

The Effects of Surface Functional Groups and Pore Sizes for 2,4-Dichlorophenoxyacetic Acid Adsorption on Activated Carbon by GCMC Simulation

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In this paper, functionalization of the structure on activated carbon was performed to investigate the effect of structure on the adsorption behavior of 2,4-dichlorophenoxyacetic acid (2,4-D) by Grand Canonical Monte Carlo method. Different pore simulation structures of activated carbon were introduced with BIOVIA material studio software to include a diverse set of functional groups, including elements S, P, N, O, and H. The results show that the 4 nm model has the maximum adsorption capacity, with the -C=O group reaching the largest adsorption capacity of 5.61 mmol/cm³. The adsorption behavior of 2,4-D in the carbon framework structure of activated carbon has been clarified by calculating both the isosteric heat parameters and binding capacity for adsorbate – adsorbent. The results of the study show that the functionalization of the activated carbon surface leads to a new direction in the synthesis of capillary materials for the application for removal of pollutants

1. Introduction

Recently, the problem of pesticide use has caused agriculture to emerge with many types of pollutants that are difficult to decompose in the environment (Paternina et al., 2022). Concerns include contamination due to overflow of arable land, poor handling of pesticides in agricultural practices, and lack of safety measures when disposing of pesticide containers without prior cleaning (Tasca et al., 2019). This study is focused on eradicating 2,4-D from the environment, as it is a licensed drug that is commonly used in agricultural activities. Studies have shown that 2,4-D can be detected both during and after application to surface water and ground water (Fan, 2017).

The removal of 2,4-D from contaminated water is done using typical conventional methods like adsorption (Ighalo et al., 2023). Activated carbon is a widely used and effective adsorbent for the removal of organic substances due to surface properties such as large surface area, high porosity and surface chemical properties containing polar functional groups favorable for adsorption by the process of forming electrostatic bonds between the surfaces of adsorbate – adsorbent (Vinayagam et al., 2023). The study of 2,4-D adsorption by different structures in terms of composition and pore size has provided an overview and effective option in the process of making adsorbent materials to capture unwanted organic components.

Yasmin Vieira et al. (2022) utilized a statistical physical model (sta-phy) to evaluate how 2,4-D adsorbs on graphene surfaces (Vieira et al., 2022). The simulation of electronic density and reaction parameters is aided by density functional theory. According to the Sta-phy model, the Hill isotherm model offers monolayer adsorption at the two most optimal energies. The amount of adsorption sites decreases as temperature increases. The concentration of saturation increases with increased temperature. The importance of thermal effects and electrostatic repulsion is evident, and their value increases when the adsorption sites are filled. The simulations of activated carbon surface structures with different functional groups used for adsorption studies have achieved results that contribute to the denaturation of graphene structures for the purposes of capturing unwanted compounds. Hongyu Chen et al. (2021) conducted the study by simulating activated carbon structures with functional groups containing different components (C, H, O, N, P, ...) (Chen et al., 2021). Functional groups are found to play a significant role in influencing the ability to absorb saturated CO₂. Activated carbon surfaces

that have been functionalized have a strong influence on adsorption capacity due to their high electron conductivity and adsorption energy. Hicham Yazid et al.(2024) investigated the mechanism of 2,4-D pesticide adsorption on activated carbon using molecular simulation (Yazid et al., 2024). The results show that the thermodynamic adsorption process indicates the exothermic mechanism. Using the Boehm method, organic functions were determined on the adsorbent surface and density function theory was applied to evaluate the adsorption mechanism on the activated carbon surface.

The studies mentioned above have nearly achieved the conclusion of assessing the adsorption capacity and the mechanism of action of simulated structures. The energy of interaction between adsorbate and adsorbent surface has not been studied in previous studies. This study established the simulated structure of activated carbon to assess 2,4-D adsorption capacity and interaction energy during the formation of adsorbate-adsorbent surface bonds.

Simulated activated carbon with surface structures bearing different pore sizes was simulated in this study to observe its effects on 2,4-D adsorption behavior. Activated carbon model calculations for 2,4-D adsorption were done using the Monte Carlo method with adsorption isotherm lines. The interaction energy value is examined in detail to provide an explanation for 2,4-D adsorption behaviour on activated carbon by examining the electron affinity differences between functional groups. This is a broad overview of the surface functionalization of carbon materials that can be used as a basis for surveys to assess the molecular dynamics of adsorption processes.

2. Methodology

2.1 Models

In this paper, the models of activated carbon established in the BIOVIA Material Studio 2017 software were simplified to a pattern of slots formed by parallel graphene sheets, whereby the dimensions of the graphene sheets were set to 17.04 Å along the x-axis and 19.68 Å along the y-axis (Jiang et al., 2022). The system of surface functional groups used in the simulated calculation included hydroxyl (-OH), carbonyl (-C=O), dihydrogen phosphate (-OP(OH)₂=O), amine (-NH₂) and bisulfite (-HSO₃). Calculations were done to investigate the effect of functional groups with different pore sizes (1 nm, 2 nm, 3 nm, 4 nm and 5 nm) on the capture of 2,4-D molecules. A simulated model of activated carbon was created in Figure 1 (BIOVIA Material studio, 2017).

2.2 Simulation method

The GCMC simulation method is a collection of useful tools that simulate the specific adsorption behavior of 2,4-D on activated carbon structures. The calculation used the sorption module, with the condensed phase optimizing the molecular potential for Atomistic Simulation Studies force field (COMPASS) (Wang et al., 2020). The parameters that have been chosen include critical state parameters and van der Waals parameters. All simulated calculations were done using the temperature of 298.15 K. One of the creation, transferring, rotating, and deleting operations in a Monte Carlo step was chosen for adsorbents that were considered rigid spheres in the simulation (Tao et al., 2022). Adsorption with different fugacity values in the range of 10⁻⁶ – 10⁵ Pa was then conducted through a series of simulations at 298.15 K.

2.3 Isothermic heat

The assessment of the criteria and properties of the adsorption process is crucial by examining the energy interaction between the molecules (E). The expression following provided the basis for determining isothermic heat E (An et al., 2019):

$$E = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \varepsilon_{ij} \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (1)$$

Where: E is isothermic heat (Cal/mol); q_i, q_j is the charge of the adsorption sites (C); r_{ij} is the distance between the adsorption sites (m); r_{ij}⁰ is the average radius of component atoms i and j (m); ε_{ij} is the average potential well depth of component atoms i and j.

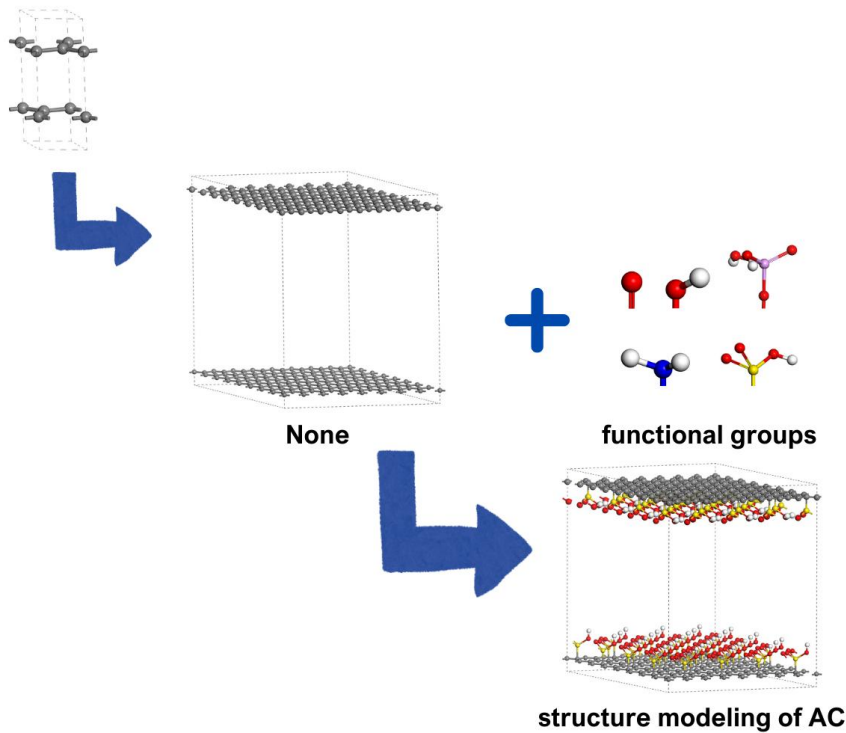


Figure 1: Structural simulation

The r_{ij}^0 and ε_{ij} values are determined according to the following equations:

$$r_{ij}^0 = \left(\frac{(r_i^0)^6 + (r_j^0)^6}{2} \right)^{\frac{1}{6}} \quad (2)$$

Where: r_i^0 and r_j^0 are the radii of atoms i and j .

$$\varepsilon_{ij} = \frac{2(\varepsilon_i \times \varepsilon_j)^{\frac{1}{2}} \times (r_i^0 \times r_j^0)^3}{(r_i^0)^6 + (r_j^0)^6} \quad (3)$$

Where: ε_i and ε_j are the average potential well depths of atoms i and j ; r_i^0 and r_j^0 are the radii of atoms i and j .

3. Result and discussion

The 2,4-D adsorption capacity on an activated carbon model with different structural simulations was estimated using the GCMC method. The following are the simulation results:

3.1 Effect of functional groups in 1.0 nm and 2 nm pore sizes

The adsorption capacity of activated carbon at its maximum for a pore size of 1 nm is shown in Figure 2. Due to the large contact between the activated carbon surface and 2,4-D, bond formation is made easier by the small pore size. The difference in adsorption capacity between functional groups due to the different binding energies between them makes the process occur quickly and there is the formation of a multilayer adsorption mechanism when the fugacity value is gradually increased. For the dihydrogen phosphate functional group ($-\text{OP}(\text{OH})_2=\text{O}$), adsorption does not occur due to the hollow size in the structure of the activated carbon being too small to be filled by 2,4-D molecules.

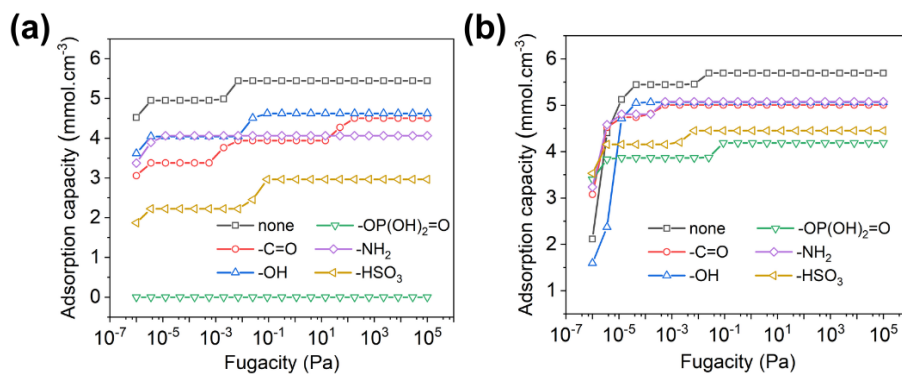


Figure 2: Adsorption isotherm of 2,4-D with different models: (a) 1 nm, (b) 2 nm

For structures with a pore size of 2 nm, adsorption occurred on all structures with functional groups established during the simulation. The maximum adsorption capacity was obtained from the none structure. This is explained by the fact that the size of functional groups affects the ability to store 2,4-D molecules and tends to increase in the direction of $-\text{OP}(\text{OH})_2=\text{O} < -\text{HSO}_3 < -\text{C}=\text{O} < -\text{OH} < -\text{NH}_2$, which occurs with a large influence on the size of functional groups. The pore size is small enough to make the effect of the size of the functional groups greater than the effect of the electron affinity between those functional groups (a characteristic property of adsorption binding) (Lin et al., 2020).

3.2 Isothermic heat in 1.0 nm and 2 nm pore sizes

Activated carbon and 2,4-D molecules have a surface interaction energy, which is represented by the isosteric heat value. The shapes of the structures in the simulation are mainly determined by their adsorption capacity. The graph has a shape that resembles the adsorption isotherms. The ability to form bonds is equivalent to the absorption energy, which is proportional to the electron affinity of the structures. The graphs in Figure 3 reveal that electron affinity plays a significant role when the bisulphite group ($-\text{HSO}_3$) reaches its maximum value at 71.6 kCal/mol.

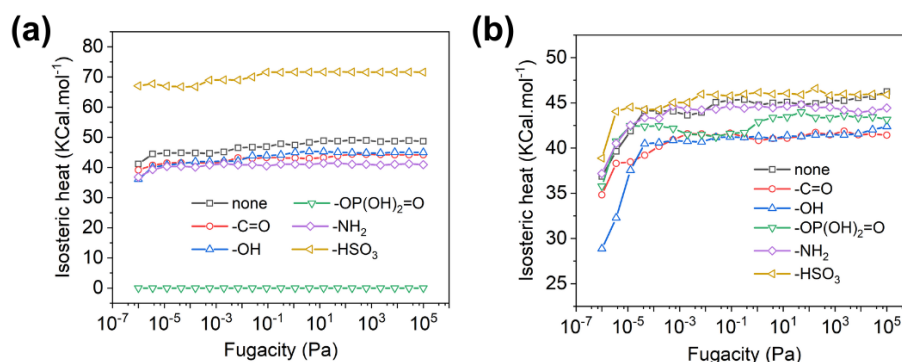


Figure 3: Isothermic heat of adsorption for 2,4-D with different models: (a) 1 nm, (b) 2 nm

When the pore size goes up to 2 nm, the impact of functional groups becomes stronger because of the change in interaction energy. The isosteric heat values in Figure 3b are closer to each other with increased fugacity than in Figure 3a. This shows that when increasing the pore size, these values will be approximately the same at the critical value of fugacity due to the greater influence of electron affinity compared to the pore size (Giraldo et al., 2019).

3.3 Effect of functional groups in large (3 nm, 4 nm, 5 nm) pore sizes

Figure 4, the influence of key determinant functional groups on 2,4-D adsorption capacity. The evidence is that in Figure 4a, the hydroxyl functional group ($-\text{OH}$) gives the maximum adsorption capacity of 5.78 mmol/cm³. The influence of functional groups that form adsorption bonds between the graphene surface and 2,4-D molecules

results in greater capture than none structure. The adsorption isotherms in Figure 4b and 4c, also in Langmuir type V, are distinct from the type I in Figure 4a (Buttersack, 2019).

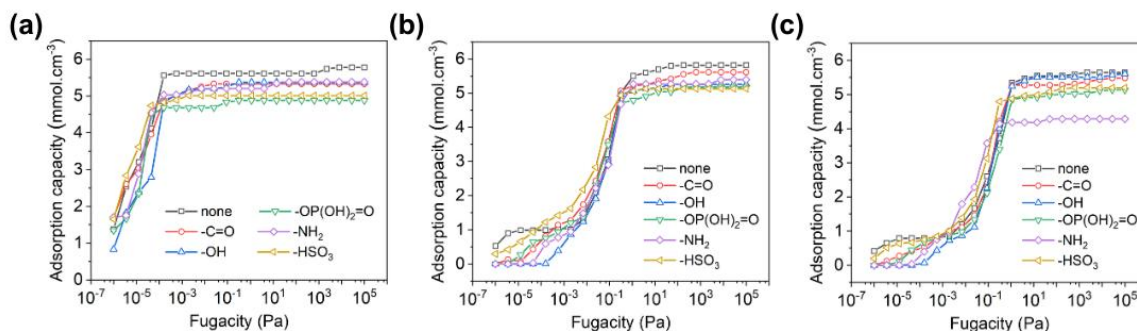


Figure 4: Adsorption isotherm of 2,4-D with different models: (a) 3 nm, (b) 4 nm, (c) 5 nm

Adsorption at low fugacity occurs faster at small sizes of 1 nm, 2 nm and 3 nm, but when the size increases to 4 nm and 5 nm, the multilayer adsorption capacity is stronger, making the capture of 2,4-D molecules increased. Electron affinity also mainly determines the adsorption capacity between them, which makes a difference between the adsorption capacity values on adsorption isotherms.

3.4 Isothermic heat in large (3 nm, 4 nm, 5 nm) pore sizes

Figure 5 shows that the interaction energy value has shifted in an increasing direction according to the electron affinity increasing value of the functional groups. This suggests that capillary condensation causes heat to evaporate which determines an important role in the energy of interactions between molecules (Yang et al., 2019).

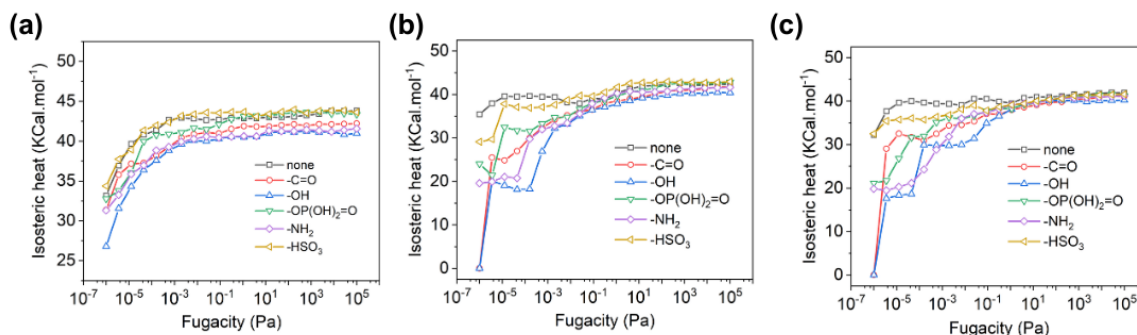


Figure 5: Isothermic heat of adsorption for 2,4-D with different models: (a) 3 nm, (b) 4 nm, (c) 5 nm

In high fugacity, the interaction energy difference is significantly reduced between different structures. At this time, the adsorption capacity is no longer influenced mainly by the interaction energy but mainly by the hollow lot size of the structures. The maximum interaction energy value was only 43.8 kCal/mol (none structure) compared to 71.6 kCal/mol on the bisulfite structure (-HSO₃) (Wang et al., 2020).

4. Conclusions

The activated carbon surface at 1 nm and 2 nm pore sizes were functionalized, which resulted in a major reduction in the adsorption capacity of 2,4-D. When the size was increased to 3 nm, 4 nm, 5 nm the adsorption capacity increased with the addition of functional groups, reaching the maximum value for the hydroxyl functional group (-OH) 5.78 mmol/cm³. Maximum interaction energy value of 71.6 kCal/mol for bisulfite structure (-HSO₃) with 1 nm pore size, as the size of the pore increases, the interaction energy value decreases, indicating a significant impact of pore size on adsorption capacity at large fugacity values. Capillary condensation occurs in large pore size structures that reduce the interaction energy but contribute to greater storage capacity of 2,4-dichlorophenoxyacetic acid molecules as a guide for the fabrication of carbon frame materials more suitable for the recovery of organic compounds.

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