



First Principle Study of the Adsorption of Glyphosate on Illite Clay for Water Depollution

Wilfried G. KANHOUNNON ^{a*},
Orou Abdal Afiz Bana N'DOURO ^a, Ezékiel LOKONON ^a,
Guy A. S. ATOHOUN ^a
and Gaston A. KPOTIN ^a

^a *Laboratoire de Chimie Physique – Matériaux et Modélisation Moléculaire (LCP3M/UCT2M),
Université d'Abomey-Calavi, Benin.*

Authors' contributions

This work was carried out in collaboration among all authors. Author WGK wrote the protocol, supervised the theoretical calculations, write parts of the manuscript. Author OAABN performed theoretical calculations and wrote some parts of the manuscript. Author EL performed theoretical calculations and wrote some parts of the manuscript. Author GASA supervised all the steps of the whole work. Author GAK designed the study and supervised the manuscript writing. All authors read and approved the final manuscript.

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ABSTRACT

The use of herbicides such as glyphosate in the agricultural sector enables agricultural intensification and thus satisfies the demand for agricultural products on the market. Glyphosate is widely used in agriculture as a herbicide for weeding fields. However, its use has a major drawback

*Corresponding author: E-mail: gbedode.kanhounnon@uac.bj;

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that calls into question its many advantages. After use, its toxic residues and metabolites end up in groundwater, which is an important source of drinking water for the population. Adsorption is the most suitable technique for recovering these toxic residues before the water is consumed. Based on Density Functional Theory, implemented in the VASP simulation code, we studied the ability of illite to adsorb glyphosate. The adsorbent properties, the abundance of illite throughout the world, particularly in Benin, and the fact that it is free from toxic products were the criteria that guide us in the use of illite clay for our work. Our work revealed that the process of adsorption of glyphosate on the illite surface is exothermic. This process does not present any risk of release of toxic by-products on five of the six studied sites. The illite clay can then be used to design water depollution filters to decrease medical as well as financial burden.

Keywords: Glyphosate; illite; DFT; VASP; adsorption.

1. INTRODUCTION

Glyphosate is the active principle in herbicides used mainly to destroy weeds (Castillo-Villalón 2005, Woodburn 2000). Thanks to the surfactants added to glyphosate (Tsui 2003), the molecule penetrates plants and blocks the biochemical processes that enable them to produce the aromatic amino acids that make up the building blocks of organic matter. As a result, plants are unable to grow and die (Sutton 1978). Every year, up to five billion kilograms of pesticides are reportedly applied worldwide, and it's expected to reach approximately 10 billion kilograms in 2050 (Özkara 2016, Popp 2013). The use of glyphosate based herbicides would present many disadvantages and as a result, had been declared by the world organization of health, a dangerous compound for the environment and the health of human beings, mammals and birds (Valle 2019, Williams 2000). Glyphosate is thought to have genotoxic effects on living organisms, a fact that places it at the origin of several pathological mechanisms, including cancer. Long-term exposure to glyphosate could also cause endocrine function disruption in humans (Gasnier 2009, Chalubinski 2006), attention-deficit/hyperactive disorder (ADHD), colitis, diabetes, heart disease, inflammatory bowel disease, amyotrophic lateral syndrome, multiple sclerosis, obesity, depression, non-Hodgkin lymphoma and Alzheimer's disease, brain and breast cancer, birth defects, celiac disease and gluten intolerance (Samsel 2013, Je 2015, Seneff 2015, Rull 2006, Paganelli 2010, Paganelli 2014, Paganelli 2013, Paganelli 2013, Paganelli 2014, Paganelli 2015).

Also, it has been evidenced that glyphosate and its derivatives can contaminate groundwater, surface waters (creeks, brooks, lakes, rivers and drains), marine sediments, seawater and rain

(Bafei 2021, Costas-Ferreira 2022, Klátyik 2024, Bradley 2017). Unfortunately, these contaminable water source constitute the main drinkable water sources of the population (Calvet 2005). This contamination of water exposes human populations, aquatic fauna and flora to all these dangerous effects mentioned above (Calvet 2004, LABAD 2018, BOUIDIA n.d.). It is therefore very important to find ways to reduce exposure to the glyphosate molecule, especially in least developed areas where access to drinking water is problematic, by removing glyphosate and its derivatives from contaminated water before their consumption.

To deal with this harmful environmental problem, many techniques have been used, namely, chemical precipitation, microbial techniques, degradation, electrocoagulation, electrolysis; membrane extraction and adsorption (Wang 2016, Rajasulochana 2016, Mansour 2011, Mansour 2004, Mansour 2009). Among all these mentioned treatment techniques, adsorption is the most suitable for trapping this type of molecule because of its effectiveness. Indeed, the precipitation method for example, although having the possibility to allow the pollutant removal at a high rate, could release in the medium many other byproducts which management could be difficult (Mansour 2021).

Different materials are used as adsorbent in the adsorption of pollutants. Activated char materials are one of the most used materials in this process (Mansour 2019, Rio *et al.* 2006) given their large specific area (Le 2024), but have the drawback to be high costing, non-efficient in aqueous medium and non-easy to be regenerated (El Qada 2008). Nanomaterial adsorbents, composite materials, soil and geominerals-like clays are also used for the removal of pollutant and particularly glyphosate from wastewater (Wang 2016, Wang 2013, Wang 2007, Jiang

2018). Among these materials, clays are of particular interest for adsorption. Indeed, after undergoing structural modifications, clays acquire a capacity similar to that of activated carbons. This acquired capacity, added to their large specific surface areas, their swelling capacity, their cation exchange capacity and their availability in nature, make them more suitable for treating contaminated water. This could explain the important number of studies devoted to the use kaolinite and of pristine or modified montmorillonite, a smectite clay, to remove glyphosate from wastewaters (Khoury 2010, Damonte 2007, Ren 2014, Ren 2002). In smectite clays, illite is also considered to treat wastewater (Yang *et al.* 2021). To the best of our knowledge, no study has been devoted to glyphosate trapping with illite clay especially by a density functional theory (DFT) study. DFT method has this advantage to provide optimal orientations to how experiments should be conducted to avoid time wasting, uncertain high costing experiment protocols.

The aim of the present work was to perform atomistic simulation studies using DFT to explore the adsorption capacity of modified illite for glyphosate. To better suit experiment structure of illite clay used in this work, we modified the basic illite primitive cell available in literature (Laibi 2017, Hamza 2023). So, illite modification led to a primitive cell containing 4 Al, 4 H, 2 K, 1 Mg, 24 O, 7 Si and 1 Na, where six potential adsorption sites called K, Na, Al, Si, O, and H were identified as described in Fig 1b. Adsorption energies of glyphosate on these six adsorption sites have been specifically calculated to elucidate adsorption mechanisms of glyphosate on illite.

2. COMPUTATIONAL DETAILS

2.1 Modelling the Adsorbent and Adsorbate Systems

The illite surface used for this work is a 3x2x1 supercell build from a modified and optimized primitive cell (Ruiz-García 2022), which has the structural parameters $a = 5.20$, $b = 8.97$, $c = 8.97$, $\alpha = 90.00^\circ$, $\beta = 101.57^\circ$, and $\gamma = 90.00^\circ$. The 3x2x1 was considered to both meet the Al/Si ratio experimentally found to be around 0.56 and the required space for the considered molecule to be adsorbed without steric clash. The primitive cell was modified to insure the chemical composition found experimentally (Laibi 2017,

Hamza 2023). So, the primitive cell contains 4 Al, 4 H, 2 K, 1 Mg, 24 O, 7 Si and 1 Na. The 3x2x1 build supercell was submitted to ab initio molecular dynamics (AIMD) simulation and the most stable geometry obtained was optimized through static DFT calculation. To avoid any interaction between the adsorbed molecule and the periodic image of the slab, a vacuum of 20Å was systematically added along the c direction (Fig. 1a). Hence, the investigated surface corresponded (the (001) surface) to the main cleavage plan, that should allow the highest adsorption capability. We have identified six potential adsorption sites on the illite modelled surface hereafter called site-Al, sit-Si, site-K, site-Na, site-O and site-H (Fig. 1b).

2.2 Calculation Methodologies for Exploiting the Results

The calculations were carried out using periodic DFT theory as implemented in the theoretical calculation code Vienna Ab-Initio Simulation Package (VASP 5.4.1) 25. (Calvet 2005). Plan waves (PAW) were used to describe the valence electron interactions (Kresse 1999). The core electrons were described using pseudopotentials. The convergence criterion for electron relaxation using the self-consistent solution of the Kohn-Sham equations is fixed at 10^{-6} eV. For ionic relaxations, calculations are allowed to converge as soon as the difference in force acting on each atom between two consecutive cycles is less than or equal to 0.02 eV/Å. The Perdew-Burke-Ernzerhof (PBE) functional of the DFT, which resulted from the generalized gradient approximation (GGA), was used (Kresse 1996, Grimme 2006). For the optimizations of all the systems studied, Brillouin zone integration was performed with the Monkhorst-Pack algorithm using only the Γ point. This was indeed dictated by the large size of the systems studied.

The total density of states (TDOS) (Haus 2016) were calculated on a finer grid (6x6x1). The plan wave cut-off energy was chosen to be 500 eV for all systems. To give a much more accurate description of the interactions occurring during adsorption processes, we took into account the dispersion forces in the calculations using Grimme's D2 method (Grimme 2006, Grimme 2004).

The adsorption energy ΔE_{ads} of the glyphosate molecule on the illite surface was calculated according to the following formula:

$$\Delta E_{ads} = E_{illite-glyphosate} - (E_{glyphosate} + E_{illite}) \quad (1)$$

Where $E_{illite-glyphosate}$ is the energy of the illite and the adsorbed chlorothalonil system, $E_{glyphosate}$ is the energy of the isolated glyphosate molecule and E_{illite} is the energy of the illite surface.

The variation in electron density caused by the adsorption of the molecule onto the surface can help gaining more insight in the nature of interactions occurred during adsorption (Daouli et al. 2022, Daouli et al. 2019). It is calculated according to formula (2) below and visualized with the VESTA software (Momma 2008).

$$\Delta\rho = \rho_{glyphosate_illite} - (\rho_{glyphosate} + \rho_{illite}) \quad (2)$$

With $\rho_{glyphosate_illite}$ being the electron density of the illite-glyphosate system after adsorption, $\rho_{glyphosate}$ and ρ_{illite} are respectively the electron densities of the chlorothalonil molecule and illite.

To assess the thermochemistry aspects of the performed adsorptions, we calculated the enthalpy and free enthalpy variation for the most stable configuration on each site. Given the big size of the studied systems, we allow only atoms of glyphosate molecule to move during frequencies calculations while atoms of illite surface were frozen. Indeed, we assumed that all motions components in the surface will compensate before and after adsorption. Once the frequencies calculations were performed, we used vaspkit tool (Wang 2001) to generate thermal corrections in the range of temperatures going from 300K to 600K with a step size of 50K. The enthalpy and free enthalpy variations (ΔH_{ads} , ΔG_{ads}) are calculated as follow:

$$\Delta H_{ads} = \Delta E_{ads} + \Delta ZPE \quad (3)$$

$$\Delta G_{ads} = \Delta E_{ads} + \Delta ZPE - T\Delta S_{ads} \quad (4)$$

ΔZPE is the variation of zero-point energy of the adsorption process and ΔS the entropy variation.

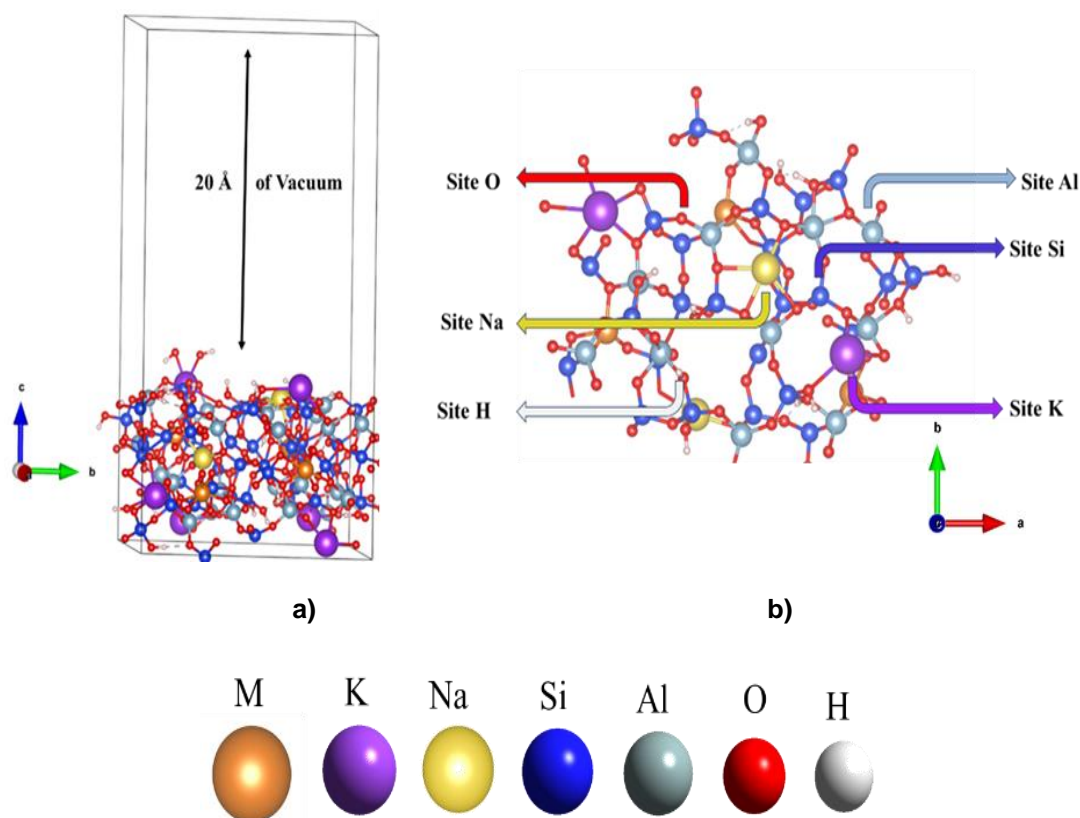


Fig. 1. The cells used for DFT study, (a) Illite 3x2x1 supercell with 25 Å of vacuum along c, (b) adsorption sites viewed from the face (001)

3. RESULTS AND DISCUSSION

Fig. 2 shows the structure of the glyphosate molecule.

Many adsorption configurations have been tested on each site of the illite surface. Indeed, three configurations have been obtained by directing toward the considered site on the illite surface each group (Car, N, Phos) highlighted on Fig. 2b when steric effect do not prevent it. The fourth configuration was obtained by setting the glyphosate molecule in a plan parallel to the surface (Flat). The tested configurations will be hereafter referred to as follow: Car-X, N-X, Phos-X, Flat-X where X represents the site.

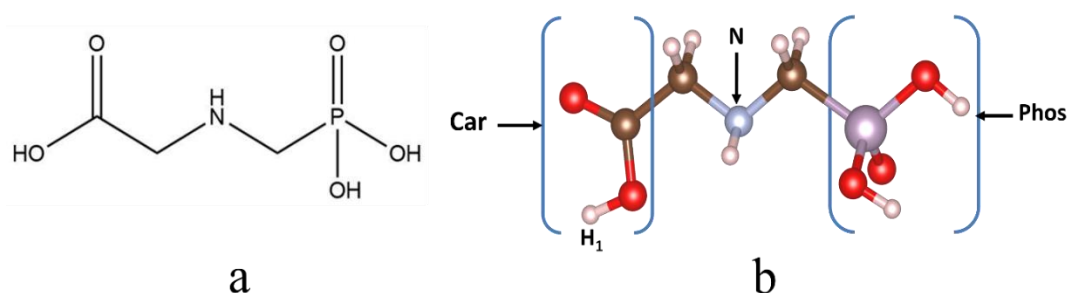


Fig. 2. Structure of glyphosate: a) 2D representation with numbering of the atoms through which glyphosate adsorbs to illite, b) 3D representation

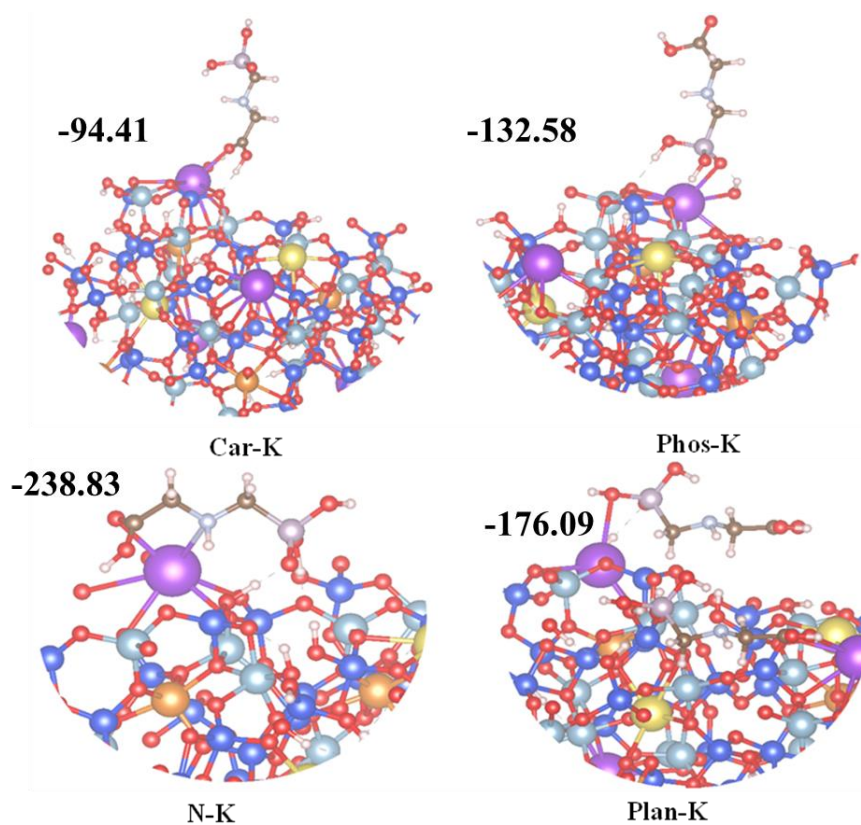


Fig. 3. Final geometries of glyphosate adsorption on K site of the illite surface and adsorption energies in kJ/mol

3.1 Adsorption Energies

3.1.1 potassium site

The geometries and the adsorption energy of glyphosate molecule on the site K in all the configurations after adsorption are presented on Fig. 3.

The analysis of adsorption energies reveals that the glyphosate molecule adsorbs more strongly in the N-K configuration. This is followed by the Flat-K, Phos-K and finally Car-K configurations. The adsorption energy of glyphosate in its N-K configuration is -238.83 kJ/mol with a dispersion energy of -56.25 kJ/mol corresponding to 23.25% of the total energy.

On this site, adsorption is dominated by chemical interactions due to the low contribution of van der Waals interactions. The adsorption of glyphosate on the Site-K of the illite surface can therefore be done according to all tested configurations. The

Car-K configuration, although possible because of the negative adsorption energy, is the least favorable.

The final geometry of glyphosate adsorption on illite in this N-K configuration showed the formation of two bonds between a potassium atom on the illite surface and a nitrogen atom and an oxygen atom of the glyphosate. In addition, two hydrogen bonds were formed between oxygen and hydrogen atoms on the illite surface and on the glyphosate. All these bonds formed during the adsorption of glyphosate on the Site-K better explain the high adsorption energy obtained as well as the contribution in dispersion energy.

3.1.2 Sodium Site

As in the previous case, glyphosate was adsorbed on the sodium site (Site-Na) of illite. The adsorption energies and geometries of the configurations after adsorption are shown in Fig. 4.

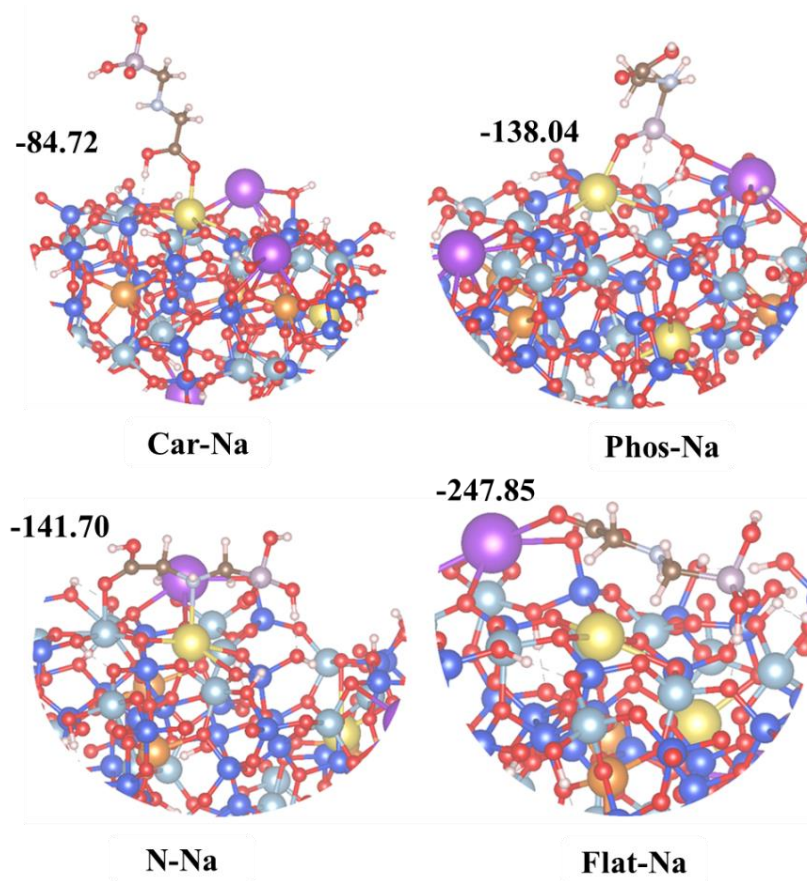


Fig. 4. Final geometries of glyphosate adsorption on sodium site of the illite surface and adsorption energies in kJ/mol

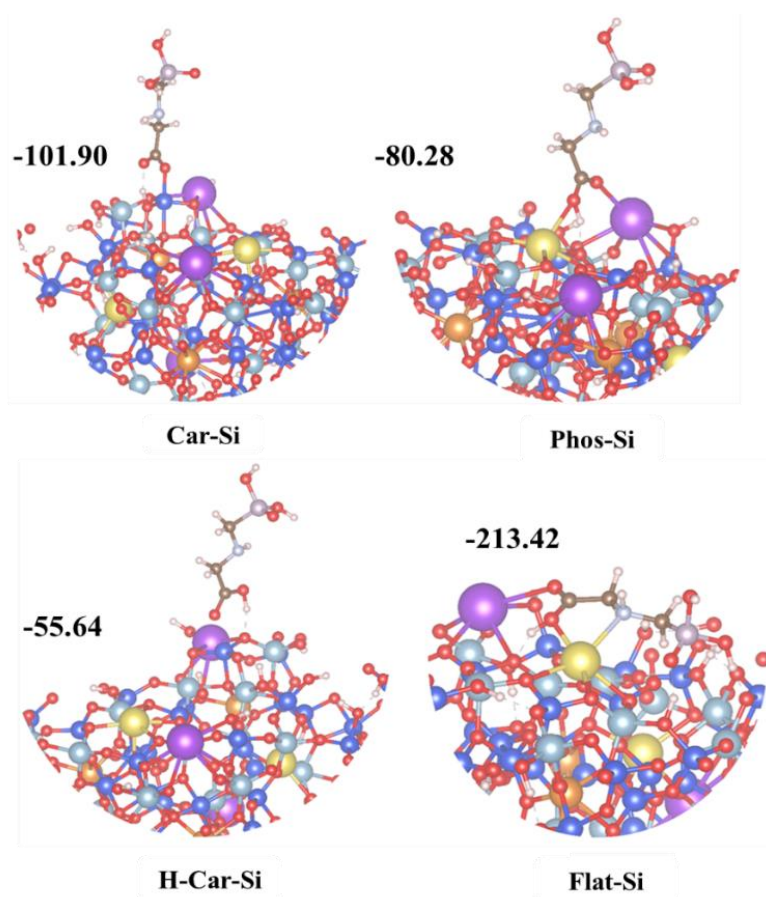


Fig. 5. Final geometries of glyphosate adsorption on Si site of the illite surface and adsorption energies in kJ/mol

On the Na site, the glyphosate molecule can adsorb in several configurations. Indeed, for all the configurations modelled, the adsorption energies are negative. The Flat-Na configuration is the one in which the interaction of the glyphosate molecule with the illite surface is the strongest, with an adsorption energy of -247.85 kJ/mol including a dispersion energy of -78.93 kJ/mol (31.85%). Adsorption in this configuration is dominated by chemical interactions with a prevalence rate around 68%. The Car-Na configuration is the least favored, as in the case of the K site.

In the final geometry of Flat-Na configuration, the adsorption of glyphosate on the sodium site of the illite was achieved by the formation of a bond between an oxygen atom of the glyphosate and a potassium atom on the illite surface. In addition, four hydrogen bonds were formed between oxygen and hydrogen atoms on the surface and the glyphosate molecule. These different bonds formed justify that the adsorption of the molecule is stronger in this configuration on this site.

3.1.3 Silicium site

The glyphosate molecule was also adsorbed on the silicon site (Site-Si) of the illite. The adsorption energies obtained (Fig. 5) are all negative and indicate that the glyphosate molecule can adsorb onto the Si site of the illite surface modelled in many configurations. The Flat-Si configuration is the most stable with an adsorption energy of -213.42 kJ/mol including a dispersion of -64.63 kJ/mol (30.28% of the total adsorption energy). Chemical interactions play the major role in the adsorption process. The H-Car-Si configuration is the least stable, as in the case of the two previous sites.

The adsorption of glyphosate in the most stable configuration (Flat-Si) occurred with the formation of a bond between a potassium atom on the surface and an oxygen atom of the glyphosate, and two bonds between a sodium atom on the surface and an oxygen atom and the nitrogen atom of the glyphosate. The formation of

these different bonds explains the high adsorption energy value obtained, indicating the strong adsorption of glyphosate on this site in this configuration. In addition, this final geometry reveals the formation of three hydrogen bonds.

Aluminum site: Adsorption of glyphosate molecule on the illite surface has also been simulated on the aluminum site of the illite surface. The obtained adsorption energies and the geometries of the configurations after adsorption are presented on Fig. 6.

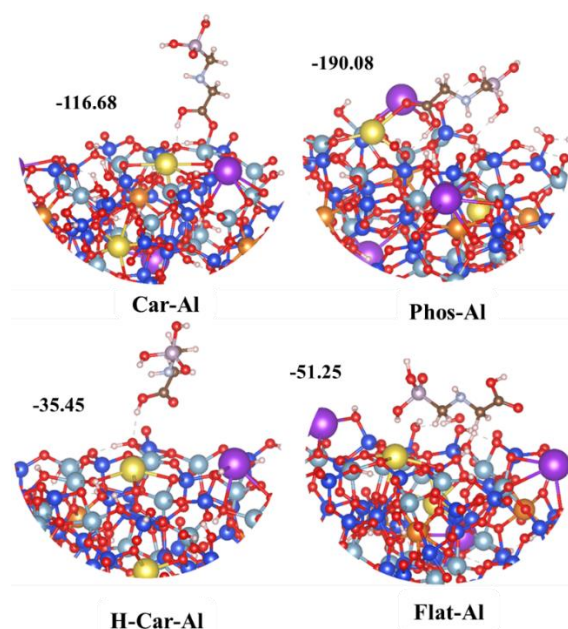


Fig. 6. Final geometries of glyphosate adsorption on Al site of the illite surface and adsorption energies in kJ/mol

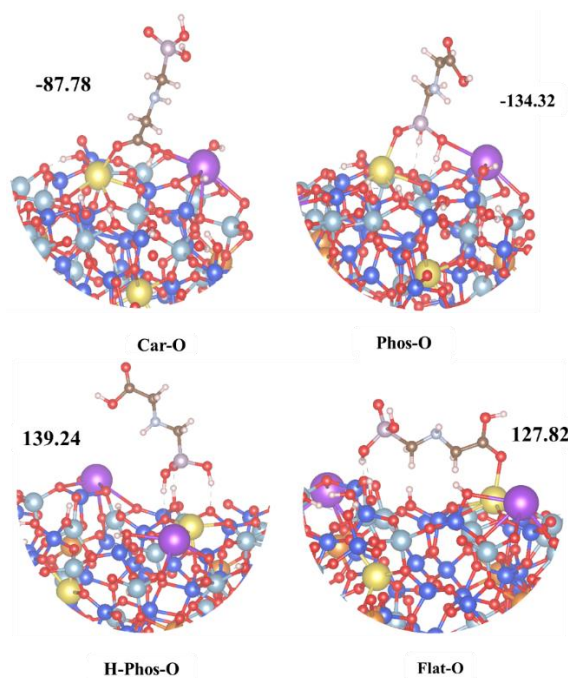


Fig. 7. Final geometries of glyphosate adsorption on O site of the illite surface and adsorption energies in kJ/mol

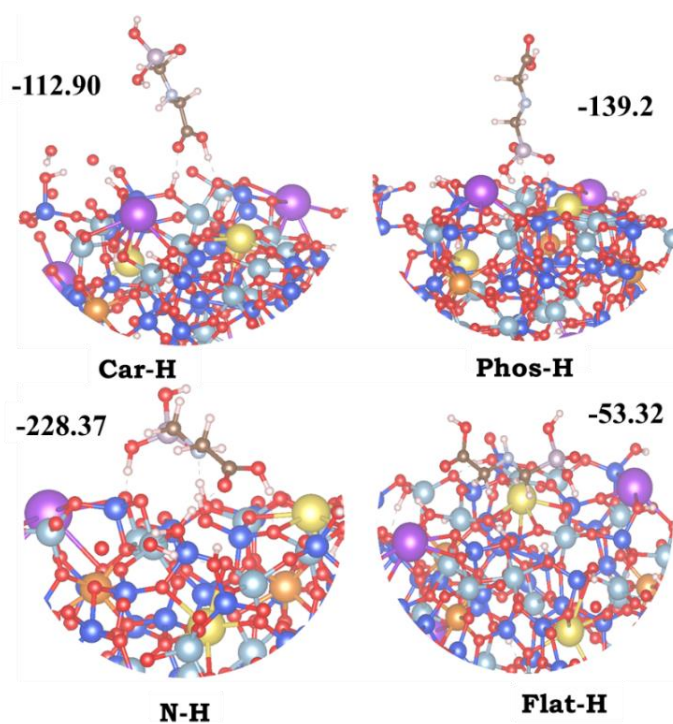


Fig. 8. Final geometries of glyphosate adsorption on H site of the illite surface and adsorption energies in kJ/mol

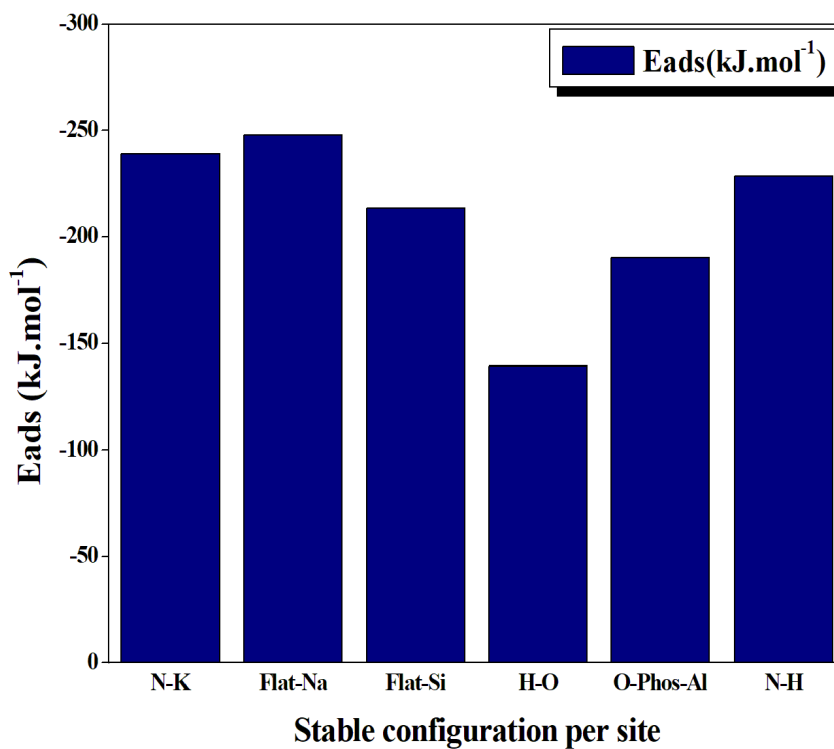


Fig. 9. Most stable Configurations per site during the adsorption of glyphosate molecule on illite surface

The information in Fig. 6 reveals that the glyphosate adsorption process on the aluminum site is exothermic since the adsorption energies for all the configurations are negative. We note a strong adsorption of glyphosate on the Aluminum site of illite in the vertical configuration (O-Phos-Al) with an adsorption energy of -190.08 kJ/mol. The dispersion energy during this adsorption process is -61.36 kJ/mol, representing 32.28% of the total adsorption energy. In this most stable configuration, adsorption occurred through the formation of a bond between a sodium atom on the surface and an oxygen atom on the glyphosate molecule. Three hydrogen bonds were also formed between oxygen and hydrogen atoms. All the bonds formed justify the relative stability of this configuration compared with the others.

Oxygen site: The glyphosate molecule was adsorbed on the oxygen site (Site-O) of the illite and the adsorption energies obtained are shown in Fig. 7.

Analysis of Fig. 7 reveals that strong adsorption of glyphosate on the oxygen site of illite is observed for all the configurations. Apart from the Car-O configuration which has a relatively low adsorption energy, the other configurations have almost equal but high adsorption energies. This indicates that glyphosate can adsorb to the O site of aluminum in several configurations. However, the H-O configuration is the one with the highest adsorption energy in absolute values. The adsorption energy of glyphosate on the Oxygen site of illite in the most stable vertical H-O configuration is -139.24 kJ/mol with a low dispersion energy (24.10 kJ/mol). This dispersion energy is evaluated at 17.31% of the total adsorption energy. The Adsorption in this configuration is thought to be largely guided by chemical interactions.

The final geometry of glyphosate adsorption on the illite oxygen site in the H-O configuration shows the formation of three hydrogen bonds, one between a glyphosate oxygen atom and a hydrogen atom on the surface, and two others between two glyphosate hydrogen atoms and a nitrogen atom and an oxygen atom on the surface.

Hydrogen site: The adsorption potential of illite via the hydrogen site (Site-H) with respect to glyphosate was investigated using various configurations. The Fig. 8 provides information

on the adsorption energies obtained and also on the geometries of configuration after adsorption.

Analysis of the adsorption energies of glyphosate on the H site of illite (Fig. 8) shows that the process is also exothermic as in the other cases. On this site, the configuration where the nitrogen atom of the glyphosate molecule is oriented towards the hydrogen atoms on the surface is the most stable. This was followed in that order by the Phos-H, Carb-H and finally Flat-H configurations. The adsorption energy in the N-H configuration is -228.37 kJ/mol with a dispersion energy of -74.98 kJ/mol. This dispersion energy represents 32.83% of the total adsorption energy. The adsorption has a prevalence of chemical interactions.

In the final geometry of glyphosate adsorption on the illite Hydrogen site in the N-H configuration, four hydrogen bonds were formed. Two are established between two oxygen atoms of glyphosate and two hydrogen atoms of the surface, and the other two, between two oxygen atoms of the surface and two hydrogen atoms of glyphosate.

Comparative study of adsorption sites: From the previous analyses, we have identified, by site, the configurations in which glyphosate is strongly adsorbed onto illite surface. The diagram in Fig. 9. shows the adsorption energies of glyphosate on illite according to the most stable configurations per site.

Analysis of this histogram reveals that glyphosate adsorption is favorable on the six different sites explored. Adsorption was very strong on the sodium site, followed by the potassium, hydrogen, silicon, aluminum and oxygen sites. On the Sodium and Silicon sites, adsorption took place in a flat configuration, but in vertical arrangements on the other sites. Furthermore, given the low dispersion rate in the total adsorption energies, we can conclude that all the adsorptions were guided by chemical interactions.

3.2 Thermochemistry of Adsorptions

To state out the exothermicity or endothermicity of the performed adsorptions, we calculated the enthalpy and the free enthalpy variations using relations (3) and (4) of subsection 2.2. The obtained values for both data are plotted on graphs of Fig. 10.

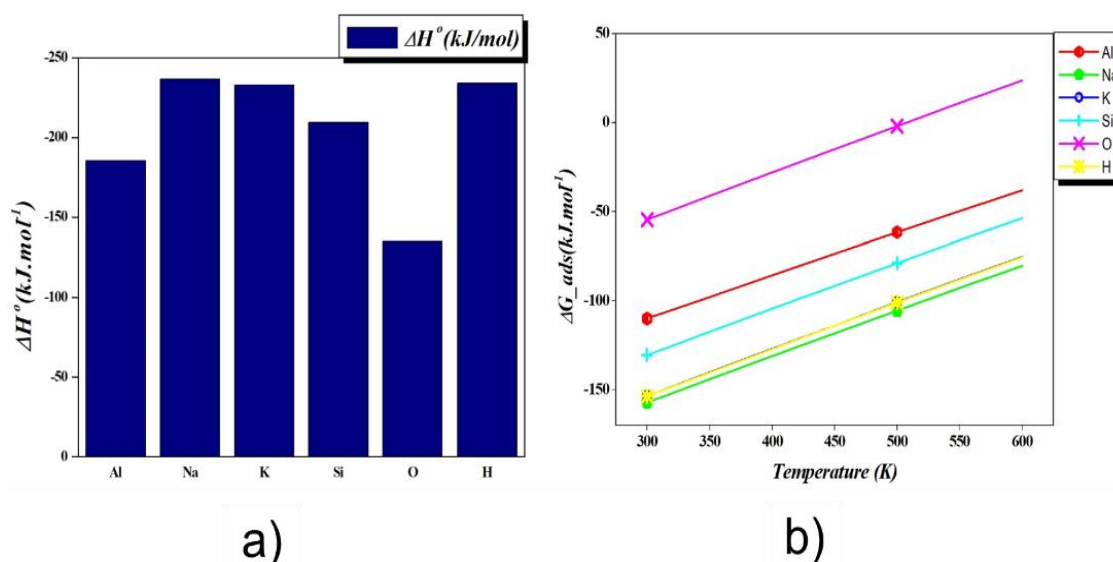


Fig. 10. Thermodynamic of the most stable configuration: a) variation of enthalpy, b) variation of free enthalpy along with temperature

Analyzing the graph a) of Fig. 10. It comes out that adsorption process is exothermic on all the sites, this because, all the ΔH_{ads} calculated are negative. Considering ΔH_{ads} , the oxygen site is also the less favored for the adsorption of glyphosate molecule on the considered illite surface. Also, all calculated ΔG_{ads} are negative meaning that adsorptions are all spontaneous. Oxygen site is also the less favored when taking into account ΔG_{ads} analysis. The desorption temperature, corresponding to the temperature from which ΔG_{ads} will become positive, apart from the oxygen site, will be very high given that ΔG_{ads} is negative for all remaining sites even at temperatures beyond 600K. This could mean that desorption rate will be very low.

3.3 Adsorption Mechanism

Assessment of the risk of formation of toxic by-products: We calculated the length variation of bonds containing atoms directly involved in the adsorption of glyphosate onto illite surface in order to assess the risk of the formation after adsorption of by-products that could be toxic. The histogram presented in Fig. 11 shows the variation in the interatomic distances of the bonds involved after the adsorption of glyphosate on illite for the most stable configurations per site.

The analysis of the graph in Fig. 12 shows slight stretching of the bonds involved in adsorption for the stable configurations of the K, Na and H sites. The elongation of the bond at the Hydrogen site is 0.005 Å, followed by those at the Sodium and Potassium sites. For the Silicon and Aluminum sites, we observed a shortening of the bonds involved. For the Oxygen site, we note a significant stretching of the bond involved. The variation in interatomic distance calculated is 0.030 Å greater than the threshold value (0.02 Å) for the plausible formation of toxic by-products.

We therefore conclude that the glyphosate adsorption process on illite at the oxygen site could present a risk of releasing toxic by-products. On the other sites, however, adsorption is favorable and there is no risk of toxic by-products being formed. Oxygen site being the least stable among the most stable configurations, one can conclude that there is no risk of by-product formation, a fact that can enhance the material recuperation for its reuse.

ISO-surface analysis: To better elucidate the interactions that occurred during the adsorption of the glyphosate molecule onto illite, we plotted the iso-surfaces variation for two configurations identified as among the most stable on the sites Si and O as shown in Fig. 12.

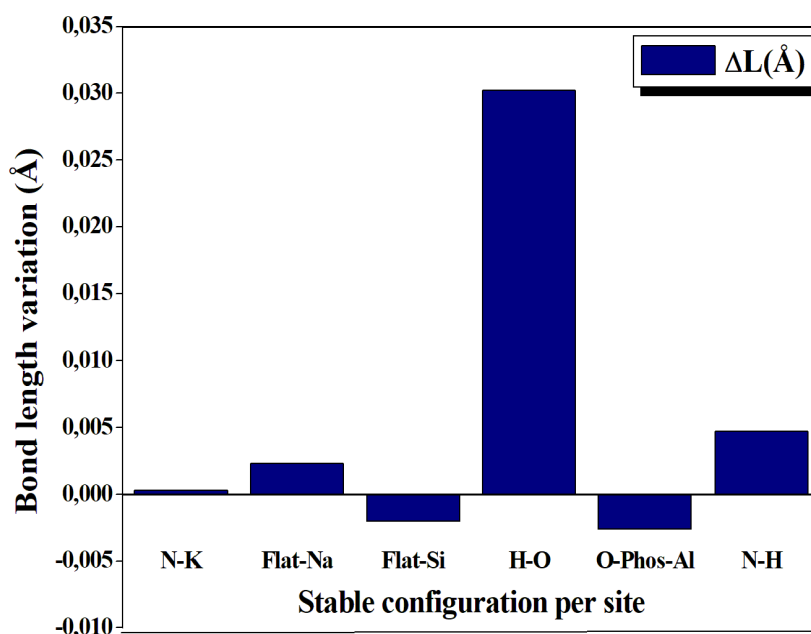


Fig. 11. Variation in the bond lengths directly involved in the adsorption of glyphosate on illite surface for the most stable configurations

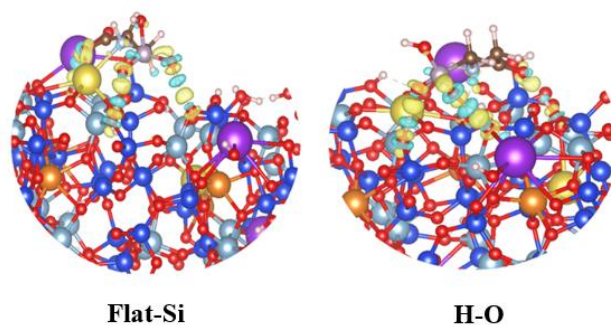


Fig. 12. The electron density changes iso-surface for the stable configuration on Si and O Sites. The yellow and blue represented iso-surfaces indicate variations of $+0.0015$ and -0.0015 electron/ \AA^3 , respectively

Analysis of Fig. 13 shows that in the stable configuration of the Si site, hydrogen bonds and electrostatic interactions between the nitrogen atom and the cations on the surface were formed, unlike in the H-O configuration where hydrogen bonds were mainly present. This justifies the fact that the adsorption energy at the Si site is higher and the configuration is more stable. The fact that electrostatic interactions and hydrogen bonds are the main parts of forces ruling the simulated adsorptions is line with conclusion of the work of Wang and coauthors (Wang 2022). They conducted both experimental and theoretical study of the adsorption of

glyphosate on montmorillonite clays and found that glyphosate adsorbed onto the montmorillonite clay, which is a smectite as illite, through electrostatic interactions and hydrogen bonding.

Total density of states (TDOS) analysis: In order to complete the understanding of the interactions between the illite surface and glyphosate molecule, the total densities of states are calculated for two of the most stable configurations (Flat-Si and H-O) per site after adsorption of glyphosate onto illite (Fig. 13).

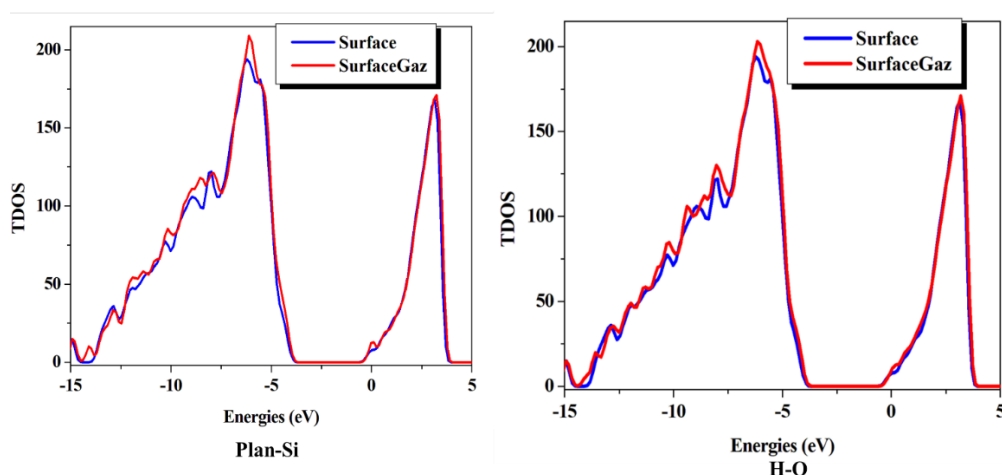


Fig. 13. Total densities of states of chlorothalonil adsorption on illite for the most stable configurations for site Si and O

The analysis of the total density of state graphs for the stable configurations on the Si and O sites shows that the peaks became more intense after adsorption. In addition, new peaks appeared on the flat-Si configuration, which is more stable than the H-O configuration. These changes attest the great electronic reorganization that occurred during the adsorption processes. It is also very important to note that the electronic changes at the surface are greater for the flat-Si configuration than for the H-O configuration.

4. CONCLUSION

We conducted the DFT study of the adsorption of glyphosate on illite. The results of this work brought out the capability of illite clay modelled in this work to trap glyphosate molecule. We firstly assessed the adsorption energies of glyphosate molecule on illite and secondly, elucidated the adsorption mechanism at the surface through the nature of the interactions produced during adsorption. It globally comes out from this study that:

- the adsorption of glyphosate on the illite surface is exothermic,
- the process of adsorption of glyphosate on illite does not present any risk of release of toxic by-products on five of the six studied sites,
- The adsorption process is mainly under chemical control in almost all the cases

All these findings elect illite clay as a performant material to design filters for the depollution of waters contaminated with glyphosate and its derivatives. We planned to extend this work to

other materials and also to consider conducting the study in aqueous area.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during writing or editing of this manuscript.

CONSENT

Not applicable

ETHICAL APPROVAL

Not applicable

COMPETING INTERESTS

Authors have declared that no competing interests exist

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