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GRAPHENE OXIDE FOR ORGANOPHOSPHATE REMOVAL – A DFT INSIGHT

DRAGANA VASIĆ ANIĆIJEVIĆ
Department of Physical Chemistry, "VINČA" Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade, Belgrade, dragana.vasic87@gmail.com

VLADAN J. ANIĆIJEVIĆ
Military Academy, University of Defence in Belgrade, Belgrade, anicijevicj.v@gmail.com

Abstract: *Organophosphate removal is crucial for protection of human health, preservation of biodiversity, and prevention of long-term contamination of soil and water systems. Organophosphate removal using carbon-based materials is widely investigated and employed because these materials are widely available, low-cost, and simple to use, making them practical for treating contamination under diverse conditions. The density functional theory (DFT) is a common tool of computational chemistry to assess the molecular aspects of the interaction between organic molecules and ordered supports such as graphene and modified graphene, including: adsorption geometry, adsorption energetics, nature of interaction (chemisorption of physisorption), and mechanistic insights. On the other hand, such task becomes more complex when the adsorbate and the support are rich in functional groups and diverse in steric properties. This contribution deals with the DFT investigation of adsorption of several selected and commonly used organophosphate model molecules on graphene oxide. The goal was to find the optimal binding geometry among several selected input positions and to find energetically most stable orientations. The obtained output geometries were further analyzed and discussed in order to design more precise carbon-based materials for advanced purposes, such as reusable adsorbents or catalysts for irreversible organophosphate hydrolysis.*

Keywords: *density functional theory, adsorption, organophosphate, graphene oxide.*

1. INTRODUCTION

Organophosphorus molecules, including warfare agents and pesticides, are highly toxic compounds that can pose serious risks to human health and the environment, including neurotoxicity and contamination of water resources, so their efficient removal is important for environmental priority, as well as for removal of warfare agents in defensive technologies. The study on the impact of graphene-based material structure shows that adsorption performance depends strongly on the nature of the graphene surface, which makes graphene-based materials promising candidates for removing these pollutants from wate [1].

Graphene oxide-based materials have attracted considerable attention for removing organophosphorus pesticides from water because their adsorption behavior depends strongly on surface structure, oxidation state, and the preservation of the sp^2 carbon network. In particular, oxidized graphene surfaces favor adsorption of more polar aliphatic compounds such as dimethoate, while graphene basal planes with a more ordered π-electron system are more suitable for aromatic pesticides such as chlorpyrifos.

Recent review work on graphene oxide (GO)-based materials for neurotoxic organophosphates also emphasizes that GO and GO composites are highly effective because their oxygen-containing functional groups, defects, and tunable surface chemistry enabl multiple interaction pathways, including hydrogen bonding, electrostatic attraction, π–π interactions, and complexation. These features make GO a versatile platform for both adsorption and remediation of organophosphate pollutants in aqueous systems [2].

Besides experimental studies, density functional theory (DFT) can also be used to investigate these systems at the molecular level. DFT helps explain adsorption energies, charge transfer, preferred binding sites, and the role of functional groups and defects, which makes it a useful complement to experiments when interpreting why some graphene-based materials remove organophosphates more efficiently than others [3].

The goal of the work was to establish a simple, general DFT-based methodology for investigation of adsorption of organophosphate molecules on graphene oxide, including warfare agents and pesticides. Tabun, as the representative of warfare agents, and dimethoate and malathion, as the representatives of pesticides, were selected for this investigation This is expected to provide insight into the general features and adsorption properties for structurally similar compounds.

2. CALCULATION DETAILS

Density functional theory (DFT) calculations were used to investigate the interaction between the organophosphate

Corresponding author: D. Vasić Anićijević
E-mail: dragana.vasic87@gmail.com

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molecule and the graphene oxide (GO) surface at the molecular level. The computational approach was chosen to provide insight into the adsorption mechanism, the strength of interaction, and the role of oxygen-containing functional groups and surface defects in stabilizing the adsorbate on the GO sheet.

DFT calculations were performed using DFTB+ code [4] using 3ob-3-1basis set. The calculation procedure began with the construction of the isolated GO model, the isolated organophosphate molecule, and the combined adsorbate–adsorbent system. Graphene oxide was modelled as a 128-atom graphene slab with 8 oxygen atoms in epoxy positions and 8 OH-groups in C-top positions to simulate oxygen-rich environment. At least 30 angstroms of vacuum above the slab were provided to minimize interactions between periodic images. All structures were then geometry optimized to obtain the most stable configuration and to ensure that the total energy corresponded to a minimum on the potential energy surface. All atoms were moved through relaxation and 300 geometry optimization steps were allowed. During optimization, the electronic convergence criteria10^{-6} eV and force thresholds 5×10^{-3} eVA^{-1}) were applied to guarantee reliable structural and energetic results.

After geometry optimization, the adsorption energy was calculated according to the following expression:

$$E_{ads}=E_{complex}-E_{GO}-E_{OPs} \quad (1)$$

where $E_{complex}$ is the total energy of the GO–organophosphate system, E_{GO} is the energy of the isolated graphene oxide surface, and E_{OPs} is the energy of the isolated organophosphate molecule. A negative adsorption energy indicates a thermodynamically favorable interaction, while a more negative value corresponds to stronger binding between the molecule and the GO surface.

3. RESULTS AND DISCUSSION

Optimized adsorption geometries os DMT, MLT and GA on GO are represented in Figures 1-3. Multiple input molecular orientations were selected to favorize the potential interaction between heteroatom moieties of organophosphate molecules (P=S, N-H and O-H binding), as well as large surface contact areas (Van der Wals forces). Structurally, the GO lattice remains intact across the configurations, preserving its hexagonal carbon framework and the distribution of hydroxyl, epoxy, and carboxyl groups that facilitate adsorption. Across all tested organophosphorus compounds (dimethoate (DMT), malathion (MLT), and tabun (GA)), the adsorption energies (E_{ads}) reveal a consistent trend of strong binding to the graphene oxide surface. Each molecule exhibits negative adsorption energies, confirming thermodynamically favorable interactions.

Stable adsorption is attributed both to physical (hydrogen bonding, Van der Wals, electrostatic) and chemical interactions (S-O and N-H binding between substrate and adsorbate). Furthermore, all three compounds demonstrate multiple stable adsorption configurations with similar adsorption energetics, highlighting the structural flexibility of GO in accommodating different orientations and binding modes.

Despite these commonalities, notable differences emerge in adsorption strength and orientation (**Table 1**). Dimethoate (DMT) shows the most stable adsorption overall, with DMT-3 reaching the lowest energy (−294.55 kJ mol^{-1}), indicating strong surface coupling through both N-H-O and C-O-H interactions (hydrogen bonding). In case of MLT-2, S-O binding is the most obvious in adsorption geometry. Malathion (MLT) exhibits weaker adsorption in MLT-1 and MLT-2 (−217.43 and −213.62 kJ mol^{-1}), but achieves significantly stronger binding in MLT-3 (−264.12 kJ mol^{-1}), suggesting the significant contribution of hydrogen binding and Van Der Wals interactions to the overall binding energy. Similarly, Tabun (GA) presents the widest variation upon the change of adsorbate-to-substrate contact area: GA-1 shows the weakest adsorption (−186.97 kJ mol^{-1}), while GA-2 demonstrates a much stronger interaction (−266.18 kJ mol^{-1}), reflecting how positional differences (flat vs. upright orientation) drastically alter binding affinity.Collectively, these results underscore that adsorption energy is highly sensitive to molecular geometry, with DMT generally outperforming MLT and GA in stability, while GA exhibits the largest configurational variability.

Table 1. Adsorption energies (E_{ads}) of malathion, dimethoate and tabun on graphene oxide, for investigated adsorption geometries.

OPs		E_{ads} (kJ mol^{-1})
dimethoate	DMT-1	-285,39774
	DMT-2	-255,07476
	DMT-3	-294,55398
malathion	MLT-1	-217,43244
	MLT-2	-213,61734
	MLT-3	-264,11796
tabun	GA-1	-186,96816
	GA-2	-266,18094

Table 1 presents the adsorption energies (Eads) of three organophosphorus compounds: dimethoate (DMT), malathion (MLT), and tabun (GA) in different adsorption configurations on graphene oxide (GO). All values are negative, confirming that the adsorption processes are thermodynamically favorable.

Optimized adsorption geometries of DMT, MLT and GA on graphene oxide are represented in **Figures 1-3**.

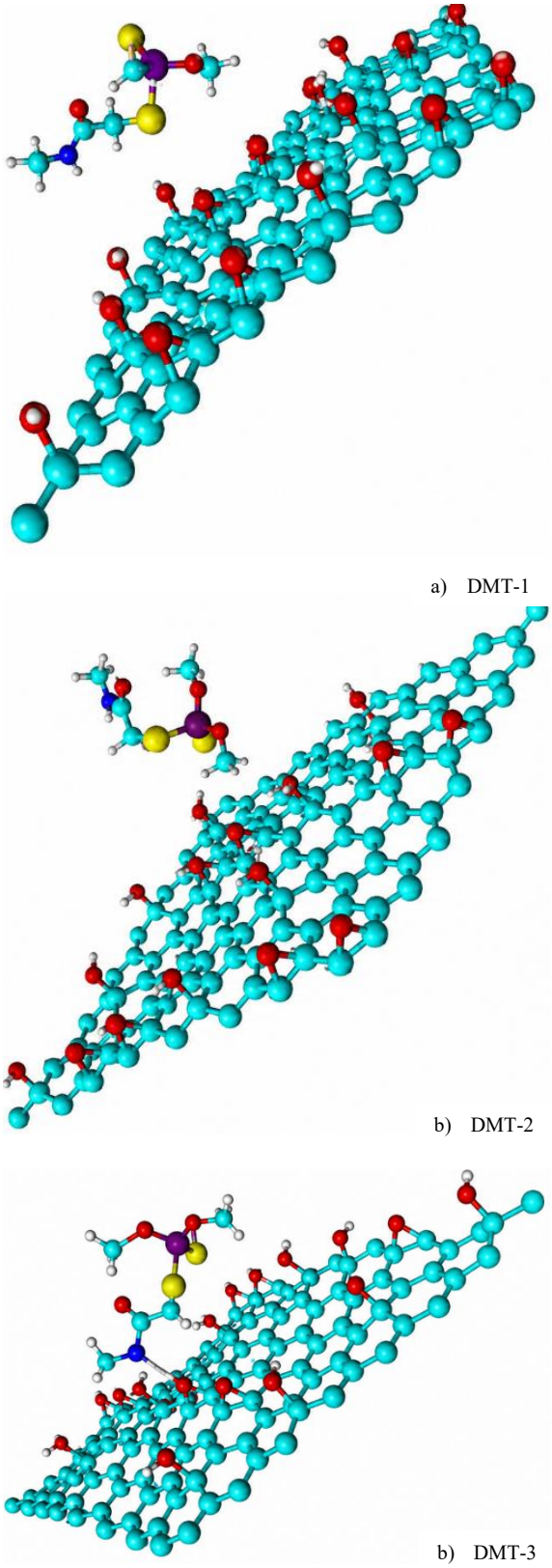


Figure 1. Optimized adsorption geometries of DMT on graphene oxide

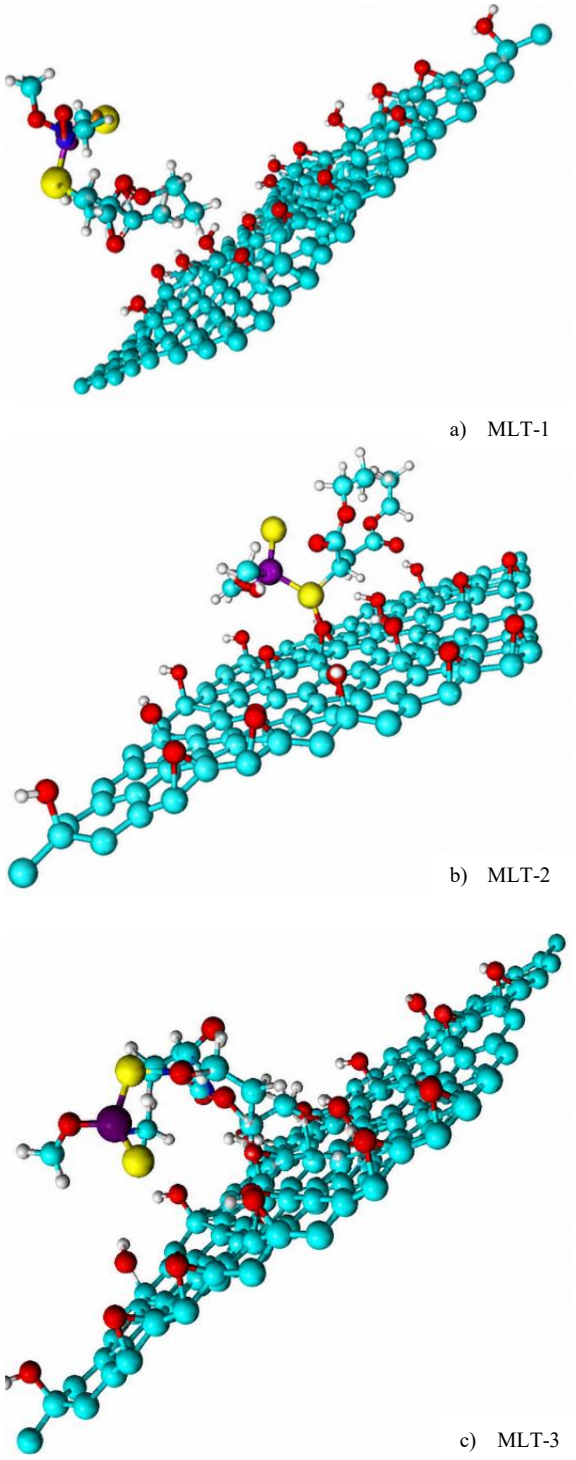
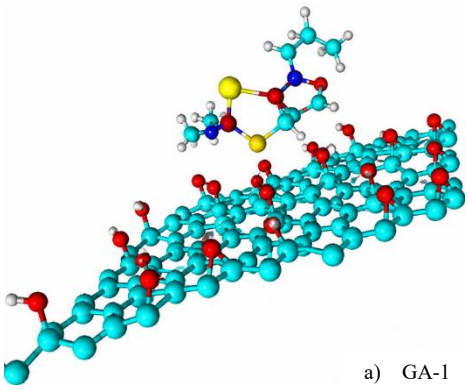
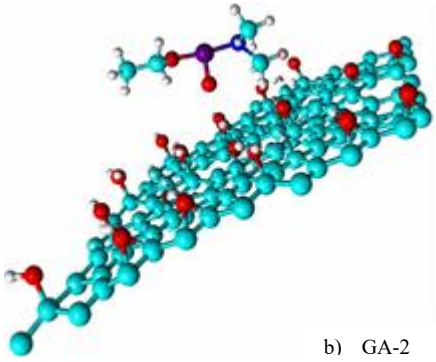


Figure 2. Optimized adsorption geometries of MLT on graphene oxide



a) GA-1



b) GA-2

Figure 3. Optimized adsorption geometries of GA on graphene oxide

4. CONCLUSION

The results presented in Table 1 and illustrated in Figures 1–3 clearly demonstrate that adsorption of organophosphorus compounds on graphene oxide is energetically favorable, with all calculated adsorption energies being negative. Among the studied systems, dimethoate (DMT) exhibits the strongest and most stable adsorption, particularly in configuration DMT-3, highlighting the importance of molecular orientation in maximizing surface interactions. Malathion (MLT) shows moderate adsorption energies, with a significant increase in stability in MLT-3, confirming that steric effects and binding geometry strongly influence adsorption strength. Tabun (GA) displays the widest variability, ranging from weak adsorption in GA-1 to markedly stronger binding in GA-2, underscoring the sensitivity of this compound to configurational changes.

Overall, the combined numerical and structural analyses indicate that graphene oxide provides a versatile platform for binding organophosphorus agents, with adsorption strength governed primarily by the spatial arrangement of phosphorus and sulfur centers relative to oxygen rich functional groups. These findings emphasize the potential of GO as an effective adsorbent material for environmental remediation and decontamination applications.

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