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Adsorption of aminomethylphosphonic acid on pristine graphene and graphene doped with transition metals: A theoretical study

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ABSTRACT

Aminomethylphosphonic acid (AMPA), a glyphosate breakdown product, exhibits environmental persistence, raising concerns. This study investigates AMPA adsorption on pristine and transition metal-doped graphene using quantum theory of atoms in molecules calculations. Results revealed favorable adsorption energies for pristine graphene, significantly enhanced by doping, with Co-doped graphene exhibiting the highest adsorption energy. Interactions were predominantly physisorption, and doping did not significantly alter graphene's electronic structure. Tight-binding dynamics simulations demonstrated efficient AMPA adsorption on doped graphene, with Co exhibiting the strongest binding affinity. These findings *highlight* the potential of transition metal-doped graphene as an effective adsorbent for removing AMPA from water sources.

1. Introduction

N(phosphonomethyl)glycine, also known as glyphosate, is an organophosphate chemical compound that is widely used in agriculture [1,2]. This compound acts by inhibiting the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), responsible for the growth and development of unwanted plant species. In studies carried out, the presence of glyphosate and its main metabolite, aminomethylphosphonic acid (AMPA), have been detected in groundwater and surface water. The concentrations found vary between 0.2 and 370 µg/L [3,4]. These concentrations can cause various damages to human health, both in direct and indirect exposure [5,6]. Glyphosate has been classified as box four by the Environmental Protection Agency (EPA). Additionally, the International Agency for Research on Cancer (IARC) has noted that glyphosate may cause potential carcinogenic problems. This classification has been supported by the World Health Organization (WHO), which has placed glyphosate in the second category of carcinogenic toxicity [7,8].

Some studies are focused on understanding the different degradation routes of the herbicide and its main metabolite, as well as its behavior in different environments [9,10]. However, the impact of excessive use of glyphosate on the environments continue to expand, making the control

and elimination of this chemical topics of great scientific interest. Some strategies have been proposed for the elimination of glyphosate and AMPA in water sources [11–14], but work is still being done in the search for selective and efficient adsorbents for this type of contaminants. The operation and availability of a wide range of adsorbents for various contaminants have been studied both theoretically and experimentally, since they allow the removal of soluble and insoluble organic, inorganic and biological contaminants [13–15]. In particular, carbonaceous materials have been widely used for the removal of contaminants from water and their modification with polymers has demonstrated the ability to adsorb up to 97 % glyphosate and 57 % AMPA [6].

However, AMPA removal is still low, posing a risk to human health and the environment. Therefore, it is essential to propose new adsorbents that allow greater removal of AMPA, with the aim of reducing the environmental impact caused by the unregulated use of glyphosate. This involves exploring different removal strategies, such as the use of selective and efficient adsorbents, as well as the modification of carbonaceous materials to improve their adsorption capacity.

Graphene, one of the allotropes of carbon, is considered as an extremely attractive candidate for the control and elimination of contaminants due to its properties such as large surface area, minimal defects, exceptional rigidity, excellent mechanical strength, and high

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electrical conductivity [13–16]. These characteristics allow its potential use in the adsorption and removal of contaminants [17]. Theoretical studies have shown that graphene has the ability to adsorb amino acids such as valine, arginine and aspartic acid, which demonstrating its effectiveness as an adsorbent for this type of compounds. Furthermore, it has been found that graphene can interact with glyphosate, that has similar characteristics similar to those of glycine, another amino acid, suggesting that graphene could also remove AMPA in an aqueous matrix [17–20]. However, pristine graphene has been observed to have limited adsorption capacity due to its low reactivity and charge transfer. To improve these properties, doped graphene has been investigated. Studies such as those by Xiaopeng Li et al. [18] have shown that doping increases the properties of graphene, while Ullah et al. [19], as well as Aramburu et al. [20], showed greater activation than pristine and a mostly reactive structure in doped graphene. Among the efficient and low-cost dopants, transition metals such as Ni, Fe and Co are presented as promising alternatives due to their availability and low cost [21]. These metals can be used to dope graphene and improve its adsorption capacity, making it a potentially effective adsorbent for the removal of contaminants, like AMPA.

The search for adsorbent materials to control and eliminate contaminants from water sources is an important challenge for the scientific community, with the aim of preserving our natural resources. Therefore, we have carried out a computational study using pristine graphene and transition metal-doped graphene to analyze their AMPA adsorption capacity. Our approach was based on conformational analysis to identify the best molecular structures, using Density Functional Theory (DFT) calculations. Furthermore, we examine the energetic and thermodynamic properties as well as intermolecular interactions using topological analysis, and tight-binding molecular dynamics (TB-MD) simulations. This information is useful for the design of more effective adsorbents in removing AMPA from water sources.

2. Methodology

For this study, graphene sheets used in previous studies were considered [22]. The model system of the pristine graphene sheet is made up of 48 carbon atoms in a hexagonal arrangement with the edges saturated with 18 hydrogen atoms. In the case of doped models, a carbon atom is replaced by a transition metal (Ni, Fe and Co). The substitution sites were obtained from experimental and theoretical studies (Fig. 1) [23,24].

All simulations were performed using Gaussian software [25]. To evaluate the adsorption of AMPA, 36 systems were explored corresponding to the synchronized horizontal rotation every 10 degrees of the AMPA on the pristine graphene sheet, in addition, the closest heteroatom of the AMPA to the graphene sheet was adjusted to a distance of 3.0 to 4.0 Å [26]. All systems were fully optimized with the Schlegel algorithm. All minimum energy states found through the optimizations

were verified by frequency calculations. Quantum mechanical calculations were performed using Density Functional Theory (DFT). To describe the exchange and correlation energy, the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) was used [27]. The valence electrons of carbon and hydrogen atoms were described by the Def2-SVP basis set, and the transition metal atoms with the LANL2DZ pseudopotential. Grimme dispersion correction was used during all calculations to incorporate Van der Waals (VdW) interactions [28].

To determine the adsorption capacity of the graphene models, different parameters were calculated. The adsorption energy (ΔE_{ads}) was estimated using the following equation:

$$\Delta E_{ads} = E_{graphene+AMPA} - (E_{graphene} + E_{AMPA}) \tag{1}$$

where $E_{graphene+AMPA}$, $E_{graphene}$ and E_{AMPA} are the total energies of the adsorbent-adsorbate, adsorbent and adsorbate, respectively. Also, the enthalpy of adsorption (ΔH_{ads}), Gibbs free energy of adsorption (ΔG_{ads}), and the equilibrium constant (*K*) at the temperature of 298.15 *K* was determined using the values of adsorbent-adsorbate system, adsorbent and adsorbate.

$$\Delta H_{ads} = H_{graphene+AMPA} - (H_{graphene} + H_{AMPA}) \tag{2}$$

$$\Delta G_{ads} = G_{graphene+AMPA} - (G_{graphene} + G_{AMPA}) \tag{3}$$

$$K = e^{-\frac{\Delta G_{ads}}{RT}} \tag{4}$$

The effect of the solvent was taken into account in the calculations by performing geometric optimizations in the aqueous medium using the polarizable continuum model IEFPCMat the same level of theory used [29,30]. The dielectric constant in PCM was set at 78.39 to simulate water, since it imitates the medium where the possible applications will be developed. The Gibbs free energy in aqueous solution (G_{sol}) was estimated in the calculations of the adsorption processes. The term G_{sol} was determined from equation (5), which includes the electrostatic and non-electrostatic interactions of the solute–solvent.

$$G_{sol} = G_{elec} + G_{dis} + G_{cav} \tag{5}$$

Where, G_{sol} represents electrostatic interactions, G_{dis} is a dispersionrepulsion term and G_{cav} is the cavitation energy between the solute and the solvent. Furthermore, the effect of AMPA adsorption on the electronic properties in the graphene sheets was evaluated by calculating the bandwidth of the HOMO-LUMO energies through the densityof-states (DOS) plot.

Intermolecular interaction forces are responsible for the formation of numerous binding critical points (BCPs) in the center of the interaction region. The nature of the intermolecular interactions presents in systems with pristine graphenes with better adsorption energy, and graphene systems doped with transition metal ions Ni, Co, and Fe, was evaluated



Fig. 1. Aminomethylphosphonic acid (AMPA) molecule and the pristine and transition metal-doped graphene models respectively.

using the Quantum Theory of Atoms in Molecules (QTAIM) implemented in MultiWFN software [31]. The BCPs between molecules of the adsorbent-adsorbate system are characterized by the values of electron density (ρ) and Laplacian of electron density ($\nabla^2 \rho$). Additionally, the non-covalent interaction index (NCI) has been used for visualization in three-dimensional space [32]. Images were rendered by the Visual Molecular Dynamics (VMD) viewer.

The assessment of kinetic stability was performed through molecular dynamics simulations utilizing the semi-empirical tight-binding method. The GFN2-xTB Hamiltonian [33], in tandem with the GBSA implicit solvation model for water, was employed across all simulations. Each simulation for the System 1, System-Ni, System-Fe, and System-Co had a duration of 1.6 ns. During these simulations, the integration of the equations of motion occurred using a 4.0 fs time step within the NVT ensemble, which maintained a constant number of atoms, volume, and temperature at 298.15 K. A Berendsen thermostat was utilized to maintain this constant temperature. Additionally, the SHAKE algorithm was implemented to ensure the stability of all hydrogen atoms. Data recording took place every 10 fs throughout the molecular dynamics runs.

3. Results and discussion

In this section, the results obtained from the theoretical simulations were analyzed in detail. The primary objective was to identify the system with the highest adsorption capacity. To achieve this, the AMPA molecule was systematically rotated by increments of ten degrees on the pristine graphene sheet, completing a full rotation of 360°. This approach allowed for a comprehensive examination of the adsorption properties of AMPA on graphene. Subsequently, the adsorption properties of pristine graphene sheets were thoroughly compared to those of graphene sheets doped with transition metal ions such as nickel (Ni), cobalt (Co), and iron (Fe). The doped graphene systems were analyzed to determine the effect of these metal ions on the adsorption efficiency and capacity for AMPA. Furthermore, the study included an in-depth analysis of the formation of several BCP in the adsorbate-adsorbent interactions. These critical points are indicative of the nature and strength of the interactions between AMPA and the graphene surface, both pristine and doped. The non-covalent interactions, including ionic bonds, hydrogen bond, VdW forces and π - π interactions, were also scrutinized to understand their role in the adsorption process. This comprehensive analysis provided valuable insights into the molecular interactions and the efficiency of different graphene systems in adsorbing AMPA, highlighting the potential modifications to enhance adsorption capacity through doping with transition metals.

3.1. Pristine and transition metal-doped graphene models

To find the systems with the highest adsorption capacity, 36 models were explored by rotating the AMPA molecule every 10 degrees on the graphene sheet. These simulations aimed to cover a comprehensive range of orientations to identify the optimal adsorption configuration. Interestingly, the simulations revealed that several initial structures converged to the same equilibrium geometry. Through this process, it was found that only a group of 10 geometrically distinct molecules could be located, illustrating the tendency of AMPA to adopt certain preferred orientations when interacting with the graphene surface (see Fig. S1). The primary characteristic of the identified systems was a pronounced orientation of the phosphate group, with a slight orientation of the amino group of AMPA towards the graphene sheets. This specific orientation was crucial for maximizing the adsorption capacity. Additionally, the average distance between the heteroatoms of the closest AMPA and the pristine graphene sheet was measured to be 3.31 Å. This finding aligns well with the values reported in the literature, validating the accuracy and reliability of the simulation results (Table 1) [26,34]. Moreover, an intramolecular hydrogen bond interaction was observed

Table 1

Adsorption energy (ΔE_{ads}) and adsorption distance (D_{ads}) of theoretical studies involving adsorption processes on pristine graphene nanosheets. Energy values are given in kcal/mol.

Adsorbate	Adsorbent	ΔE_{ads} (kcal/mol)	D _{ads} (Å)	Reference
AMPA	Pristine Graphene	-26.3	3.2	This work
Glyphosate	Pristine Graphene	-32.7	_	[37]
Naproxen	Pristine Graphene	-22.5	3.3	[26]
Ibuprofen	Pristine Graphene	-19.3	3.3	[26]
Paracetamol	Pristine Graphene	-15.1	3.2	[26]
Tramadol	Pristine Graphene	-19.3	3.2	[26]
Histidine	Pristine Graphene	-34.4	3.0	[34]
Alanine	Pristine Graphene	-20.9	3.2	[34]
Aspartate	Pristine Graphene	-26.9	4.0	[34]
Tyrosine	Pristine Graphene	-37.6	3.0	[34]
AMPA	Graphene-Ni	-51.6	1.9	This work
O ₂	Graphene-Ni	-20.0	_	[20]
AMPA	Graphene-Fe	-58.2	1.9	This work
O ₂	Graphene-Fe	-42.2	_	[20]
AMPA	Graphene-Co	-60.6	1.8	This work
02	Graphene-Co	-65.4	_	[20]
SO_2	Graphene-Co	-80.0	2.0	[38]

within the AMPA molecule in what was identified as System 1 (Fig. S1). This interaction significantly contributed to the geometric stability of the system, with an average distance between the acceptor and the donor atoms measured at 1.68 Å. Given the enhanced stability conferred by this hydrogen bond, System 1 was deemed the reference structure for further investigation into the adsorption behavior of AMPA on a graphene sheet doped with the metals Fe, Ni, and Co. Dopants can significantly alter the properties of graphene, affecting the adsorption energy, chemical reactivity and electronic distribution. Validating and analyzing different dopant configurations helps to better understand the adsorption mechanism and provides valuable information for the design of materials with specific and improved properties. Thus, based on the studies of the adsorption of H₂CO on Al-doped graphene sheets and the adsorption of CH₂O, H₂S and HCN on a graphene sheet doped with a manganese atom, where the choice of the position is given by the substitution of a central carbon atom by a metal atom [35]. Furthermore, the study by Mollaamin and Monajjemi [36] exposes that doping with transition metals such as Fe, Ni and Zn improves the adsorption efficiency of toxic gases due to significant charge transfer and variations in charge density. This being so, our choice is based on previous studies that have demonstrated the feasibility and efficacy of these dopings on graphene. Furthermore, the development of new materials as adsorbents is crucial in the application towards emerging contaminants, where transition metals with Co, Fe and Ni may have high availability and low cost and can serve as a promising alternative, due to their electronic and catalytic properties that significantly improve the reactivity and adsorption of graphene. These metals can provide additional active sites and facilitate specific interactions with AMPA. Overall, the analysis highlighted the significance of the phosphate group orientation in enhancing the adsorption interaction, providing a detailed understanding of how AMPA interacts with graphene at the molecular level.

3.2. Adsorption properties

To evaluate the adsorption capacity of the selected systems, the geometric and thermodynamic parameters were calculated both in the gas phase and in aqueous solution (Table 2) using equations 1–5. These calculations include parameters such as bond lengths, bond angles, adsorption energies, and Gibbs free energies. The results show that the inclusion of solvent does not significantly modify the optimized structures of any of the systems explored. However, the presence of the solvent does decrease the adsorption energies to a lesser extent compared to the gas phase. This decrease is attributed to the solvation effects, where the solvent molecules interact with both the adsorbate and the adsorbent, thereby stabilizing the system. The adsorption energies

Table 2

Adsorption energies (ΔE_{ads}), adsorption enthalpies (ΔH_{ads}), Gibbs free energies (ΔG_{ads}) and equilibrium constant (*K*) for the systems formed by AMPA and graphene sheets both in the gas phase and in aqueous solution. Energy values are given in kcal/mol.

Systems	ΔE_{ads}		ΔH_{ads}		ΔG_{ads}		K	
	Gas	Water	Gas	Water	Gas	Water	Gas	Water
System-1	-27.0	-26.3	-15.7	-15.2	-4.6	-20.9	$2.36 imes 10^3$	2.01×10^{15}
System-2	-24.3	-20.9	-13.5	-10.6	-2.7	-14.7	$1.01 imes 10^2$	5.58×10^{10}
System-3	-24.1	-20.7	-13.3	-10.4	-3.3	-15.4	$2.84 imes 10^2$	1.83×10^{11}
System-4	-24.6	-22.3	-12.5	-10.8	-2.0	-16.1	$3.32 imes10^1$	6.35×10^{11}
System-5	-24.5	-22.0	-12.5	-10.6	-2.3	-17.2	5.25×10^{1}	4.07×10^{12}
System-6	-23.9	-21.8	-12.2	-10.2	-2.0	-16.5	$3.01 imes10^1$	1.32×10^{12}
System-7	-23.9	-21.8	-12.2	-11.8	-2.0	-16.9	$3.01 imes 10^1$	2.55×10^{12}
System-8	-23.6	-22.8	-11.9	-10.1	-2.0	-17.0	$2.96 imes 10^1$	$3.13 imes10^{12}$
System-9	-19.4	-21.8	-8.5	-10.2	-2.5	-16.2	$1.45 imes 10^2$	8.03×10^{11}
System-10	-23.5	-22.8	-11.6	-10.7	-1.5	-18.1	$1.35 imes10^1$	2.00×10^{13}
System-Ni	-66.9	-51.6	-58.7	-40.6	-46.4	-40.6	1.01×10^{34}	6.02×10^{29}
System-Fe	-77.7	-58.2	-69.9	-48.6	-57.2	-46.2	8.02×10^{41}	7.43×10^{33}
System-Co	-83.7	-60.6	-77.4	-49.2	-66.1	-47.7	2.78×10^{48}	9.83×10^{34}

obtained for all systems are negative values, indicating that the adsorption process is exothermic and spontaneous. Specifically, the negative adsorption energies suggest a release of energy upon adsorption, which favors the stability of the adsorbed state. Given the practical applications of these systems, we present the energy results obtained through simulations in aqueous solution. This choice is crucial as it mimics the real-world environment where these systems are likely to be employed, such as in wastewater treatment, biosensors, and other aqueous-based applications [39]. The aqueous environment can influence the adsorption behavior due to factors such as solvation and ionic strength, making these results more relevant for practical use. Furthermore, the thermodynamic parameters such as adsorption enthalpies (ΔH_{ads}) , Gibbs free energies (ΔG_{ads}) , were calculated to provide a comprehensive understanding of the adsorption process. The negative values of ΔG_{ads} confirm the spontaneity of the adsorption, while the enthalpy and entropy changes give insights into the nature of the interactions between the adsorbate and the adsorbent. For example, a negative ΔH_{ads} indicates an exothermic process, which is consistent with the observed negative adsorption energies.

We have observed that doping graphene sheets with the transition metals Ni, Fe and Co significantly improves the adsorption capacity. When comparing these doped systems with the undoped System 1, it has been found that the adsorption energy increases notably. Specifically, a greater increase has been recorded in the case of Co, with an adsorption energy of - 60.598 kcal/mol, followed by Fe (-58.245) kcal/mol and finally Ni (-51.625) kcal/mol. It is relevant to highlight that glyphosate and AMPA present structural similarities to each other. When comparing the values obtained in this study with the findings where the adsorption of graphene doped with transition metals was evaluated, adsorption energies ranging between - 31.82 and - 65.26 kcal/mol were found [20]. On the other hand, when comparing the adsorption energies reported in the literature for the case of the adsorption of O_2 [20] and SO_2 [38] on graphene sheets doped with the metals Ni, Fe and Co, it is possible to observe more negative values of adsorption energy, suggesting stronger interaction between the adsorbates and the doped graphene sheet. This improvement is also reflected in the thermodynamic parameters, indicating that the systems under study could exhibit spontaneous adsorption, given that the values of $\Delta G_{ads} <$ 0, and the equilibrium constants exceed those of pristine graphene. In addition, values were found in a range similar to other theoretical studies that have used graphene sheets in adsorption processes (Table 1).

This increase in adsorption efficiency is largely attributed to the adoption of a tetrahedral structure by the metals (Fig. S1), which maximizes the surface area and expands the interaction sites for the possible binding of the AMPA molecule to the graphene sheet. According to the argument presented by Yam et al. In 2020 [40], this spatial arrangement provides a greater number of active sites, which in turn boosts reactivity and adsorption capacity. This improvement derives from the ability of

transition metals to take advantage of their empty d orbitals and receive lone pairs of electrons from oxygen atoms, which find accommodation in their antibonding *d* orbitals through retrodonation. These orbitals can interact with adsorbates through coordination bonds [40].

These findings suggest that doping with transition metals, such as Ni, Fe, and Co, can have a significant impact on the adsorption capacity of graphene sheets. These results are promising and open the possibility of using these doped sheets in applications related to the adsorption of substances such as glyphosate and AMPA. However, it is important to note that more research and studies are needed to fully understand the adsorption mechanisms. These findings represent an advance in the field and provide new perspectives for future research on this topic.

To better understand how transition metal-doped graphene affects the AMPA adsorption capacity and the electronic properties of the system, we performed density of states (DOS) plots (Fig. S2). In this analysis, we focus on the systems with the highest adsorption capacity: System 1 and System-Co. In the case of System 1, we observe that pristine graphene has a bandgap of 2.36 eV. However, when AMPA is adsorbed onto pristine graphene, the bandgap maintains the same energy value of 2.36 eV. This suggests that AMPA adsorption does not significantly alter the electronic structure of pristine graphene.

On the other hand, when examining graphene doped with a cobalt atom, we noticed an increase of 0.23 eV in the bandwidth of the bandgap. This modification could be related to the interactions between the cobalt atom and the adsorbed AMPA, which could slightly influence the conductivity properties of the material. Although our results indicate that cobalt-doped graphene could offer a more favorable environment for AMPA adsorption, it is important to *highlight* that the bandgap energies for both pristine graphene and cobalt-doped graphene are within the reported range in literature [41].

3.3. Topological analysis

AMPA has ionic groups in its molecular structure, which significantly influences its interactions with surfaces such as graphene. Specifically, the amino group is a weak base that can accept a proton, becoming positively charged and forming the ammonium ion. In addition, the phosphonic acid group contains two ionisable hydroxyl groups that can give up protons and become negatively charged, forming the phosphate ion. These functional groups allow AMPA to form strong electrostatic ion-ion interactions with the graphene surface, especially if the graphene is doped with transition metals, which modifies its electronic properties. VdW interactions and induced dipole interactions also play an important role in the adsorption of AMPA on graphene. The intensity of these electrostatic interactions determines the degree of adsorption of the molecule, with strong ionic intermolecular interactions combined with VdW interactions being one of the reasons for the favourable adsorption capacities in these systems. In System 1, electrostatic interactions were observed with an average acceptor–donor distance of 2.6 Å, and an intramolecular hydrogen bridge in the AMPA with a distance of 1.68 Å. In addition, VdW interactions were detected between one of the oxygens in the AMPA and pristine graphene (CP 155–156), see Fig. 2. In transition metal doped systems, the interactions seem to be influenced by electrostatic ionic interactions and weak long-range interactions. In the System-Fe and System-Co, strong interactions were

observed with distances of 2.25 Å (CP 104) and 3.50 Å (CP 125) respectively. In the System-Ni, intramolecular hydrogen bonding was detected with a distance of 1.92 Å (CP 118). The AMPA adsorption capacity in these systems is determined by a combination of electrostatic, van der Waals and hydrogen bonding interactions, suggesting that modification of graphene with different transition metals can optimise AMPA adsorption. Furthermore, the thermodynamic parameters



Fig. 2. NCI analysis and reduced density gradient plot (RDG) of System 1, System-Ni, System-Fe, and System-Co with the best adsorption properties. PCs indicate the different bond critical points (BCP). The surfaces are colored according to the sign(λ_2) ρ in the range - 0.020 to 0.035 au.

indicate a spontaneous adsorption of AMPA, $\Delta G_{ads} < 0$. The System-Co presented the highest equilibrium constant with a value of 9.83 \times 10³⁴ (Table 2).

To understand the interactions, present between AMPA and pristine and doped graphene sheets, the QTAIM methodology was used, which provides a definition of intermolecular bond critical points (BCP) [42,43]. In the first instance, the positive values of $\nabla^2 \rho_{BCP}$ in the BCP indicate that G_{BCP} is greater than V_{BCP} , which implies the existence of hydrogen bond type interactions, thus specifying their classification as weak, medium, strong and very strong in relation to $\nabla^2 \rho_{BCP}$ and H_{BCP} [43]. The Table 3 provides an in-depth topological analysis of BCPs, offering insights into the nature and strength of the chemical bonds. The ρ_{BCP} is observed in the O₅₃...Fe₂₁ bond in System-Fe at 0.1125 a.u., indicating a strong covalent interaction, while the lowest ρ_{BCP} is found in the H₅₇...C₄₆ bond in System-Co at 0.0015 a.u., suggesting a weak, closed-shell (ionic) interaction. The $\nabla^2 \rho_{BCP}$ most positive value, 0.7170 a.u. for the O₅₃...Co₂₁ bond in System-Co, indicates a closed-shell interaction. Other significant values include 0.6619 a.u. for the O₅₃... Ni₂₁ bond in System-Ni, suggesting a mixed interaction, and 0.6514 a.u. for the O₅₃...Fe₂₁ bond in System-Fe, supporting its strong covalent character [22,42]. Since according to Cremer and Kraka [44], the point analysis of G_{BCP} and V_{BCP} indicates that for covalent bonds the local energy density $H\rho_{BCP=} G_{BCP} + V_{BCP}$ in the sites of highest concentration of ρ_{BCP} is always negative. This can be observed at the critical points in which atoms or different transition metals interact intramolecularly with AMPA [45,46]. The highest G_{BCP} value of 0.1993 a.u. is found for the O₅₃...Co₂₁ bond in System-Co, suggesting a significant covalent contribution. Other high values include 0.1879 a.u. for the O53...Fe21 bond in System-Fe and 0.1644 a.u. for the O₅₃...Ni₂₁ bond in System-Ni, both indicative of strong covalent bonds. The $V_{\rm BCP}$ shows the strongest nuclear-electron attraction in the O_{53} ... Co_{21} bond in System-Co with a value of - 0.2193 a.u.. Similarly, the $\mathrm{O}_{53}...\mathrm{Fe}_{21}$ bond in System-Fe, with a $V_{\rm BCP}$ of -0.2130 a.u., reinforces its strong covalent nature. The most negative H_{BCP} value of -0.0251 a.u. for the O_{53} ...Fe₂₁ bond in System-Fe suggests a robust covalent bond. Other notable negative values include - 0.0200 a.u. for the O_{53} ... Co_{21} bond in System-Co and -0.0110 a.u. for the $H_{59}...N_{54}$ bond in System 1. The only positive H_{BCP} value observed is 0.0011 a.u. for the O53...Ni21 bond in System-Ni, indicating a unique interaction profile. The topological analysis of BCPs reveals significant variations in bonding interactions, reflecting the diverse nature of chemical bonds. System 1 shows a range of bond distances and electron densities, indicating a mixture of interaction strengths. System-Ni and System-Fe exhibit strong covalent bonds, particularly evident in the high ρ_{BCP} and significant negative H_{BCP} values for the O53...Ni21 and O53...Fe21 bonds. System-Co, while also showing strong covalent characteristics, displays a notable closed-shell

interaction in the O₅₃...Co₂₁ bond.

Furthemore, the non-covalent interaction (NCI) index is used as an additional tool for the study of interactions in the mentioned systems. The NCI is based on the graphical representation of the reduced density gradient and the sign(λ_2) ρ , which allows the identification of attractive, weak and repulsive interactions. Strong attractive interactions are shown in blue, while strong repulsive interactions are shown in red. On the other hand, weak interactions are *highlighted* with a green isosurface. Fig. 2 shows the presence of strong interactions through ionic bonds and hydrogen bonds. Furthermore, green zones can also be identified that correspond to weak VdW dispersion and interactions between glyphosate and pristine and doped graphene. These weak interactions appear to play an important role in the adsorption process, reinforcing the previous conclusion that AMPA adheres to adsorbents through physisorption analogous to glyphosate and to transition metals an ionic or covalent chemisorption [47].

3.4. Tight-binding molecular dynamic simulations

Tight-binding molecular dynamics (TB-MD) simulations have emerged as a powerful computational tool to study the interactions and dynamics of graphene and carbon nanostructures on metal surfaces at the atomic scale.

In this study, TB-MD simulations were conducted to explore the adsorption process of AMPA on both pristine graphene surfaces (System 1) and those doped with Nickel (System-Ni), Iron (System-Fe), and Cobalt (System-Co), see Fig. S3. The simulations aimed to provide a comprehensive understanding of the interaction mechanisms at the molecular level. It was observed that AMPA does not adsorb onto the pristine graphene surface and detaches from it around 1.0 ns, indicating a weak interaction and lack of binding affinity. Conversely, on doped graphene surfaces (Ni, Fe, and Co), AMPA exhibits efficient adsorption, demonstrating a strong affinity for the doped materials. This efficient adsorption is particularly notable with Cobalt, where the interaction is strongest. The strength of this interaction is indicated by lower Root Mean Square Deviation (RMSD) fluctuations compared to those observed with Nickel and Iron. These lower RMSD fluctuations suggest a more stable and consistent binding of AMPA to the cobalt-doped graphene surface, highlighting Cobalt as the most effective dopant for AMPA adsorption among the three metals studied.

Fig. 3 presents the RMSD values for the four systems under investigation: System 1, System-Ni, System-Fe, and System-Co. The data indicates that System-Co has the lowest RMSD value, signifying that this system experienced the least structural deviation from its initial configuration throughout the duration of the simulation. This low RMSD value suggests a high level of structural stability and minimal

Table 3

Topological analysis of the bonding critical points (BCP) of System 1, System-Ni, System-Fe, and System-Co. Bond Distance (r) in Angstroms, Electron Density (ρ_{BCP}), Electron Density Laplacian ($\nabla^2 \rho_{BCP}$), Kinetic Energy Density (G_{BCP}), Potential Energy Density (V_{BCP}) and Total Energy Density (H_{BCP}). All parameters were calculated at the PBE-D3/Def2-SVP level. Energies are given in atomic units (a.u.).

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Bond	CP	r	$ ho_{ m BCP}$	$ abla^2 ho_{ m BCP}$	$G_{ m BCP}$	V _{BCP}	$H_{\rm BCP}$
$H_{56} \cdots C_{15}$	115	2.71	0.0076	0.0231	0.0048	-0.0039	0.0009
$H_{55} \cdots C_{14}$	129	2.95	0.0053	0.0169	0.0033	-0.0025	0.0009
$H_{60} \cdots C_7$	170	2.31	0.0144	0.0393	0.0089	-0.0079	0.0009
$H_{59} \cdots N_{54}$	118	1.68	0.0621	0.1267	0.0427	-0.0537	-0.0110
O53C45	155	3.42	0.0054	0.0168	0.0035	-0.0028	0.0007
O ₅₃ …C ₂₁	156	3.33	0.0055	0.0181	0.0037	-0.0029	0.0008
O53Ni21	159	1.91	0.0874	0.6619	0.1644	-0.1633	0.0011
$H_{59} \cdots O_{51}$	118	1.92	0.0332	0.0892	0.0226	-0.0228	-0.0003
$H_{59} \cdots C_{51}$	82	1.85	0.0382	0.1023	0.0260	-0.0263	-0.0004
$H_{60} \cdots C_{22}$	104	2.25	0.0171	0.0380	0.0090	-0.0086	0.0005
O53Fe21	102	1.85	0.1125	0.6514	0.1879	-0.2130	-0.0251
$O_{51} \cdots C_{45}$	131	3.07	0.0094	0.0305	0.0066	-0.0056	0.0010
H57C46	125	3.50	0.0015	0.0057	0.0010	-0.0007	0.0004
O ₅₃ …Co ₂₁	97	1.84	0.1115	0.7170	0.1993	-0.2193	-0.0200
$H_{59} \cdots O_{51}$	134	1.98	0.0290	0.0787	0.0199	-0.0201	-0.0002
	$\begin{tabular}{ c c c c c } \hline Bond \\ \hline H_{56} \cdots C_{15} \\ \hline H_{55} \cdots C_{14} \\ \hline H_{60} \cdots C_7 \\ \hline H_{59} \cdots N_{54} \\ \hline O_{53} \cdots C_{21} \\ \hline O_{53} \cdots C_{21} \\ \hline O_{53} \cdots N_{21} \\ \hline H_{59} \cdots O_{51} \\ \hline H_{59} \cdots C_{51} \\ \hline H_{60} \cdots C_{22} \\ \hline O_{51} \cdots C_{45} \\ \hline H_{57} \cdots C_{46} \\ \hline O_{53} \cdots C_{21} \\ \hline H_{59} \cdots O_{51} \\ \hline H_{59} \cdots O_{51} \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Bond & CP \\ \hline $H_{56} \cdots C_{15}$ & 115 \\ $H_{55} \cdots C_{14}$ & 129 \\ $H_{60} \cdots C_{7}$ & 170 \\ $H_{59} \cdots N_{54}$ & 118 \\ $O_{53} \cdots C_{45}$ & 155 \\ $O_{53} \cdots C_{21}$ & 156 \\ $O_{53} \cdots N_{21}$ & 159 \\ $H_{59} \cdots O_{51}$ & 118 \\ $H_{59} \cdots C_{51}$ & 82 \\ $H_{60} \cdots C_{22}$ & 104 \\ $O_{53} \cdots Fe_{21}$ & 102 \\ $O_{51} \cdots C_{45}$ & 131 \\ $H_{57} \cdots C_{46}$ & 125 \\ $O_{53} \cdots C_{91}$ & 97 \\ $H_{59} \cdots O_{51}$ & 134 \\ \end{tabular}$	$\begin{tabular}{ c c c c c } \hline Bond & CP & r \\ \hline $H_{56} \cdots C_{15}$ & 115 & 2.71 \\ \hline $H_{55} \cdots C_{14}$ & 129 & 2.95 \\ \hline $H_{60} \cdots C_7$ & 170 & 2.31 \\ \hline $H_{59} \cdots N_{54}$ & 118 & 1.68 \\ \hline $O_{53} \cdots C_{45}$ & 155 & 3.42 \\ \hline $O_{53} \cdots C_{21}$ & 156 & 3.33 \\ \hline $O_{53} \cdots N_{21}$ & 159 & 1.91 \\ \hline $H_{59} \cdots O_{51}$ & 118 & 1.92 \\ \hline $H_{59} \cdots C_{51}$ & 82 & 1.85 \\ \hline $H_{60} \cdots C_{22}$ & 104 & 2.25 \\ \hline $O_{53} \cdots Fe_{21}$ & 102 & 1.85 \\ \hline $O_{51} \cdots C_{45}$ & 131 & 3.07 \\ \hline $H_{57} \cdots C_{46}$ & 125 & 3.50 \\ \hline $O_{53} \cdots C_{21}$ & 97 & 1.84 \\ \hline $H_{59} \cdots O_{51}$ & 134 & 1.98 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline Bond & CP & r & ρ_{BCP} \\ \hline $H_{56}\cdots C_{15}$ & 115 & 2.71 & 0.0076 \\ $H_{55}\cdots C_{14}$ & 129 & 2.95 & 0.0053 \\ $H_{60}\cdots C_7$ & 170 & 2.31 & 0.0144 \\ $H_{59}\cdots N_{54}$ & 118 & 1.68 & 0.0621 \\ $O_{53}\cdots C_{45}$ & 155 & 3.42 & 0.0054 \\ $O_{53}\cdots C_{21}$ & 156 & 3.33 & 0.0055 \\ $O_{53}\cdots N_{121}$ & 159 & 1.91 & 0.0874 \\ $H_{59}\cdots O_{51}$ & 118 & 1.92 & 0.0332 \\ $H_{59}\cdots C_{51}$ & 82 & 1.85 & 0.0382 \\ $H_{60}\cdots C_{22}$ & 104 & 2.25 & 0.0171 \\ $O_{53}\cdots Fe_{21}$ & 102 & 1.85 & 0.1125 \\ $O_{51}\cdots C_{45}$ & 131 & 3.07 & 0.0094 \\ $H_{57}\cdots C_{46}$ & 125 & 3.50 & 0.0015 \\ $O_{53}\cdots C_{21}$ & 97 & 1.84 & 0.1115 \\ $H_{59}\cdots O_{51}$ & 134 & 1.98 & 0.0290 \\ \hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



Fig. 3. Density-bar plots of Root-mean-square deviation (RMSD) from tightbinding molecular dynamics simulations of System 1, System-Ni, System-Fe, and System-Co.

conformational changes, indicating a strong and stable interaction between AMPA and the cobalt-doped graphene surface. In contrast, System-Ni and System-Fe exhibit similar RMSD values, both higher than those of System-Co. This suggests that while the adsorption of AMPA on nickel and iron-doped graphene surfaces is more stable than on pristine graphene, it is less stable than on cobalt-doped graphene. The RMSD values for these systems indicate moderate structural deviations, reflecting a balance between stability and flexibility in the interaction between AMPA and the doped surfaces. System 1, has the highest RMSD values, which are more evenly distributed in the point density of the bar. This distribution suggests that System 1 underwent the largest structural changes or deviations from its initial structure during the molecular dynamics simulation. The high RMSD values and even distribution further indicate that AMPA did not bind to the pristine graphene surface during the simulation and was released from the surface. The RMSD values provide crucial information on the structural stability and conformational flexibility of the four investigated systems. Higher RMSD values are indicative of larger structural deviations and greater flexibility, suggesting weaker interactions and less stable configurations. Conversely, lower RMSD values reflect more stable and rigid conformations, signifying stronger interactions and greater structural stability. This analysis underscores the superior performance of System-Co in maintaining structural integrity and stability in the presence of AMPA, compared to System-Ni, System-Fe, and System 1, providing further insights into the enhanced interaction observed with the doped graphene surfaces.

4. Conclusions

This study provides valuable insights into the adsorption behavior of AMPA on pristine graphene and graphene doped with transition metals (Fe, Ni, Co). The results demonstrate that doping graphene with these transition metals significantly enhances its adsorption capacity for AMPA compared to pristine graphene. Among the doped systems, Codoped graphene exhibited the highest adsorption energy of - 60.5 kcal/mol, followed by Fe (-58.2 kcal/mol) and Ni (-51.6 kcal/mol). Detailed analysis of the intermolecular interactions through QTAIM and NCI methods revealed that the adsorption is predominantly governed by physisorption involving VdW forces and electrostatic interactions. Furthermore, the electronic structure analysis showed that doping does not significantly perturb the electronic properties of graphene. In addition, the inclusion of solvent does not affect the optimized structures for any of the systems explored, but the presence of the solvent decreases the adsorption energies to a lesser extent. TB-MD simulations corroborated the efficient adsorption of AMPA on the doped surfaces, with Co exhibiting the strongest binding affinity. Collectively, these findings highlight the promising potential of transition metal-doped graphene as an effective adsorbent material for the removal of persistent organic pollutants like AMPA from water sources. However, further experimental validation and exploration of practical implementation strategies are warranted to fully realize the applications of these doped graphene systems in environmental remediation.

Future research on AMPA adsorption on graphene should focus on several key areas. Investigating the long-term stability and reusability of graphene-based adsorbents in various environmental conditions is crucial for practical applications. The potential toxicity and environmental impact of metal-doped graphene in aqueous environments need to be thoroughly assessed. Studies on competitive adsorption of AMPA in the presence of other pollutants and ions would provide valuable insights. Examining adsorption kinetics and mechanisms on different graphene functionalizations could lead to improved designs. Developing scalable, cost-effective synthesis methods and enhancing the selectivity of graphene-based materials for AMPA adsorption are also important avenues for future work.

CRediT authorship contribution statement

Dumer S. Sacanamboy: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Luis Quispe-Corimayhua:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Elkin A. Tilvez:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation. **Osvaldo Yañez:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Resources, Project administration, Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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