Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 19, n. 3, p. 319-327, 2018.
Recebido em: 21.09.2018. Aprovado em: 11.11.2018.

ISSN 2176-462X

ADSORPTION OF ORGANIC DYES IN GRAPHENE: AN AB INITIO STUDY[1]

ADSORÇÃO DE CORANTES ORGÂNICOS EM GRAFENO: UM ESTUDO AB INITIO

Jessica Cargnelutti[2], Patricia Viera de Oliveira[3], Iuri Medeiros Jauris[4], Ivana Zanella da Silva[5] and Solange Binotto Fagan[5]

ABSTRACT

Inadequate disposal of organic dyes in aquatic effluents can cause unfavorable effects on flora and fauna by obstructing the transmittance of solar radiation, thus preventing photosynthesis by algae and causing serious damage to humans such as irritation, allergy, mutagenic and carcinogenic effects. On looking for new efficient alternatives and a low cost of adsorption of these organic compounds, we propose a study of graphene in interaction with the Methylene Blue (MB), Acridine Orange (AO) and Red Alizarin S (ARS) dyes via computational simulations evaluating their electronic and structural properties. In this study, the Density Functional Theory (DFT) was implemented in the SIESTA computational code to perform the electronic structure calculations of the systems. It has been observed that the most stable configurations are those in which graphene is in the planar position with the nanostructure. The MB dye is the one with the highest stability with a binding energy of 1.86 eV. Upon comparing this same configuration with the methodology of the carbon nanotubes we have the energy of 1.14 eV. Thus, we can conclude that graphene becomes more efficient than nanotubes in the adsorption of organic dyes.

Keywords: computational simulation, Density Functional Theory (DFT), nanostructures.

RESUMO

O descarte inadequado de corantes orgânicos em efluentes aquáticos pode causar efeitos desfavoráveis na fauna e flora ao obstruir a transmitância da radiação solar impedindo assim a realização da fotossíntese pelas algas, além de causar sérios danos aos seres humanos como irritação, alergia, efeitos mutagênicos e carcinogênicos. Em busca de novas alternativas eficientes e de baixo custo de adsorção destes compostos orgânicos propõem-se um estudo do grafeno interagindo com os corantes Azul de Metileno (MB), Laranja de Acridina (AO) e Vermelho de Alizarina S (ARS) via simulações computacionais avaliando suas propriedades eletrônicas e estruturais. Neste estudo fez-se uso da Teoria do Funcional da Densidade (DFT) implementada no código computacional SIESTA para a realização dos cálculos de estrutura eletrônica dos sistemas. Observou-se que as configurações mais estáveis são aquelas em que o grafeno está na posição planar com a nanoestrutura. O corante MB é o que apresenta maior estabilidade com uma energia de ligação de 1,86 eV, comparando esta mesma configuração com a metodologia dos nanotubos de carbono tem-se uma energia de 1,14 eV. Sendo assim, pode-se concluir que o grafeno se torna mais eficiente do que os nanotubos na adsorção de corantes orgânicos.

Palavras-chave: *simulação computacional, Teoria do Funcional da Densidade (DFT), nanoestruturas.*

---

[1] Study of Scientific Initiation - FAPERGS.

[2] Student of the Medical Physics Course - Franciscan University. E-mail: jessicacargnelutti@gmail.com

[3] Student the Nanosciences Posgraduate Program - Franciscan University. E-mail: patiolivera@yahoo.com.br

[4] Colaborator at the Nanosciences Posgraduate Program - Franciscan University. E-mail: iuri.jauris@gmail.com

[5] Advisor. Professor at the Nanosciences Posgraduate Program - Franciscan University. E-mails: solange.fagan@gmail.com; ivanazanella@gmail.com

INTRODUCTION

Effluents from firms that make extensive use of dyes, such as textiles, leather, among others, when not treated properly can reach natural waters leading to environmental damage. It is estimated that about 15% of the world's production of dyes is lost to the environment during its industrialization process (GUARATINI; ZANONI, 2000).

If a considerable amount of dye is released into aquatic effluents, it may lead to a change in the color of the rivers, causing a change in pH and conductivity of the medium (ZANONI; CARNEIRO, 2001). Contamination of rivers and lakes with these compounds can cause unfavorable effects on aquatic life by obstructing light and preventing photosynthesis (CARDOSO et al., 2012).

For human health it can cause allergies, itchy skin or wounds, allergic reactions in the eyes and irritation of the mucous membrane and respiratory tract. In extreme cases, it can induce mutation and cancer (CARITÁ; MARIN-MORALES, 2008). Therefore, the treatment of contaminated water with organic dye is a very important environmental concern.

The most efficient method for the removal of synthetic dye from aqueous effluents is the adsorption procedure (ROYER et al., 2010). The adsorption capacity of an adsorbent is mainly determined by its texture (surface area and porosity). For this reason, among the wide range of adsorbent materials, activated carbon is the most used. However, it is not very effective in the removal of dye, because it is highly soluble. In addition, adsorption with activated carbon represents a high investment due to the difficulty of desorption (KERMER; RICHTER, 1995).

In the search for new adsorbent materials and a lower cost there is graphene (G), which is formed by the few hexagonal layers that form the graphite. The organic properties and the large surface area are some of the most interesting characteristics for the adsorption of organic functional groups (ZANELLA et al., 2008).

An experimental study developed by Liu et al. (2012) analyzed the graphene prepared using the Hummers method to remove the methylene blue dye, the adsorption isotherm followed the Langmuir model and the maximum 293K adsorption capacity was 153, 85 mg/g, and the kinetic adsorption study conforms to the pseudo-second-order model and indicated that the process is endothermic and spontaneous. The results obtained in this study show that graphene is a good nano-adsorbent for the removal of methylene blue.

However, the methylene blue (MB), acridine orange (AO) and alizarin red (ARS) dyes are interesting for computational simulation, since they have planar structures, and are reasonably small molecules (20 to 30 atoms) which make the computational cost reasonable.

In the work, looking for new efficient and low-cost alternatives for adsorption of these organic compounds, the interaction of the MB, AO and ARS dyes with G are evaluated, and the previous results with the same molecules interacting with carbon nanotubes (JAURIS et al., 2012) are compared.

MATERIAL AND METHODS

The electronic and structural properties of the dyes MB, AO and ARS interacting with graphene were studied by means of the DFT Density Function Theory (KOHN; SHAM, 1965) implemented in the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) (SOLER et al., 2002). For the approximation to the exchange and correlation potential, the Local Density Approximation (LDA), parameterized by Perdew and Zunger (1981) was used. The (TROULLIER; MARTINS, 1991) pseudopotential was used to describe the interaction between valence electrons. The pseudo atomic orbitals were utilized by means of double zeta bases plus polarization (DZP) functions (SOLER et al, 2002).

To calculate the adsorption energy (E_{ads}) the following equation was used:

$$E_{ads} = - \{E(A + B) - E(A) - E(B)\} \quad (1)$$

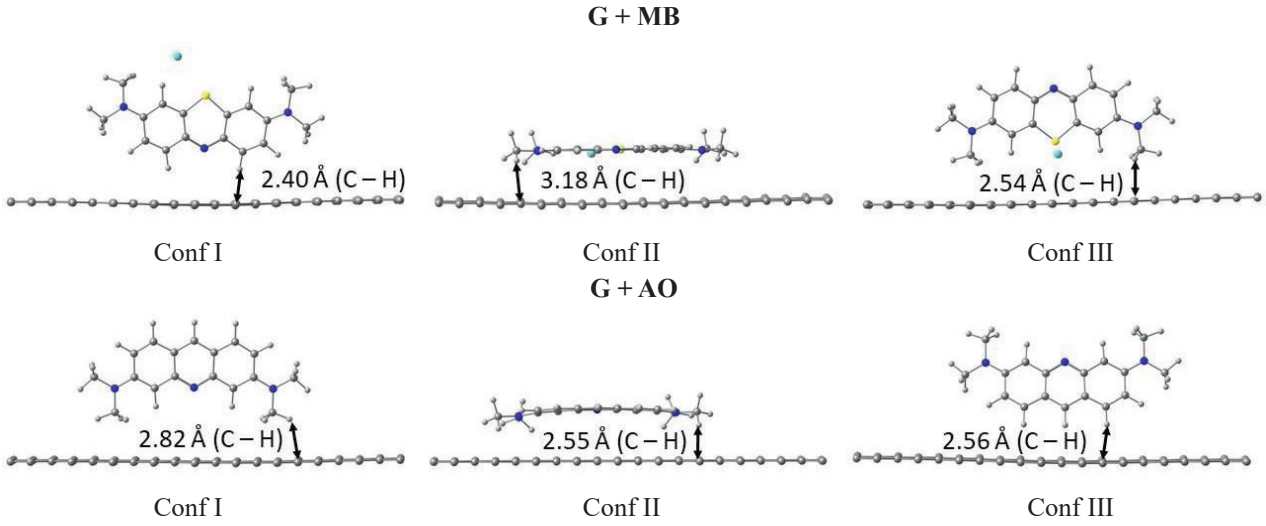
with E (A + B) the total energy of the system, where A (dye) and B (graphene), E (A) is the total energy of the isolated dye, and E (B) is the total energy of the graphene isolated.

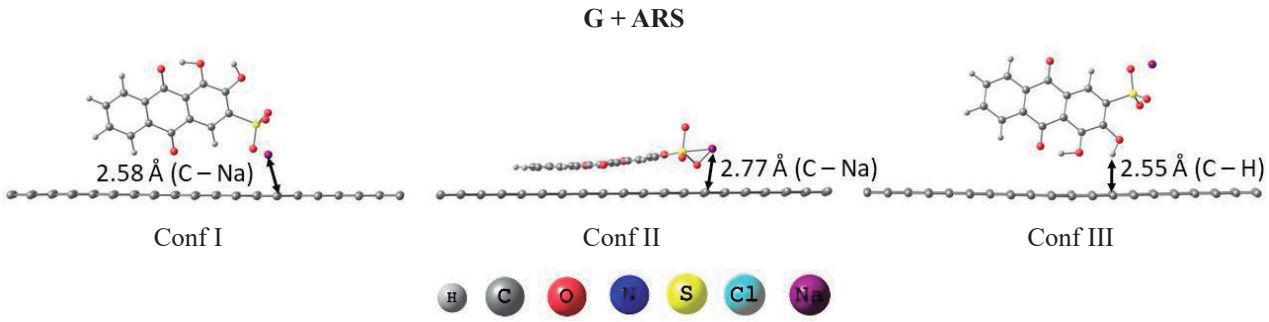
RESULTS

In order to analyze the electronic and structural properties of the dyes interacting with graphene, three different configurations were performed for each molecule and the initial distance for each configuration was 2.5 Å between the nanostructure and the molecule.

The final configurations of the interaction of graphene with the methylene blue, acridine orange and, alizarin red dyes are shown in figure 1, below.

Figure 1 - Final configurations of graphene interacting with the methylene blue, acridine orange and alizarin red dyes.





Source: author's construction.

The table 1 shows the electronic properties of the graphene interacting with the MB, AO, and ARS dyes, indicating the smallest distance between nanostructure and molecules, and adsorption energy calculated according to equation 1.

Table 1 - Results of the interaction of graphene with the dyes MB, AO and ARS, where d is the smallest distance between the dye atoms with graphene, E_{ads} is the adsorption energy, ΔQ is the charge a transfer (positive sign indicates transfer of charge from graphene to the molecule). In bold are the most stable configurations of systems.

Configuration	d (Å)	E_{ADS} (eV)	ΔQ (e-)
G + MB I	2.4 (C - H)	0.49	0.05
G + MB II	**3.18 (C - H)**	**1.86**	**0.08**
G + MB III	2.54 (C - H)	0.43	0.02
G + AO I	2.82 (C - H)	0.52	0.02
G + AO II	**2.55 (C - H)**	**1.42**	**0.09**
G + AO III	2.56 (C - H)	0.41	0.04
G + ARS I	2.58 (C - Na)	0.94	0.18
G + ARS II	**2.77 (C - Na)**	**1.57**	**0.17**
G + ARS III	2.55 (C - H)	0.88	0.03

Source: author's construction.

Table 1 shows that the most stable configuration, having the highest modulus value. For the interaction of the methylene blue dye with the graphene the configuration II is the most stable. In this arrangement the dye is in planar position with respect to π-π interaction between the dye and graphene atoms, providing a more effective interaction in the system with an adsorption energy of 1.86 eV and a distance of 3.18 Å between the graphene carbon and the hydrogen of the molecule. The charge transfer was 0.08 electrons from graphene to the dye.

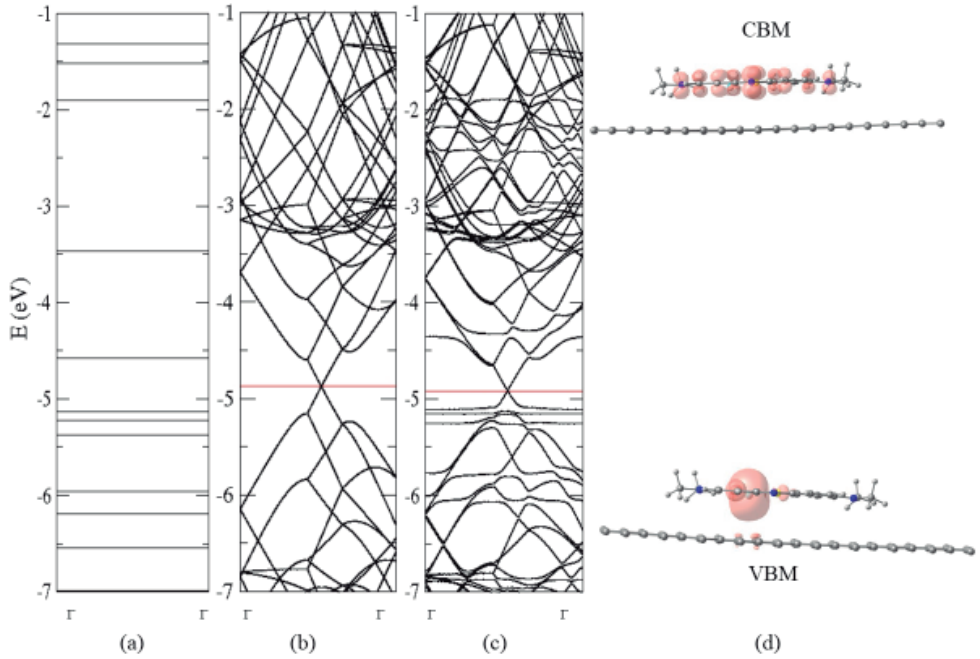
Comparing this result with the same configuration for the carbon nanotube nanostructure (JAURIS et al., 2012) we have a binding energy of 1.14 eV. Analyzing the two nanostructures it is verified that graphene would be a better nanoadsorvent for the removal of methylene blue dye present in industrial effluents.

Figure 2, which shows the energy levels of the isolated dye molecule, the energy band of isolated graphene and the energy band of the methylene blue and graphene interaction for the most stable configuration II, it is observed that an overlap occurs of the energy levels, and the concentration of

charge density for the CBM (conduction band minimum) is located in the dye atoms only, and for the VBM (valence band maximum) the concentration of charges is smaller and only in one part center of the dye and at the basal plane of the graphene.

As can be seen in figure 2, there was an overlap of energy levels, the electronic characteristic of graphene was maintained after the interaction of the nanostructure with the methylene blue dye.

Figure 2 - Level energy (a) methylene blue and bands of energy (b) graphene and (c) configuration II methylene blue interacting with graphene, (d) plot of charge density, contour plot 0.003756 eV / Å^3



Source: author's construction.

Observing these electronic and structural properties it is suggested that the interaction of methylene blue with graphene presents a physical adsorption.

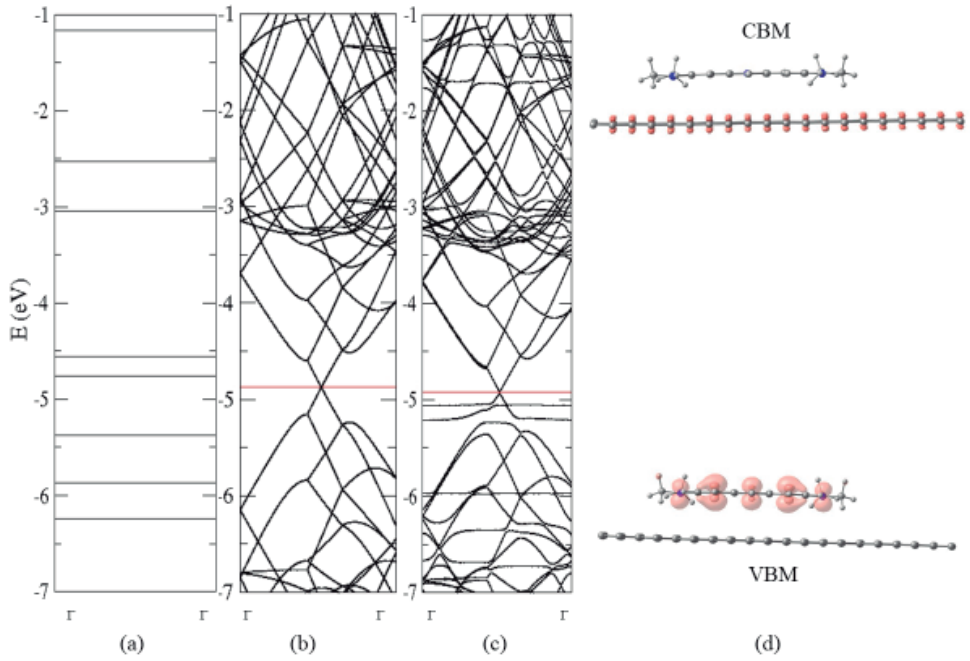
For the interactions of graphene with the acridine orange dye the most stable configuration is the one in which the dye is in parallel with the nanostructure, having an energy of adsorption of 1.42 eV and a distance of 2.55 Å between the carbon of the graphene and the hydrogen of the molecule. The charge transfer was 0.09 electrons from the graphene to the molecule.

The results obtained by Jauris et al. (2012) in which it uses the same computational methodology and analyzes the interaction of the carbon nanotubes with the acridine orange dye obtained a binding energy of 1.06 eV and an adsorption of the physical regime, comparing these results it is verified that the graphene becomes more efficient than the carbon nanotubes in the adsorption of the acridine orange organic dye.

As can be seen in figure 3, the energy levels of the isolated dye and the energy bands of the isolated nanostructure and the interacting system, an overlap of energy levels is also observed and graphene retains its electronic characteristic even after interaction. The concentration of charge

density in the CBM is located only in the nanostructure, and in the VBM it is concentrated only in the molecule of the dye.

Figure 3 - Energy level (a) acridine orange and energy bands (b) graphene and (c) configuration II acridine orange interacting with graphene, (d) plot of charge density, contour plot 0.003756 eV / Å3.



Source: author's construction.

Observing the results obtained in table 1, the most stable configuration of the graphene interactions with the red dye of alizarin s was the configuration II in which the molecule is planar in relation to the nanostructure, having an adsorption energy of 1.57 eV and a distance of 2.77 Å between graphene and sodium carbon of alizarin red dye s. The charge transfer was 0.03 electrons from graphene to the molecule.

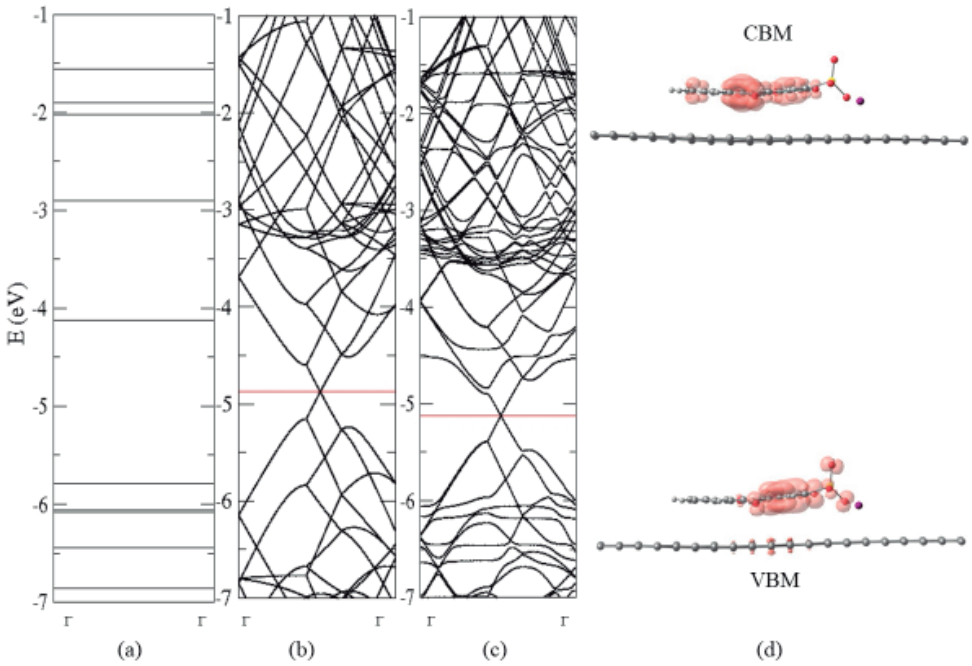
In figure 4, it was observed that a shift in the fermi level also occurred when compared to the pristine graphene band and the graphene interacting with the alizarin red s, also, the electronic characteristic of the graphene was maintained after the interaction. The concentration of charge density for the most stable configuration for both CBM and VBM is found only in the dye molecule.

It is suggested by observing the electronic and structural properties of the graphene interacting with the red dye of alizarin S, that the system obeys an adsorption of the physical type.

Comparing this result with the same configuration obtained in the work of (JAURIS et al., 2012) the interaction of the carbon nanotube with the red dye of alizarin s obtained a binding energy of 1.05 eV, and an adsorption of the physical type.

Thus, by observing these two nanomaterials under analysis, graphene shows to be more efficient in adsorption of alizarin s dye.

Figure 4 - Energy level (a) Alizarin red and energy bands (b) graphene and (c) alizarin red configuration II interacting with graphene, (d) plot of charge density, contour plot 0.003756 eV / Å^3 .



Source: author's construction.

CONCLUSION

For the more stable interactions of graphene interacting with the organic dyes methylene blue, acridine orange and alizarin red s the adsorption energies obtained were 1.86 eV, 1.42 eV and 1.47 eV respectively. The adsorption energies for methylene blue, acridine orange and alizarin red dyes were 1.14 eV, 1.06 eV and 1.05 eV, respectively, in the work developed by (JAURIS et al., 2012) in which the nanotube was used as nano-adsorbent.

The most stable configuration was the II of graphene interacting with the methylene blue dye having an adsorption energy of 1.86 eV and in relation to the methodology of the carbon nanotubes (JAURIS et al., 2012) it is noticed that the preference is also for the with planar structures with binding energy of the order of 1 eV, being that the graphene becomes more efficient in the adsorption of organic dyes due to its planar structure.

The most stable configurations for all the systems present the structural arrangements with the molecule parallel to the graphene surface. Also, this theoretical study shows that the interaction of organic dyes with graphene obeys a physical adsorption regime, which would be ideal for the system to be used as an environmental filter because it has a weak interaction that can remove undesired molecules in the environment, and after physical treatments the system can be reused.

REFERENCES

CARDOSO, N. F. et al. Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents. **Journal of hazardous materials**, v. 241, p. 146-153, 2012.

CARITÁ, R.; MARIN-MORALES, M. A. Induction of chromosome aberrations in the Allium cepa test system caused by the exposure of seeds to industrial effluents contaminated with azo dyes. **Chemosphere**, v. 72.5, p. 722-725, 2008.

GUARATINI, C. C. I.; ZANONI, M. V. B. Corantes têxteis. **Química Nova**, v. 23, p. 71-78, 2000.

JAURIS, I. M. et al. **Adsorção de corantes em nanotubos de carbono**: uma abordagem de primeiros princípios. 2012. Dissertação (Mestrado em Nanociências) - Programa de Pós-graduação em Nanociências, UNIFRA, Santa Maria-RS, 2012.

KERMER, W. D.; RICHTER, I. S. Entfärbung von Färbereiabwasser durch Ionenpaarextraction. **Melliand Textilberichte**, v. 76, n. 6, p. 433-437, 1995.

KOHN, W.; SHAM, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. **Physical Review**, v. 140, n. 4A, p. 1133-1138, 1965.

LIU, T. et al. Adsorption of methylene blue from aqueous solution by graphene. **Colloids and Surfaces B: Biointerfaces**, v. 90, p. 197-203, 2012.

PERDEW, J. P.; ZUNGER, A. Self-interaction correction to density-functional approximations for many-electron systems. **Physical Review B**, v. 23, n. 10, p. 5048, 1981.

ROYER, B. et al. A useful organofunctionalized layered silicate for textile dye removal. **Journal of hazardous materials**, v. 181, n. 1-3, p. 366-374, 2010.

SOLER, J. S. et al. The SIESTA Method for Ab Initio Order-N Materials Simulation. **Journal of Physics: Condensed Matter**, v. 14, n. 11, p. 2745-2779, 2002.

TROULLIER, N.; MARTINS, J. L. Efficient Pseudopotentials for Plane-Wave Calculations. **Physical Review B**, v. 72, p. 1993-2006, 1991.

ZANELLA et al. Chemical doping-induced gap opening and spin polarization in graphene. **Phys. Rev. B**, v. 77, p. 73404-73407, 2008.

ZANONI, M. V. B.; CARNEIRO, P. A. O descarte dos corantes têxteis. **Ciência Hoje**, v. 29, n. 174, p. 61-64, 2001.