Computational Analysis of Electrochemical Behavior and Fullerene-Based Adsorbents for Extraction of Acetamiprid

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ABSTRACT: *Using density functional methods, the results of the analysis of traditional adsorbents and adsorbents based on nanosized particles capable of trapping acetamiprid molecules in fruits and plants are presented. We considered the following interacting compounds: acetamiprid@ fullerene C20, a fragment of the structure of activated carbon. We determined the optimal configurations of the corresponding interacting structures, estimated their electrochemical parameters and binding energies, and chemical potentials. The highest binding energy was obtained -0.70 eV adsorbed on C20 fullerene. At the same time, the energy gaps between the occupied HOMO and unoccupied LUMO molecular states were calculated, which makes it possible to characterize the reactivity and stability of molecules. acetamiprid has rather large gaps HOMO-LUMO. Using the concept of the electronic localization function, we found that a covalent bond is formed between acetamiprid and C20 fullerene with a sufficiently high degree of electron localization in the bond region. In other cases, the value of the localization function indicates the absence of a chemical bond between the compounds. The proposed study gives recommendations on the adsorption of acetamiprid for further electrochemical analysis, which will allow them to be found in fruits and plants by gas chromatography using a flame ionization detector.*

KEYWORDS: *Adsorption, Acetamiprid, Density functional theory, Electrochemical properties.*

INTRODUCTION

Neonicotinoids are a relatively new class of synthetic insecticides used primarily to control aphids, leafhoppers, whiteflies, and other sap-sucking pests [1]. Neonicotinoids from a rapidly increasing group of insecticides, utilized across the world since carbamates and pyrethroids were introduced performing the role of full or partial agonists of insect nicotinic acetylcholine receptors (nAChRs). Imidacloprid and acetamiprid [2-7] are two major neonicotinoids present in the market, which specifically act on the nicotinic acetylcholine receptors (nAChR) within the central nervous system of insects. The design of new members of these compounds has led to promising results in recent years. The nitro group fixation in a cis configuration for different neonicotinoid types has yielded compounds with certain biological functions and behaviors, supporting their potential efficiency in elucidating

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Table 1: optimized X Y Z structure of C20

C20(ih)	X	Y	Z
C	1.6186	-0.6631	-0.9481
C	1.8147	0.6626	-0.478
C	0.4899	-0.6645	-1.8098
C	-0.0094	0.6633	-1.8762
C	0.8085	1.4827	-1.0539
C	-0.5095	-1.4851	-1.2229
C	-1.6298	-0.663	-0.9299
C	-1.3211	0.6635	-1.3321
C	0.0026	-1.9894	0.0019
C	-0.8072	-1.4831	1.0529
C	-1.8145	-0.6637	0.4781
C	1.3176	-1.4815	0.1728
C	1.3212	-0.6619	1.3324
C	0.0093	-0.6633	1.876
C	1.6291	0.6646	0.9299
C	0.507	1.4824	1.2276
C	-0.4958	0.6622	1.809
C	-1.6217	0.6639	0.9436
C	-1.3127	1.4844	-0.1735
C	0.0032	1.989	0.0004

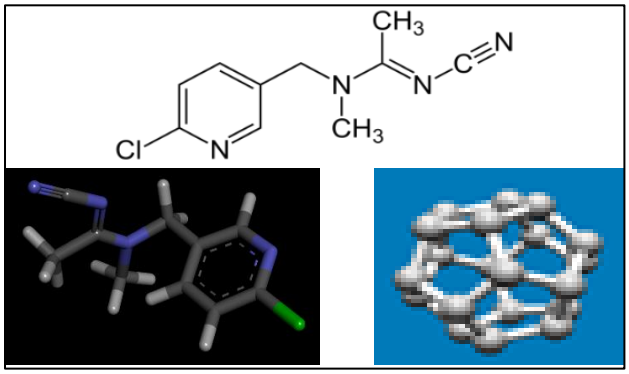

Fig. 1: Acetamiprid structure and C20 structure

the pharmacology and characteristics of the neonicotinoid binding sites. The current developments in carbon materials have led to graphene as a fundamental component of graphitic materials [8-14] of all other ranges, representing a single atomic layer of graphite with hexagonally bonded and sp^2 hybridized carbons. Scientists and researchers have been interested in this material since it was discovered in 2004, because it showed specific characteristics, including considerable quantum Hall impacts, high mobility, great electronic and mechanical properties, specific magnetism, and high thermal conductivity, There have been investigations on the use of graphene-based materials [11] to manage the environmental issues related to pollution. Activated carbon as a well-known sorbent is used in the field of pharmacology [15,16], in the food industry, in the military, in devices for purifying drinking water, and many other areas of life. Further, fullerenes are stable, biocompatible, and highly reproducible nanoparticles. It was shown that fullerenes, fullerene-, graphene-like materials, due to their large specific surface area, can chemically bind a large number of particles. Although C60 and nanotubes are more suitable due to their larger area, we consider C20 as the minimum fullerene; it is the most curved and therefore the most active. The efficiency of adsorption using functionalized nanoparticles by different groups is also an interesting research subject. In this study, C20 was selected for the adsorption of acetamiprid from fruits and plants. All electrochemical and adsorption parameters were calculated.

EXPERIMENTAL SECTION

The considered atomic model was driven to energy-optimal configurations using the Gaussian [17] software package. Based on the density functional theory using the set of basic functions B3LYP / 6-311++G(2d,2p) [18], the diameter of the molecules, their total energies corresponding to a given local energy minimum, and the bond lengths were calculated. All structures are optimized while a Hellman-Feynman force convergence exceeds 10−2 eV/Å. Iteration tolerance is 10−5. The dispersion interaction was taken into account by the DFT-D2 method of Grimme [19]. The density functional theory method is also used to calculate the HOMO-LUMO sites. The full visualization process is carried out in the ChemCraft package.

Fig. 1 shows the 3D structure for the considered acetamiprid, fullerene C20, and activated carbon. All of the considered molecules were optimized as described above. The dark grey balls denote the carbon atoms, the light grey balls denote the hydrogen atoms, the green balls denote the color atoms, and the blue balls denote the nitrogen atoms.

Further, we constructed the atomistic models of interacting structures: acetamiprid — fullerene C20, (Table 1) a fragment of the structure of activated carbon. We performed the optimization procedure again. The initial configurations of the interacting structures were chosen so that the space between them contained as many atoms as possible.

Table 2: Electronic parameters of acetamiprid

HOMO(eV)	-6.8906604
LUMO(eV)	-1.7221209
IP(eV): ionization potential	6.8906604
EA(eV):electron affinity	1.7221209
χ(eV):electronegativity	4.30639065
η(eV):hardness	2.58426975
σ(eV):softness	0.386956509
ω(eV): electrophilicity	3.58805431
μ(eV): chemical potential	-4.30639065
ΔE(LUMO-HOMO) (eV):band gap	5.1685395

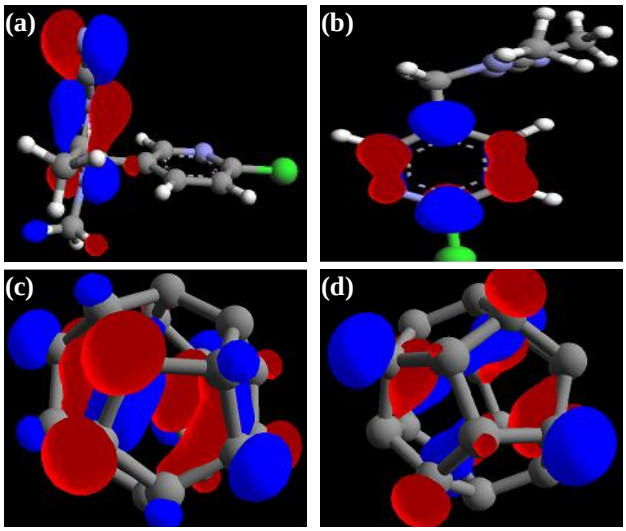

Fig. 2: Acetamiorid HOMO(a) and LUMO(b) C20 HOMO(c) and LUMO(d)

RESULTS AND DISCUSSIONS

Oxidation and reduction process in chemical media have been affected on health and fresh properties of fruits and vegetables. One of chemical properties which is important to consider for health on fruits is rest of pesticides. In this study the adsorption method applied for elimination of acetamiprid as pesticide. For this propose the binding (adsorption) energy of acetamiprid on fullerene C20, and a fragment of the structure of activated carbon was given by [20]:

$$E_b = E_{tot} - (E_{acetamiprid} + E_{C20}) \quad (1)$$

Where E_{tot} is the totally optimized energy of the complex interacting structures, $E_{acetamiprid}$ is the energy of the free, relaxed acetamiprid, and E_{C20} is the same energy of adsorbents.

Electronics chemical properties is very important for participating chemical compounds in all reactions. HOMO and LUMO is the most physical properties to consider for electronics chemical characteristics. As shown in [21], the density functional theory allows getting a set of physical quantities. One of them is the HOMO-LUMO gap. It is defined as the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital [21]. So, the optimized parameters for the adsorption of acetamiprid@C20 adsorption species were tabulated in Table 2 and the HOMO and LUMO orbitals of C20 and acetamiprid showed in Fig. 2.

As shown in Table 1, the largest bonding was found for acetamiprid @ fullerene C20 because the Eb = −0.70 eV. The value is close to the adsorption energy of oxygen molecule's covalent bonds (chemisorbed) [22]. As to the HOMO-LUMO gap, acetamiprid has a large HOMO-LUMO gap. The HOMO-LUMO gap is reduced as one moves to other adsorbents.

HOMO energy shows a molecule’s capability of donating electrons; therefore, higher E HOMO values indicate a greater possibility of donating electrons by the molecule. On the other hand, LUMO energy represents a molecule’s ability to accept electrons, which means that lower E LUMO values result in a greater possibility of receiving electrons from the molecule. The main parameter has been the energy gap that exists among the energy levels of HOMO and LUMO as it is a function of the molecules’ reactivity. Ionization potential can describe an atom's chemical reactivity, and the high ionization potential of molecules reflects their highly stable status. Hard molecules possess larger energy gaps, while their soft counterparts show higher reactivity associated with their higher potential for electron donation. The electrophilicity index describes the molecule's capability of electron acceptance. The compounds’ electronic parameters are presented in Table 2. As shown in this table, acetamiprid donates electrons in chemical media, and shows the high ionization energy that refers to the simplest electrochemical behavior. Considering the bandgap energy, acetamiprid showed to have higher reactivity, acting better in biological chemical media. This result was supported by other thermodynamic as well as electronic parameters of the compounds Table 3. According to the ΔG, we can calculate the reduction potential by ΔG=-nFE. Where F= 96485 C and n is the number of electrons.

The ElectroStatic Potential (ESP) is used to analyze the positively and negatively charged regions of a molecule

Table 3: Thermodynamic parameters of acetamiprid by B3LYP/6-311++G(2d,2p)

	ΔG (kJ)	ΔH (kJ)	ΔS (cal/mol.K)	Cv (cal/mol.K)
Acetamiprid	-4.6×10^{-18} kJ	-4.6×10^{-18} kJ	120.39 cal/mol.K	49.050 cal/mol.K

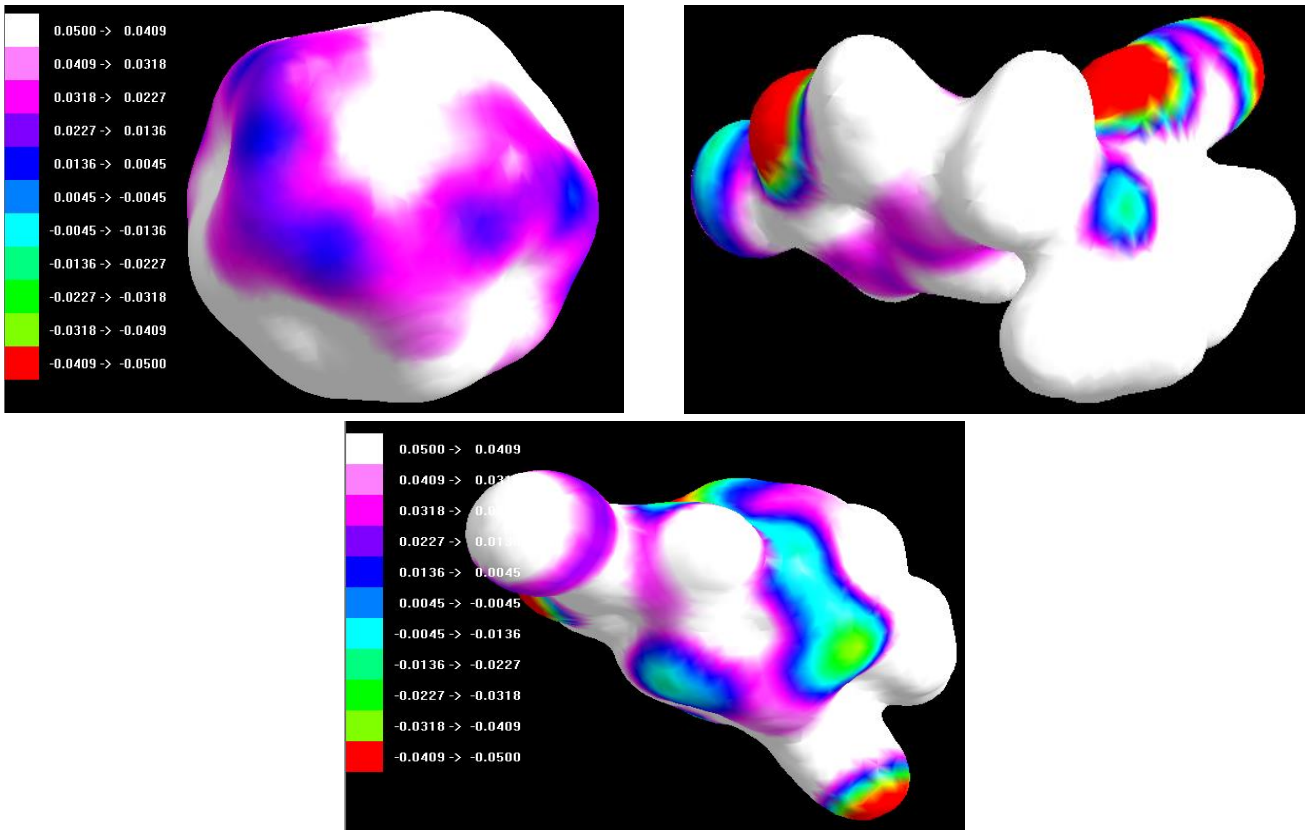

Fig. 3: Electron surface potential of a) C20, b) acetamiprid, c) acetamiprid@C20

Fig. 3. In atomic units, it is defined as the interaction energy of the molecule with an infinitesimal positive point charge, per unit charge. Fig 3 shows the positive and negative sites of acetamiprid. Typically, hard acids/electrophiles attack a molecule where the electrostatic potential is most negative, and hard bases/nucleophiles attack a molecule where it is mostly positive. The value of the electrostatic potential at a nucleus is often interesting, because it shows how the energy changes when the atomic number of the nucleus changes (to first order). Therefore, it is relevant for alchemical changes as an atom changes to an adjacent atom in the periodic table.

CONCLUSIONS

Quantum chemistry is a powerful tool for predicting the properties of new materials and their compounds. But often, the results obtained in the course of quantum chemistry turn out to be divorced from practice. In this study, we have provided an appropriate link, since the obtained results will help to understand which classical or new materials can be used for the effective adsorption of toxic acetamiprid. This information will help to carry out electrochemical analysis and find them in fruits and plants. The data of electronic chemical parameters show that acetamiprid is an active molecule with good potential behavior and thermodynamic data has illustrated the good adsorption on C20. Calculating the HOMO and LUMO surface energy can provide the active band gap and electrochemical ability of acetamiprid and C20@acetamiprid composite in chemical media. Thermodynamic properties of acetamiprid and C20@acetamiprid composite showed the stability of these compounds in chemical media for electrochemical experimental study.

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