

## Article

# Experimental and Modeled Results Describing the Low-Concentration Acetone Adsorption onto Coconut Shell Activated Carbon

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**Abstract:** Polar VOCs represented by ketones deteriorate indoor air quality and affect human health. Adsorption by activated carbons can effectively remove harmful gases, but relatively little is known about the adsorption capacity of polar VOCs at a low concentration level. So, this paper adopted acetone as the typical polar VOC to test its adsorption on the coconut shell activated carbon and developed a prediction model to estimate the breakthrough time. The results will help users master the acetone adsorption behavior under realistic conditions and thus estimate the service life of the filters. The adsorption test of acetone with concentrations of 0.5, 1.0, 2.0, 3.0, and 4.0 ppm was carried out. Four adsorption isotherms, namely, Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin, were used to fit the data. The Freundlich model fitted best when was used to determine the equilibrium capacity of acetone. An approach based on the Thomas model was proposed to predict the acetone breakthrough curve. The mass transfer coefficient of acetone adsorption with a relatively high concentration (1.0–4.0 ppm) was calculated based on the Thomas model, and the relationship between the mass transfer coefficient and acetone inlet concentration was established to obtain the mass transfer coefficient of acetone at the predicted concentration. The equilibrium capacity and mass transfer coefficient were substituted into the Thomas model to predict the breakthrough curve of acetone at a lower concentration. The results showed that the shape of the predicted curve was much closer to the measured data of acetone adsorption. The relative deviation between the predicted service life and measured data was 10%, indicating that the Thomas model was suitable for predicting acetone adsorption at low concentrations.

**Keywords:** coconut shell activated carbon; acetone; low concentration; Thomas model



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## 1. Introduction

Volatile organic compounds (VOCs) are indoor air pollutants emitted from building materials and the usage of daily necessities [1]. Urban residents spend nearly 90% of their lifetime indoors [2], and long exposure to VOCs causes headaches, weakness, anxiety, dizziness, and functional decline of the nervous system [3]. Hundreds of VOCs are detected indoors. In general, ventilation is a fast and efficient way to remove VOCs. Still, when ventilation is insufficient, air-cleaning technologies are applied to reduce the concentrations of indoor VOCs. Currently, VOC removal through adsorption is proven to be the most effective method [4], and activated carbons are the most commonly used adsorbents due to their high sorption capacity owing to large specific surface area and high porosity. Some activated carbons made of various agricultural bio-wastes were not only effective in the pollutant's removal but also low-cost [5].

Numerous studies have been conducted to explore the adsorption performance of activated carbons on indoor organic gaseous pollutants. Compared with polar compounds, activated carbons are apt to adsorb non-polar compounds, and therefore most research has focused on non-polar VOCs. The representative non-polar VOCs included toluene [6],

benzene [7], naphthalene [8], anthracene [9], and so on. However, the pollution of polar VOCs is also severe. For instance, a large amount of acetone and formaldehyde were identified in nail salons [10]. This situation was worse in developing countries: it was reported that the indoor concentration of aldehyde and ketone in Beijing was 1.25 times that of Paris, 2.7 times that of New York, and 12 times that of Uppsala, and acetone ranked first in the polar substances of air samples collected in 40 households [11]. An indoor air quality investigation in France indicated that the acetone concentration was the highest among VOCs measured in school buildings [12]. In the study of Kiurski et al., it was found that the concentration of acetone was up to 1.1 ppm in a screen printing workshop [13]. Long exposure to acetone would cause serious health problems such as headache and narcosis [14].

To enhance the adsorption performance for polar VOCs of activated carbons, coatings of metal nanoparticles have been explored by some researchers. For example, Rengga et al. made a bamboo-based activated carbon covering with silver nanoparticles and found it 2.36 times more effective for formaldehyde than untreated activated carbon [15]. Tseng et al. prepared Au-Ag-, nano silver-, and chitosan-coated activated carbon to test the removal of formaldehyde, acetone, and CO. The results showed that the removal of formaldehyde and CO were promoted, but the same gain was not observed for acetone [16]. Although a few attempts received positive outcomes, the improvement of the adsorption capacity for ketone was dubious. In the actual application for indoor pollution control, untreated activated carbon is still the preferred adsorbent. However, the studies on the adsorption performance of polar VOCs mainly focused on industrial occasions when challenged with VOCs of a concentration at least in the hundreds ppm [17–19]; relatively little is known about the adsorption capacity at a lower concentration level.

Moreover, from the user's point of view, it is desirable to know the adsorption behavior under realistic conditions and thus estimate the service life of the filters. In the past, phenomenological models based on the theory of mass and heat transfer were developed to predict the breakthrough curve and life span, with the main difficulty being the requirement of detailed information about adsorbents [20]. Later, semi-empirical equations for prediction were also proposed, such as the Yoon–Nelson model [21,22], Wheeler–Jonas model [23], Tomas model [24], Clark model [25], Wolborska model [26], and Adams–Bohart model [27]. Among these, the Yoon–Nelson and Wheeler–Jonas models were singled out for breakthrough prediction with high precision [28]. With the equation of the Yoon–Nelson model, the breakthrough time could be calculated as a function of inlet and breakthrough concentration of pollutants with the kinetic parameters of 50% breakthrough time and constant rate that could be experimentally available. The Wheeler–Jonas model then required more property parameters of adsorbents (i.e., bulk density, mass, and equilibrium capacity of the adsorbent). The equilibrium capacity of the adsorbent was generally described by isotherms such as the Langmuir, Freundlich, and Dubinin–Radushkevich model (D-R model). Vizhemehr et al. [28] predicted the breakthrough curves of MEK (methyl ethyl ketone) and n-Hexane using a set of isotherms as well as the Yoon–Nelson and Wheeler–Jonas model derived from the experimental data of 15–300 ppm. Ligotski et al. [29] applied the Wheeler–Jonas model to forecast the breakthrough curve of a toluene concentration of 0.09 ppm from the measurement data at 9 or 90 ppm suggested in ISO 10121. They found that the Freundlich and Dubinin–Radushkevich isotherms accurately predicted the equilibrium capacity. Shiue et al. [30] modified the Yoon–Nelson model to boost the prediction performance to larger than 50% breakthrough fraction based on the measurement data of toluene in 10–70 ppm. It was found that only in the study of Laskar et al. [31] the mathematical model was mentioned for predicting acetone, but the concentration far exceeded the indoors levels. Based on previous studies, it can be concluded that the semi-empirical equations had an excellent experience in predicting the adsorption of non-polar VOCs, but whether they are suitable for polar VOCs needs a deep discussion.

As mentioned earlier, polar VOC pollution in buildings is severe and has a negative impact on human health. However, the removal of polar VOCs at a low concentration based

on adsorption has rarely been studied. Then, in this paper, acetone was adopted as the representative of polar VOCs, and the dynamic adsorption behavior of low-concentration (ppb~ppm level) acetone by commercially available coconut shell activated carbon was experimentally investigated. The different adsorption isotherms and prediction models were elaborated and a suitable method was proposed to predict acetone adsorption using activated carbon.

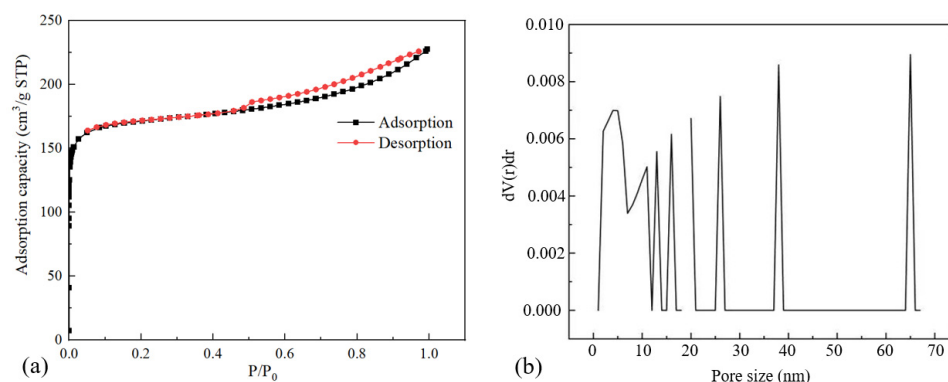
## 2. Experiment

### 2.1. Materials

The experiment used a commercially available coconut shell-based granular activated carbon (GAC, purchased from Starlight Activated Carbon Co., Ltd., Hainan, China). The sample's adsorption and desorption curve at 77 K were measured using nitrogen as a probe with the Accelerated Surface Area and Porosimetry System (ASAP 2020, Micromeritics, Norcross, GA, USA). The specific surface area was calculated via the Brunauer–Emmett–Teller (BET) equation using the desorption curve. The total pore volume was equal to the nitrogen adsorption amount at a relative pressure of 0.99. Pore size distribution was obtained based on Barrett–Joyner–Halenda (BJH). The main characteristics of the GAC sample are summarized in Table 1 and Figure 1.

**Table 1.** Characteristics of coconut shell-based granular activated carbon.

| Property                                     | Value  |
|----------------------------------------------|--------|
| Specific surface area (m <sup>2</sup> /g)    | 519.8  |
| Average pore size (nm)                       | 2.71   |
| Total pore volume (cm <sup>3</sup> /g)       | 0.0994 |
| Micropore volume (cm <sup>3</sup> /g)        | 0.0030 |
| Mesoporous pore volume (cm <sup>3</sup> /g)  | 0.0849 |
| Macroporous pore volume (cm <sup>3</sup> /g) | 0.0115 |



**Figure 1.** The adsorption and desorption curves of the activated carbon in N<sub>2</sub> (a) and the pore distribution (b).

### 2.2. Test Facility

The diagram of the test facility is shown in Figure 2, including the challenge gas generation unit, activated carbon adsorption unit, and challenge gas monitoring unit. Acetone was adopted as the challenge gas. It was listed as an alternative gas in the standard ISO 10121-1 [32], and the acetone concentration tested was high among indoor polar VOCs [11]. The adsorption performance of toluene was also investigated, in order to compare the kinetic behavior between polar and non-polar compounds. The compressed air successively passed through the silica gel column and high-efficiency particulate air (HEPA) filter to be dehumidified and purified. Then, the air was mixed with high-concentration acetone (100 ppm) to reach the desired concentration by means of controlling the mass flow. When the challenge gas was delivered to the empty adsorber, the desired inlet

concentration was real-time checked and measured by a photoionization detector (ppbRAE, Honeywell, NJ, USA). The inlet concentration was fixed at 0.5, 1.0, 2.0, 3.0, and 4.0 ppm with  $\pm 5\%$  deviation. When the challenge gas was switched to the activated carbon adsorption column, the concentration downstream was monitored and recorded. It was reported in the reference of [33] that a uniform spatial distribution of challenge gas could be reached when the diameter of the fixed bed was eight times larger than the particle size of the adsorbent. Then, the length of the adsorption bed was determined as 3 mm with a diameter of 10 mm. The GAC sample was crushed and sieved to 20~30 mesh (0.6~0.9 mm) and filled in the adsorption bed with a mass of 0.12 g. The experiments were performed at an airflow rate of 2.5 L/min and at a temperature of 20 °C which was controlled by the air conditioner in the laboratory. The specifications of the main measurement devices are listed in Table 2.

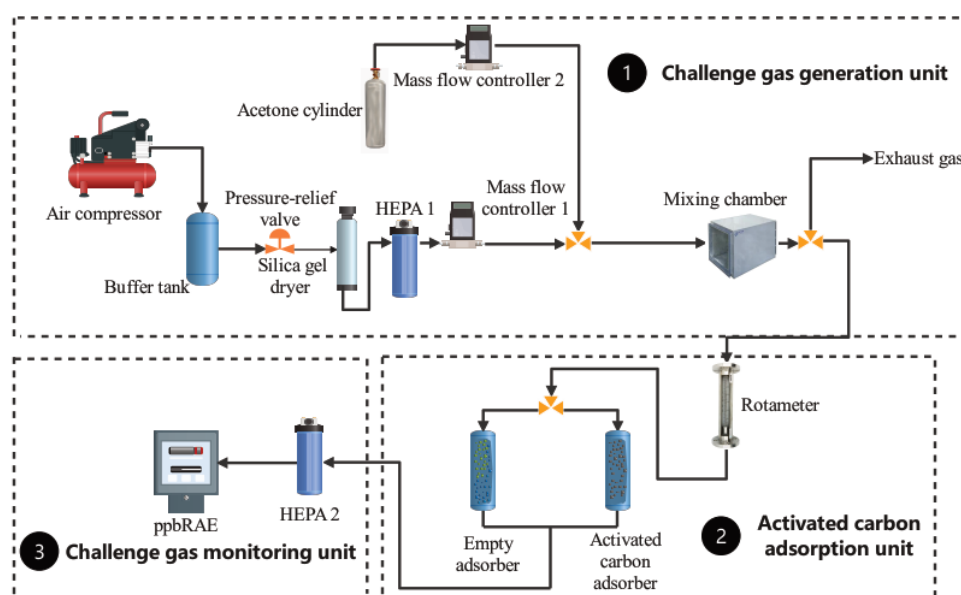


Figure 2. Test Facility.

Table 2. Specifications of the measurement device.

| Device            | Measurement Range | Accuracy                                               |
|-------------------|-------------------|--------------------------------------------------------|
| ppbRAE 3000       | 1 ppb~10,000 ppm  | $\pm 3\%$ (10~2000 ppm isobutene),<br>1 ppb resolution |
| Mass flow meter 1 | 0~10 L/min        | $\pm 1\%$                                              |
| Mass flow meter 2 | 0~2 L/min         | $\pm 1\%$                                              |

### 2.3. Experimental Results

For each test concentration, the experiment was conducted until the concentration downstream of the activated carbon adsorber became equal to the inlet concentration. After completing the breakthrough test, the equilibrium adsorption capacity  $q_e$  can also be calculated as Equation (1) through numerical integration:

$$q_e = \frac{Q[C_i t_f - \int_0^{t_f} C_b dt]}{m_{GAC}} \quad (1)$$

where  $Q$  is the flow rate through the adsorption bed,  $\text{m}^3/\text{min}$ ;  $C_i$  is the inlet concentration,  $\text{mg}/\text{m}^3$ ;  $C_b$  is the breakthrough concentration,  $\text{mg}/\text{m}^3$ ;  $t_f$  is the time at 100% breakthrough fraction, min; and  $m_{GAC}$  is the quality of activated carbon, g.

Figure 3 shows the breakthrough curves of acetone and toluene at different concentrations. It was found that the profiles of both acetone and toluene tended as S-shape, while the curve of acetone was steeper, and accordingly, the breakthrough time was significantly

reduced. With increasing concentration of contaminants, the concentration gradient between the surface of activated carbon and indoor air was increased, leading to a stronger driving force and a faster penetration through the boundary layer, and finally resulting in a shorter penetration time. Figure 4 shows the comparison of equilibrium adsorption capacity between acetone and toluene. The adsorption capacity of toluene was approximately 13 times that of acetone due to the weak affinity to the adsorption sites. It is known that the molecular diameter of acetone is less than that of toluene which results in a quicker motion and a weak intermolecular force to the active sites of activated carbon. Thus, the activated carbon was more likely to adsorb toluene than acetone.

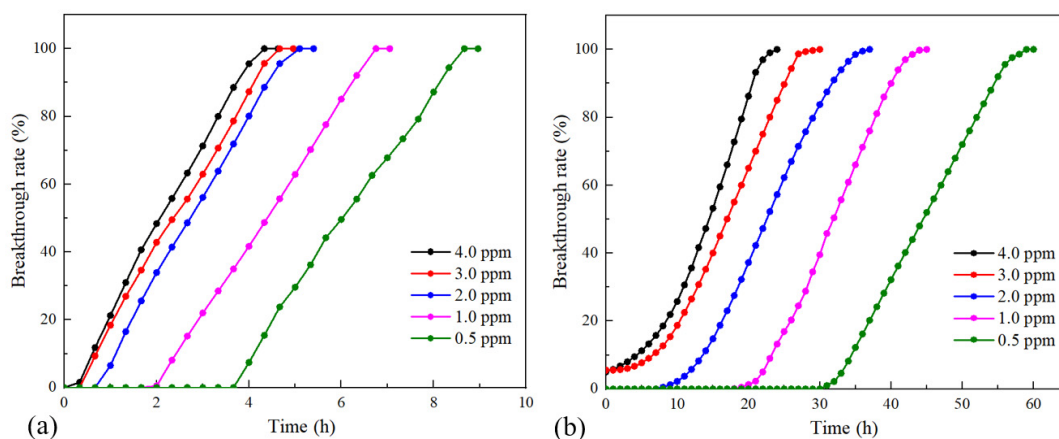


Figure 3. Breakthrough curves of acetone (a) and toluene (b) at different concentrations.

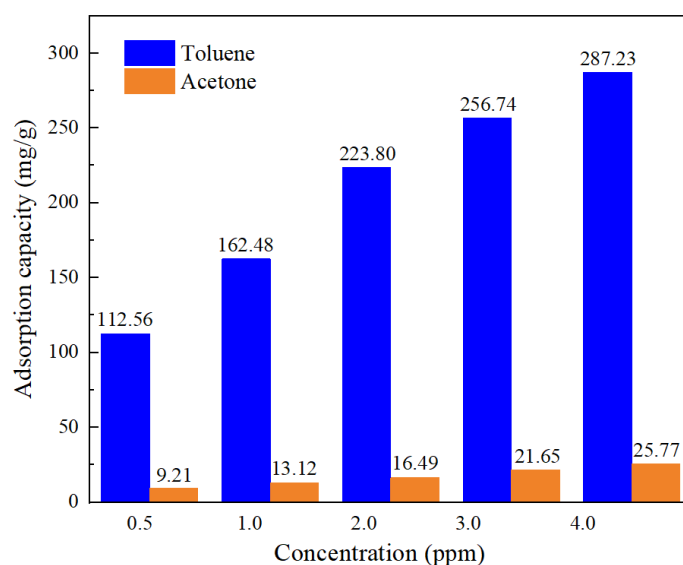


Figure 4. Equilibrium adsorption capacity of acetone and toluene at different concentrations.

### 3. Equilibrium Capacity Models

#### 3.1. Isotherms

The Langmuir model is the theoretical model for monolayer adsorption and has been widely used to describe the VOCs adsorption in the adsorbents [34]. The expression is

$$\frac{q_e}{q_m} = \frac{K_L C_i}{1 + K_L C_i} \quad (2)$$

where  $C_i$  is the inlet concentration of the adsorbate,  $\text{mg}/\text{m}^3$ ;  $q_e$  is the equilibrium adsorption capacity at  $C_i$  concentration,  $\text{mg}/\text{g}$ ;  $q_m$  is the maximum adsorption capacity in theory,  $\text{mg}/\text{g}$ ; and  $K_L$  is the equilibrium adsorption constant,  $\text{m}^3/\text{mg}$ .

The Freundlich model is an empirical model based on experimental results without theoretical derivation [35]. It is expressed as

$$q_e = K_f C_i^{\frac{1}{n}} \quad (3)$$

where  $K_f$  is the equilibrium adsorption constant describing how strongly the adsorbate is attached to the surface of the adsorbent.  $n$  is a constant, and  $1/n$  represents the difficulty in the adsorption process.

The D-R model is a semi-empirical equation based on the theories of adsorption potential and micropore filling. The model expression is as follows [36]:

$$W_e = W_0 \exp \left\{ - \left( \frac{1}{E} \right)^2 \left[ RT \ln \left( \frac{p_0}{p} \right) \right]^2 \right\} \quad (4)$$

where  $W_e$  is the pore volume occupied by the adsorbate,  $\text{cm}^3/\text{g}$ ;  $W_0$  is the micropore volume of adsorption,  $\text{cm}^3/\text{g}$ ;  $E$  is the adsorption free energy of the adsorbate,  $\text{J/mol}$ ;  $RT \ln(p_0/p)$  is the adsorption potential.  $R$  is the gas constant,  $8.314 \text{ J}/(\text{mol} \cdot \text{K})$ ;  $T$  is the absolute temperature,  $\text{K}$ ;  $p_0/p$  is the adsorbate's relative pressure;  $p_0$  is the saturation pressure of the adsorbate at the adsorption temperature,  $\text{Pa}$ ; and  $p$  is the pressure of the adsorbate vapor,  $\text{Pa}$ .

The Temkin model assumes that the adsorption heat of all molecules in the adsorption layer decreases linearly with the coverage rate due to the adsorbent–adsorbent interaction, and is characterized by the uniform distribution of bond energy up to a maximum binding energy, which is suitable for describing chemisorption. The formula is as follows [37]:

$$q_e = a + 2.303b \log C_i \quad (5)$$

where  $a$  is the equilibrium binding energy constant corresponding to the maximum binding energy,  $\text{mg/g}$ ; and  $b$  is the parameter related to adsorption heat,  $\text{m}^3/\text{g}$ .

### 3.2. Fitting Results

The equilibrium adsorption capacity was obtained by integrating the experimental data according to Equation (1), after which the data were fitted to the adsorption isotherms. The Langmuir, Freundlich, D-R, and Temkin models were used to fit the adsorption isotherm of acetone. The fitting results are shown in Figure 5, and the parameters and fitting degree  $R^2$  in the formula are shown in Table 3.

The comparison of  $R^2$  between the four models showed that the Freundlich model fitted best ( $R^2 = 0.9847$ ). The comparison showed a significant error in the predicted adsorption capacity of the D-R model. The Langmuir and Temkin models also had better fitting results but not as good as the Freundlich model. When the concentration was between 1 and 3.5 ppm, the equilibrium adsorption capacity predicted by the Langmuir model was higher than that predicted by the Freundlich model, and the predicted values were lower in other concentration ranges. This was because the Langmuir model assumed that the surface of the adsorbent was uniform, and each adsorption site had the same affinity for gas molecules. One adsorption site could only adsorb one molecule and form a single molecular layer. The Freundlich model assumed that the surface of the adsorbent was uneven, with different types of adsorption sites, and the affinity to gas molecules was not the same. Affected by the adsorbate concentration, air temperature, and other factors, both single and multi-molecular layer adsorption might occur. The Temkin model was related to the bonding energy for describing the chemical reaction, and the fitting effect was not as good as the Freundlich model, indicating that the adsorption of acetone by activated carbon was more inclined to a physical process.

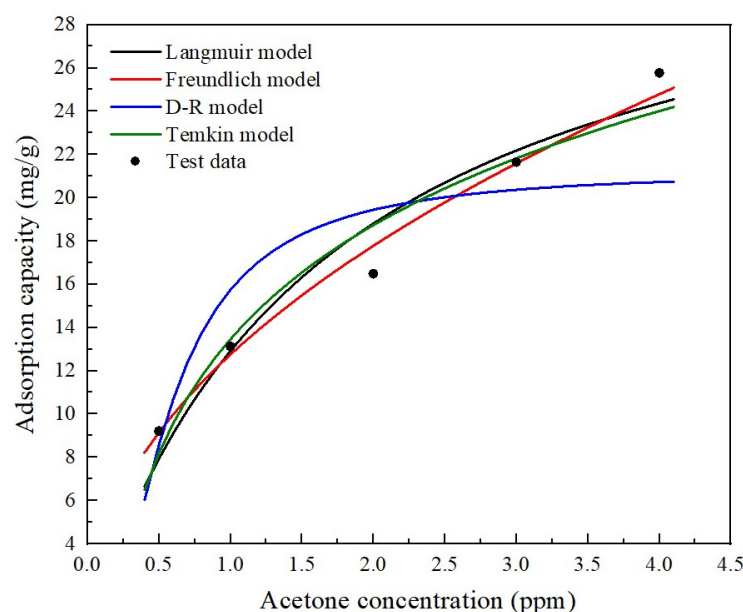


Figure 5. Fitting curve of acetone adsorption isotherms.

Table 3. Adsorption isotherm model fitting results of acetone.

| Adsorption Isotherm | Parameter                                                   | Fitting Degree $R^2$ |
|---------------------|-------------------------------------------------------------|----------------------|
| Langmuir            | $q_m = 34.602 \text{ mg/g}$ , $K_l = 0.247$                 | 0.9457               |
| Freundlich          | $K_f = 8.360$ , $1/n = 0.479$                               | 0.9847               |
| D-R                 | $q_m = 21.235 \text{ mg/g}$ , $E = 2183.636$                | 0.7664               |
| Temkin              | $a = 6.763 \text{ mg/g}$ , $b = 7.605 \text{ m}^3/\text{g}$ | 0.9464               |

#### 4. Prediction Model

##### 4.1. Prediction Based on Wheeler–Jonas Model

##### 4.1.1. Wheeler–Jonas Model

The Yoon–Nelson and Wheeler–Jonas models are widely used in the description of adsorption of VOCs by porous materials. They have similar forms, but the Wheeler–Jonas model contains more detailed parameters; therefore, we choose the Wheeler–Jonas equation to establish the prediction process.

The Wheeler–Jonas model was originally derived from the mass balance of the adsorption bed between the challenge gas inlet and the sum of the gas adsorbed and penetrating the bed. The Wheeler–Jonas model is simple and has no strict requirements on property parameters such as adsorbent types and adsorption bed characteristics, making it easy to calculate and widely used. The Wheeler–Jonas model is described below [38]:

$$t_b = \frac{q_e m_{GAC}}{C_i Q} + \frac{q_e \rho_b}{K_v C_i} \ln\left(\frac{C_b}{C_i - C_b}\right) \quad (6)$$

where  $t_b$  is the breakthrough time, min;  $K_v$  is the adsorption rate constant, 1/min;  $C_b$  is the breakthrough concentration of the adsorbate, ppm;  $C_i$  is the initial concentration of the adsorbate, ppm;  $t_b$  is the breakthrough time at the concentration  $C_b$ ;  $\rho_b$  is the bulk density of the activated carbon, g/m<sup>3</sup>; and  $Q$  is the flow rate of the carrier gas through the adsorption column, m<sup>3</sup>/min.

##### 4.1.2. Prediction Process

The equilibrium adsorption capacity and total mass transfer coefficient were two critical parameters to be obtained in Equation (6). It could be seen from the previous section that the Freundlich isotherm equation of acetone adsorption on the sample was

$q_e = 8.360C_0^{0.479}$ , and the equilibrium adsorption capacity at any adsorption concentration could be calculated.

For the calculation of the mass transfer coefficient, Wu [39] and Busmundrud [40] carried out extensive research through classical diffusion theory. Based on the analysis of a large number of experimental data, a semi-empirical equation was proposed as follows:

$$K_v = 800\beta^{0.33}v_L^{0.75}d_p^{-1.5}(q_e/M_W) \quad (7)$$

The dependence of  $K_v$  on adsorbent particle size  $d_p$ , airflow linear velocity  $v_L$ , adsorbate affinity coefficient  $\beta$ , and molar adsorption capacity  $q_e/M_W$  was considered. Compared with the complicated calculation process and error problem of the semi-empirical formula, it was simpler and more accurate to determine the mass transfer coefficient by measuring and considering  $K_v$  as a function of concentration.

The calculation of mass transfer coefficient  $K_v$  at higher concentrations (4, 3, 2, and 1 ppm) was based on the principle of least squares. Taking  $K_v$  as the only fitting variable, the measured breakthrough curve was linearly fitted by the Wheeler–Jonas equation with the Levenberg–Marquardt algorithm. In order to improve the accuracy of fitting, the gas film diffusion process at the beginning of adsorption and the surface diffusion process at the end of adsorption were simplified, and only the adsorption process with a breakthrough rate in the range of 20–80% was studied. In Figure 6, with breakthrough time  $t_b$  as abscissa and logarithmic concentration  $\ln(C_b/(C_i - C_b))$  as ordinate,  $K_v$  was calculated by the slope of the curve. To estimate the total mass transfer coefficient of acetone at a lower concentration (0.5 ppm), a polynomial regression method was used to fit the value of  $K_v$  at higher concentrations (1.0, 2.0, 3.0, and 4.0 ppm), and the functional relationship between  $K_v$  and adsorption concentration was obtained. As shown in Figure 7, the relationship between  $K_v$  and the initial acetone concentration satisfied the quadratic function:  $K_v = 0.0002C_i^2 - 0.0017C_i + 0.0055$ . Through the calculation of the quadratic function, the mass transfer coefficient  $K_v$  of all concentrations (0.5, 1.0, 2.0, 3.0, and 4.0 ppm) could be obtained.

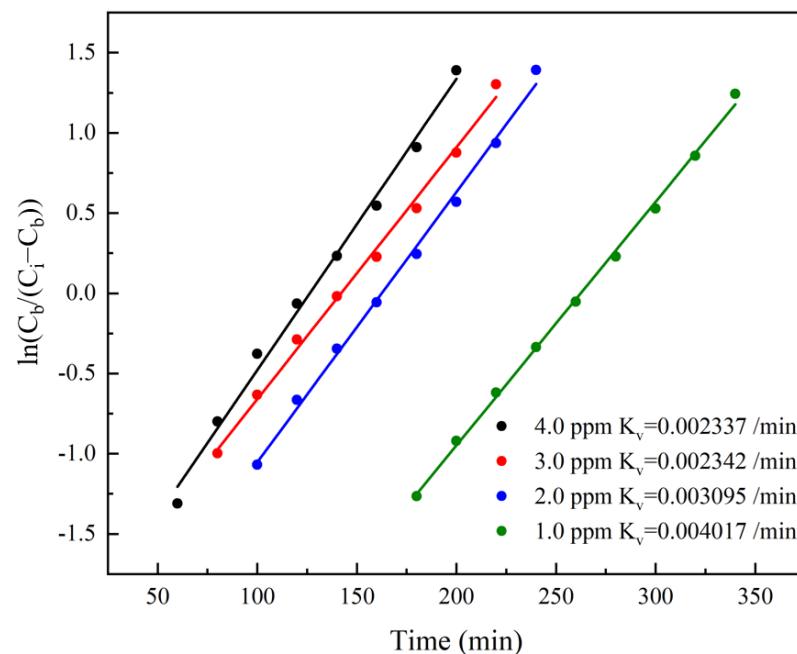


Figure 6. Calculation of mass transfer coefficient by the Wheeler–Jonas equation.

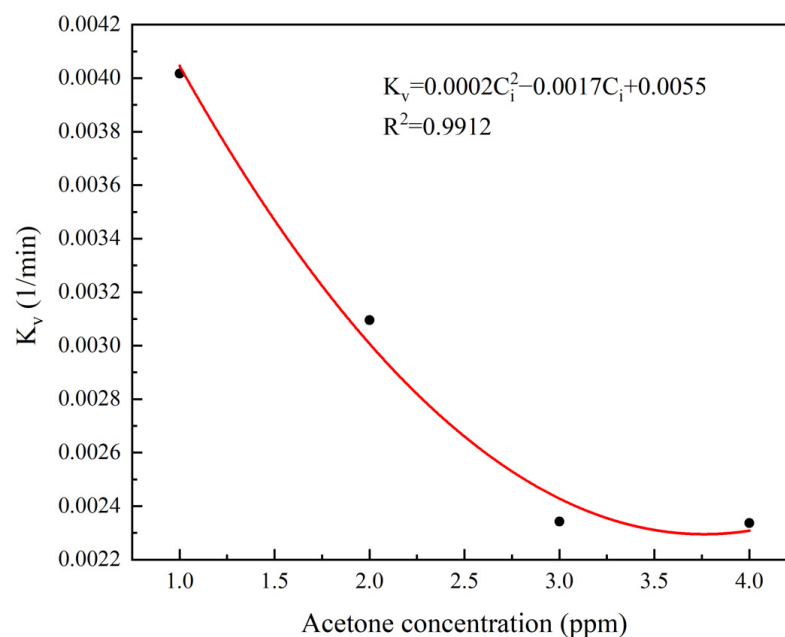


Figure 7. Relationship between mass transfer coefficient  $K_v$  and acetone concentration.

The mass transfer coefficient  $K_v$  of the Wheeler–Jonas equation at different concentrations was obtained through the above derivation, and the equilibrium adsorption capacity  $q_e$  calculated by the Freundlich isotherm was combined to establish a prediction model based on the Wheeler–Jonas equation. It can be seen from Figure 5 that the model can describe the penetration of downstream acetone gas in detail. To verify the accuracy of the model at low concentrations, the breakthrough curves by the described prediction method at 0.5, 1.0, 2.0, 3.0, and 4.0 ppm were compared with the measured data (Figure 8).

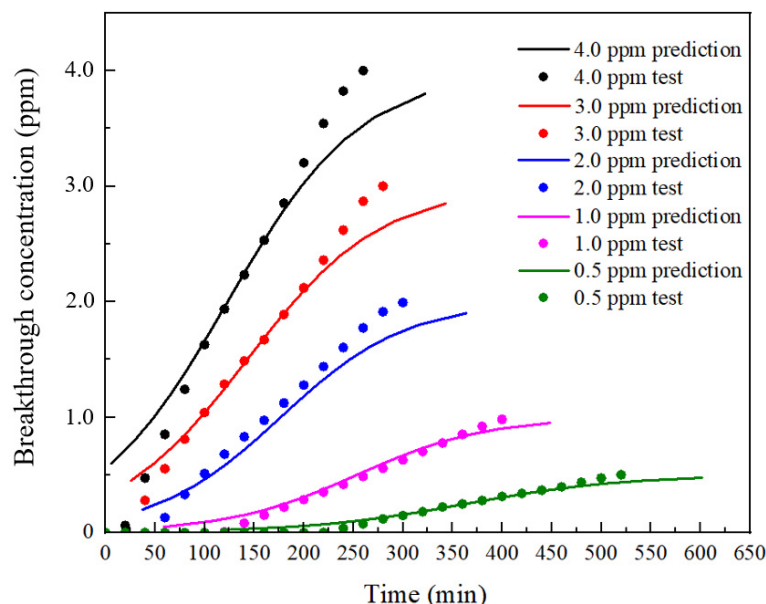


Figure 8. Comparison of predicted breakthrough curves by the Wheeler–Jonas model and measured data at the acetone concentration of 0.5–4.0 ppm.

The predictions seemed accurate, but there was still a difference from the measured data. The forecast greatly increased the adsorption rate of acetone in the initial stage and reduced the breakthrough rate in the end stage. In the initial stage, there were a number of unsaturated adsorption sites on the surface of the activated carbon, the acetone was

wholly adsorbed by the activated carbon, and the actual breakthrough time was longer than predicted. However, when the breakthrough rate of acetone was greater than 85%, many adsorption sites were saturated, the acetone penetrated the activated carbon bed faster than predicted, and the actual service life was shorter than predicted. Compared to the prediction, the acetone penetrated the activated carbon at a relatively constant rate and the activated carbon was saturated more quickly.

#### 4.2. Prediction Based on the Thomas Model

##### 4.2.1. Thomas Model

Li et al. [41] found that the Thomas model was suitable to fit the adsorption curve of acetone when the water content of activated carbon was less than 20%. However, it was noted that the inlet concentration of acetone was 4628 ppm which was in the range of industrial process. Whether it was still the most acceptable model for adsorption prediction needed a validation.

The Thomas model follows the Langmuir isotherm and quasi-second-order kinetics. The Thomas model assumed that the whole process was interfacial mass transfer and that the external and internal mass transfer resistance could be ignored. The model expression is as follows [42]:

$$\frac{C_b}{C_i} = \frac{1}{1 + \exp\left(\frac{K_v q_e m_{GAC}}{Q} - K_v C_i t_b\right)} \quad (8)$$

where  $K_v$  is the total mass transfer coefficient, L/(mg·min); and  $t_b$  is the breakthrough time, min.

##### 4.2.2. Prediction Process

Similar to the process described in Section 4.1.2, the equilibrium adsorption capacity was also calculated by the Freundlich model. According to the Thomas model, the mass transfer coefficient  $K_v$  was obtained by linear fitting with  $t_b$  as the horizontal coordinate and  $\ln(C_i/C_b - 1)$  as the vertical coordinate at 1.0~4.0 ppm (Figure 9), and the relationship of mass transfer coefficient  $K_v$  against acetone inlet concentration was established. It fitted as a power function, and the fitting degree was as high as 0.9974 (Figure 10). Using the equation, the mass transfer coefficients of each concentration could then be calculated. Finally, the equilibrium adsorption capacity and the mass transfer coefficient were substituted back into the Thomas equation to obtain the breakthrough curve, as shown in Figure 11.

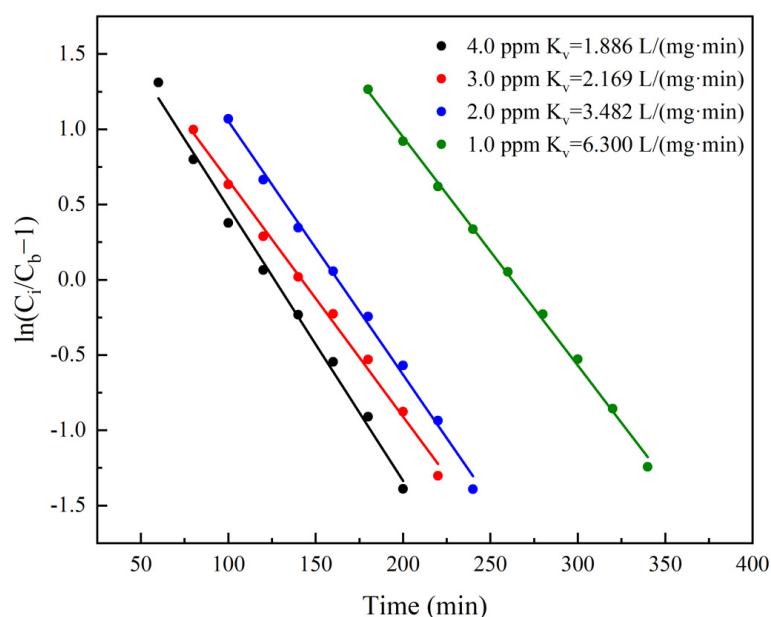


Figure 9. Calculation of mass transfer coefficient by the Thomas equation.

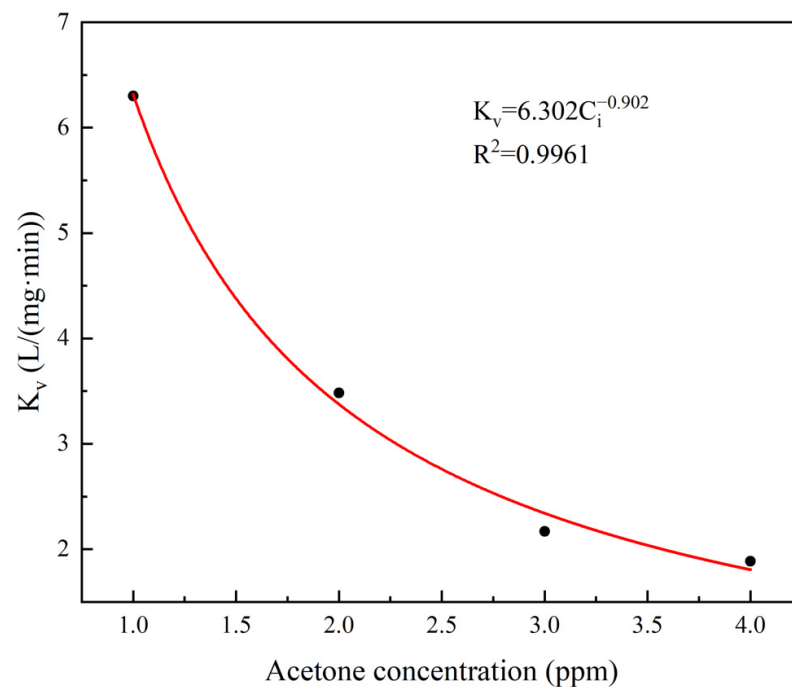


Figure 10. Relationship of mass transfer coefficient and acetone inlet concentration.

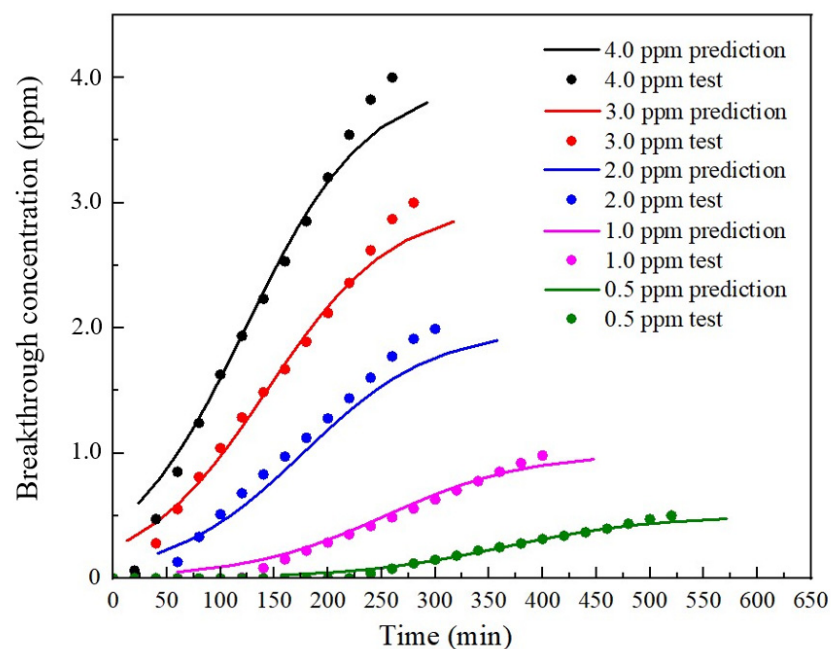
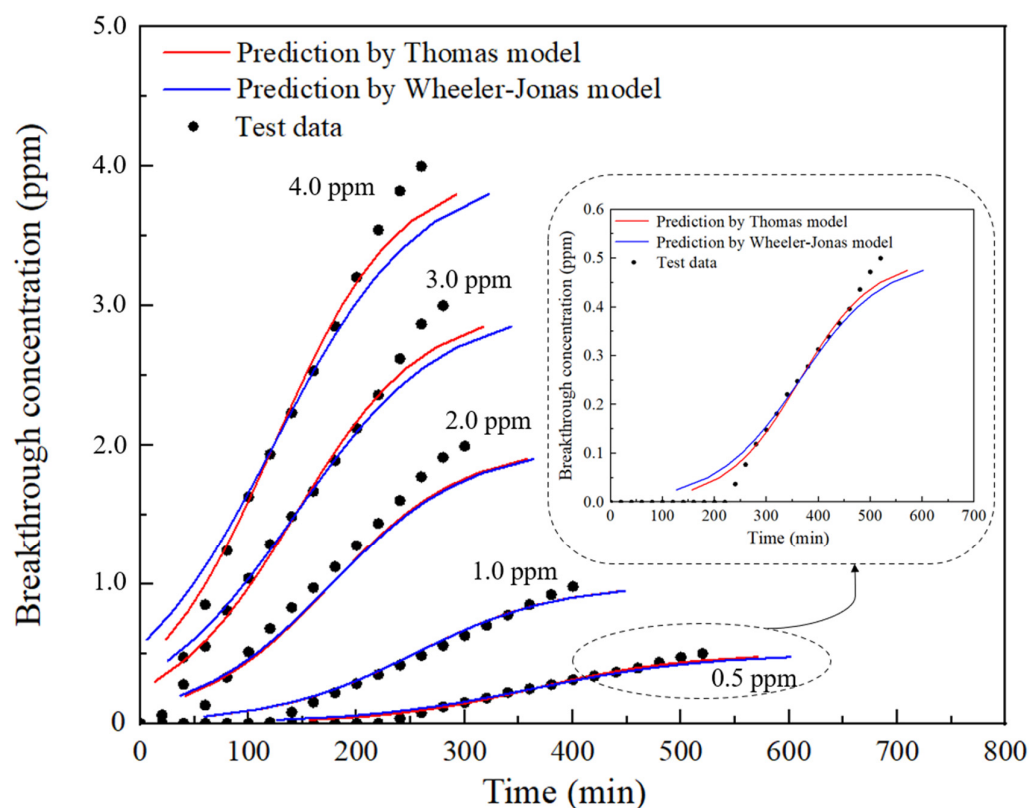


Figure 11. Comparison of predicted breakthrough curves by the Thomas model and measured data at the acetone concentration of 0.5–4.0 ppm.

## 5. Discussion

When comparing Figures 10 and 11, it seemed that there was no significant difference. When the predicted breakthrough curves based on the two methods were displayed in one figure (Figure 12), the differences emerged clearly. It was found that the predicted curve based on the Thomas model was closer to the measured data, especially at the initial and the end stage of the adsorption. When the concentration of acetone was higher (4.0 ppm), the prediction accuracy was higher. When the concentration of acetone was lower (0.5 ppm), the two predicted curves seemed to coincide and the prediction quality could not be distinguished. The magnified validation of the proposed methods at 0.5 ppm

of acetone showed that the predicted curve by the Thomas model still displayed a better adsorption shape of acetone.



**Figure 12.** Comparison of predicted breakthrough curves based on the Thomas and Wheeler–Jonas models.

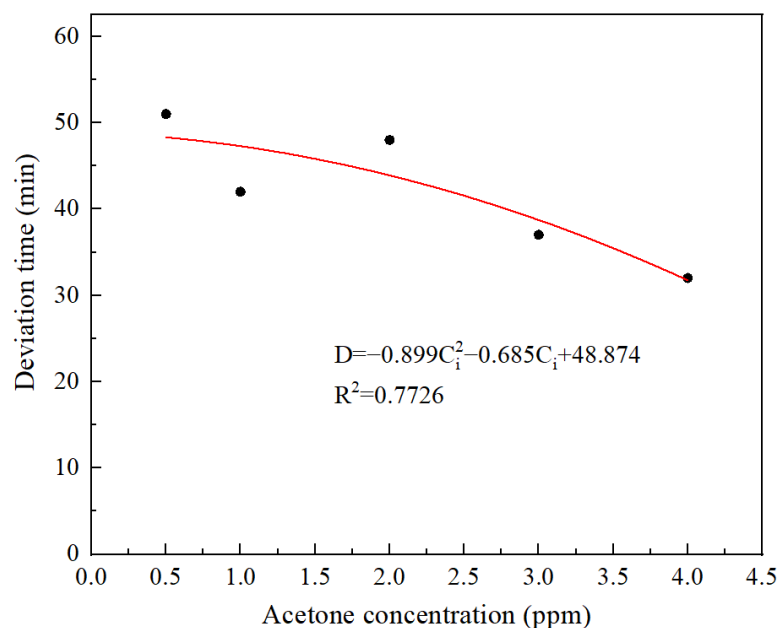
The predicted service life based on the two proposed methods was compared in Table 4. It was found that the predicted service life based on the Thomas model was closer to the measured service life at any inlet concentration of acetone. For example, for the curve at 0.5 ppm of acetone, the predicted service life according to the Thomas model differed from the actual service life by 10%, which was 6% more accurate than that predicted by the Wheeler–Jonas model. So, the Thomas model was more suitable to predict the acetone adsorption when the acetone concentration was at ppb–ppm level.

**Table 4.** Deviation of predicted and measured service life from the two proposed methods.

| Inlet Concentration of Acetone (ppm) | Test Data of Service Life (min) | Predicted Value Based on the Wheeler–Jonas Model (min) | Predicted Value Based on the Thomas Model (min) | Relative Deviation Based on the Wheeler–Jonas Model | Relative Deviation Based on the Thomas Model |
|--------------------------------------|---------------------------------|--------------------------------------------------------|-------------------------------------------------|-----------------------------------------------------|----------------------------------------------|
| 4.0                                  | 260                             | 322                                                    | 292                                             | 24%                                                 | 12%                                          |
| 3.0                                  | 280                             | 343                                                    | 317                                             | 23%                                                 | 13%                                          |
| 2.0                                  | 310                             | 364                                                    | 358                                             | 17%                                                 | 15%                                          |
| 1.0                                  | 405                             | 448                                                    | 447                                             | 11%                                                 | 10%                                          |
| 0.5                                  | 520                             | 601                                                    | 571                                             | 16%                                                 | 10%                                          |

To increase the accuracy of the predicted service life, the deviation time  $D$  between the predicted value based on the Thomas model and the measured service life was calculated, and a relationship was established between the deviation time and the inlet concentration (Figure 13). The expression was  $D = -0.899C_i^2 - 0.685C_i + 48.874$  ( $R^2 = 0.7726$ ). The predicted value minus the deviation time  $D$  computed by the equation was the modified service life, which was listed in Table 5. It was also found that the relative error between

the modified and the measured service life was in the range of 0.1% to 4.7%, which further improved the accuracy of the predicted service life.



**Figure 13.** The relationship between deviation time and acetone concentration.

**Table 5.** Deviation of modified and measured service life.

| Inlet Concentration of Acetone (ppm) | Deviation Time (min) | Modified Service Life (min) | Test Data of Service Life (min) | Relative Error |
|--------------------------------------|----------------------|-----------------------------|---------------------------------|----------------|
| 4                                    | 32                   | 260                         | 260                             | 0.1%           |
| 3                                    | 37                   | 278                         | 280                             | 0.6%           |
| 2                                    | 38                   | 314                         | 310                             | 4.7%           |
| 1                                    | 37                   | 400                         | 405                             | 0.1%           |
| 0.5                                  | 51                   | 523                         | 520                             | 0.5%           |

In the early study of [43], the curve described by the Wheeler–Jonas equation was symmetric about the time point at 50% breakthrough and was a standard S-shape. It was presumed that the Wheeler–Jonas equation was suitable for cases when the breakthrough curve was an S-shape or close to an S-shape. For the activated carbon with actual breakthrough curves of an S-shape, the predicted and measured curves were close, and the deviation between the measured and predicted breakthrough rates at 50% of the time was slight (between  $-12.4$  and  $+124$  min) [30]. As for the activated carbon with a convex breakthrough curve, the model could not be matched. The breakthrough curves in some experiments were asymmetrical S-shaped, but the variation of breakthrough rate was close to the S-shaped curve, and the Wheeler–Jonas model successfully predicted the breakthrough curves [28]. The change in the breakthrough rate of the breakthrough curve for toluene adsorption on activated carbon was also close to the S-shape, undergoing a gradual change from slow to fast and fast to slow, and the Wheeler–Jonas model also presented better prediction results [44]. In contrast, although the breakthrough curve of acetone in this study was atypical of the S-shaped curve, the breakthrough rate was faster, and there was no process of the faster breakthrough rate at the early stage of adsorption and no asymptotic process of slowing down at the end of adsorption. This may be the reason for the bias in predicting the Wheeler–Jonas equation.

The Thomas model might be suitable for steep breakthrough curves. Ang et al. [44] found that the Thomas model could describe a steeper S-shaped breakthrough curve in sevoflurane adsorption using activated carbon. Although the adsorption curve of acetone

in the experiment was S-shaped, the mass transfer resistance during the adsorption process was small, and the breakthrough curve was steeper, which was suitable to be described by the Thomas model. The Thomas model considered that the limiting step in the process was the interfacial mass transfer rather than the external and internal mass transfer. It was presumed that the adsorption of acetone was controlled by the interfacial mass transfer process with low external and internal mass transfer resistance. In summary, the Thomas model was more suitable for the adsorption process where the breakthrough curve was a steep S-shape.

## 6. Conclusions

In this paper, the acetone adsorption performance by coconut shell activated carbon was tested under the concentration of 0.5–4.0 ppm, and an approach to predict the breakthrough curve of acetone based on the Thomas model was proposed. The breakthrough curve for acetone on activated carbon was steeper, reaching saturation rapidly and showing a non-standard S-shape. Different adsorption isotherms were used to fit the breakthrough curve to obtain the equilibrium adsorption capacity. The equilibrium adsorption capacity predicted by the D-R model deviated significantly from the actual ( $R^2 = 0.7664$ ) and was not as good as the predictions of the Langmuir ( $R^2 = 0.9457$ ), Freundlich ( $R^2 = 0.9847$ ), and Temkin ( $R^2 = 0.9464$ ) models. The Freundlich model fitted best, indicating that multilayer adsorption occurred during the adsorption process, and acetone adsorption was dominated by physical adsorption. A prediction method for acetone adsorption was developed. As the breakthrough curve of acetone was asymmetric S-shaped and steep, it could not be described by the Wheeler–Jonas model. For this case, the Thomas model was more suitable for an accurate prediction of service life and breakthrough performance. And the relative deviation between the predicted service life and measured data was ~10%.

It should be pointed out that the conclusions above are obtained from the experimental cases considered. Different outcomes or trends may occur when the conditions change. The feasibility of the prediction method in a wider concentration range of acetone should be implemented in a further study, as well as the application for other polar VOCs. Nonetheless, the current prediction model would be useful in mastering the acetone adsorption performance at ppb–ppm level by coconut shell activated carbon and estimating its service life.

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