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ADSORPTION OF BISPHENOL A AND DIBUTYL PHTHALATE IN GRAPHENE OXIDE: AN AB INITO STUDY[1]

ADSORÇÃO DE BISFENOL A E DIBUTILFTALATO EM ÓXIDO DE GRAFENO: UM ESTUDO AB INITO

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ABSTRACT

Endocrine disruptors encompass a wide class of substances that cause adverse effects to organisms or their progeny. In this work, we emphasize bisphenol A and dibutyl phthalate, both constituents of plastics, which are widely used in modern life. These compounds were detected in effluent treatment plants, and new technologies were required for the treatment of these substances. Adsorption is a promising technique for the treatment of effluents due to its low cost and efficiency. Highlighting here the graphene oxide, a material used as nano adsorbent due to its high surface area, stands out for this application. In this work, we evaluated the interaction of graphene oxide and the endocrine disruptors' bisphenol A and dibutyl phthalate via computer simulation, analyzing the electronic and structural characteristics of the systems isolated and adsorbed. The results show that the interactions occur in the physical adsorption regime, with the adsorption energy of approximately 1 eV for the most stable configurations, promising for the application of this system as a filter to absorb the pollutants.

Keywords: density functional theory, endocrine disruptors, nano adsorbent.

RESUMO

Os interferentes endócrinos englobam uma ampla classe de substâncias que causam efeitos adversos nos organismos ou na sua prole. Destaca-se neste trabalho o bisfenol A e dibutilftalato, ambos constituintes do plástico, que são amplamente utilizados na vida moderna. Estes compostos foram detectados sem estações de tratamento de efluentes, tornando-se necessárias novas tecnologias para o tratamento destas substâncias. A adsorção é uma técnica promissora para o tratamento de efluentes, devido ao seu baixo custo e eficiência. Destacando aqui o óxido de grafeno, um material usado como nanoadsorvente devido a sua alta área superficial. Neste trabalho, avalia-se a interação do óxido de grafeno e os interferentes endócrinos bisfenol A e dibutilftalato, via simulação computacional, analisando as características eletrônicas e estruturais dos sistemas isolado e adsorvido. Os resultados mostram que as interações ocorrem no regime de adsorção física, com energia de adsorção de aproximadamente 1 eV para as configurações mais estáveis, mostrando-se promissoras para a aplicação deste sistema como um filtro para adsorver os poluentes.

Palavras-chave: *teoria do funcional de densidade, interferentes endócrinos, nanoadsorvente.*

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INTRODUCTION

Plastic is widely used in modern life; this compound has in its chemical composition bisphenol A and dibutyl phthalate that can reach the environment. They are classified as endocrine disruptors, which are exogenous substances or mixtures that alter the function of the endocrine system causing adverse effects on an organism or its progeny (SINGH; LI, 2012; DAMSTRA et al., 2002).

Recent studies show the adverse effects of bisphenol A (BPA) on both the environment and human health. Adoamnei et al. (2018) examined BPA exposure and male reproductive function and the results suggest that exposure to BPA may be associated with a reduction in Leydig cell capacity (increased LH levels) and decreased spermatozoa in young men. Rochester, Bolden and Kwiatkowski (2018) associate early exposure of BPA to hyperactivity, and the substance has been shown to disrupt neurodevelopment in rodents and humans. Seachrist et al. (2016) in studies conducted in rats suggests that BPA can be reasonably anticipated as a human carcinogen in the breast and prostate because of its tumor-promoting properties.

Dibutyl phthalate (DBP) has mutagenic, teratogenic and carcinogenic effects (KONG et al., 2018). Yin et al. (2018) performed DBP studies evaluating early developmental neurotoxicity as well as cytotoxicity using mouse embryonic stem cells; the results suggest a potential developmental toxicity in mammals, especially for the specification of neural ectoderm. Chen et al. (2011) suggest that exposure to DBP and BaP (benzopyrene), in separate or combined doses, may adversely affect the male reproductive system through mechanisms related to oxidative stress.

Thus, Sobré et al. (2007) point out that the presence of endocrine disruptors in water is related to effluent and sewage treatment efficiency, however, many endocrine disruptors are not detected in surface water due to the lack of sewage and effluent treatment.

Therefore, the use of nano adsorbents such as graphene oxide has attracted the attention of researchers due mainly to the presence of functional groups such as carboxyl, carbonyl, epoxy and hydroxyl. These functional groups provide negative charges to the GO that can provide adsorption sites for a wide variety of adsorbents, especially those with positive charge such as heavy metal ions, synthetic dyes and other organic compounds (BERGMANN; MACHADO, 2015).

Graphene oxide has already been used in experimental works such as the one carried out by Bele, Samanidou and Deliyanni (2016). Graphene oxide was reduced to different reduction grams and then characterized to the performance of the nanomaterial for the adsorption of BPA. It was observed that the adsorption capacity was increased by increasing the degree of reduction of the GO with the maximum adsorption capacity (Qmax=94.06 mg/g), and the adsorption followed a pseudo-second-order kinetics and thermodynamic analysis indicated that the reaction is spontaneous and endothermic.

Another study, developed by Yin, Lin and Jia (2014), shows graphene oxide-functionalized magnetic nanoparticles (GO-MNPs) used for the removal of phthalate esters, and the maximum adsorption capacity of diethyl phthalate was 8.71 mg/g according to the Langmuir adsorption isotherm.

In this way, the objective of this work is to analyze the electronic properties of the interaction of graphene oxide (GO) with the endocrine interferences bisphenol A (BPA) and dibutyl phthalate (DBP) by means of an *ab initio* computational simulation, in order to be used in the removal of organic compounds present in wastewater and to help in the understanding of the adsorption process in future experimental studies.

MATERIAL AND METHODS

To evaluate the properties of the interaction of graphene oxide with the endocrine disruptors (BPA and DBP), we used the *ab initio* computational simulation methodology (first principles), which makes use of the Density Functional Theory (DFT) (1965), proposed and tested in the computation of the electronic structure of atoms, molecules and solids to deduce their chemical and physical properties. To find these properties in the DFT, however, it is necessary to make use of some approximations to allow the simulation of many bodies, such as the Born-Oppenheimer approximation, pseudopotential, supercell and base function (BEVILAQUA et al., 2010).

We used the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code (SOLER et al., 2002), in which we performed self-consistent calculations to solve the Kohn-Sham equations and to evaluate the main properties resulting from the interaction between the systems (KOHN; SHAM, 1965). We used double-base base functions plus a polarized function (DZP), the term of exchange and correlation is the LDA (local density approximation) parameterized by Perdew et al., (1992). For the representation of electronic charge space, we use a radius cut-off of 300 Ry. The atomic forces of the structures were relaxed until the residual forces were less than 0.05 eV/Å for all the atoms of the system. For the pseudopotential, we used the model proposed by Troullier and Martins (1991).

In order to calculate the binding energy, we used the BSSE (Basis Set Superposition Error) (ARTACHO et al., 2008) by equation (01).

$$E_B = - \{E[A + B] - (E[A + B_{ghost}] + E[A_{ghost} + B]\} \quad (01)$$

where, E [A + B] is the total energy of system A (graphene oxide) interacting with B (endocrine disruptors BPA or DBP);E [A + Bghost] / E [Aghost + B] is the total energy of the A / B system, taking into account all its set of functions of bases and atoms, however, considering the base set of B / A without the presence of their atoms.

RESULTS AND DISCUSSION

To analyze the electronic and structural properties of the system under study, we first analyzed the isolated structures. Figure 1 (a) shows the graphene oxide that agrees with the theoretical and experimental study of Yin, Lin and Jia (2014) and Yadav et al. (2018). This structure was successfully studied to evaluate the physical properties of 2D (two-dimensional) structures such as carbon sheets and nitride boron. However, in the work developed by Rosas et al. (2011) it was suggested that this type of structure could be applied to graphene oxide (0D) templates and analyzed with different functional groups.

The graphene oxide structure used in this work has a circular shape to avoid anisotropic effects. The incorporation of hydroxyl and carboxyl groups tended to "bend" the structure of the graphene, in addition, the edge effect was eliminated with the passivation with hydrogen atoms, resulting in a curved surface.

In figure 1 (a), we can see the structure of the graphene oxide $C_{55}H_{21}O_6$, where one COOH (carboxylic acid) and one OH (hydroxyl) functional group are localized in the border, two OH and one epoxy functional group at the basal plane.

The difference between the highest occupied molecular (HOMO) orbital and LUMO (lowest unoccupied molecular orbital) obtained for graphene oxide in the work developed by Rosas et al. (2011) was 0.42 eV, which is very similar to the obtained in our work.

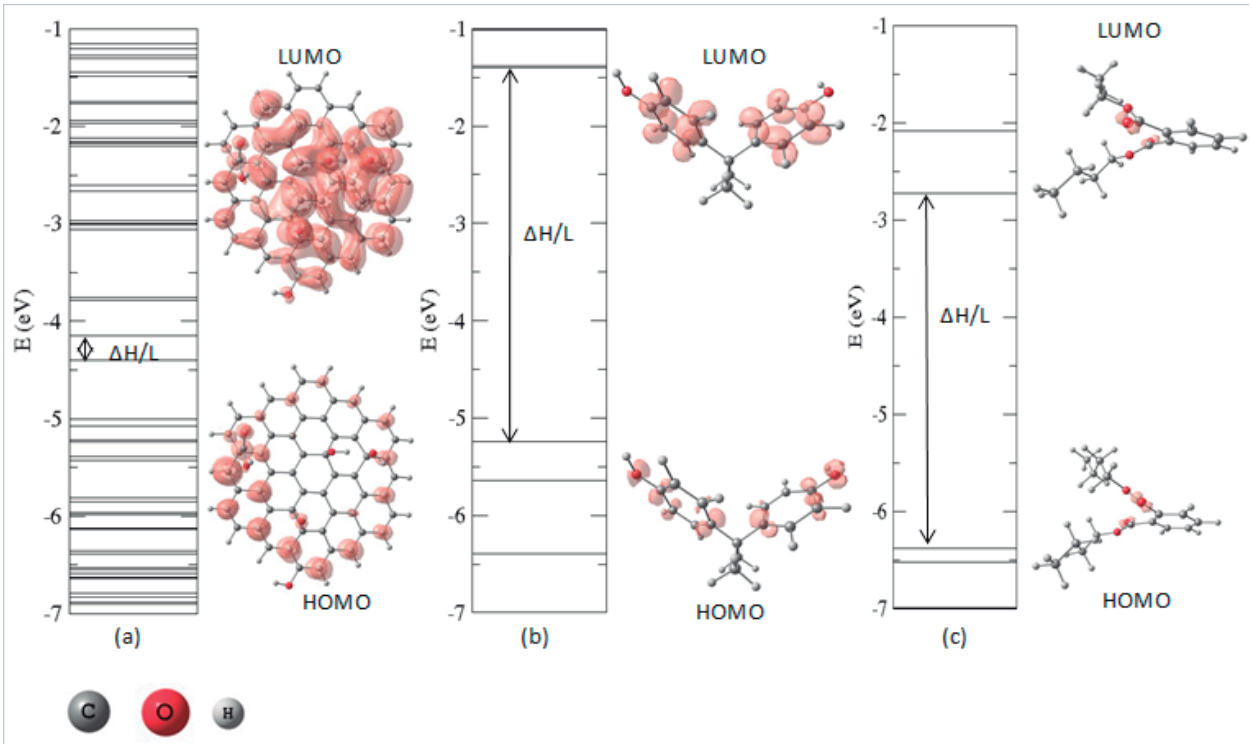
The electronic charge in the graphene oxide nanostructure for the LUMO is concentrated in the center of the structure and for the HOMO orbital it is mainly localized at the edge of the nanostructure.

The molecule of bisphenol A, chemical formula ($C_{15}H_{16}O_2$), shows a difference between the HOMO and LUMO of about 3.84 eV. The charge concentration for the LUMO is in the benzene rings of the structure and for the HOMO as well in the benzene rings and in the oxygen atoms of the molecule, as we can see in figure 1 (b).

In figure 1 (c), the dibutyl phthalate ($C_{16}H_{22}O_4$) molecule shows a difference between the HOMO and LUMO orbital of about 3.65 eV. The concentration of charges in the HOMO and LUMO are concentrated in the oxygen atoms of the molecule. These regions present a characteristic acceptor or donor of electrons and therefore become a site of great interest for the subsequent interaction with graphene oxide.

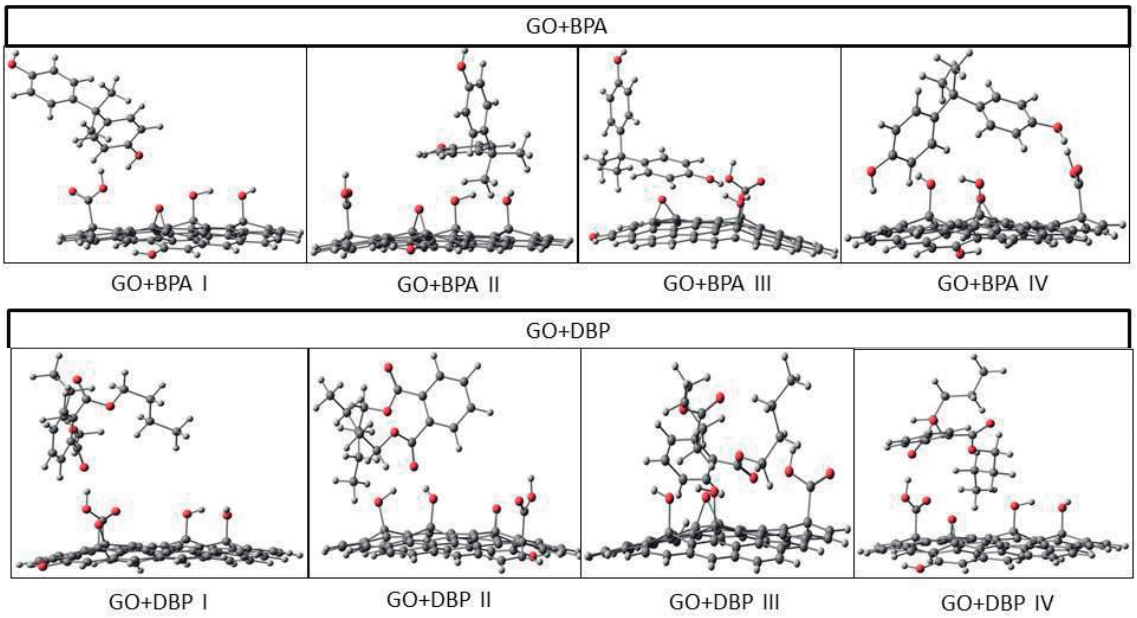
In table (1) we can observe the electronic and structural properties for each studied system, highlighting the smaller distance between atoms, binding energy, charge transfer and the difference between the HOMO and LUMO orbitals for the systems. Figure 2 shows the eight optimized configurations of each system, graphene oxide and bisphenol A and graphene oxide and dibutyl phthalate, in different positions.

Figure 1 - Energy levels, highlighting the HOMO and LUMO (a) graphene oxide (b) bisphenol A and (c) dibutyl phthalate, a contour of the plot of charge is 0.000005 eV / Å^3.



Source: author's construction.

Figure 2 - Relaxed configurations of the graphene oxide and bisphenol A (GO + BPA) and graphene oxide and dibutyl phthalate (GO + DBP), configurations I, II, III and IV.



Source: author's construction.

Table 1 - Results of the optimized structures of the isolated systems graphene oxide (GO), bisphenol A (BPA) and dibutyl phthalate (DBP), highlighting the smaller distances between D (Å) atoms of the nanostructure and molecule, respectively. Binding energy E_B (eV), calculated with equation (01), ΔQ charge transfer in electrons where the positive sign represents transfer of charge from the nanostructure to the molecule, and the negative sign represents charge transfer of the molecule for the nanostructure, and the difference between the HOMO and LUMO (ΔH / L (eV)). In bold it is highlighted the most stable configuration.

Configuration	$D_{nano\ mol}$ (Å)	E_B(eV)	Δ Q(e-)	ΔH/L (eV)
GO	-	-	-	0.44
BPA	-	-	-	3.84
DBP	-	-	-	3.65
GO+BPA I	2.38 O-H	0.41	-0.24	0.62
GO+BPA II	2.85 O-C	0.32	+0.04	0.63
GO+BPA III	1.62 O-H	1.02	+0.08	0.60
GO+BPA IV	**1.45 H-O**	**1.70**	**+0.06**	**0.64**
GO+DBP I	1.48 H-O	0.66	-0.05	0.56
GO+DBP II	1.65 H-O	0.98	+0.04	0.66
GO+DBP III	2.26 O-H	0.68	+0.02	0.59
GO+DBP IV	**1.46 H-O**	**1.03**	**-0.12**	**0.54**

Source: author's construction.

The most stable configuration for the interaction of graphene oxide and BPA was the configuration IV, with binding energy of about 1.70 eV, binding distance of 1.45 Å between the hydrogen atoms present in the graphene oxide and oxygen present in BPA molecule. The charge transfer was 0.06 electrons and occurred from the nanostructure to the BPA.

Figure 3 shows the energy levels of the isolated structures together with the interaction of BPA and graphene oxide with to the most stable configuration (IV). The difference between the HOMO and LUMO for the bisphenol A molecule is 3.84 eV, while for the graphene oxide is 0.44 eV, and for the interaction of the nanostructure and endocrine disruptors is 0.64 eV. The concentration of the electronic charge density for the HOMO and LUMO remain in the structure of graphene oxide, on carbon and oxygen atoms.

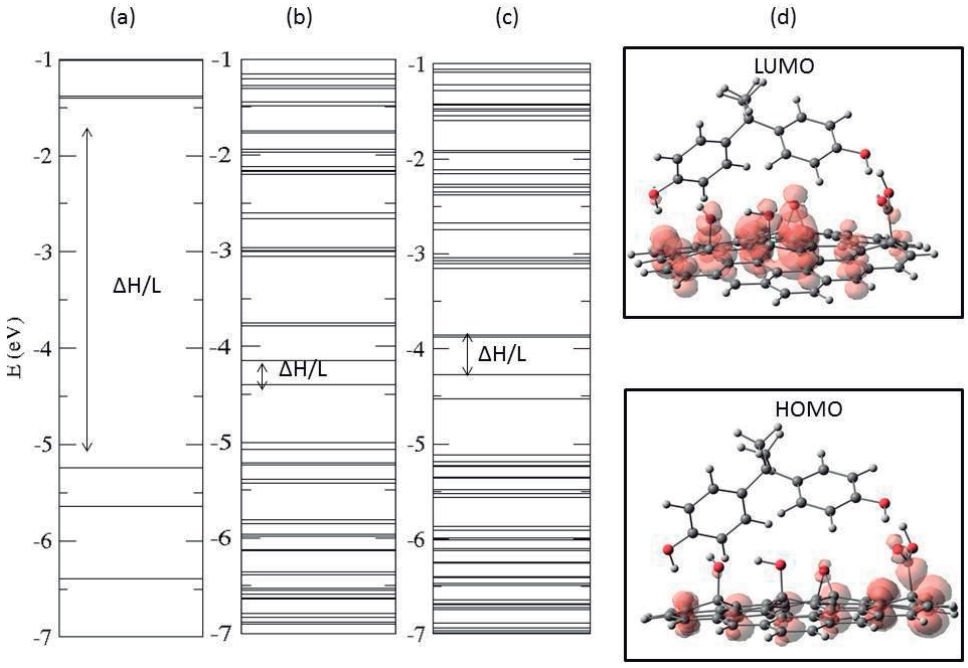
Analyzing the electronic and structural properties of the system, points out to a physical adsorption regime between BPA and graphene oxide.

For the interaction of graphene oxide and DPB, the most stable configuration was IV, with adsorption energy of 1.03 eV and the lowest distance between the atoms was 1.46 Å between the hydrogen atoms of graphene oxide and oxygen of the endocrine interfering. The charge transfer was 0.12 electrons and occurred from the DPB molecule to GO.

The energy levels of the isolated and interacting structures for the most stable configuration can be observed in figure 4. It is noted that there is an overlap of energy levels, the difference between the HOMO or LUMO orbital of the dibutyl phthalate molecule is 3.65 eV for graphene oxide is 0.44 eV and for the interaction between the nanostructure and the endocrine disruptors was 0.54 eV.

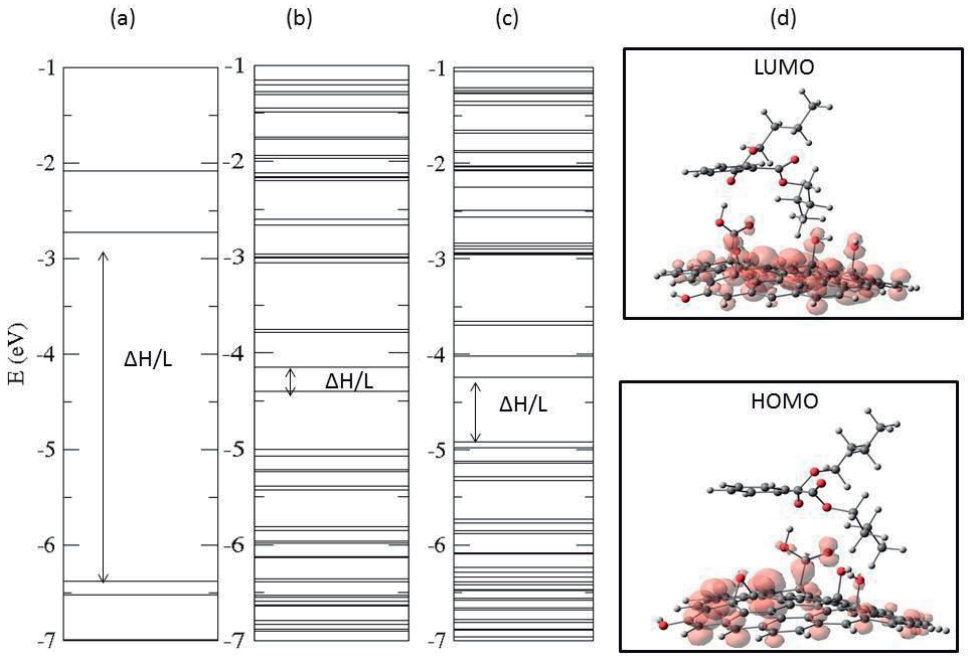
The concentration of electronic charge for the HOMO and LUMO is localized only on the structure of the graphene oxide. Observing these properties, it is suggested that the adsorption process of the system is of the physical adsorption type.

Figure 3 - Energy levels (a) BPA (b) graphene oxide and (c) more stable configuration of the interaction graphene oxide and BPA the configuration IV, contour of the plot of charge is 0.000005 eV / Å^3**.**



Source: author's construction.

Figure 4 - Energy levels (a) DBP(b) graphene oxide and (c) more stable configuration of the interaction graphene oxide and DBP configuration IV, a contour of the plot of charge is 0.000005 eV / Å^3



Source: author's construction.

Both the most stable configurations of the BPA interaction with graphene oxide and dibutyl phthalate and graphene oxide occur when we approached the BPA from carboxylic acid functional group (-COOH). This is because the chemical group presents a strong polar moment and form hydrogen bonds between the functional group and the molecule.

In addition, in both systems studied, the adsorption energy of both bisphenol A and dibutyl phthalate interacting with graphene oxide present adsorption energy around 1eV. Machado et al. (2012) in a theoretical and experimental study of the adsorption of dyes by carbon nanotubes establish a relationship between the enthalpy of the system and binding energy, where they considered that the enthalpy values in the order 80 $KJ.mol^{-1}$ (~ 0.83 eV) are representative for a physical adsorption process.

CONCLUSION

From the *ab initio* computational simulations, of the 0D graphene oxide and bisphenol A and dibutyl phthalate molecules we can observe a physical adsorption regime. The most stable configuration of the graphene oxide and bisphenol A/ dibutyl phthalate present binding energy of 1.70/1.03 eV, respectively.

The system area may have an application as filters for pollutants adsorption present in waste-water due to the physical adsorption. In this way, we consider that this study may contribute to future experimental studies in adsorption of endocrine disruptors present in the treatment plants of effluents and it may also contribute to solve public health problems.

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