Measurement and prediction of breakthrough curve of low-concentration toluene adsorbed by activated carbon

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Abstract. People spend most of their time indoors. The volatile organic compounds (VOCs) in indoor air represented by toluene inevitably affect people's health. Activated carbon can effectively reduce indoor VOCs pollution. The experiments in the previous studies were carried out at the concentration of tens or hundreds of ppm, which could not reflect the actual adsorption performance of activated carbon in the actual conditions. In this study, a method was proposed to predict breakthrough curve of toluene at ~1 ppm. The method was based on Wheeler-Jonas model, the equilibrium adsorption capacity was predicted by the Freundlich equation, and the adsorption rate constant was obtained by Yoon-Nelson equation. The predicted breakthrough curves were in good agreement with the experimental data in the range of 0.5–4.0 ppm. The adsorption rate constant was predicted using the relationship with inlet concentration of toluene. When the breakthrough fraction was 20-85%, the relative deviation was 5.54% and 4.08% at 0.5 and 1.0 ppm. This method can predict the adsorption performance and service life of activated carbon for toluene at ppb–ppm level.

1 Introduction

People spend about 90% of their time indoors, and indoor air quality has a significant impact on people's health and productivity. Volatile organic compounds (VOCs) are vital pollutants leading to the deterioration of indoor air quality [1]. People exposed to the harmful VOCs for a long time may suffer from a variety of diseases such as SBS (Sick Building Syndrome), respiratory diseases, cardiovascular diseases, leukemia and cancer [2]. As one of the most promising VOCs removal methods, adsorption has the advantages of low cost, simple operation and no by-products. Activated carbon is widely used in the field of gaseous pollution control [3]. The standard of ISO 10121-2 defined the test procedures for the performance of gas-phase air cleaning media, and recommended toluene at concentrations of 9 or 90 ppm as a representative substance for VOCs [4]. In the standard of ASHRAE 145.1, the concentration of toluene was recommended at 100 ppm to accelerate the adsorption [5]. The concentrations of VOCs indoors are only at ppb–ppm level. The performance of the adsorbent may differ from the actual results when tested at concentrations specified in the standard. Therefore, the existing test methods in the standard cannot evaluate the long-term performance of air purification media indoors. Using low concentration of pollutants to test the adsorption performance of gas phase filter consumes long time and has high requirements for measurement devices, so it is not worth adopting [6].

In contrast, using high concentration experimental data to predict the adsorption performance of gas-phase air filters at low concentrations is a fast and effective method. Ligoski et al. [7] predicted toluene breakthrough curves at concentrations of 0.09 or 0.9 ppm using experimental data of 9, 40 and 90 ppm. However, the prediction curve was only in good agreement with the S-type breakthrough curve. Freundlich and Dubinin-Radushkevich (D-R) equations were more accurate to predict equilibrium adsorption capacity. Shiue et al. [8] studied the influence of surface velocity and inlet concentration of toluene on the breakthrough curve, and established a model based on D-R equation and modified Yoon-Nelson model to estimate the service life of chemical filters. However, the range of concentrations (4–96 ppm) in experiments were carried out at low surface velocity (0.076, 0.114 and 0.152 m/s), which was different from the actual filter surface velocity.

As aforementioned, there were many limitations in the existing prediction methods, which could not accurately evaluate the adsorption performance of the gas-phase air cleaning media under the actual operating conditions. Therefore, the prediction method to access the performance of low-concentration VOCs adsorption is still a topic worth exploring. In this paper, we proposed a method to predict the adsorption performance of toluene adsorption by activated carbon at ppm level derived from the experimental data. We tested and verified the breakthrough curves of toluene by activated carbons by this method at 0.5–4.0 ppm.

2 Methods

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2.1 Activated carbon

Granular activated carbon made by coconut shell was selected in the experiment, namely sample GAC. Fig. 1 shows the pore size distribution. The total pore volume of GAC was 0.1020 cm³/g, and the specific surface area was 1143.9 m²/g. The microporous volume of GAC accounted for 34.9%, with an average pore size of 1.79 nm.

![Fig. 1. Pore size distribution of GAC](image)

2.2 Experimental facility

The experimental system consisted of the components of carrier gas pretreatment, gas-phase pollutant generation, adsorption column and gas concentration measurement, as shown in Fig. 2. After passing through pressure-relief valve, silica gel drying column and HEPA (high efficiency particulate air) filter, carrier air became dry and clean. The required concentration of toluene was controlled by mixing pressurized air and toluene in the cylinder with a fluctuation within 5%. Mass flow controller 1 and 2 controlled the flow rate of pressurized gas and toluene. The rotameter controlled the flow rate of the adsorption column at 2.5 L/min. Exhaust gas was discharged into the atmosphere after treatment. The activated carbon sample was ground to 20-30 mesh (0.6-0.9 mm) and fixed on the adsorption column. The inner diameter of the column was 10mm, and the filling height was 3 mm. The ppbRAE 3000 device was used to continuously measure the concentration of toluene, and recorded every 1 minute. The device had a detection range of 1 ppb to 10,000 ppm, reaching the resolution of 1 ppb.

![Fig. 2. Schematics of experimental system](image)

2.3 Adsorption isotherm

The Langmuir model was the theoretical model based on monolayer adsorption [9]. The equation is expressed as:

$$\frac{q_e}{q_m} = \frac{K_f C_i}{1 + K_f C_i}$$

(1)

Where $C_i$ is the inlet concentration, mg/m³; $q_e$ is the equilibrium adsorption capacity, mg/g; $q_m$ is the maximum equilibrium adsorption capacity in theory, mg/g; $K_f$ is the equilibrium adsorption constant related to the nature of adsorbate.

The Freundlich adsorption isotherm was an empirical equation [10]. The equation is expressed as:

$$q_e = K_f C_i^{1/n}$$

(2)

Where $K_f$ is the equilibrium adsorption constant related to the intensity of the adsorption; $1/n$ represents the difficulty in the adsorption process. The value is between 0 and 1 in most cases. Smaller value of $1/n$ indicates the adsorption occurs easier. Once the value is more than 2, it means the adsorption is difficult to occur.

The D-R model was a semi-empirical equation [11]. The expression of D-R model is:

$$q_e = q_m \exp \left( 1 - \exp \left( \frac{RT \ln(1 + \frac{1}{C_i})}{E_f} \right) \right)$$

(3)

Where $E$ is the adsorption free energy of adsorbate, J/mol; $R$ is the gas constant, 8.314 J/mol·K; $T$ is absolute temperature, K.

The equilibrium adsorption capacity $q_e$ can be calculated as Eq. (4) by means of numerical integration:

$$q_e = \frac{Q[C_t - \int_{0}^{t_b} C_i dt]}{m_{GAC}}$$

(4)

Where $Q$ is the flow rate of carrier gas through the adsorption column, m³/min; $C_i$ is the breakthrough concentration, mg/m³; $t_f$ is time at 95% breakthrough fraction, min; $m_{GAC}$ is the quality of activated carbon, g.

2.4 Breakthrough models

The Yoon-Nelson model was simple. The application of this model was not restricted to the physical and chemical properties of absorbent [12]. The expression is expressed as:

$$t_e = \tau + \frac{1}{K_v} \ln\left( \frac{C_b}{C_i - C_b} \right)$$

(5)

Where $K_v$ is the adsorption rate constant, 1/h; $t_b$ is the breakthrough time, h; $\tau$ is the breakthrough time required for 50% breakthrough, h.

The Wheeler-Jonas model was used for predicting the adsorption of organic vapor on activated carbon. The equation can be expressed as [13]:

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Where \( \rho_b \) is the bulk density of activated carbon, g/cm\(^3\).

3 Results

3.1 Breakthrough curves and adsorption isotherms

The breakthrough curves of toluene at different inlet concentrations were shown in Fig. 3. In theory, the adsorption process of activated carbon includes three basic steps: 1) Film diffusion. 2) Pore diffusion. 3) Surface diffusion. Since each stage has a different diffusion rate, the slowest stage determines the adsorption process. It was found that pore diffusion was the key process \[14\]. The diffusion rate of toluene in the pores increased with the increased inlet concentration, and the adsorption equilibrium was reached faster \[8\].

![Fig. 3. Breakthrough curves of toluene adsorption on GAC](image)

The equilibrium adsorption capacity of toluene was calculated as Eq. (4). The least-square method was used to fit the data, and the adsorption isotherms could be obtained (Fig. 4). It was found Freundlich model fitted well, and \( R^2 \) was 0.9904 (Table 1). Wang et al. also found that Freundlich model could predict the equilibrium adsorption capacity of low-concentration toluene by activated carbon through molecular simulation \[15\]. It was indicated that the adsorption sites with different affinity for gas molecules were existed on the surface of activated carbon. The toluene molecules were adsorbed first by the adsorption site with strong activity, and then by other adsorption sites, which might be multilayer adsorption.

![Fig. 4. Adsorption isotherms of toluene adsorption on GAC](image)

### Table 1. Adsorption isotherms

| Model     | Equation                        | \( R^2 \) |
|-----------|---------------------------------|-----------|
| Langmuir  | \( q_e = 325.48 \times \frac{C_i}{1 + 0.18C_i} \) | 0.9847    |
| Freundlich| \( q_e = 69.08C_i^{0.46} \)      | 0.9904    |
| D-R       | \( q_e = \frac{223.7 \times 1.16 \times 10^{-16}}{C_i} \) | 0.8507    |

3.2 Prediction method

The prediction method was established using the experimental data of GAC. In the first step, the equilibrium adsorption capacity at different concentrations was calculated by the Freundlich equation in Table 2. The second step was to calculate the adsorption rate constant as Eq. (5) using experimental data. And the adsorption rate constants could be estimated at 0.5 and 1.0 ppm by the relationship between inlet concentration and adsorption rate constant. Third, the mass of activated carbon, toluene inlet concentration, equilibrium adsorption capacity and adsorption rate constant were put into the Wheeler-Jonas equation (Eq. (6)) to obtain the predicted breakthrough curve (Fig. 5).

![Fig. 5. Predicted breakthrough curves of toluene on GAC](image)

It was found that the deviation the predicted curve and at 2.0 ppm deviated from the experimental data. That might be due to the difference of the equilibrium adsorption capacity between predicted and actual value. When the breakthrough fraction was 20–85%, the deviation between the predicted curve and the measured data at different concentrations is shown in Table 2. The relative deviations at 0.5 and 1.0 ppm in average were 5.54% and 4.08%, respectively. When the breakthrough fraction was 0–20%, the deviation was larger, and the initial breakthrough time was longer than prediction. Due to a large number of empty adsorption sites on the
surface of adsorbent, the probability of toluene contact with adsorbent was high. The actual adsorption of more toluene molecules than predicted, so the initial penetration time was longer. When the breakthrough fraction reached 85%, the predicted value gradually deviated from the measured data and activated carbon reached saturation faster in actual. With the adsorption process going, the empty adsorption site decreased, and the diffusion resistance increased, so the actual adsorption rate was low. More toluene molecules penetrate the adsorption column directly, and the saturation was reached faster than the predicted curve.

**Table 2. Deviations between predicted value and experimental data**

| Concentration (ppm) | Average relative deviation (%) | Minimum relative deviation (%) | Maximum relative deviation (%) |
|---------------------|--------------------------------|-------------------------------|--------------------------------|
| 0.5 ppm             | 5.54                           | 2.69                          | 8.34                           |
| 1.0 ppm             | 4.08                           | 0.44                          | 6.77                           |

4 **Conclusion**

A new method for predicting the breakthrough curve of toluene by activated carbon at about 1 ppm was proposed and verified. The method was established based on the Wheeler-Jonas equation. The equilibrium adsorption capacity was predicted by Freundlich model and the adsorption rate constant was obtained by Yoon-Nelson equation. The relationship between concentration and adsorption rate constant was used to predict the adsorption rate constant. To verify the accuracy of the method, the breakthrough curves of activated carbon adsorption toluene were measured at 0.5–4.0 ppm and compared with the prediction. The results showed that the method had good prediction effect and could get the breakthrough curve at about 1 ppm quickly and efficiently. This method can be used to predict the adsorption performance and service life of filters.

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