Development of Computational Method to Calculate Organic Pollutant Load on Nano-Material's Surface

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ABSTRACT
Nanomaterials have been demonstrated to be very effective adsorbent for various impurities because of their large volume-to-surface area and high adsorption potential. This research elucidates the attempt of designing computational model and procedure to access the maximum possible load of endosulfan, a persistent insecticide, on graphene nanosurface. We, here, present a strategy to calculate the maximum area covered by a molecule of endosulfan based on shape and its orientation on graphene surface. We have also modified the popular Langmuir's model to calculate the maximum adsorbate load on adsorbent by including steric hindrance caused by a adsorbate molecule to others due to shape and adsorption configurations.

General Terms
Environmental remediation, Nanotechnology, Adsorption, Computational model

Keywords
Graphene, Endosulfan, Langmuir's model, steric hindrance.

1. INTRODUCTION
Nanomaterials are microscopic particles that have at least one dimension less than 100-nm being evaluated in many fields in material sciences. Now a days, nanomaterials have gained a lot of attention in various scientific endeavors due to their distinguished properties in comparison to the bulk form. These unique properties are contributed for high surface to volume ration. Recently, nanomaterials are being used for the environmental remediation processes [1]. These materials adsorb various pollutants and used for the removal of toxic gases, (CO, NOx, SO_2, etc), organic pesticides, heavy metals, biological substances (bacteria, virus, amino acids, antibiotics) from a range of biological matrices [2]. Organic pollutant adsorption on carbon nanomaterials (CNMs) are commercially used for purifying drinking water, for example, in the removal of arsenic [3]. Among the nanomaterials available, graphene has been widely used for this purpose. Graphene is a carbon sheet with thickness of one atomic layer produced by processing from either silicon carbide or graphite flakes [4]. Graphene is a two-dimensional array of sp2-bonded carbon atoms arranged to produce a honeycomb lattice made of hexagonal rings [5], adsorb small molecules by charge transfer mechanism.

2. MATERIALS AND METHODS

2.1 Load calculation of adsorbate on the adsorbent
Adsorption process occurs in most natural physical, chemical and biological systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption processes are usually described through isotherm which calculates the amount/ maximum load of adsorbates on the adsorbent. Langmuir isotherm is one such isotherm which calculates the maximum load on the substrate [6] based on the four hypothesis; 1) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal; 2) Adsorbed molecules do not interact.; 3) All adsorption occurs through the same mechanism; and 4) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on each other. Langmuir's model is used to calculate maximum amount of adsorbate adsorbed per gram of adsorbent for the formation of monolayer can be calculated as:

$$x_m\left(\frac{mg}{g}\right) = \frac{A\left(\frac{m^2}{g}\right) \times M}{S\left(\frac{m^2}{molecule}\right) \times N}$$

Where, Xm = maximum amount of adsorbate adsorbed per gram of adsorbent for monolayer formation; A = Surface area of the adsorbent (m2/g); M = molecular weight of adsorbate (mg/molecule); N = Avogadro's number; S = Contact surface area by each molecules (m^2).

In the Langmuir isotherm, the orientation of the adsorbate was ignored, which is one of the decisive factor to calculate the maximum pollutant load on the adsorbent surface. The importance of adsorbate orientation to calculate the maximum pollutant load on the unit surface area of adsorbent can be properly understood by the representation in Figure 1.

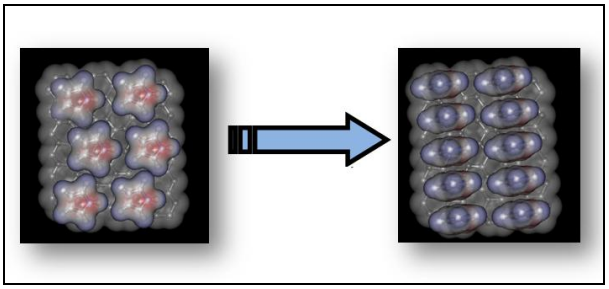


Figure 1 Total load of the adsorbate on the adsorbent largely depends on its orientation with respect to the surface. In the left panel, only 6 molecules of adsorbate can be loaded, however the change in the orientation lead to load maximum 10 molecules of the adsorbate on the adsorbent surface (right panel).

In the present work, we provide a methodology to use the orientation of adsorbate as an important parameter to accurately calculate the maximum possible load of adsorbate on adsorbent. For this purpose, organic pollutant endosulfan, a polychlorinated insecticide used for controlling a variety of insects, has been used as adsorbates and graphene nanosheet as adsorbent. It has been investigated that, the adsorption of organic pollutant on graphene sheet is based on the adsorption position and orientation of pollutants on the surface and also depend on molecular doping, i.e., charge transfer between the pollutants and the graphene surface [7].

2.2 Computational model for Graphene sheet and Endosulfan

A realistic atomistic model of pristine graphene sheet arranged in arm chair configuration was designed using 3D sketcher of Material studio (MS) software package, Accelrys Inc. The three dimensional structure of the endosulfan was retrieved from the PubChem Database (CID: 3224).

2.3 Adsorption of Endosulfan on Graphene sheet

To investigate the detail insight of adsorption phenomenon of endosulfan on graphene sheet, the Adsorption Locator module of Accelrys Material Studio (MS) V 6.0 was employed. Adsorption Locator in MS allows us to find low energy adsorption sites on both periodic and nonperiodic substrates. The probability of a configuration is based on canonical ensemble. Simulated annealing algorithm was used to perform canonical Monte Carlo sampling at fine quality level of simulation with endosulfan selected as adsorbate. In the canonical ensemble, the loading of all adsorbate components on the substrate, as well as the temperature, are fixed. The COMPASS forcefield with atom based summation method was selected for the Electrostatic and van der Waals energy calculation with the load of maximum ten molecules of endosulfan on the graphene sheet.

2.4 Calculation of contact surface area between adsorbate and adsorbentof Endosulfan on Graphene sheet

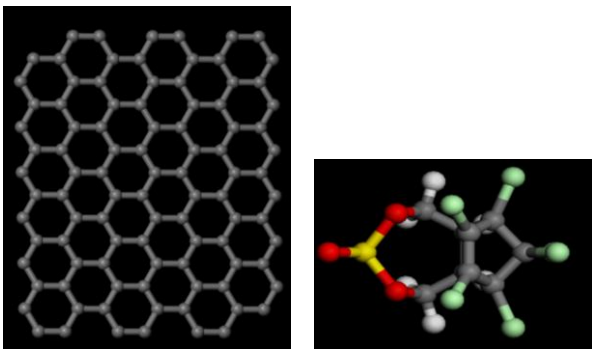
To calculate the contact surface area between adsorbate and adsorbent, the 3D slices was created using volume visualization dialogs of MS. The slice was created as a best fit to the graphene sheet. Total area of graphene sheet was chosen so that all points within the visible field volume intersecting with the slice plane forms as a part of the slice. Further, we realigned 3D slices at various heights, parallel to graphene surface, to calculate the maximum area occupied by endosulfan molecules. The maximum area occupied is much larger than the actual contact area between two interacting entities. This difference may be considered as the steric hindrance caused due to the geometry of one adsorbate molecule to other on the nano surface. Finally, the maximum load of endosulfan on the graphene sheet was calculated by the following formula:

$$x_m\left(\frac{mg}{g}\right) = \frac{A\left(\frac{m^2}{g}\right) \times M}{Smax\left(\frac{m^2}{molecule}\right) \times N}$$

Where, Xm = maximum amount of adsorbate adsorbed per gram of adsorbent for monolayer formation; A = Surface area of the adsorbent (m2/g); M = molecular weight of adsorbate (mg/molecule); N = Avogadro's number; Smax = maximum area covered by each adsorbate molecules (m2) on nanosurface.

3. RESULTS AND DISCUSSION

The computational model of graphene sheet with a total of 96 carbon atoms arranged in hexagonal carbon rings of length 16.00 Å and breadth of 13.86 Å is shown in Figure 2a. The 3D structure of endosulfan, downloaded from PubChem Database is shown in Figure 2b.



(A) **(B)**

Figure 2 The computational model of Graphene sheet (A) and endosulfan (B)

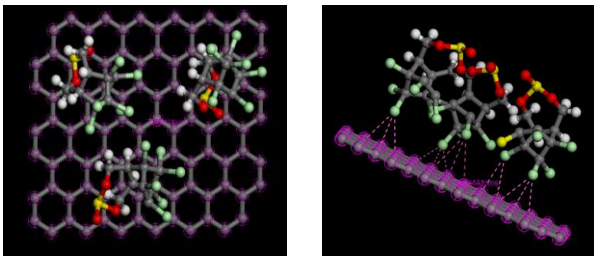
Adsorption of organic molecules on nanomaterials is a complex relationship between non-electrostatic and electrostatic interactions. Both interactions depend on the characteristics of the adsorbent. The adsorption process solely depends on the surface characteristics of particles including surface chemistry and surface energy. Adsorption Locator of

Table-1: Various energy parameters of top 10 poses of endosulfan molecules loaded on the graphene surface

Structures	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	endosulfan1 : dEad/dNi
Pose-1	-14.83281116	-252.5666298	-76.05774609	-176.5088837	-98.10699232
Pose-2	-12.25263698	-249.9864556	-73.19970394	-176.7867517	-99.70499972
Pose-3	-5.5713893	-243.3052079	-67.04820405	-176.2570039	-91.4546427
Pose- 4	-5.32391513	-243.0577338	-66.60673766	-176.4509961	-92.43473369
Pose- 5	-4.25389344	-241.9877121	-65.01740159	-176.9703105	-83.89884165
Pose - 6	-3.45907442	-241.192893	-64.11285118	-177.0800419	-91.53948856
Pose - 7	0.89797918	-236.8358394	-60.30871332	-176.5271261	-78.31856086
pose - 8	1.47920478	-236.2546139	-60.39955651	-175.8550573	-83.94287979
Pose - 9	7.91968075	-229.8141379	-52.48526972	-177.3288682	-78.42302284
Pose - 10	12.27291754	-225.4609011	-48.32326289	-177.1376382	-75.7364017

MS used for this purpose, identifies the possible adsorption configurations by carrying out Monte Carlo searches. The Metropolis Monte Carlo method used in Adsorption Locator, samples the configurations in canonical ensemble by generating a chain of configurations [8]. A low energy adsorption site is identified by carrying out a Monte Carlo search of the configurational space of the substrate-adsorbate system as the temperature is slowly decreased. This process was repeated to identify further local energy minima. The COMPASS force field was used for energy calculation. A total of 10 best poses of endosulfan molecules adsorbed on the nanosurface was generated based on the total energy, adsorption energy, rigid adsorption energy and deformation energy (Table-1).

In total 3 endosulfan molecules were found to adsorb on the graphene surface. The best orientation of graphene molecules on the nanosurface along with van der Waals (vdW) interaction are shown in Figure-3.

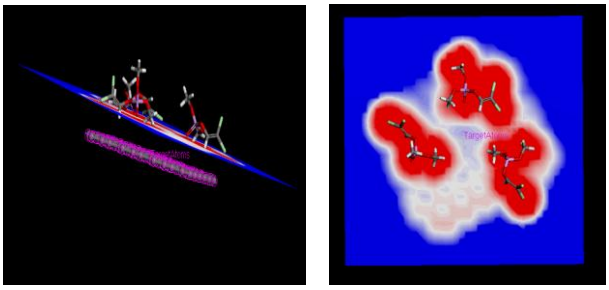


(A) **(B)**

Figure 3 A total of 3 endosulfan molecules loaded on the graphene surface. (A) orientation of the endosulfan molecules; (B) van der Waals interactions between endosulfan molecules and carbon atoms of graphene (pink dotted lines)

The vdW surface area was calculated for both the adsorbate and adsorbent molecules. For graphene, the vdW surface area was 865.29 $Å^2$, while for endosulfan molecule it was 267.87 $Å^2$. In order to identify maximum possible load of endosulfan molecules on the prepared graphene sheet, first we have identified the contact surface areas between two entities. The 3D slice was generated for this purpose as shown in Figure 4.

The 3D slices was further moved in the perpendicular direction to the graphene sheet to identify the contact surfaces of endosulfan molecules. In each of the slice configuration, the maximum contact surface area (red color) was calculated. The instance, at which the red color contour was highest, selected for the load calculation of the endosulfan on the graphene sheet at a given orientation Figure 5(A-C). From the figure, it is clear that the red contour area is maximum when the 3D slice was place at the distance of 0.6 Å from the graphene sheet as when the 3D slice was further moved toward/ away the graphene sheet, the red contour area was decreased (Figure 4B).



(A) Side view **(B) Top view**

Figure 4 Three dimensional slice (blue color) was generated to find the contact surface area of the pollutant adsorbed on graphene. the red color contour shows the area of contact of the adsorbate on the blue colored slice at the distance 0.45 Å from the graphene sheet

The area occupied by the endosulfan molecules is much larger at the distance 0.6 Å from the graphene sheet in comparison to the actual contact area between two entities. This area is more realistic to handle the steric hindrance caused due to the geometry and orientation of adsorbate to adsorb other molecules on the surface that was previously ignored in the Langmuir's model.

4. CONCLUSION

Nanomaterials have gained lots of attention in the environmental cleanup and remediation process due to their high adsorption potential. In order to design a viable remediation system, it is very important to calculate the load of impurities on the nanosurfaces. The load depends on the physico-chemical properties of the adsorbate and adsorbent. Also, the orientation of adsorbate on the surface is one of the most deterministic factors to calculate the adsorption load. Langmuir's model was generally in use to calculate this load.

However, the orientation and the steric hindrance due to the shape and geometry of the adsorbate were ignored in the calculation. We, here, modified the Langmuir's model by incorporating the orientation of the adsorbate along with the shape on the nanosurface. Our strategy require the computational modeling of adsorption process for proper load calculation of various environmental impurities on variety of nanosurfaces, in order to select the best nanomaterial for the remediation process.

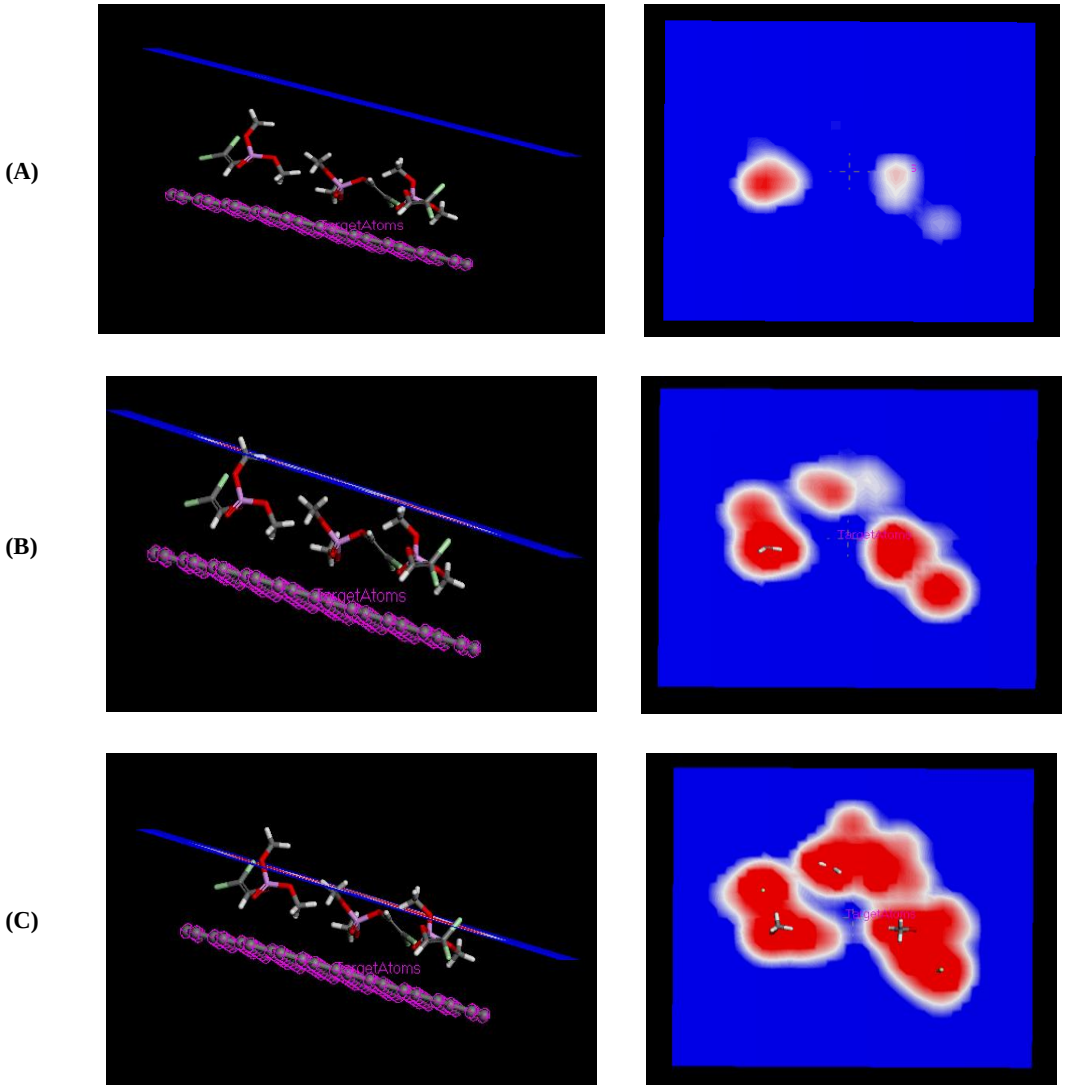


Figure 5 Various configurations of 3D sliced to calculate the maximum contact surface area occupied by endosulfan molecules. 3D slice was placed at A) 0.8 Å; B) 0.7 Å; C) 0.6 Å from the graphene sheet

5. ACKNOWLEDGMENTS

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