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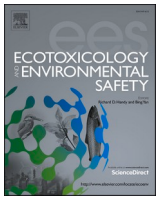

Molecular modeling investigation on mechanism of diazinon pesticide removal from water by single- and multi-walled carbon nanotubes

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ABSTRACT

In this study, the mechanism of diazinon adsorption on single-walled carbon nanotubes (SWNTs), as well as multi-walled carbon nanotubes (MWNTs), was investigated using molecular modelling. Determination of the lowest energy sites of different types of carbon nanotubes (CNTs) was demonstrated. The adsorption site locator module was used for this purpose. It was found that the 5-walled CNTs are the best MWNTs for diazinon elimination from water due to their higher interactions with diazinon. In addition, the adsorption mechanism in SWNT and MWNTs was determined to be wholly adsorption on the lateral surface. It is because the geometrical size of diazinon molecules is larger than the inner diameter of SWNT and MWNTs. Furthermore, the contribution of diazinon adsorption on the 5-wall MWNTs was the highest, for the lowest diazinon concentration in the mixture.

1. Introduction

In the current modern era, world population growth and addressing its daily requirements have been considered major challenges. One of the most important issues is the enhancement of the efficiency of the agricultural sector for increasing food production (Moradi et al., 2022). Fertilizers or pesticides are used in order to increase and preserve food crops. In modern agricultural methods, pesticides play the most vital role to prevent weeds, small animals, insects, etc. attack and damage on agricultural products (Pawar et al., 2006). Organophosphorus pesticides are widely used in the agricultural sector for the enhancement of food production around the world (Toolabi et al., 2018). Diazinon as an organophosphorus is categorized as a substance that is only mildly dangerous by the World Health Organization (Wang and Shih, 2015). The maximum diazinon concentration in drinking water was defined as 0.6 μg/L by USA Environmental Protection Agency (Mahmoodi et al., 2015; Pirsaheb et al., 2022). Therefore, diazinon can have an adverse impact on freshwater resources and all aquatic animals, mammals, and humans' lives (Nasrollahi et al., 2020; Roselló-Márquez et al., 2021). In terms of human life, diazinon causes a disturbance of the human nervous system by preventing the acetylcholinesterase enzyme (Zhang et al., 2010).

A number of approaches have been proposed and implemented for the treatment of wastewater streams containing diazinon. Wang and Shih (2015) used sono-Fenton process for diazinon degradation. It was found that there are three degradation by-products to develop the

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possible oxidation mechanism. The membrane is another technique, which has been used for pesticide removal from wastewater (Mukherjee et al., 2018). The ceramic microfiltration and ultrafiltration membranes' performance was studied and ultrafiltration membranes showed a 15% enhancement in pesticide removal, less membrane fouling as well as fully separation of the biomass in the synthetic system (Mukherjee et al., 2018). The coagulation/flocculation method was developed to remove methyl parathion as well as chlorpyrifos pesticides from synthetic wastewater (Saini and Kumar, 2016). Adsorption is the most common method for the treatment of wastewater containing pesticides. Enhanced photocatalytic degradation of diazinon using Au/Ag-decorated titanium dioxide nanorods was applied for diazinon degradation and it demonstrated better efficiency due to the dual features such as e^- trapping proficiency of Au/Ag as well as having higher surface area and also pore size (Jalili-Jahani et al., 2022). Tabasideh et al. (2017) investigated the degradation of diazinon in wastewater by iron-doped titanium oxide nanoparticles.

The CNTs have been proven as useful adsorbents for the higher elimination of organic contaminants and the protection of the environment. These adsorbents have a number of advantages including large specific surface area, appropriate mechanical and thermal stability, as well as high permeability. They have higher adsorption capacity because of their large surface area as well as the particular hollow and layered structure (Agarwal et al., 2016). Sbai et al. (Sbai et al., 2014) investigated vibrational breathing modes (VBMs) in the Raman spectrum of MWNTs with various diameters and numbers of layers. It was found good agreement between experimental data and calculated values. The SWCNT is considered the fundamental structural unit. MWNTs were discovered in 1991 (Latha et al., 2022). The MWNTs structure is like a ring with nestled single-walled CNTs that are insufficiently stretched via the Vander Waals' force. Carbon atoms make up MWCNTs which are graphite-structured and constructed in a number of cylindrical tubes that are coaxially aligned (Latha et al., 2022; Šušteršič, 2021). Wastewater containing diazinon pesticide treatment using SWCNTs and MWCNTs was investigated by Dehghani et al. (2019). The results indicated that MWCNTs have great potential to use as a useful and highly efficient adsorbent for the entire removal of diazinon pesticides from wastewater. The adsorption mechanism of diazinon on SWCNTs and MWCNTs has not been studied so far, and it can be highly valuable to investigate for further understanding of the process. Using the development of a suitable model and theory can improve understanding of the process. Furthermore, the development of theoretical models and simulation can help to reduce the cost related to experimental works (Rezakazemi et al., 2018). Therefore, novelty of this paper will be molecular level investigation diazinon adsorption on the SWCNTs and MWCNTs.

In the current study, a number of molecular as well as quantum chemical calculations such as adsorption site analysis are investigated for diazinon removal from wastewater using MWNTs and SWNTs. In this study, BIOVIA Materials Studio as a complete modeling and simulation environment was used to determine the adsorption mechanisms of diazinon on various types of CNTs.

2. Materials and method

2.1. Materials

The built structures of diazinon and H_2O are provided in Fig. 1. The oxygen, nitrogen, hydrogen, carbon, phosphorus, and sulphur atoms are illustrated in red, blue, white, grey, purple, and yellow colours respectively. 100 H_2O molecules, and 1, 5, and 10 diazinon molecules, were considered to simulate 0.01, 0.05, and 0.1 (fraction) diazinon/water mixture. Computational time reduction and determination of the active adsorption sites are the main reasons for the selection of these concentrations. the Build-module as well as build nanostructure submenus in the BIOVIA Material Studio software was used for making different types of CNTs (1–18 walls).

2.2. Method

2.2.1. Analysis of adsorption site

To further recognise, the possible interactions of diazinon and H_2O

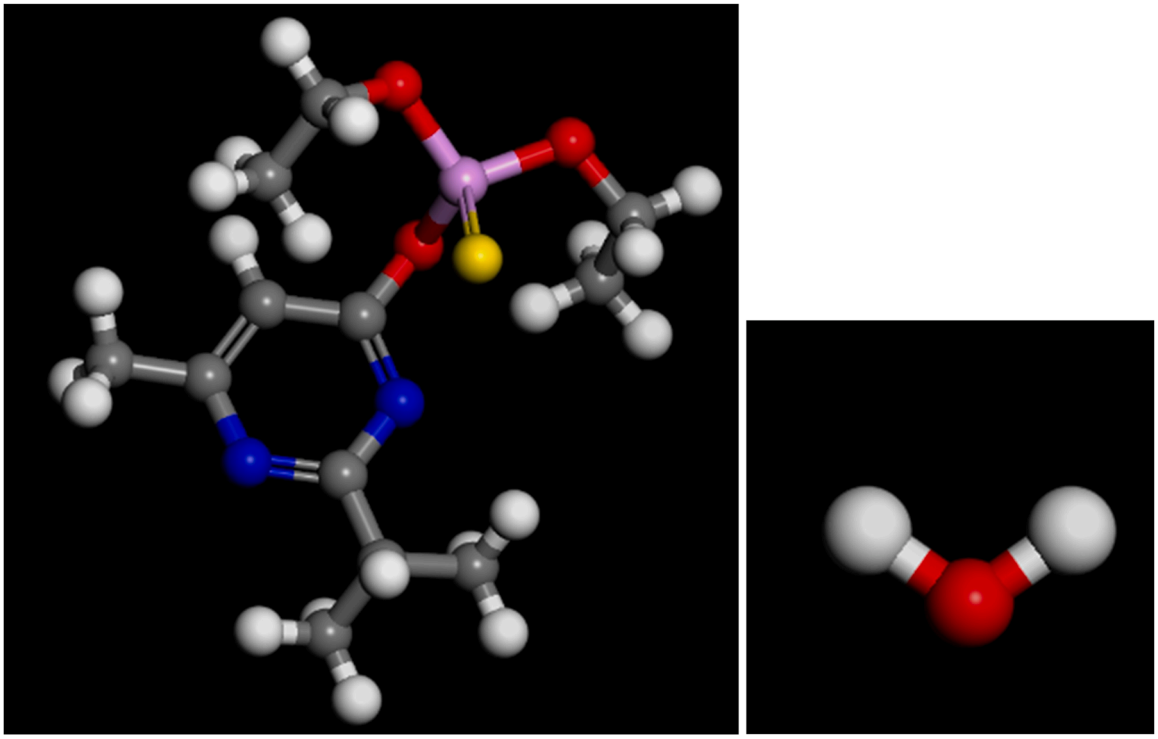

Fig. 1. : The molecular structures of diazinon and water.

on CNTs, a module known as the adsorption locator in Materials Studio software was used. This module is usually used to determine low-energy adsorption locations as well as investigation of preferential adsorption compounds including diazinon and water on the CNTs. In this method, the potential CNTs-diazinon/water layouts are chosen from a canonical statistical ensemble where the total content of water/diazinon compounds on the CNTs as well as the temperature are fixed.

This module identified using performing Monte Carlo searches configurational space of the CNTs-diazinon system's as the T is gradually decreased, and the loading of all diazinon on the CNTs and T is fixed. The probability of the configuration, m, in the canonical statistical ensemble is provided as follows (Frenkel and Smit, 2002):

$$P_m = C\exp[-\beta E_m] \quad (1)$$

where C, and β, E_m denotes an arbitrary normalization constant, the reciprocal temperature, and the configuration (m) total energy respectively. The reciprocal temperature is determined as follows (Frenkel and Smit, 2002):

$$\beta = \frac{1}{k_B T} \quad (2)$$

where k_B, T refers the Boltzmann constant as well as the absolute temperature respectively. The following equation is used for the calculation of the total energy of configuration (Frenkel and Smit, 2002):

$$E_m = E_m^{AA} + E_m^{AS} + U_m^A \quad (3)$$

where E_m^{AA}, and E_m^{AS} are the inter-molecular and the interaction energies between the diazinon and the CNTs, and U_m^A denotes the sum of the diazinon intra-molecular energy. The intra-molecular energy of the CNTs is not considered due to its fixed structure is fixed in the simulation. Furthermore, the total intra-molecular energy can be expressed as follows (Frenkel and Smit, 2002):

$$U^A = \sum_{\{N\}_m} U_{intra} \quad (4)$$

where $\{N\}_m$ is defined diazinon loading in the configuration m.

The constructed components should be firstly geometrically as well as energetically optimized for using the adsorption locator module. In this regard, the Forcite module in Material Studio Software was used with evaluating the same minimization as well as settings for energy in the module of the adsorption locator. The setting for energy was COMPASS III and it was used in the Forcite module (Černý, 1985; Frenkel and Smit, 2002; Kirkpatrick et al., 1983; Metropolis et al., 1953). The mono-walled CNTs (a), and CNTs with 10 walls (b) were shown in Fig. 2.

3. Results and discussion

Table 1 provides the results related to energies of CNTs- (water/diazinon) layouts of CNTs for diazinon (5 molecules) and water (100 molecules). The rigid adsorption, the adsorption, and the deformation energies are combined to determine the total energy of the CNTs-(water/diazinon) configuration. It should be pointed out that the adsorption energy is required for the relaxed diazinon/water molecules adsorption on the CNTs. The whole of this energy is made of the deformation as well as the rigid adsorption energies for the water or diazinon. There is another type of energy known as rigid adsorption energy. This energy is required for adsorption of the unrelaxed water or diazinon on the CNTs. The relaxation of the adsorbed water/diazinon on the CNTs is defined as the deformation energy. Furthermore, the energy that is required for the separation of diazinon or water from the CNTs surface is defined as the dEad/dNi's. Greater energy is needed for the desorption of diazinon from SWNTs as well as MWNTs when it is compared with H_2O. Moreover, the best favourable dEad/dNi is achieved for 5-walled MWNTs provided in Table 1. It is revealing the highest contribution of 5-walled

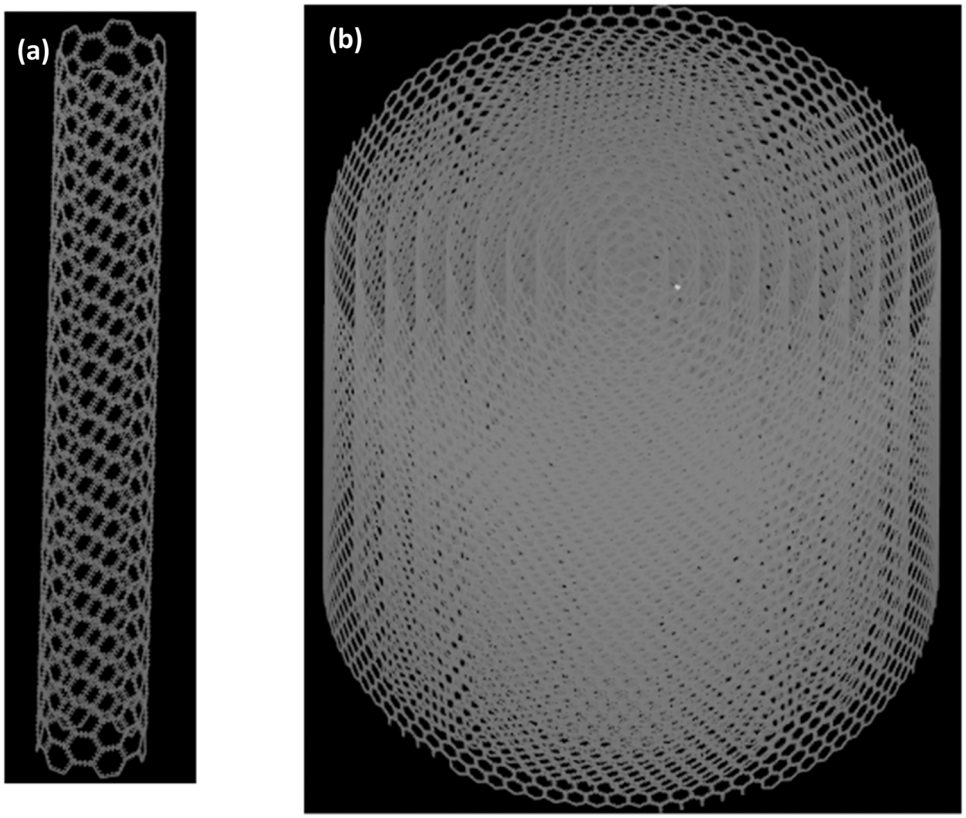

Fig. 2. : The CNTs with 1 wall (a), and CNTs with 10 walls (b).

Table 1
Adsorption locator module calculation results for SWNTs and MWNTs.

Structures	Total energy (kJ/mol)	Adsorption energy (kJ/mol)	Rigid adsorption energy (kJ/mol)	Deformation energy (kJ/mol)	dEad/dNi (kJ/mol)	
					Water	Diasin
SWNT	-1001.65	-4160.87	-524.41	-3636.46	-19.40	-362.10
MWNT2W	-1231.38	-4390.60	-766.42	-3624.18	-19.42	-364.99
MWNT3W	-1137.54	-4296.76	-666.08	-3630.68	-19.39	-364.96
MWNT4W	-1161.51	-4320.73	-690.24	-3630.49	-19.41	-368.95
MWNT5W	-1215.08	-4374.30	-747.94	-3626.37	-19.42	-374.62
MWNT6W	-1255.13	-4414.35	-786.30	-3628.05	-19.42	-366.95
MWNT7W	-1054.42	-4213.64	-580.08	-3633.56	-19.42	-369.88
MWNT8W	-1162.64	-4321.86	-688.41	-3633.45	-19.42	-365.80
MWNT9W	-1099.27	-4258.49	-625.74	-3632.75	-19.42	-368.96
MWNT10W	-1126.45	-4285.67	-653.06	-3632.61	-19.42	-367.52
MWNT11W	-1176.38	-4335.61	-703.63	-3631.97	-19.42	-369.26
MWNT12W	-1133.26	-4292.49	-658.58	-3633.91	-19.42	-365.63
MWNT13W	-1136.86	-4296.08	-663.50	-3632.58	-19.42	-365.53
MWNT14W	-1085.72	-4244.94	-608.11	-3636.83	-19.42	-369.41
MWNT15W	-1050.07	-4209.30	-576.71	-3632.58	-19.40	-367.64
MWNT16W	-1043.64	-4202.86	-567.79	-3635.07	-19.42	-365.65
MWNT17W	-1058.00	-4217.22	-579.84	-3637.38	-19.42	-369.16
MWNT18W	-1018.84	-4178.06	-535.23	-3642.83	-19.42	-366.21

MWNTs in the adsorption of diazinon.

The CNTs-(diazinon/water) configurations for SWNTs are provided in Fig. 3. The outputs of the adsorption site analysis reveal the primary mechanism of diazinon elimination within SWNTs is adsorption on the lateral surface. The molecular modelling outputs for an adsorption site analysis of 2-walled CNTs are given in Fig. 4. According to simulations, with the enhancement of CNTs walls from one to two, the adsorption on the lateral surface of CNTs increases as can be observed in Fig. 4. There are fewer trapping mechanisms for both SWNTs and 2-walled MWNTs. Furthermore, the primary mechanism of diazinon elimination in SWNTs and MWNT2W is adsorption onto the lateral surface. It seems that the adsorption of water/diazinon onto the lateral surface in 2-walled CNTs is higher than SWNTs. This could be attributed to the lower inner diameter as well as the gap between the walls of multi-walled CNTs. In addition, the outputs for analysis of the adsorption site of 3-walled CNTs are provided in Fig. 5. According to simulations, the adsorption of diazinon/water on the lateral surface is the main mechanism and no considerable trapping mechanism can be seen. The molecular modelling was implemented for up to 18-walled CNTs and it was found approximately the same results as found for 2-walled CNTs. In all MWNTs, the main adsorption mechanism was lateral surface adsorption and the trapping mechanism did not play a significant role in the adsorption of diazinon on MWNTs due to the lower inner diameter of MWNTs in comparison to the geometrical size of diazinon, so the role of the adsorption mechanism on the lateral surface of CNTs would be more vital. The trapping mechanism may improve with increasing the inner tube diameter as well as distance between layers.

3.1. *Effect of diazinon concentration*

It was found that the MWNTs with 5 walls have the highest contribution of diazinon adsorption as its dEad/dNi was the maximum. Therefore, the total, adsorption, rigid adsorption, deformation energies, and water and diazinon dEad/dNi for the MWNTs with 5 walls were determined for different diazinon concentrations including 0.01, 0.05, and 0.1 mol%. Fig. 6 demonstrates different energies as a function of diazinon concentration in the mixture. There was increase in diazinon dEad/dNi from 366 kJ/mol to 377 kJ/mol with decreasing diazinon concentration from 0.1 to 0.01 mol%. It means that there is more interaction between diazinon and MWNTs with decreasing diazinon concentration. It obtained an increase in total, adsorption and deformation energies with the enhancement of diazinon concentration. The highest rigid adsorption energy was obtained for 0.05 mol% of diazinon concentration. Furthermore, Fig. 7 provides adsorption site analysis

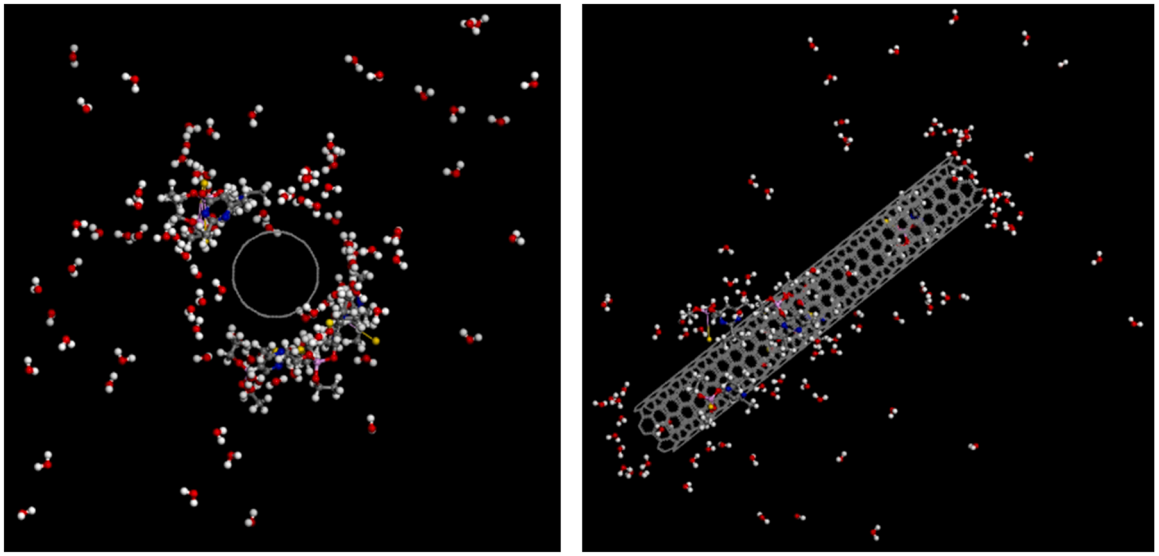

Fig. 3. : Adsorption site analysis for single-walled carbon nanotubes.

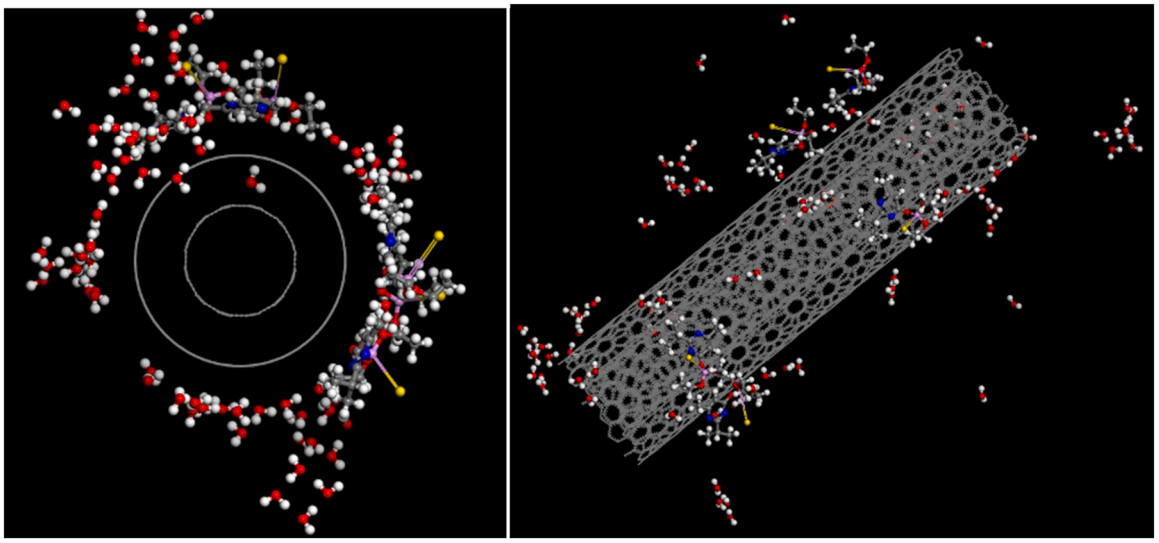

Fig. 4. : Results of adsorption site analysis of two-walled carbon nanotubes.

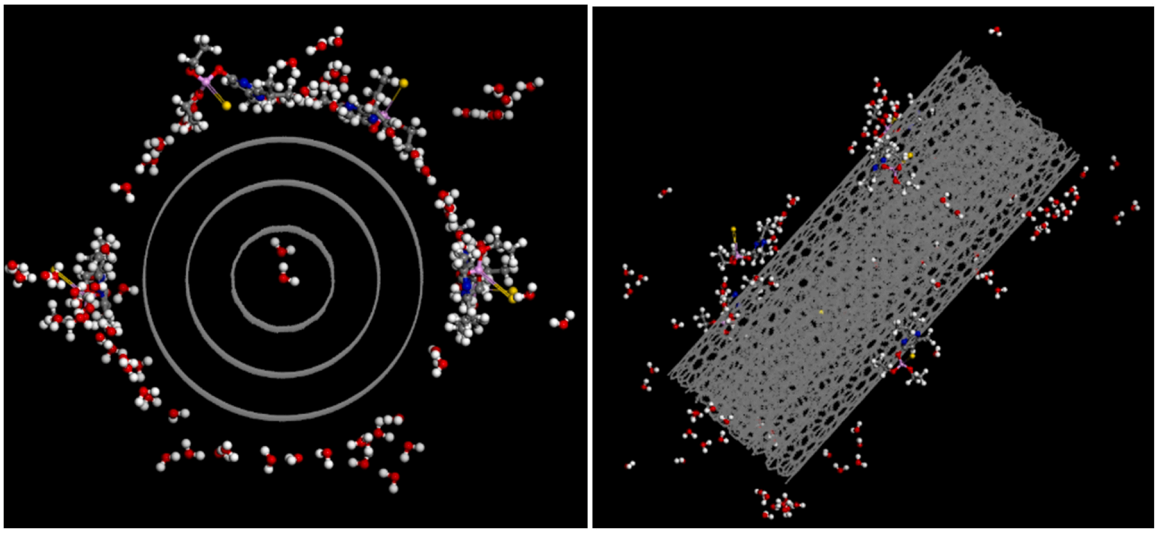

Fig. 5. : Results of adsorption site analysis of three-walled carbon nanotubes.

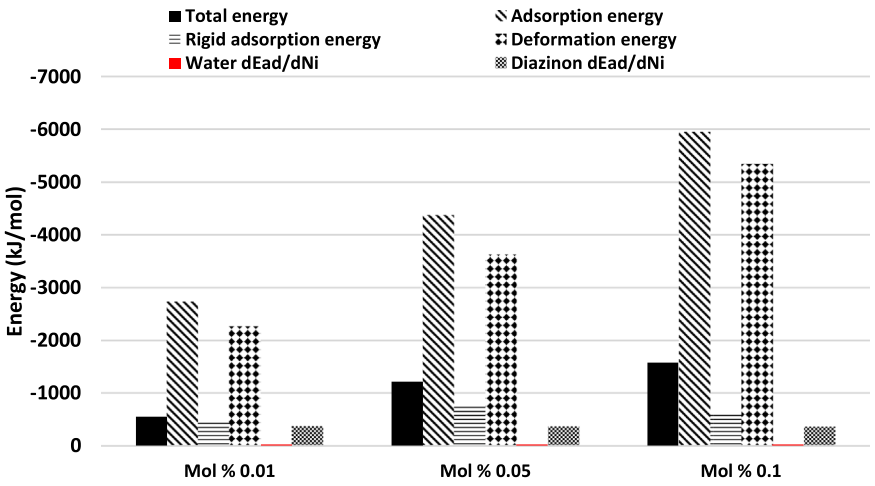

Fig. 6. : Total, adsorption, rigid adsorption, deformation energies, and water and diazinon dEad/dNi for the MWNTs with 5 walls as a function of diazinon concentration.

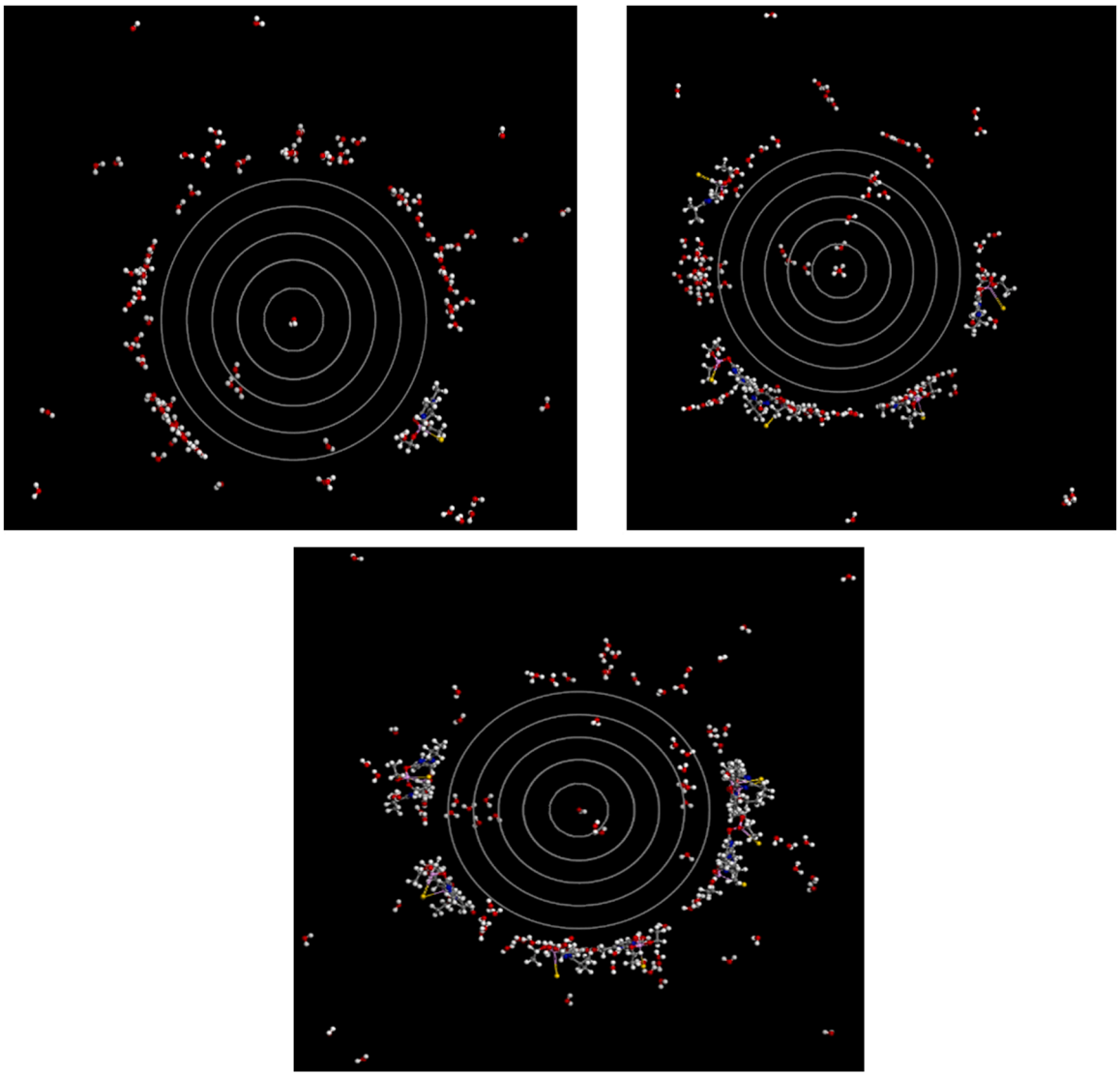

Fig. 7. : Adsorption site analysis results of diazinon and water on MWNTs with 5 walls with different diazinon concentrations.

results of diazinon and water on the MWNTs with 5 walls with different diazinon concentrations. Based on Fig. 7, the most significant adsorption mechanism is the adsorption on the lateral surface of MWNTs with 5 walls.

3.2. Effect quality of calculation

There is Quality Set in the Adsorption Locator module. The factors that govern the simulation's precision and speed are determined by this option. Available choices are Course, Medium, then Fine, and Ultrafine. The Quality option impacts all important task factors that control the accuracy of the simulation. The effect of Quality setting on the total, adsorption, deformation and rigid adsorption energies, and water and diazinon dEad/dNi were demonstrated in Fig. 8. As can be observed, the quality has a significant effect on the energies and it indicates that the calculations should be performed when the quality setting is ultrafine. The total, adsorption, and rigid adsorption energies, and diazinon dEad/dNi were increased from − 339 to − 1215, − 4398 to − 4374, − 71 to − 748, and − 303 to − 372 kJ/mol. Furthermore, there was no change in deformation energy when the quality set was medium, fine, or ultrafine.

4. Conclusion

The molecular mechanism of diazinon removal from wastewater using SWNTs and MWNTs was investigated in the current work. Materials Studio software was used for the determination of the adsorption sites. The simulation showed the high performance of single-WNTs as well as multi-WNTs in diazinon elimination from wastewater with molecular features. It was found that main the adsorption mechanism of diazinon on SWNTs and MWNTs is the adsorption on the lateral surface. The 5-walled CNTs showed the highest contribution to diazinon removal from wastewater. The increase in diazinon concentration led to the reduction of diazinon adsorption on the MWNTs with 5 walls. Also, an investigation of the Quality setting indicated that the calculation should be performed when the quality is Ultrafine in order to achieve accurate results.

CRediT authorship contribution statement

Xinbao Fu, Alaa Mohammed Hussein Wais, Yaser Yasin: Conceptualization, Methodology, Modeling, Writing – original draft preparation. **Israa Taha Ibrahim, Ahmed Subhi Ali, Kadhum Al-Majdi:** Writing – review & editing, Data curation, Formal analysis. **Waleed Mohammed Khazaal, Salema K. Hadrawi**: Writing – review &

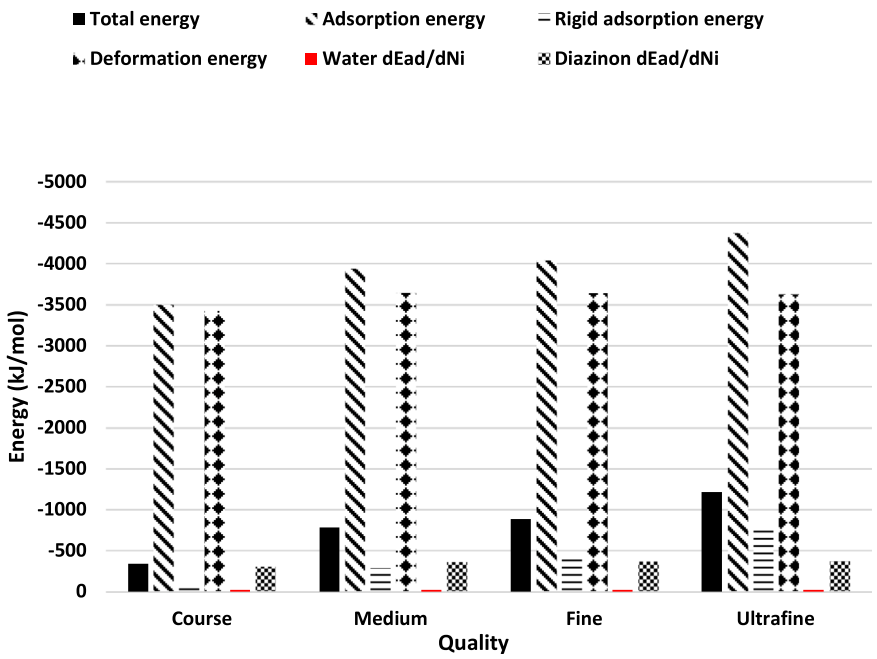

Fig. 8. : The effect of Quality setting on the total, adsorption, rigid adsorption, and deformation energies, and water and diazinon dEad/dNi.

editing, Project administration, Data curation. **Ahmed S. Abed, Yassin Riyahi, Yan Cao**: Supervision, Writing – review & editing, Funding acquisition.

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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