

Theoretical Investigations of the Herbicide Glyphosate Adsorption on the B₁₂N₁₂ Nanocluster

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Abstract: Nowadays is emergent the development of new materials which can be used in the adsorption process to remove herbicide glyphosate from the aquatic environment. Therefore, density functional theory (DFT) calculations were performed to study the adsorption process of the glyphosate on the B₁₂N₁₂ nanocluster in aqueous media. The optimized structures of adsorbed glyphosate do not affect the nanocluster structure indicating its structural stability. The chemisorption of this herbicide is an exothermic process with -43.89 kcal.mol⁻¹. The most stable complex displayed an adsorption energy and ΔG values of -53.97 and -40.79 kcal.mol⁻¹, respectively. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies are located in the glyphosate implying that this herbicide can be removed by chemical reaction. Our results show that the B₁₂N₁₂ nanocluster can be a suitable new nanomaterial to remove the glyphosate from wastewater.

Keywords: glyphosate@B₁₂N₁₂ complex; adsorption process; thermodynamic properties; DFT

1. INTRODUCTION

The high growth of agricultural activity is associated with the incorporation of various technologies to the agricultural modernization process, among which stands out the use of pesticides, and Brazil presents the largest market of pesticides in the world [1]. The variables that build this indicator involve the planted area, in hectares, and the amount of consumed pesticides in accordance with the principal classes of use (herbicides, fungicides, insecticides, bactericides, and others) [2]. Among the herbicides, the glyphosate (*N*-(phosphonomethyl)glycine) is the most active ingredient used worldwide, having a broad spectrum of action, and it is classified as systemic and post-emergent which belonging to the chemical group of phosphonated amino acids. Glyphosate is absorbed by the living tissue and is translocated, via phloem, through the plant to the roots and rhizomes and acts as

a potent inhibitor of the activity of the enzyme 5-enolpyruvylshikimate 3-phosphate synthase (EPSPS), which is a catalyst of aromatic amino acid synthesis reactions, as phenylalanine, tyrosine and tryptophan [3,4].

The glyphosate and its salts are crystalline solids which has excellent water solubility (12 g/L at 25 °C) [5] and practically insoluble in common organic solvents such as acetone and ethanol. Its molecular structure has a phosphonate group, amino and carboxylate that may be coordinated as a tridentate ligand with metal ions which puts it in a unique position among herbicides [3,6]. Glyphosate presents different dissociated species as function of pH, showing positive net charge at low pKa and negative charge with an increasing of pKa, reaching a trianionic form in pKa higher to 11. In aqueous solution and pH between 5.6 and 10.6, the glyphosate is negatively charged (-2) [7].

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Epidemiological studies have been evaluated in order to determine whether exposure to the herbicide glyphosate can generate cancer risk in humans [8, 9], Parkinson's disease [10], changes in embryonic cells [11], as well as studies with other animals [12, 13]. On this way, the removal of glyphosate from the water sources is very important and emergent. Experimentally, different methods for removing this herbicide have been used: reverse osmosis, microfiltration, ultrafiltration, and adsorption by biopolymer membrane, filtration using sand, and biological degradation [14]. However, some of these processes are expensive, while the adsorption is an attractive method due to its efficiency, convenient and recyclable technique. Experimental studies reported the effectiveness of some solid adsorbents, i.e. layered double hydroxides [15], ferric-supported active carbon [16], montmorillonite [17], Zr-based metal-organic frameworks (MOFs) [18], to remove glyphosate from wastewater. These studies show clearly that the adsorption process is a promising experimental procedure for removal of glyphosate in water. In order to decrease the cost in a trial and error process, the use of computational chemistry methods can be an alternative technique to study adsorption of small molecules in metal surfaces. Therefore, in the present work, the adsorption of the glyphosate

molecule in the $B_{12}N_{12}$ nanocage was investigated using quantum chemistry methods. The $B_{12}N_{12}$ is a nanocluster with spherical form consisting of eight hexagons rings and six squares rings, and it satisfies the tetragonal rule. This nanocage was obtained and characterized experimentally in the period of 1998-2004 [19–21]. The $B_{12}N_{12}$ has some interesting properties like high-temperature stability, large thermal conductivity, low dielectric constant and oxidation resistance [22, 23]. Recently, density functional theory (DFT) methods were used to study and to predict the absorption/adsorption of different molecules, i.e. pyridine [24], arsenite and arsenate [25], methylamine [26], urea [27], caffeine and nicotine [28], and also ammonia [29] on $B_{12}N_{12}$ nanocage. Moreover, we reported [30] the structural and stability of the different $M_{12}O_{12}$ ($M = Zn, Ca, Ti,$ and Fe) nanocluster like $B_{12}N_{12}$ using DFT. Therefore, this method was used here to study the adsorption process of the glyphosate molecule on spherical $B_{12}N_{12}$ nanocluster. To date, there is no similar study performed, indicating the importance of our approach and therefore giving support for future experiments. The structures of the herbicide glyphosate and the $B_{12}N_{12}$ nanocage are shown in Figure 1.

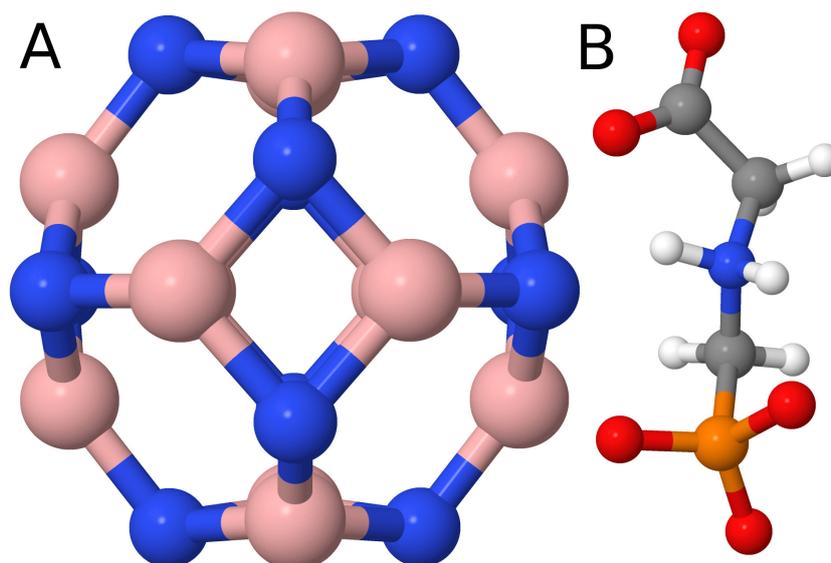


Figure 1. Structural representation of the $B_{12}N_{12}$ nanocage (A) and glyphosate molecule (B) at pH 6.5. Nitrogen in blue, oxygen in red, phosphorous in yellow, carbon in gray, hydrogen in white and boron in salmon colors.

2. MATERIAL AND METHODS

The structures of the $B_{12}N_{12}$ nanocage, glyphosate molecule and complexes (glyphosate@ $B_{12}N_{12}$) were optimized using the

ORCA package [31]. Glyphosate was considered as charged molecule because at pH higher than 6.5 it has a dianion form in aqueous solution. All calculations were carried out using the DFT with B3LYP hybrid

functional, and the 6-31+G(d,p) basis set was considered. This level of theory was chosen to balance the results accuracy and computational cost. The adding of diffuse function on the basis set is justified by having charged species to be investigated and then its effect on the properties is considered. The COSMO (Conductor-like Screening Model) was used to take in account the solvent effect. In this solvation model, the solvent is treated as continuum dielectric, with dielectric constant of 80 to represent the water solvent [32]. The COSMO was considered due its efficient to study large molecules with irregular form, and its accuracy to describe solvents with a higher permittivity, like water. All the stationaries points were characterized as a point of minimum energy using the harmonic vibrational states, and were not observed negative frequencies. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies were used to calculate the reactivity parameters based in the Koopman's theorem [33]. The adsorption energy (E_{ads}) between $B_{12}N_{12}$ and glyphosate molecule was calculated using the following equation:

$$E_{\text{ads}} = E_{\text{complex}} - (E_{B_{12}N_{12}} + E_{\text{glyphosate}})$$

where E_{complex} is the total energy of the complex (glyphosate@ $B_{12}N_{12}$), $E_{B_{12}N_{12}}$ and $E_{\text{glyphosate}}$ are total energies of the $B_{12}N_{12}$ nanocage and the glyphosate molecule isolated, respectively. The thermodynamics properties (ΔG , ΔH and ΔS) of formation of the complexes were calculated from standard conditions (298.15 K) from the optimized structures.

3. RESULTS AND DISCUSSION

In order to evaluate the use of a spherical nanocluster ($B_{12}N_{12}$) as a possible candidate to remove the herbicide glyphosate from environment, we used the most stable structures of $B_{12}N_{12}$ nanocluster, glyphosate conformations and the complexes obtained from the DFT calculations, as presented in Figure 2.

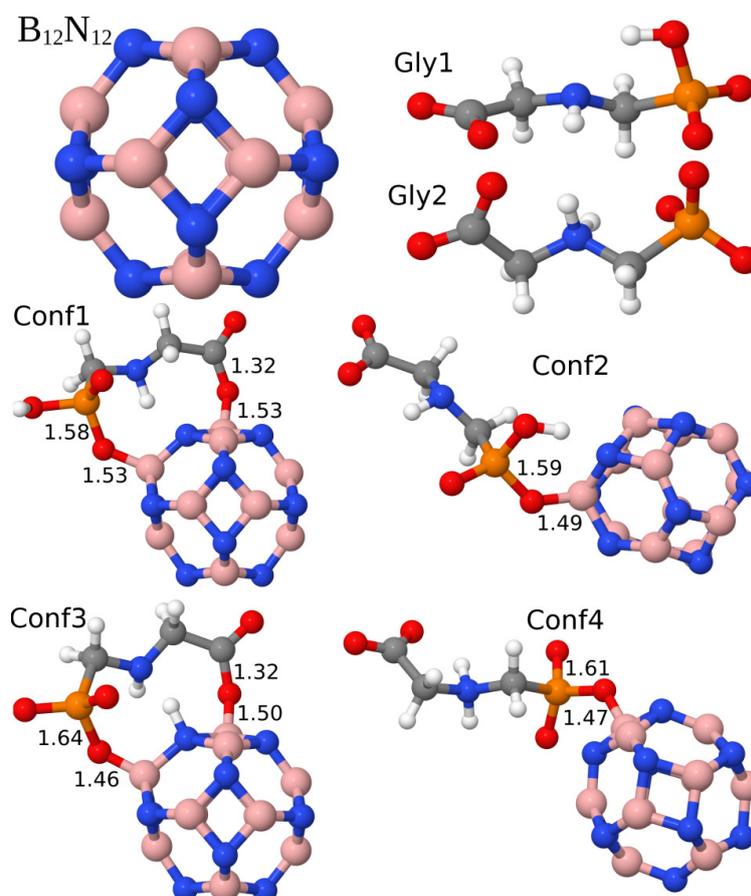


Figure 2. Structures of the $B_{12}N_{12}$ nanocage, glyphosate conformations (Gly1 and Gly2), complexes (Conf1, Conf2, Conf3 and Conf4) optimized with DFT//B3LYP/6-31G+(d,p). Intramolecular distances are in Å.

The structure optimization process revealed two stable glyphosate conformations with proton at different position (Gly1 and Gly2, Fig. 2). In the Gly1 is possible to observe an intramolecular interaction via hydrogen bond between the H (bonded to the PO_3^-) and N (bonded to the $-\text{NH}-$) with distance of the 2.13 Å. For all complexes were not observed significant structural change in the spherical form of $\text{B}_{12}\text{N}_{12}$ nanocluster. Figure 2 shows undoubtedly the formation of covalent bond between the glyphosate structures and $\text{B}_{12}\text{N}_{12}$ nanocage. These bonds occur between the B atom from $\text{B}_{12}\text{N}_{12}$ and O atom of the glyphosate. For Conf1 and Conf3 complexes, there are formations of two covalent bonds: one between the oxygen from CO_3^{2-} and B atom, and another one between the O from phosphate anion and B atom, both with bond order of ~ 1 . In the Conf1, the distance between the O (PO_3^-) and O (CO_3^{2-}) with B atom is about 1.53 Å (Fig. 2), while for the Conf3 these distances are 1.46 and 1.50 Å, respectively. The lowest distance observed for Conf3 imply in a strong

interaction between the Gly2 and $\text{B}_{12}\text{N}_{12}$ compared to the Gly1 molecule. Moreover, in the Conf3 complex there is a proton transfer from NH_2^+ group (glyphosate) to nitrogen atom of the $\text{B}_{12}\text{N}_{12}$. After this transference, this proton makes an intermolecular hydrogen bonding with the NH group from glyphosate with distance of 1.83 Å. It is worth noting that the intramolecular hydrogen bonding for Gly1 (Fig. 2), commented previously, was break with formation of an intermolecular interaction between H (PO_3^-) and N atom ($\text{B}_{12}\text{N}_{12}$), which displayed a distance of 2.55 Å. For others complex were observed the formation of only one covalent bond. For Conf2 and Conf4, the distances between the O (from phosphate ion) and B ($\text{B}_{12}\text{N}_{12}$) are 1.49 and 1.47 Å, respectively. In the Conf2 there is formation of a hydrogen bonding between the H (PO_3^-) and N ($\text{B}_{12}\text{N}_{12}$) with distance of 1.72 Å. To understand the energetic process involved in the glyphosate chemisorption on the $\text{B}_{12}\text{N}_{12}$, we presented in Table 1 some electronic and thermodynamics properties obtained in our calculations.

Table 1. Electronic and thermodynamics properties obtained from DFT//B3LYP/6-31G+(d,p) level. It is shown the ground state energy with ZPE correction, frontier molecular orbitals energies and thermochemistry data for each structure.

Structures	E(ZPE) ^a	ϵ_{HOMO} (eV)	ϵ_{LUMO} (eV)	E_g (eV)	E_{ads}^b	ΔG^b	ΔH^b	$T\Delta S^b$
$\text{B}_{12}\text{N}_{12}$	-955.627	-7.79	-0.98	6.81	–	–	–	–
Gly1	-890.270	-6.02	0.13	6.15	–	–	–	–
Gly2	-890.270	-5.80	0.14	5.94	–	–	–	–
Conf1	-1845.970	-5.85	-0.10	5.75	-45.81	-28.67	-43.89	-15.22
Conf2	-1845.954	-6.20	-0.46	5.74	-35.77	-17.73	-35.00	-17.27
Conf3	-1845.983	-6.10	-0.28	5.82	-53.97	-38.23	-53.98	-15.75
Conf4	-1845.962	-6.68	-0.33	7.01	-40.79	-23.66	-39.61	-15.95

^ain atomic unit; ^bin kcal.mol⁻¹

The total energies presented in the Table 1 indicated that all structures are energetically favorable with following sequence for the complexes: Conf3 < Conf1 < Conf4 < Conf2. Although, the total energy can not be used to measure the stability of a molecule, however this sequence is the same of the free energy of Gibbs. The order of the lowest ΔG values are: Conf3 (-38.23) < Conf1 (-28.67) < Conf4 (-23.66) < Conf2 (-17.73 kcal.mol⁻¹), and these negative values show that all complexes are thermodynamically stable. The relationship between the total energy and ΔG values can be attributed to the similar entropic contributions as can see in the Table 1. Therefore, the enthalpic factor is crucial to measure the stability of the glyphosate on $\text{B}_{12}\text{N}_{12}$ nanocage. Consequently, the ΔH values follow the same sequence of the ΔG and their negative values show that the adsorption is an exothermic process. The Conf3 complex is the most

stable with lowest ΔG , and at experimental level would be expected the formation of this particular complex in aqueous solution. Moreover, except for Conf4, the energy gap (~ 6 eV) is similar for all complexes, indicating that they have similar reactivity in chemical reactions. Due to the high-temperature resistance of the $\text{B}_{12}\text{N}_{12}$ nanocage, the complexes formed can be submitted to calcination process, resulting into the glyphosate degradation.

The chemisorption of the glyphosate by the $\text{B}_{12}\text{N}_{12}$ nanocage is an exothermic process with the following order of adsorption energies (E_{ads}): Conf3 (-53.97) < Conf1 (-45.81) < Conf4 (-40.79) < Conf2 (-35.77 kcal.mol⁻¹). The lowest E_{ads} values for the Conf1 and Conf3 are attributed to the two covalent bonds formed between the glyphosate molecule and the $\text{B}_{12}\text{N}_{12}$ nanocluster, Fig. 2. The Conf3 is the most stable complex and with lowest E_{ads} , and this can be

attributed to two mainly process: i) highest reactivity (lowest E_g) of the Gly2 compared to the Gly1; ii) the capacity of the Gly2 to transfer its hydrogen to the B₁₂N₁₂ nanocluster.

The E_g ($|HOMO - LUMO|$ energy) for B₁₂N₁₂ obtained here (6.81 eV) is in agreement with previous calculations, with a value of 6.85 eV, considering that the authors used a different basis set [24]. Baei studied [24] the removal of pyridine by using (BN)₁₂ based on B3LYP/6-31G(d) level of theory and they obtained the values of -7.71 and -0.86 eV for the HOMO and LUMO energies, respectively, for B₁₂N₁₂ isolated. Based in the gap energy, the B₁₂N₁₂ should not be a good sensor for glyphosate detection because the gap energy of this nanocage does not change significantly after the glyphosate adsorption. Our results are in good agreement, considering that the adding of p polarization function and an implicit solvent model decrease slightly the E_g value. As also mentioned by Baei, the solvent effect plays an important role in the reactivity of the B₁₂N₁₂ nanocage. Moreover, it is also clear the effect of the diffuse function on the LUMO

energies in accordance with recent works for the (BN)₁₂ nanocage studied by DFT calculations in gas phase [27,28,34]. Thus, it can suggest that the B₁₂N₁₂ nanocage acts as electron acceptor (highest IP), while the glyphosate acts as electron donor (lowest IP). This is in agreement with the CHELPG charge analysis [35], where we observed the transference of the -0.97, -0.50, -0.80, -0.55 |e| charges from glyphosate to B₁₂N₁₂ in Conf1, Conf2, Conf3 and Conf4 complexes, respectively. As a consequence, it was observed an increase in the dipole moment after the chemical adsorption of glyphosate (Gly1 and Gly2) into B₁₂N₁₂ surface. For instance, the dipole moment obtained for Gly1 is 5.30 Debye, and those ones complexed with B₁₂N₁₂ are 7.02 and 38.40 Debye for Conf1 and Conf2, respectively. For Gly2, the dipole moment is 10.93 Debye, while after its adsorption by the B₁₂N₁₂, this value increase to 13.64 and 26.05 Debye in the Conf3 and Conf4 complexes, respectively.

The Figure 3 shows the HOMO and LUMO energies and their surface representations obtained in our calculations.

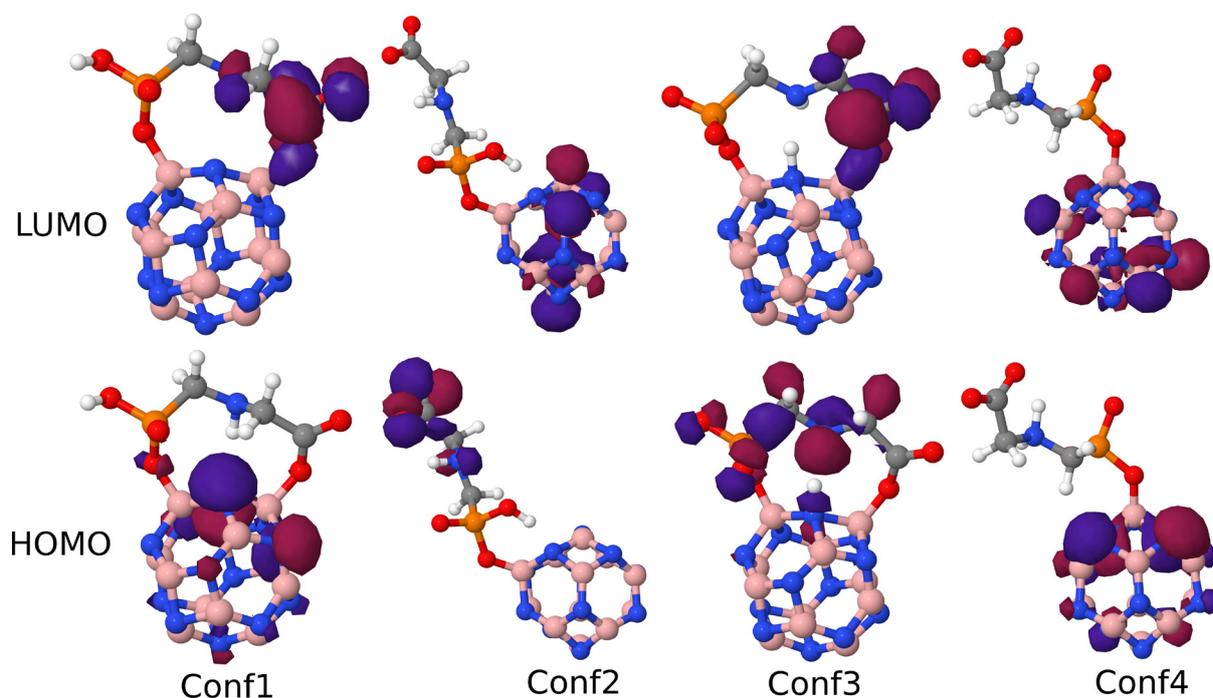


Figure 3. Representation of the HOMO and LUMO orbitals for all complexes obtained from DFT/B3LYP/6-31G+(d,p).

The Figure 3 shows that the HOMO and LUMO orbitals in the Conf3 are located only in the glyphosate bonded to the B₁₂N₁₂ nanocage. This indicates that the structure of the B₁₂N₁₂ is stable in

the chemical reaction, while the glyphosate presents more reactivity. Therefore, we suggest that the glyphosate absorbed by the B₁₂N₁₂ can be removed from the nanocage surface using specific chemical

reaction in agreement with the thermodynamics properties as reported in the Table 1.

4. CONCLUSION

In the present work, DFT method was used to study the adsorption process of the glyphosate by the B₁₂N₁₂ nanocage in aqueous media. We analyzed four complexes conformations with lowest energy. In all complexes were observed the formation of covalent bond between glyphosate and the B₁₂N₁₂. The optimized structures of glyphosate absorbed do not affect the spherical form of the nanocage, indicating its structural stability. The adsorption energies and ΔH values of the complexes show that the chemisorption of the glyphosate on nanocluster is an exothermic process. The Gibbs free energy shows that all complexes are stable at 298 K, while the most stable complex has the ΔG value and adsorption energy of -38.23 and -53.97 kcal.mol⁻¹, respectively. The HOMO and LUMO energies of this stable complex are located only in the glyphosate indicating the herbicide reactivity. In general, the present results show that the B₁₂N₁₂ nanocage can be a new nanomaterial to remove the herbicide glyphosate from aquatic environment.

5. ACKNOWLEDGMENTS

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