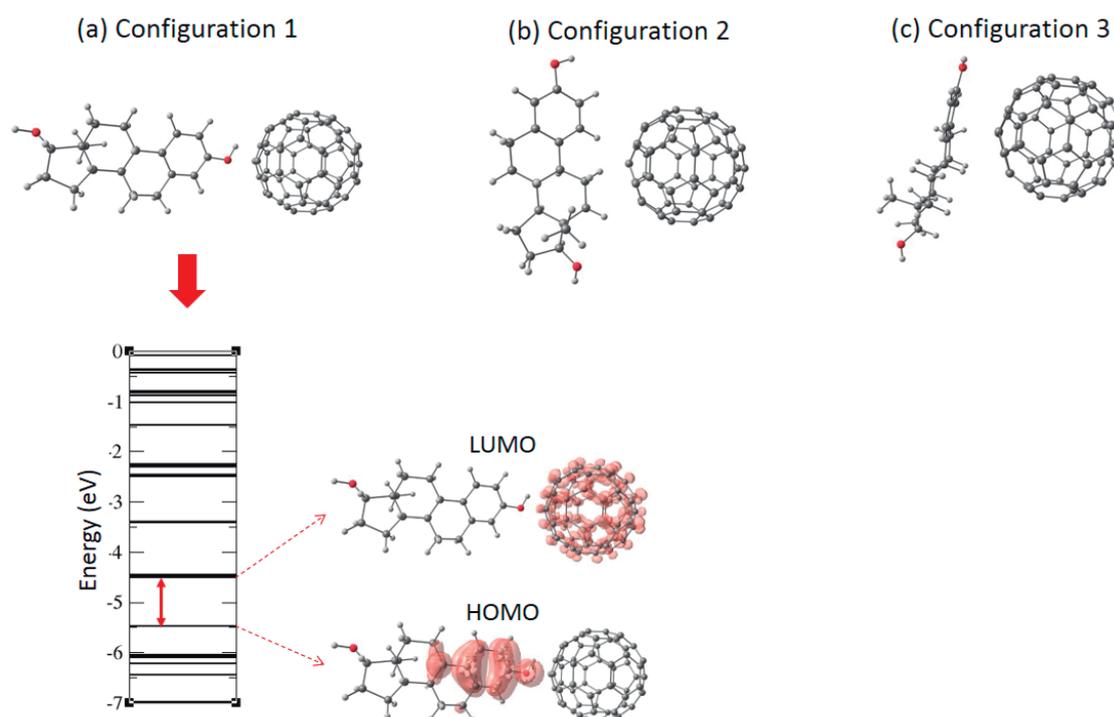
Source: author's construction.

Table 1 - Initial distance, final distance, binding energy, ΔH-L and charge transfer of the
configurations studied for the C_{60} + 17β-estradiol systems.

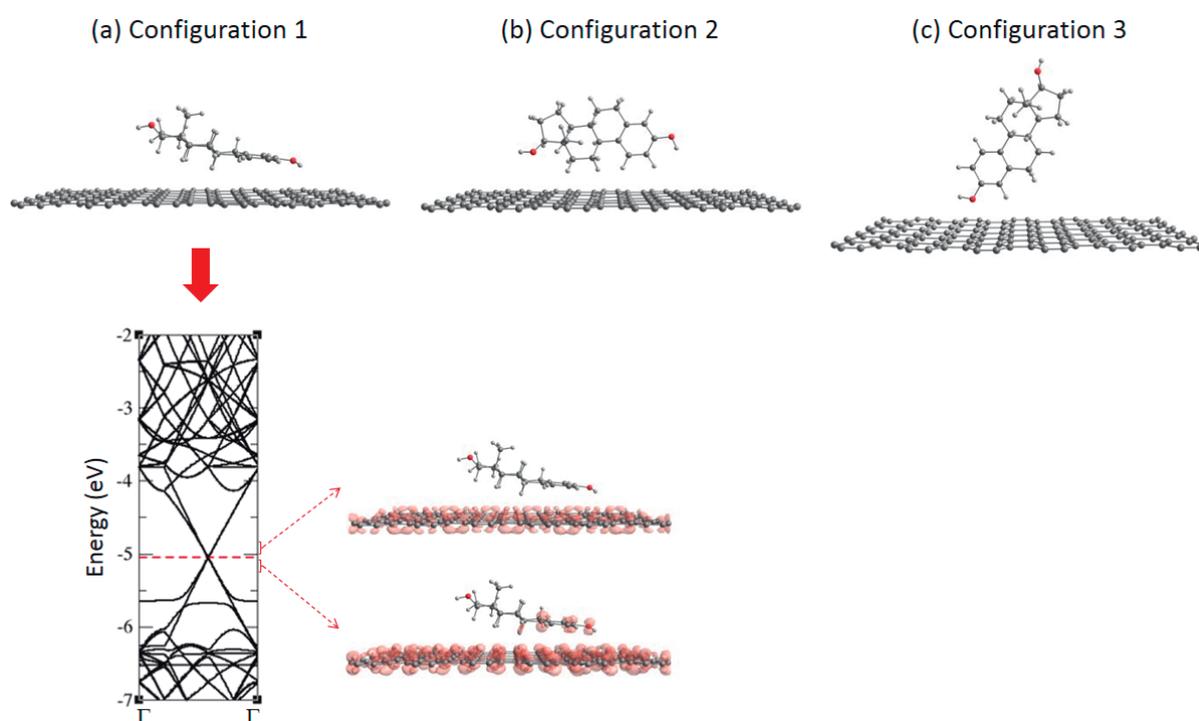| Configuration	Initial distance (Å)	Final distance (Å)	Binding energy (eV)	ΔH-L (eV)	Δq (e⁻)
1	2.23 (C-H)	2.41 (C-H)	-0.90	1.01	+0.09
2	2.25 (C-H)	2.37 (C-H)	-0.65	0.88	+0.19
3	2.20 (C-C)	2.94 (C-C)	-0.87	1.25	+0.04

Observing the table 1, we can see that the binding energies present negative values, indicating attraction between the molecules. The positive values for the charge transfer indicate electrons transfer of fullerene to the 17β-estradiol. The most stable configuration found for this complex was the configuration 1, which showed the highest binding energy in module. In addition, it was analyzed the final distances between the nearest atoms, which have not undergone significant changes when compared to the initial distances, indicating that there is no chemical bonding in the systems studied. The plot of local density for HOMO and LUMO corroborated that there is only overlapping of the energy levels of the 17β-estradiol molecule with the fullerene one. The HOMO is localized on the 17β-estradiol and the LUMO only on fullerene.

Graphene + 17β-estradiol

The optimized structures for interaction of the graphene with 17β-estradiol and the representation of the plots of the electronic charge density for the most stable configuration are shown in the figure 4. The initial and final distances of and binding energies of three conformations studied are shown in the table 2.

By the values of binding energy and final distance (Table 2), the interaction between 17β-estradiol molecule and graphene occurs via a physical adsorption process. The positive values for charge transfer indicate that there is transference of graphene to the 17β-estradiol. The configuration 1 is the most stable, similar to the fullerene case. In figure 4 it can be seen that the concentration of the electronic charges for the two regions analyzed has homogeneously distributed on the graphene surface. In addition, the electronic charge is present also in the benzene ring and OH group in the molecule of 17β-estradiol for the region analyzed below of Fermi energy.

Figure 4 - Optimized configurations for the graphene interaction with 17β-estradiol and (a)-(c) representation of the energy levels and plots of the electronic charge density for the most stable configuration of the system (configuration 1). The value of the isosurface plot was 0.001 e-/Bohr³.

(a) Configuration 1   (b) Configuration 2   (c) Configuration 3

Source: author's construction.

Table 2 - Initial distance, final distance, binding energy and charge transfer of the configurations studied for the interaction graphene + 17β-estradiol.

Configuration	Initial distance (Å)	Final distance (Å)	Binding energy (eV)	Δq (e⁻)
1	2.23 (C-H)	2.45 (C-H)	-0.87	+0.16
2	2.14 (C-H)	2.32 (C-H)	-0.47	+0,15
3	2.19 (C-O)	2.94 (C-O)	-0.58	+0,10

SWNT (8,0) + 17β-estradiol

The arrangements studied for the SWNT + 17β-estradiol as well as the electronic band structures and electronic charge density to the top of the valence band and for the bottom of the conduction band of the more stable configuration found are shown in figure 5. The initial and final distances of atoms closer, the binding energy and the gap of the three conformation studied can be seen in table 3.

Figure 5 - Configurations optimized for the SWNT (8,0) interacting with 17β-estradiol and (a)-(c) representation of the energy band and plots of charge density for the most stable configuration of the system (configuration 1). The value of the isosurface plot was 0.001 e-/Bohr³.

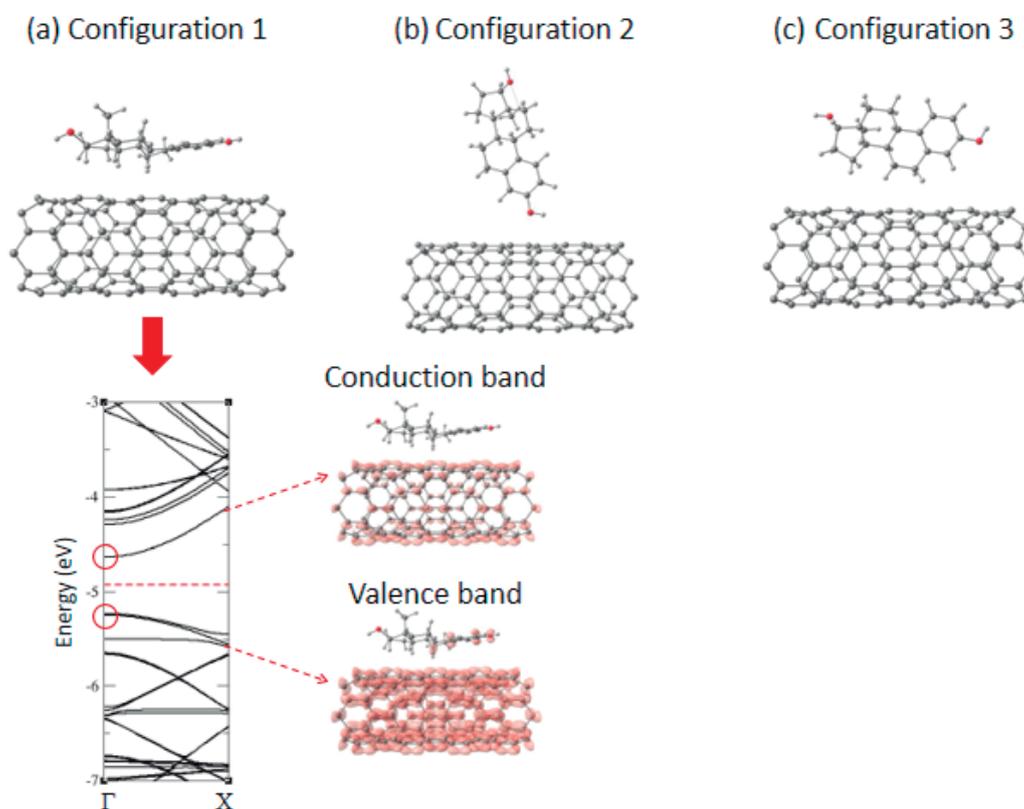
Source: author's construction.

Table 3 - Initial distance, final distance, binding energy, gap and charge transfer of the configurations studied for the interaction of the SWNT (8,0) + 17β-estradiol.

Configuration	Initial distance (Å)	Final distance (Å)	Binding energy (eV)	Gap (eV)	Δq (e⁻)
1	**2.20 (C-H)**	**2.27 (C-H)**	**-1.05**	**0.6**	**+0.15**
2	2.25 (C-O)	2.60 (C-O)	-0.61	0.6	+0.01
3	2.21 (C-H)	2.33 (C-H)	-0.77	0.6	+0.12

As can be seen in table 3, the most stable configuration is the configuration 1, as well as for fullerene and graphene. The values of binding energy are higher than the other nanostructures. Although the binding energy value is greater than 1 eV, the system does not form a chemical bond. Since there are no significant changes in the electron structure in the Fermi region of the pristine SWNT and the interaction distances are smaller than the maximum binding distance for these atoms, the interaction between the systems also occurs via a physical adsorption. As well as in the study with the fullerene and graphene, the positive values for the charge transfer indicate that there are electrons transfer of the nanotube to the 17β-estradiol.

The distance between the top of the valence band and the bottom of the conduction band (gap) was 0.6 eV for all configurations studied for the interaction of the nanotube with estradiol. Regarding to

the electronic properties of this interaction, it is possible to see, in figure 5 that both, in the conduction band and in the valence band, there is an homogeneous distribution of the charges in the SWNT, with a small concentration of charges in the region of the benzene ring and hydroxyl on the 17β-estradiol molecule for the valence band.

For all studies CNTs interacting with 17β-estradiol the adsorption occurs via physical interactions. Although the binding energy value is around 1 eV. This binding energy value is a result of the choice of the exchange and correlation potential (LDA), which is known in the literature (JAURIS et al., 2016; TOURNUS et al., 2005) to overestimate the binding energy values. This behavior was also observed by other works. There were also found binding energies in the order of 1 eV, but the system interaction occurs through physical adsorption (JAURIS et al., 2016; MACHADO et al., 2016).

The binding energy values, smaller interaction distances and more stable configurations are different for each nanostructure studied. This behaviour is due to the difference in curvature of each nanostructure and not planarity of the 17β-estradiol molecule. Greater curvature associated with a non-planar molecule implies a greater number of interactions, thus increasing the binding energy of the system. In our case, the greatest interaction occurs between the molecule and the SWNT (8.0), which is the nanostructure with the greatest curvature.

CONCLUSION

The interaction of the fullerene (C_{60}), graphene and SWNT (8,0) with the 17β-estradiol was studied through computer simulations from first principles simulations. The results indicated that for all the arrangements studied, the 17β-estradiol interacts with the CNTs via physical adsorption, since there were no significant changes in structural and electronic part of its constituents. For all studied conformations, the carbon nanostructures behave as charge donors.

The highest stability was found for the 17β-estradiol interacting with SWNT, with binding energy of -1.05 eV. In addition, the distances between the atoms closer and negative values of the binding energies reveal that there is attraction between the molecules. However, this attraction is weak, making these complexes candidates for sensing and filtering, since the intention of these systems is the subsequent removal of the adsorbed compound in the nanostructure. Therefore, this study demonstrated that the complexes studied can be considered promising for the development of a possible filter for the adsorption of effluents in wastewater.

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