Computer aided design of water-resistant adsorbent for formaldehyde abatement

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Abstract. Formaldehyde is a well-known indoor air pollutant that is regulated by authorities worldwide. Formaldehyde has adverse health effects in humans, especially as a sensory irritant to the eyes and to the upper air way, and more importantly, it is a known carcinogen. Adsorption by carbon adsorbents is an old, but indispensable cleaning technology for combating indoor formaldehyde. In this study, we report isotherms and 2D-density distributions by conducting comprehensive Monte Carlo simulation. The effects of the functional group and pore size were investigated. We found that formaldehyde has a different response when the number of functional group and pore size change from that of water. Therefore, by tuning pore size and functionalities it may be feasible to produce real materials that retain effective capture of formaldehyde but which avoid pore blocking by water based on the differences in adsorption properties between water and formaldehyde.

1. Introduction

Formaldehyde is one of the main volatile organic compounds in indoor air and atmospheric environment. Since it not only reacts with ozone to form secondary organic aerosols (SOA) in atmospheric environment, but also it has a certain risk of cancer in indoor air even at low concentrations, formaldehyde has attracted broad attention recently. Acute exposure to formaldehyde can cause eye, nose, throat and skin allergies, while long-term exposure has been linked to certain cancers (such as nasal sinuses) and asthma [1]. In the United States, the statutory occupational limit for formaldehyde exposure is 2 PPM for short-term (i.e. <15 minutes) and 0.75 PPM for long-term (i.e. > 1.5 minutes) [2]. In contrast, the national institute for occupational safety and health recommends limiting exposure to lower levels: 0.016 PPM (long-term) and 0.1 PPM (short-term). Short-term exposure guidelines recommended by the world health organization (WHO) are 0.1 mg/m³ (about 80 PPB, 30 minutes on average) [3], and long-term exposure indicators, known as chronic reference exposure limits (REL), are provided by the California office of environmental health hazard assessment (OEHHA), as low as 9 ug/m³

Due to the use of building materials in the home, such as particleboard, MDF, paints and varnishes, the concentration of formaldehyde in the indoor air tended to exceed the standard limits of WHO or OEHHA [4]. Gilbert et al., has invested the formaldehyde concentrations in 155 homes in Canada, the resulted showed that the concentration of formaldehyde exceeding 50 μg m⁻³ in 16 out of 59 homes (27%) in Prince Edward Island and 11 out of 96 homes (11%) in Québec City [5]. Therefore, it is imperative to carry out effective formaldehyde purification.

For the formaldehyde purification, lots of purification techniques has been used to work on it, such as photocatalysis, catalytic combustion, adsorption, absorption and so on. Among these purification technologies, adsorption is the most suitable technology for indoor formaldehyde, because of its simple form and high efficiency. As many publications reported, activated carbons (ACs) were extensively used...
as highly effective adsorbent for adsorption of formaldehyde from air. [6]. Many studies have forced on the further improve the adsorption performance of formaldehyde by carbon, such as functional groups modify, change the pore structure, change the structure and so on. Ma et al. has studied the effect of functional group modification on the adsorption of formaldehyde by activated carbon, and showed that the addition of amino group could effectively improve the adsorption performance. [7] Shen et al., has changed the form of carbon to improve the adsorption performance of formaldehyde[8].

Surface functional groups, pore structure and activated carbon form all affect the adsorption performance of activated carbon. In addition to the above influencing factors, competitive adsorption is an important factor affecting the adsorption of formaldehyde by activated carbon. In particular, water molecules, which are combined with activated carbon in the low pressure region, occupy the adsorption site and reduce the adsorption of formaldehyde molecules. At the high pressure region, water condenses in the mesopores, which blocks the pores and reduces the adsorption of formaldehyde [9] Therefore, reducing the competitive adsorption in the presence of moisture is a new challenge for formaldehyde adsorption. In this paper, we aim to design of water-resistant adsorbent for formaldehyde abatement by Monte Carlo simulation and the effect of functional groups and pore size has been researched.

2. Theory

2.1 Formaldehyde model

Formaldehyde, an organic polar molecule with effective size ~2.5 Å and large 2.6 D dipole moment, which was described by the OPLS model [10]. The molecule is planar and is modeled by 4 dispersive sites located at the centers of the atoms and 2 partial charges located at the centers of the oxygen and carbon atoms. The molecular parameters are given in Table 1. The intermolecular potential energy is described by the 12 –6 Lennard-Jones (LJ) equation for the dispersive-repulsive interaction and the Coulomb law for the electrostatic interaction.

| Site | q/e | ε/kB(K) | σ |
|------|-----|---------|---|
| C    | +0.45 | 52.9    | 0.375 |
| H    | 0.00  | 7.6     | 0.242 |
| O    | -0.45 | 105.8   | 0.296 |

2.2. Pore model

Figure 1a is a schematic diagram of the slit carbonaceous pore, with both ends open to the gaseous surroundings. On the basal plane of the innermost pore walls several rows of functional groups (FGs) were placed along the y-direction. The hydroxyl group (OH) was chosen as the functional group because it is the most abundant oxygen-carrying group in carbonaceous materials [11]. Solid-state nuclear magnetic resonance (NMR), ultra-high-resolution transmission electron microscopy (TEM) and near-edge X-ray absorption fine-structure (NEXAFS) [12] studies suggest that OH groups tend to attach to the basal plane surfaces rather than at their edges. The molecular parameters of an OH group are given in Figure 1b.
2.3. Vapor pressure

The saturation vapor pressures for the potential models of formaldehyde and water, which are used to plot isotherms as a function of reduced pressure, were fitted to a virial equation calculated from the kinetic Monte Carlo (kMC) simulations of the vapor-liquid equilibria (VLE) [13].

3. Results and discussion

3.1 Comparison between simulation and experiment

Figure 2. (a) Simulated isotherms in 1.25 nm pores with FGs at 298 K over the full reduced pressure scale. (b) Experimental water adsorption-desorption isotherm in a microporous carbon (ACF-10) at 298K (c) Comparison of the simulated isotherms for formaldehyde adsorption in the 1.25 nm pore and experimental isotherm.
The simulation of water adsorption-desorption isotherm by 1.5nm graphitic slit pore at 298k is shown in Figure 2a. Figure 2b shows the experimental data in microporous carbon (ACF-10). Although the pore model in Figure 1 is idealized, the key features of the experimental isotherm has been captured by simulated adsorption-desorption isotherm, including the type V adsorption isotherm, the H1 hysteresis loops and the onset of pore-filling occurring around a reduced pressure of 0.5. Figure 2c shows the simulation adsorption isotherm for the 1.25nm graphitic pore. The simplified model structure also corresponds to the experimental data of formaldehyde adsorption in microporous activated carbon. In Figure 2a,2b, the experimental adsorption branch is slightly more skewed than the simulated one, possibly due to the size distribution of the pores of the real material. Therefore, the simplified model for carbon can calculate the adsorption-desorption isotherm of water and formaldehyde, and it can effectively present the characteristic information of adsorption isotherm, such as the type of sorption isotherm, adsorption capacity and hysteresis loops for desorption.

3.2 Adsorption mechanism

![Figure 3](image-url)  
**Figure 3.** Simulated isotherms at 298k for water and formaldehyde plotted against reduced pressure in the 1.55nm pore with FGs.

![Figure 4](image-url)  
**Figure 4.** 2D-density distributions at the selected points marked in Fig. 3. Columns from left to right: formaldehyde and water. The axes are in units of nm, and the scale bars are in units of kmol/m³.
Due to water and formaldehyde are found in indoor environment, and competitive adsorption has been found on activated carbon for adsorption of two substances, the isotherms of water, formaldehyde has been simulated and showed in Fig 3, which adsorbed by the 1.55 nm slit carbon pore with FGs at 298 K. Water and formaldehyde are small molecules with different polarities. The adsorption isotherms show different types, I type for formaldehyde and V type for water. The onset of pore-filling occurs at different reduced pressures for these adsorbates: 0.1P/P0 for formaldehyde to 0.5P/P0 for water. Figure 8 shows the 2D-density distributions as the marked point in Figure 7 to illustrate the adsorbates behave of water and formaldehyde. At low loadings (Point A’), the water molecules preferentially adsorb around the groups to form clusters at both ends of the pore. With increasing the molecules, the clusters were first grown normal to the walls (Point B’Ⅰ), and pore condensation is induced by growth of the two pore-spanning clusters in the axial direction (Point B’Ⅱ). While the process of formaldehyde adsorption shares some similarities with that of water, the major difference stands out: the cluster growth direction. In the process from point A to point B, the clusters grow along pore walls. As the loading is increased to Point C, the new layer has been formed at the center. The relative strengths of the FF and SF interactions can explain the difference of the adsorption behave. The large the ratio of SF/FF interactions, the tendency of layers is greater than that of clusters. The ratios of SF/FF are in the order: formaldehyde (0.56) > water (0.09). With decrease the rate of SF/FF, the clusters grow changes from pore wall to normal.

3.3 The effect of functional group

![Graph showing isotherms](image)

Figure 5. (a) Simulated isotherms of formaldehyde in 1.55nm pores with 8 rows of FGs and without FGs at 298K. (b) Simulated isotherms of water in 1.55nm pores with 8 rows of FGs and 4 rows of FGs at 298K. Figure 5. shows the simulated isotherms with different concentration of groups in 1.55nm pores at 298K. For functional groups, formaldehyde adsorption has a certain sensitivity. Without functional groups, the saturated adsorption capacity decreases, and the adsorption performance is more obvious in the low-pressure area. Although the adsorption capacity decrease, the type of adsorption isotherms has not changed, which belongs to I type. when the FG concentration is reduced by half, the rate of SF/FF significantly decrease, then the water molecules tend to attract to each other rather than to pore walls. Due to the unabsorbed water molecules, the pore condensation could not occur with increase the load pressure of water molecules. Therefore, it is speculated that there may be a rate of SF/FF that is the boundary point of water molecules adsorption.
3.4 The effect of pore size

![Graph showing simulated adsorption-desorption isotherms in pore of different pore sizes at 298k with different concentration of function groups.](image)

Figure 6. Sumilated adsorption-desorption isotherms in pore of different pore sizes at 298k with different concentration of function groups.

Figure 6. shows the effect of pore sizes for water adsorption at 298K. Water is very sensitive to the change of pore size. With increase the pore size from 1.55 nm to 1.8 nm, the onset of pore-filling occurs at reduced pressures from 0.5 to 0.8, which is outside the ambient RH range suggested by ASHRAE. Therefore, the pore size control may improve the adsorption performance of formaldehyde under high humidity conditions.

4. Conclusion

In this paper, we have conducted a comprehensive Monte Carlo simulation of formaldehyde and water adsorption in functionalized carbon nanopores. The effects of FG density and pore size were investigated in terms of isotherm and 2D-density distribution. The results showed that formaldehyde and water showed different growth directions in the pore of activated carbon. The functional group and pore structure showed different effects on the adsorption of formaldehyde and water. Therefore, by tuning pore size and functionalities it may be feasible to produce real materials that retain effective capture of formaldehyde but which avoid pore blocking by water based on the differences in adsorption properties between water and formaldehyde revealed in this paper. Similarly, the removal of other polar pollutants, such as ammonia and hydrogen sulfide might be engineered. Future studies will be focused on the simulation of mixtures of formaldehyde and water.

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