Molecular simulation to analyze the effect of ultrafine particles on indoor organic gaseous pollutants removal by activated carbon

Ying Sheng[1*] and *Mingyang* Wang[1]

[1]School of Environmental Science and Engineering, Tianjin University, 300350 Tianjin, China

Abstract. Activated carbons are usually used to control the gas phase pollutants in the indoor environment. Actually, there are substantial ultrafine particles (UFPs) in air that have an impact on the gas pollutants removal by activated carbons in the actual implementation. In this paper, the influence of UFPs on the adsorption performance of activated carbon was analyzed by molecular simulation. The nanoporous carbon model was developed to describe the activated carbon. The adsorption of low concentration toluene with/without NaCl UFPs in the activated carbon was simulated and evaluated from the perspectives of adsorption capacity, diffusion coefficient, adsorption site, radial distribution function, adsorption heat and energy distribution. The results showed that the toluene adsorption was decreased by 21~29% since the existence of NaCl UFPs blocked the pores to some extent and occupied a portion of adsorption sites of toluene. The morphology of toluene molecules adsorbed in the activated carbon was double-layer. The optimal adsorption sites were at a distance of 4.4 Å from the activated carbon skeleton. As the concentration of toluene was increased, the toluene molecules were adsorbed on the active sites that released more energy and gradually moved to the common sites that released less energy. The existence of NaCl UFPs neither affected the optimal adsorption distance of toluene in the activated carbon, nor the energy distribution and adsorption heat. This study revealed the mechanism of gas-solid coupling mass transfer in the porous materials and would help master the actual adsorption performance of adsorbent.

1 Introduction

Indoor air quality is closely related to people's life and health. Long-term exposure to harmful volatile organic compounds (VOCs) such as toluene can cause sick building syndrome, reproductive diseases and a variety of respiratory diseases [1,2]. Adsorption is considered to be the most effective [3] technologies to remove VOCs and activated carbon is a widely used adsorbent. According to the study of National Quality Inspection Centre in China, it was found that 30% of activated carbon samples couldn't recover the initial adsorption rate after high temperature desorption of 120°C [4]. The reasons except for the destroy of chemical properties of activated carbon by high temperature regeneration, the existence of ultrafine particles (UFPs) in air was also an important factor affecting the adsorption performance [5]. Although the high efficiency particulate air (HEPA) filters are normally pre-installed to remove UFPs, the filtration efficiency for the UFPs below 200 nm was no more than 60% [6]. Even if the particles had been filtered by fibers, some of them returned to the air due to the rebound effect and caused secondary pollution [7,8]. Therefore, it is necessary to explore the influence of UFPs on the adsorption performance of activated carbon, so as to help master the actual adsorption performance of adsorbent.

Molecular simulation is an effective method to analyze the adsorption performance.

Molecular simulation is an effective method to analyze the adsorption performance. Alberto et al. [9] assembled a nanoporous carbon model by randomly combining a certain density with graphite flakes, and used this model to analyze the competitive adsorption relationship between CO_2 and CH_4. Chen et al. [10] calculated the equilibrium adsorption capacity of N_2 and CH_4 by activated carbon and calculated their diffusion coefficients by molecular simulation. Huang et al. [11] found that low concentration benzene was double-layer adsorption on the activated carbon by the radial distribution function (RDF). Wu et al. [12] found that the adsorption energy distribution of CO_2 in dry coal was changed with concentration.

Based on previous studies, it is feasible to apply the molecular simulation to study the influence of UFPs on the adsorption characteristics of activated carbon for VOCs. In this paper, toluene and NaCl were used as the representatives of VOCs and UFPs, respectively. The methods of Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) were used to study the gas-solid two-phase mass transfer on the activated carbon.

---

* Corresponding author: ysheng@tju.edu.cn

2 Simulation method

We considered a cubic box and randomly packed it with rigid carbon fragments to obtain the activated carbon model as shown in Fig. 1, which was completed in the module of Amorphous Cell in the Materials Studio (MS) software. The activated carbon model was characterized in the module of Atom Volumes & Surfaces. Nitrogen atoms were used as probes to roll on the resulting activated carbon model structure and the accessible surface was the contact area of nitrogen atoms. The BET specific surface area of activated carbon was 2551 m^2/g, which was close to the result of activated carbon microporous/mesoppore model constructed by Huang et al. based on HRTEM images [11]. Meanwhile, the model of toluene quoted from Pubchem and the model NaCl quoted from Materials Project were used for simulation.
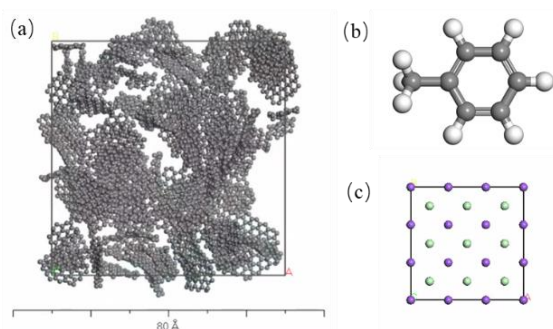

Fig. 1. Molecular model of activated carbon (a), toluene (b) and NaCl (c).

GMGC method performed in 2×10^6 steps was used to calculate the adsorption of toluene. The first half of steps was used to make the absorbent molecules reach equilibrium states and the last steps was used to calculate the amount of absorbate molecules captured to obtain the adsorption sites, adsorption isotherms, adsorption heat and potential distribution. The simulations ran using the metropolis algorithm with the parameters of the temperature at 298 K, the Dreiding field [13] adopted, the fugacity at 1×10^{-4} kPa. The electrostatic force was calculated by Ewald-group, and the van der Waals force was calculated by Atom-based method with a cut-off distance of 12.5 Å.

The movements of absorbent molecules in the activated carbon were obtained by MD method, then the radial distribution function and diffusion coefficient were calculated [14]. MD simulations were conducted in the NPT ensemble for 10^5 steps with the following parameters: the temperature at 298 K, the pressure at 0.1MPa, and the total simulate time of 100 ps with 1 fs interval. The initial velocities were set as random, the option of thermostat chose Nose and the option of Barostat was Berendsen. The parameter settings of non-bond energies were the same as that in GCMC simulation.

3 Results

3.1 Adsorption sits

Fig. 2 shows the adsorption sites of toluene and NaCl during the adsorption. The size of NaCl was more than ten times that of toluene. Given that the size limitation of activated carbon model, the amount of NaCl entering the activated carbon was much less than that of toluene. It was found that NaCl not only blocked the pores inside the activated carbon but also occupied the adsorption sites of toluene. After calculation, the number of toluene adsorbed on activated carbon was significantly decreased by 28% when the NaCl entered the activated carbon.
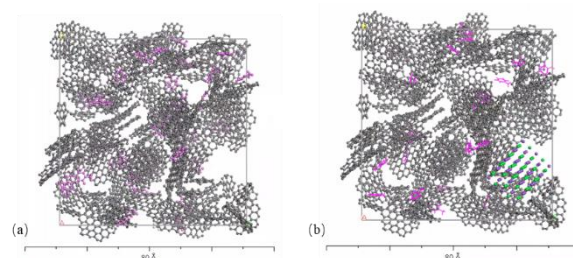

Fig. 2. Adsorption sites. (a) Adsorption sites for single component adsorption of toluene; (b) Adsorption sites for the mixture adsorption of toluene and NaCl.

3.2 Radial distribution function

Radial Distribution Function (RDF) was defined as the probability of atoms distributed in the space at a certain distance to the referenced atom. In this study, RDF expressed the optimum adsorption sites of toluene on the activated carbon structure. It was found in Fig. 3 that when the toluene concentration was 1 ppm, the values of RDF under the conditions of toluene adsorption with/without NaCl were almost the same. The main peak indicated that most of toluene molecules were adsorbed at a distance of 4.4 Å from the pore wall of the activated carbon. This was the most optimum adsorption distance of toluene on the activated carbon. The secondary peak indicated that double-layer adsorption of toluene occurred and the adsorption sites were located at the distance of 7.4 Å from activated carbon. The existence of NaCl did not affect the optimum adsorption distance of toluene, nor changed the double-layer adsorption characteristics of toluene on activated carbon.
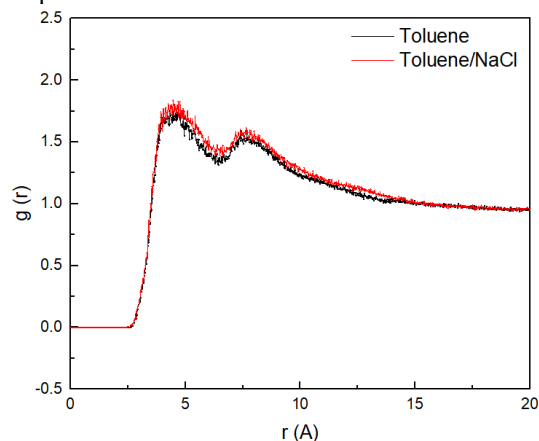

Fig. 3. Radial distribution function of toluene on the activated carbon model.

3.3 Adsorption capacity and mean square displacement

Fig. 4 shows the adsorption curve of activated carbon for toluene. At the same toluene concentration, the adsorption capacity of activated carbon for toluene was significantly greater than that for toluene/NaCl, indicating that the ultrafine particles affected the adsorption capacity of toluene on activated carbon. When the concentration of toluene was between 1~10 ppm, the existence of NaCl particles could reduce the adsorption capacity of toluene by 21~29%. It was speculated that this phenomenon was related to the change of diffusion coefficient. NaCl particles entered the interior of activated carbon and occupied proportion of the adsorption sites. Meanwhile, NaCl particles are difficult to be removed after entering the pores of activated carbon that would prevent toluene molecules from entering the interior of activated carbon.

The mean square displacement was usually used to calculate the diffusion coefficient. Fig. 5 shows the plots of mean square displacement inside the activated carbon when toluene concentration was 1 ppm, including single component of toluene and toluene containing NaCl particles. A straight line was fitted by the least square method, and 1/6 of the slope of the straight line was the diffusion coefficient of toluene in the activated carbon. The calculated diffusion coefficient of single component of toluene was 0.27×10^{-8} m^2/s, and that of toluene containing NaCl particles was 0.20×10^{-8} m^2/s. The diffusion coefficient of toluene decreased by 27%, which proved that the existence of NaCl particles limited the diffusion of toluene in the activated carbon, causing the decrease of adsorption capacity.
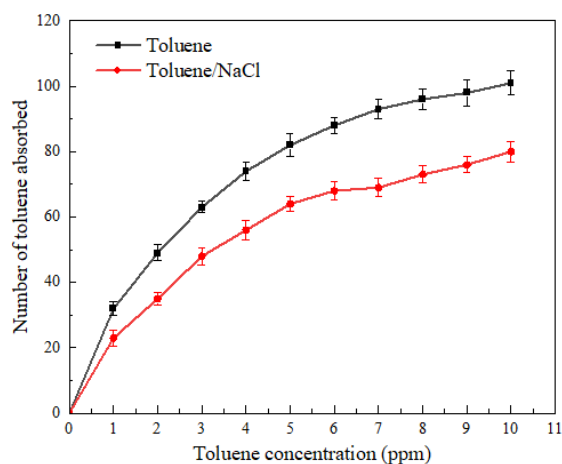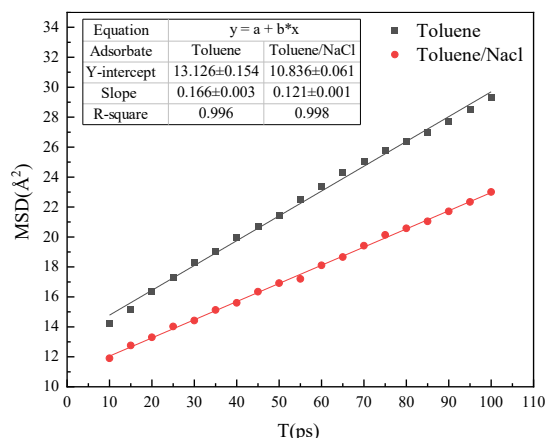

Fig. 4. Adsorption isotherms of toluene.

Fig. 5. Plots of mean square displacement of toluene.

3.4 Adsorption heat and energy distribution

Fig. 6 shows the curves of average adsorption heat of toluene absorbed on the activated carbon when the toluene concentration was between 1~10 ppm. When the toluene concentration was 1 ppm, the adsorption heat was 17.2 kcal/mol, namely the maximum value in toluene concentration interval. Because of low concentration, less toluene molecules entered the activated carbon and occupied the favorable adsorption sites. As the toluene of adsorption increased, the favorable adsorption sites became saturated. Then the toluene was adsorbed on common adsorption sites instead, and each toluene molecule released less adsorption heat compared with the formers. Whether the NaCl particles existed or not, the average adsorption heat decreased with the increase of toluene concentration.

Fig. 7 shows the energy distribution of activated carbon adsorbing toluene. In the constructed adsorption system, van der Waals force was the dominated interaction force. The change of van der Waals energy after toluene adsorbed reflected the change of system energy. Compared the energy distribution of single component of toluene adsorption with the energy distribution of toluene/NaCl, it was found that the distribution of the two curves was basically consistent. The existence of NaCl particles did not affect the distribution of adsorption energy. When the concentration of toluene was 1 ppm, the energy released by the favorable adsorption sites was around -17.00 kcal/mol. The calculated weighted average of each energy point on the energy distribution curve was -17.18 kcal/mol. This result was close to the average adsorption heat, proving that van der Waals energy was the main source of adsorption heat. However, when the concentration of toluene was 10 ppm, the energy released by the favorable adsorption sites was around -16.2 kcal/mol, indicating that the favorable adsorption site of toluene on activated carbon would change at different concentrations.
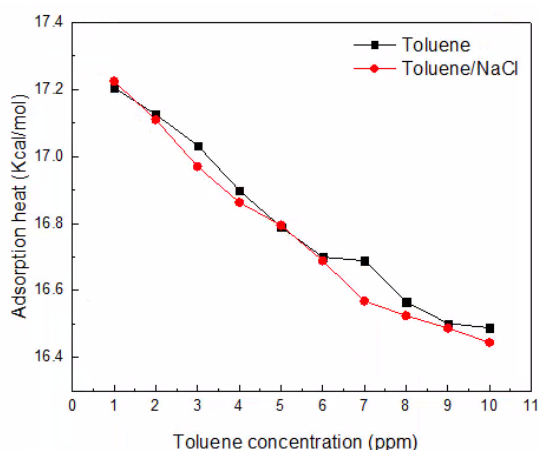
Fig. 6. Adsorption heat of adsorption of toluene without/ with NaCl in the activated carbon.
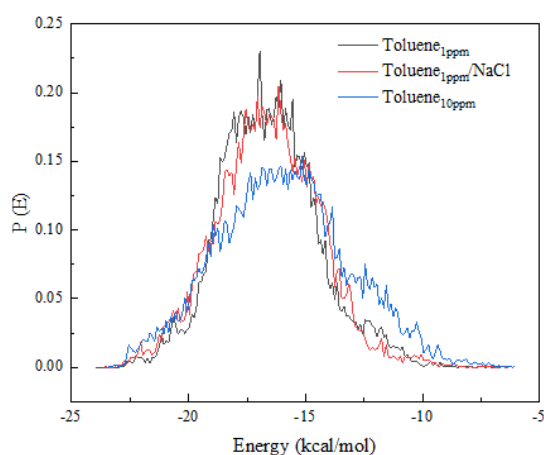

Fig. 7. Energy distribution of van der Waals in the activated carbon model.

4 Conclusions

In this paper, molecular simulation was used to study the adsorption of toluene on activated carbon. A nanoporous carbon model consisted of different kinds of graphite fragments was constructed to adsorb indoor low-concentration toluene and toluene containing NaCl particles. The adsorption sites, radial distribution function, adsorption capacity, diffusion coefficient, adsorption heat and energy distribution were analyzed. The main conclusions were as follows:

(1) Toluene was double-layer adsorption on the activated carbon. The best adsorption distance between toluene and the pore wall of activated carbon was 4.4 Å, and it did not be affected by NaCl particles.

(2) With the existence of NaCl particles, the adsorption capacity of toluene was significantly reduced. Because the NaCl particles occupied part of the pores and the adsorption sites of the activated carbon, which affected the diffusion of toluene in the activated carbon. When the toluene concentration was 1ppm, the diffusion coefficient of toluene containing NaCl particles on the activated carbon dropped by 28%.

(3) The change of energy distribution in the system reflected the change of toluene adsorption heat. As the concentration of toluene increased, activated carbon was prior adsorbed on favorable sites that could release higher energy, and then adsorbed on less favorable adsorption sites. The existence of NaCl particles did not affect the energy distribution, but it was found that the favorable adsorption sites of toluene on activated carbon changed with toluene concentrations.

Acknowledgements

References

1. L. Mølhave, B. Bach, O.F. Pedersen, Environ Int, 12, 167 (1986)
2. X.Y. Zhang, B. Gao, A.E. Creamer, C.C. Cao, Y.C. Yi., J. Hazard. Mater, 338, 102 (2017).
3. L.Q. Li, J. Song, Z. Sun, S. Wang, X. Yao, W. Liu, Z. Liu, The Chemical Industry and Engineering Society of China, 62, 2784 (2011)
4. B. Zhang, C. Chen, P.J. Hu, J. Xiao, Environ. Sci. Technol., 31, 28 (2018).
5. C. Kim, H. Lee, A. Juelfs, C.L. Haynes, D.Y.H. Pui, Carbon, 121, 63 (2017)
6. M.S. Waring, J.A. Siegel, R.L. Corsi, Atmospheric Environ., 42, 5003 (2008)
7. C.S. Wang, Y. Otani, Ind. Eng. Chem. Res., 52, 5 (2013).
8. Z.W. Zhuang, Z.Z. Zhang, F. Jiang, Res. Environ. Sci., 27, 835 (2014)
9. A.G. Albesa, M. Rafti, J.L. Vicente, H. Sánchez, P. Húmpola, Adsorp Sci Technol, 30, 669 (2012)
10. G.F. Chen, Y.X. An, Y.H. Shen, Y.Y. Wang, Z.L. Tang, B. Lu, D.H. Zhang, Chin. J. Chem. Eng., 28, 1062 (2020)
11. Y. Huang, F.S. Cannon, J.K. Watson, B. Reznik, J.P. Mathews, Carbon, 83, 1 (2015).
12. S.Y. Wu, C.B. Deng, X.F. Wang, J Nat Gas Sci Eng, 71, 102980 (2019)
13. S.L. Mayo, B.D. Olafson, W.A. Goddard, J. Phys. Chem. B, 94, 8897 (1990).
14. Z.Y. Li, X.Y. Liu, X. Yang, Y. Xing, C.J. Tsai, M.M. Meng, R.T. Yang, Microporous Mesoporous Mater., 239, 9 (2017)