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The Influence of The Functional Groups and Pore Sizes on Activated Carbon for 4-Chlorophenol Adsorption by Molecular Simulation

Van Linh Nguyen*, Anh Kien Le, Van Thanh Huy Ngo, Thanh Tung Nguyen, Thuy Nguyen, Anh Khoi Tran

Institute for Tropicalization and Environment (ITE), 57A Truong Quoc Dung Street, Ward 10, Phu Nhuan District, Ho Chi Minh City, Vietnam
linhnguyen40496@gmail.com

In this study, hydrogen, hydroxyl, carbonyl, carboxyl, amine, epoxy functional groups are introduced into various pore structures of activated carbon, to investigate their effect on the adsorption of 4-chlorophenol by molecular simulation. Adsorption isotherm of 4-chlorophenol is then calculated by sing Grand Canonical Monte Carlo (GCMC) simulation. The simulation results showed that, on the none structure, the 4-chlorophenol adsorption capacity reached the maximum value with a pore size of 1.5 nm. In contrast, when a functional group is present on the surface, activated carbon with a 4 nm pore is more dominant in terms of adsorption capacity. All functional groups exert a great influence on the threshold pressure and reduce the adsorption capacity at high pressure. But at medium and low pressures, the adsorption capacity of activated carbon increases rapidly in the presence of functional groups. The simulation results also showed that the carboxyl functional group gives superior adsorption capacity at medium and low pressures. The ability of activated carbon to form adsorption bonds with 4-chlorophenol was further investigated by comparing the adsorption energy between them. It can be seen that the surface functionalization has provided additional information during the synthesis of carbon materials for the treatment of organic compounds.

1. Introduction

Environmental pollution by organic compounds has always been a problem in recent years. 4-chlorophenol is one of them with very durable characteristics in the environment, which is a threat to human health and the environment (Sarno and Iuliano, 2019). In recent years, the application of adsorbent materials has always been a useful method to remove the above compounds (Zhang et al., 2020). Its advantage over other methods is that it does not create toxic intermediates, which are easily recovered and removed. Activated carbon is an excellent adsorbent material that is frequently applied in adsorption processes that remove toxic compounds without causing secondary effects. Due to the developed capillary structure, large specific surface area, activated carbon is researched and applied in the current technology of environmental pollution treatment (Chengyu et al., 2017).

The investigation of the influence of surface functional group structure, pore size on the adsorption capacity of activated carbon by simulation method has been studied a lot in recent years. With the help of molecular simulation methods have contributed to the design options of activated carbon structures suitable for the purposes of adsorption of different molecules. There have been many studies applying the molecular simulation method in the investigation of the adsorption process of activated carbon for pollutant compounds. Arriagada et al. (2013) conducted a study to remove 4-chlorophenol by different graphene surface structures (Arriagada et al., 2013). The research team set up a series of molecular simulations of graphene (G), graphene oxide (G-O) and graphene with doped functional groups G-COOH, G-CO, G-OH, A-doped graphene (A = N, B). The results showed that the functionalization of the graphene molecule showed better 4-chlorophenol removal potential than pristine graphene through hydrogen bonding interaction. The study's results indicate that functionalized

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structures are a more appropriate alternative to graphene pristine. Kuntail et al. (2019) conducted a study on the adsorption of p-chlorophenol, phenol and p-nitrophenol molecules on magnetic surface (Kuntail et al., 2019). The functional groups involved in the absorbate – adsorbent interaction was determined by radial distribution density function. Data from isotherms show that the adsorption constant is highly dependent on the polarity of the functional group and the formation of hydrogen bonds. The comparative order of the adsorption energy between them is consistent with this. Wei et al. (2019) conducted a chlorophenol adsorption study on the graphene surface by calculating density functional theory and molecular dynamic (Wei et al., 2019). The calculation results elucidated the adsorption mechanism of chlorophenol on the graphene surface. The team found that adsorption was improved by hydroxyl (-OH) groups, as they could provide more adsorption sites during chlorophenol capture. The adsorption affinity is also weakened when increasing the number of chloro-groups.

The above studies have elucidated the influence of surface functional groups related to 4-chlorophenol adsorption capacity but have not included the gap factor between graphene layers to study monolayer and multilayer adsorption in the capillary structure of graphene. Parameters related to the onset of adsorption, threshold fugacity, have not been investigated. This study, in addition to inheritance, will further investigate the effects of different pore sizes and threshold fugacity values for adsorption isotherms.

In this study, models representing different activated carbon structures in terms of functional group and pore size were established to study 4-chlorophenol adsorption on activated carbon using the GCMC simulation method. The change in adsorption capacity under different values of fugacity is studied in the form of adsorption isotherm lines and has been discussed in detail. The accessible volume and adsorption energy have also been studied the adsorption of 4-chlorophenol.

2. Theory and Compulational Methods

2.1 Models

In this study, the pore structure of activated carbon is simulated by parallel graphite plates, oriented in x, y, z axis. Where the dimensions according in the x axis is 39.5 Å, in the y axis is 34.2 Å. The intervals of the two graphite sheets in z-direction simulate the effective pore size of the graphite layers of 1, 1.5, 2, 3 and 4 nm. The pattern of activated carbon is shown in Figure 1.

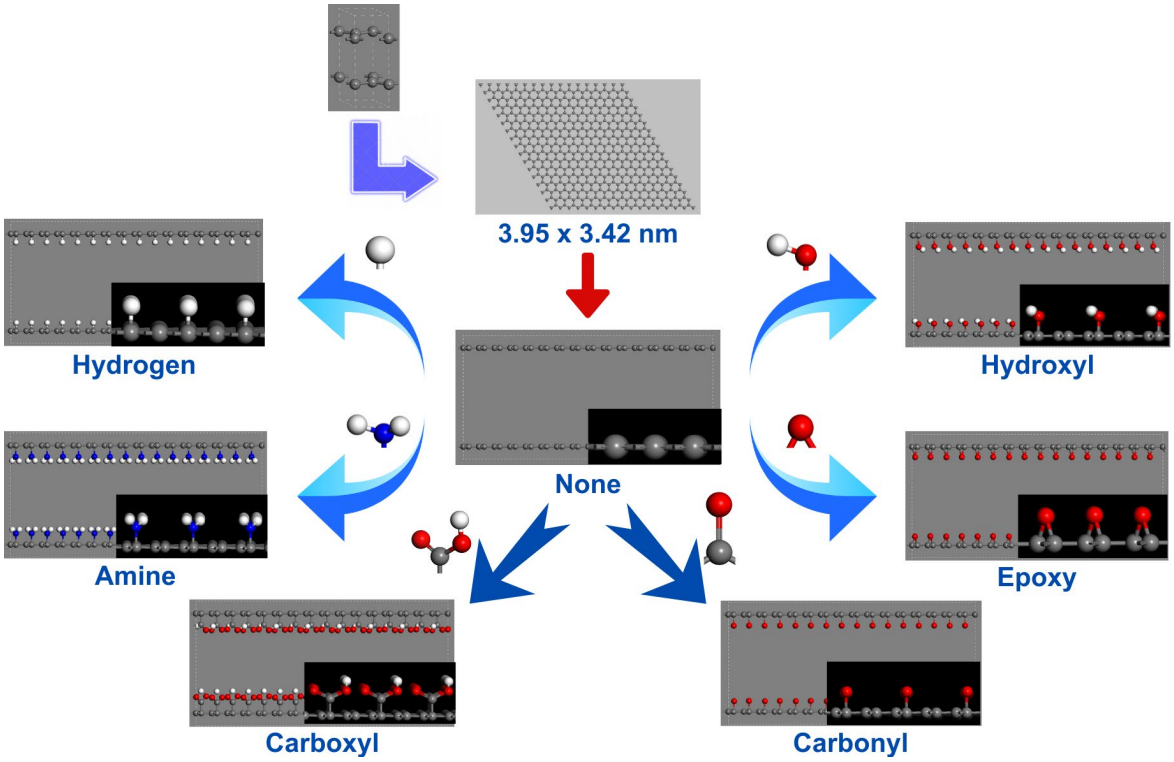

Figure 1: Activated carbon models

In this study, hydrogen (-H), hydroxyl (-OH), carbonyl (-C=O), carboxyl (-COOH), amine (-NH_2) and epoxy (-C-O-C-) functional groups were used to study the influence of surface functional groups on the 4-chlorophenol adsorption capacity of activated carbon by GCMC simulation. The optimization structure performed with selected parameters is the orbital polarization function (DNP), a generalized slope approximation (GGA) optimization method with a high-precision Perdew-Burke-Emzerhof (PBE) function in the description of van der-Waals forces (Huang et al., 2019).

2.2 Grand canonical Monte Carlo simulation

The GCMC simulation is a widely used tool for simulating adsorption of molecules. The molecular is optimized by the Dmol3 module, the critical state parameters, and the van der-waals parameter activated in the simulation (Zhu et al., 2022). The pressure selected in adsorption isotherm simulation is 10^{-8} – 10^{7} Pa. 4-chlorophenol adsorbents are considered hard balls in the GCMC method. A temperature value of 298 K was selected to conduct the study in the simulation.

2.3 Threshold fugacity

The threshold fugacity is calculated from the constants of the Langmuir isothermal adsorption model (see Eq(1)), which gives information about the fugacity value at which adsorption begins to occur (Liang et al., 2018).

$$Q = Q_0 \frac{kP}{1+kP} \tag{1}$$

Where: Q, Q_0 are the adsorption capacity at pressure P and the maximum adsorption capacity calculated from the model (mmol/cm^3); k is the Langmuir constant (cm^3/mmol).
The expression for determining the pressure threshold value of the adsorption isotherm is determined by constants from the Langmuir adsorption isotherm model (see Eq(2)).

$$P_{threshold} = \frac{1}{k(Q_0-1)} \tag{2}$$

2.4 Accessible volume

This value is determined by the method for He_2 gas adsorption activated carbon structures (because Helium is an inert gas, it is almost difficult to be adsorbed by activated carbon, so they are almost applied to compare accessible volumes in activated carbon structures by molecular simulation). The relationship between the number of helium molecules that can be adsorbed in the activated carbon structure with fugacity can be expressed by the Eq(3) (An et al., 2019).

$$N_t = \frac{VM_{He_2}}{RT} P \tag{3}$$

Where: Nt is the number of helium molecules adsorbed (per.cell); $M_{He_2}$is the molar mass of the Helium gas molecule (g/mol); V is the empty volume of the pore structure (L); R is the ideal gas constant (R = 8.314 KJ/mol); T is the temperature kelvin at the survey site (K); P is the fugacity value at the time of the survey (Pa).

3. Result and Discussion

3.1 Adsorption in activated carbon with different structures

Figure 2 depicts adsorption isotherms of 4-chlorophenol on activated carbon structures with different pore sizes and functional groups (none representing a non-functional structure).
From Figure 2 it is observed that adsorption isotherms of 4-chlorophenol are of type V (IUPAC nomenclature). In experimental studies, the 4-chlorophenol adsorption isotherms are of type IV (Tun and Chen, 2021). This diference is due to limited experimental research on low fugacity value. In the experiment, the inflection point of isothermal lines is difficult to recognize as clearly as the simulation studies and so not easy to be verified by conventional experiments. The isotherm data shows that the 4-chlorophenol adsorption capacity of activated carbon reaches its maximum value for the none structure. This may explain that activated carbon surface-mounted functional groups reduce the volume of space in the pore structure.
For different pore structures the 4 nm pore structure gives the largest adsorption capacity for structures containing the polar functional group (the capacity reaching the maximum value for the epoxy polar functional group). For less polar structures (none and hydrogen) the adsorption capacity reaches the maximum value on the 1.5 nm structure (the maximum value is 8.43 mmol/cm^3 on the none structure). This difference can be attributed to the fact that, for a low spatial volume structure, the effect of electrostatic binding forces and Der-Waals valves force is negligible in large pore structure. At large sizes 4-chlorophenol molecules are more readily trapped when there are electrostatic interactions between the polar structure of the hydroxyl (-OH) and -Cl

groups in 4-chlorophenol with functional groups containing highly electronegative (N, O) atoms on the surface of activated carbon (Domenicano and Vaciago, 1979). To further clarify the different adsorption capacity of the 4-chlorophenol constituents of the activated carbon surface with different functional groups, the parameters of threshold fugacity, accessible volume and adsorption energy were further investigated.

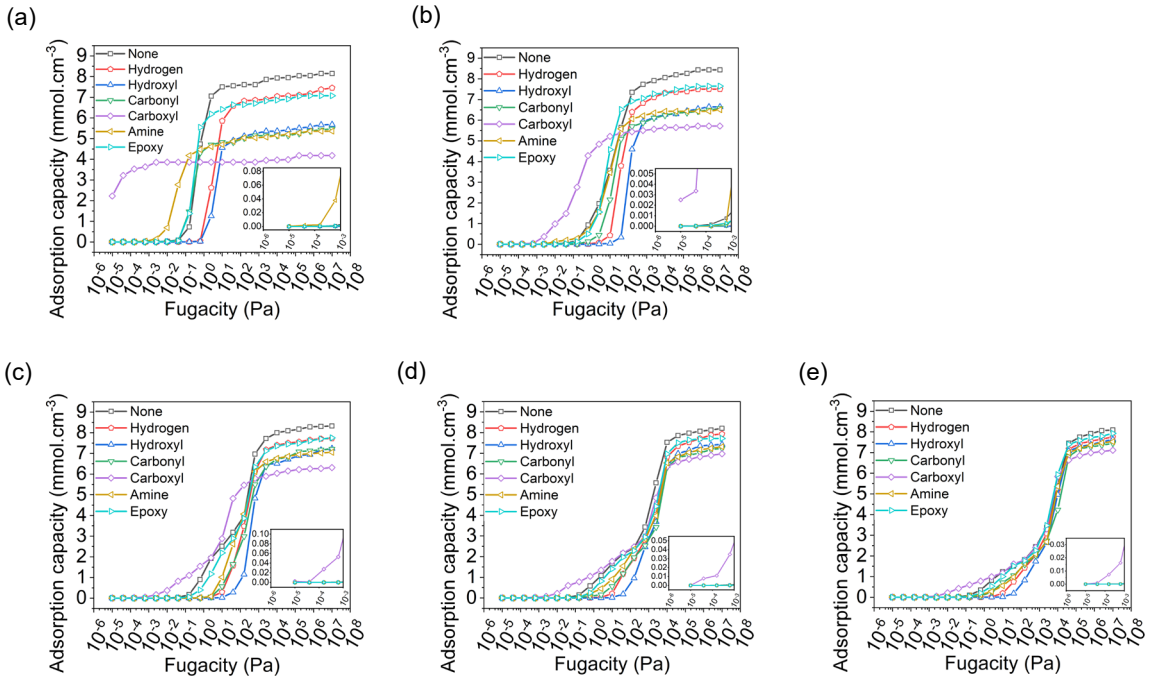

Figure 2: Adsorption capacity with different structures: (a) 1 nm, (b) 1.5 nm, (c) 2 nm, (d) 3 nm, (e) 4 nm

3.2 Threshold fugacity with different structures

The results of the calculation of threshold fugacity from 4-chlorophenol adsorption isotherm lines of various structures of activated carbon are presented as Figure 3.

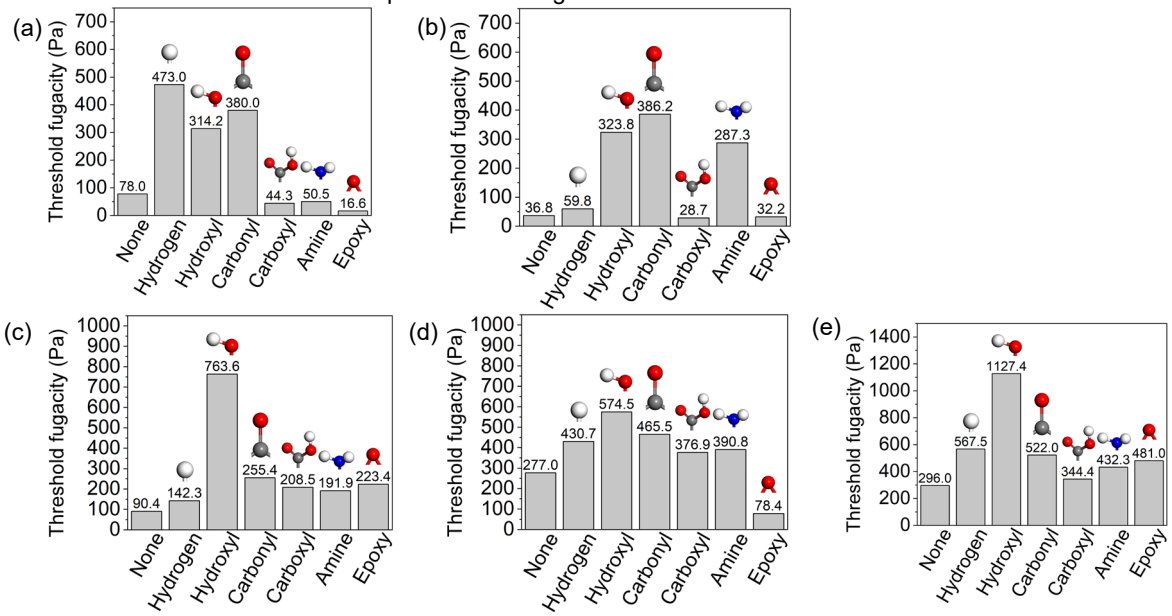

Figure 3: Threshold fugacity with different pore sizes: (a) 1 nm, (b) 1.5 nm, (c) 2 nm, (d) 3 nm, (e) 4 nm

The threshold fugacity value gives us complete information about the adsorption capacity of various structures, the 4-chlorophenol adsorption of activated carbon begins when the fugacity exceeds the threshold fugacity (Liang et al., 2018). It was found that, at 1 nm and 1.5 nm pore sizes, none, epoxy, carboxyl structures have a much lower threshold fugacity than the rest of the structures (ranging from 16.6 – 78 Pa). The result proves that the interoperability of none, epoxy, carboxyl structures is greater than hydrogen, hydroxyl, carbonyl and amine structures. Their adsorption capacity starts to increase sharply when fugacity reaches these values. When the threshold fugacity value is passed, the slope of the isotherm gradually decreases and enter the process of reaching saturation. At 2 nm and 4 nm pore sizes, the hydroxyl group structure has an unusually high threshold fugacity compared to the other structures. The result shows that the hydroxyl structure has a lower threshold fugacity than the other structures. At the 3 nm pore structure, the epoxy group easily surpasses the threshold fugacity value compared to other structures with a threshold fugacity of only 78.4 Pa. The low threshold fugacity of the carboxyl structure also explains the difference in their adsorption isotherm compared to the rest of the structures in Figure 2a.

3.3 Accessible volume and adsorption energy

To explain the 4-chlorophenol adsorption capacity of activated carbon when adding functional groups, the accessible volume and adsorption energy were further investigated (An et al., 2019).

The adsorption energy characterizes the ability to create a sustainable, accessible volume that characterizes the volume of space in which 4-chlorophenol molecules are stored, these values add and subtract each other. Their combination is the largest for none structure describing the largest adsorption capacity. Investigate these values to understand adsorption behavior at low fugacity (Liu et al., 2012). In Figure 2 with low fugacity the adsorption capacity of polar groups is greater than that of less polar groups but at large fugacity the effect of volume accessible is dominant due to the main spatial volume for the adsorption behavior of 4-chlorophenol on the structures of activated carbon (Herrera et al., 2010).

From the results of Figure 4, it is easy to see that the increase in adsorption energy when attaching functional groups is always less than the approachable volume decrease. This further confirms the influence of pore size in this study clearly greater than the influence of the formation of interaction links of functional groups. This shows that the epoxy functional group gives the combined influence of the larger elements than the rest of the structures.

The value of accessible volume tends to decrease gradually in the direction of none > hydrogen > epoxy > hydroxyl > amine > carbonyl > carboxyl. The results reflect the ability of activated carbon structures to store 4-chlorophenol molecules in the pore structure, which is perfectly suited to explain differences in adsorption capacity through simulation (Herrera et al., 2010).

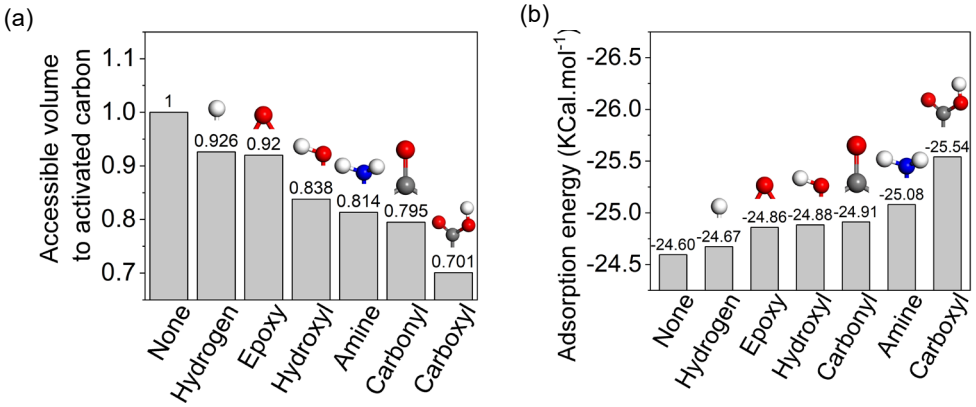

Figure 4: (a) accessible volume, (b) adsorption energy

Comparison results of adsorption energy decreasing in the polarization direction of the functional group (none < hydrogen < epoxy < hydroxyl < carbonyl < amine < carboxyl). This accounts for the difference in the threshold fugacity of structures containing carboxyl groups compared to other functional structures. Oxygen-containing functional group structures has a large polar structure to create a more stable bond, so the energy released from the bonding process also increases completely in accordance with theory and practice (Inglezakis and Zorpas, 2012). From this, it can be seen that bringing the functional group to the surface of activated carbon will create more stable forms of adsorption, which can be applied to recover organic substances under adverse conditions for adsorption to take place.

4. Conclusions

The addition of hydrogen, hydroxyl, carbonyl, carboxyl, amine, epoxy functional groups mostly reduces the adsorption capacity of 4-chlorophenol. The diminish according to the size of the functional groups, the carboxyl group for the smallest adsorption capacity at the survey values. The epoxy, hydrogen functional group gives a larger adsorption capacity than the other polar functional groups. The research results show that the 1.5 nm pore structure has a large adsorption capacity on none, hydrogen functional groups, while the 4 nm structure has a large adsorption capacity on epoxy, hydroxyl, carbonyl, carboxyl and amine functional groups. A survey of the overall effect of pore size and functional groups showed that the structure containing the epoxy group has the greatest adsorption potential. The results of the study have provided more information for the process of making carbon materials to recover organic compounds, contributing to environmental protection.

Acknowledgments

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