



## Breakthrough of methylethylketone and benzene vapors in activated carbon fiber beds

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### Abstract

The breakthrough of low concentration methylethylketone (MEK) and benzene vapors in beds packed with rayon-based activated carbon fiber (ACF) with different surface areas was investigated. The breakthrough characteristics depend on the properties of the ACF and the vapors, as well as on the adsorption conditions. The results of dynamic adsorption in an ACF bed were consistent with those of equilibrium adsorption by gravimetric methods. The breakthrough adsorption indicates that ACF, with an appropriate surface area, could be utilized in controlling volatile organic compounds (VOCs) in indoor air.

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### 1. Introduction

Indoor air quality has caused much concern recently since it is directly related to human health. Many toxic gases can be emitted by daily activities such as cooking, smoking and modern equipment such as computers, photocopy machines, etc. The critical toxic gases are volatile organic compounds (VOCs), which are significantly higher in indoor air than in outdoor air [1]. These contaminants may cause infection to eyes, nose and could even cause cancer if people are exposed for a long time. One common way to minimize this harmful effect is to reduce the concentration of the VOCs by ventilation. Other ways include adsorption, thermal or catalytic oxidation, liquid absorption [2] and photocatalytic oxidation

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Table 1  
Pore structure parameters of ACF samples

ACF	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{mi}}^{\text{b}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{tot}}^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )
ACF6	640	0.172	0.220
ACF14	1460	0.320	0.549
ACF16	1680	0.432	0.759

<sup>a</sup>  $S_{\text{BET}}$ : BET surface area.

<sup>b</sup>  $V_{\text{mi}}$ : micropore volume.

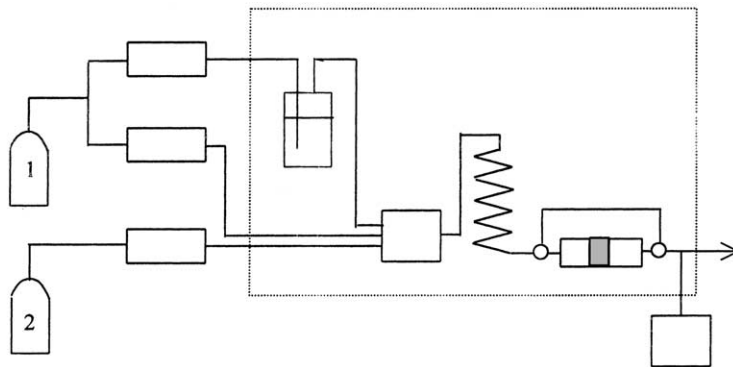
<sup>c</sup>  $V_{\text{tot}}$ : total pore volume.

[3,4]. Adsorption on porous carbon [5,6] is an extensive method because it possesses a large specific area and has a high adsorption capacity. Micropores, due to the overlap of attractive forces of opposite pore walls, are primarily responsible for the adsorption of gases at low concentration [7].

Microspores dominate in activated carbon fibers (ACFs), which exhibit a higher adsorption capacity and have faster adsorption kinetics than granular activated carbon (GAC). Moreover, activated carbon fibers are easier to use than GAC since they can be formed in various forms of cloth, felt, etc. Therefore, activated carbon fibers are more suitable as an adsorbent for removing indoor VOCs. The adsorption of VOCs on phenolic resin-based activated carbon fibers at various concentrations was investigated [8–12]. In our previous work [13], the equilibrium adsorption of polar methylethylketone (MEK) and non-polar benzene vapors on viscose rayon-based activated carbon fibers was measured.

In order to fit a realistic application, dynamic adsorption tests using packed beds can be performed. Yoon and Nelson [14] have presented a semi-empirical gas adsorption model that can predict the whole breakthrough curve

$$C = C_0 \frac{1}{1 + \exp[k'(\tau - t)]} \quad (1)$$



- 1.High-purity nitrogen    2.VOC in nitrogen calibrated standard    3.Mass flow controller  
4.Humidifier    5.Mixer    6.Thermostat    7.Adsorber    8.Gas Chromatograph

Fig. 1. Schematic experimental flow diagram.

where  $C_0$  and  $C$  are inlet and outlet concentrations of VOCs,  $k'$  the rate constant,  $t$  the time, and  $\tau$  the time at 50% breakthrough.

In the present work, we studied the breakthrough of methylethylketone and benzene vapors in beds packed with the same activated carbon fibers as those used previously [13]. We expected that a comparison of the trends in breakthrough times (the time to reach an outlet concentration equal to 50% of the inlet concentration) for the ACF packed bed could be consistent with the trends observed with the adsorption isotherms.

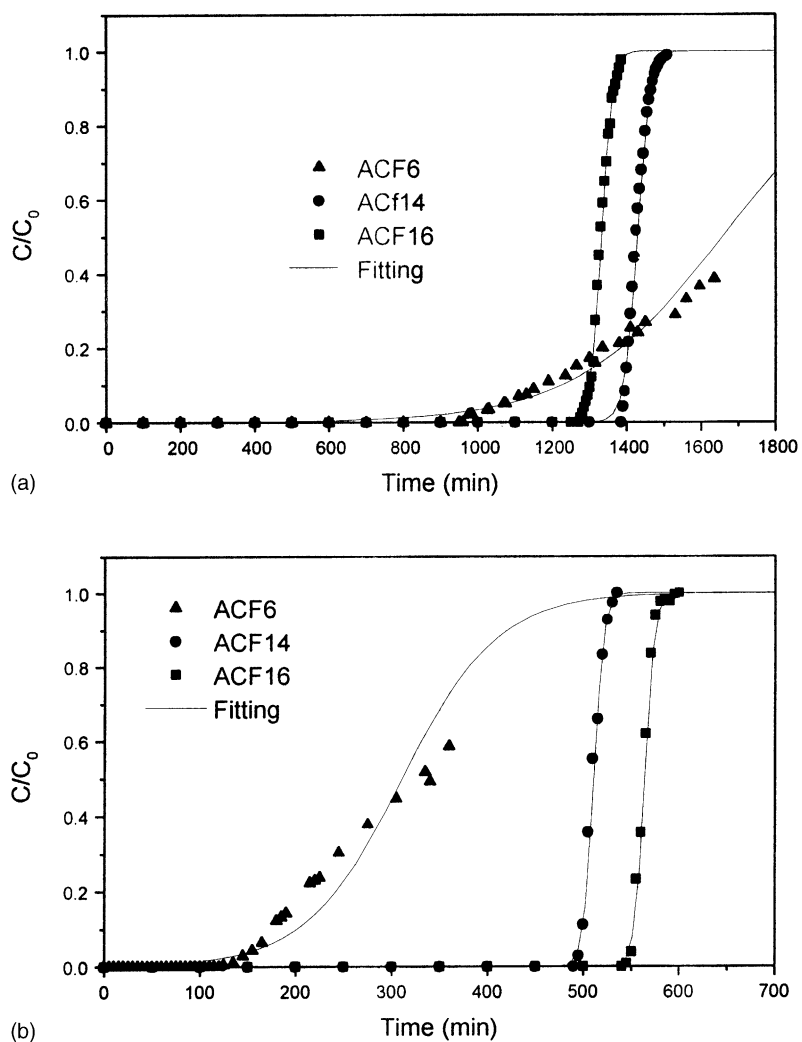


Fig. 2. Comparison of breakthrough curves of ACFs for MEK with (a) 50 ppm, (b) 250 ppm, and (c) 1000 ppm at 30 °C.

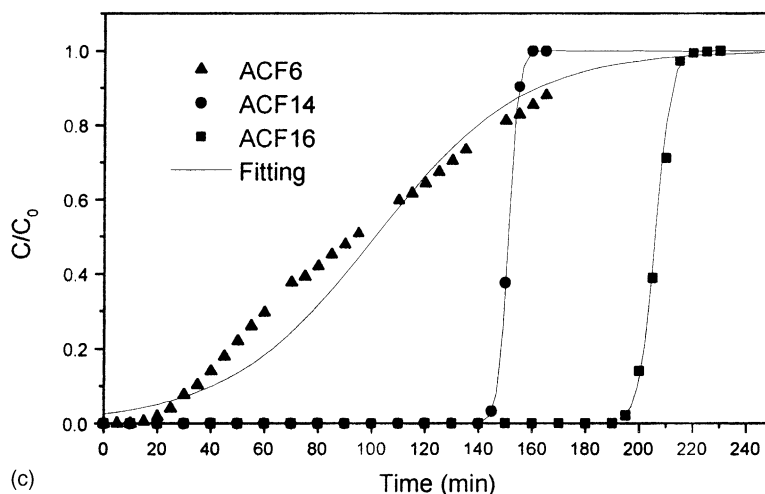


Fig. 2. (Continued).

## 2. Experimental

Three viscose rayon-based ACF samples (made in Anshan Activated Carbon Fiber Company, PR China) with different specific surface areas were used and denoted as ACF6, ACF14 and ACF16, respectively, referring to their specific surface areas. The pore structure parameters of ACFs are listed in Table 1. Methylketone and benzene vapors were selected as the adsorbates. Certified standard gases were used in the experiment. High purity nitrogen was used to dilute the standard gas to the required concentration.

The schematic experimental flow diagram is shown in Fig. 1. The adsorption vessel was a 20-cm long, 8-mm outside diameter and 5-mm inside diameter stainless steel pipe. All samples were initially dried under vacuum at 120 °C overnight and then packed in the adsorption column. The column temperature was maintained at  $30 \pm 1$  °C. The gas flow rate was controlled with a mass flow controller. The gas inlet was switched to test gas after high pure nitrogen outgassing for 2 h. The total flow rate was kept at 60 ml/min. The relative humidity was controlled by regulating the ratio of the nitrogen flow rate through the water bubbler to the overall flow rate. A Shimadzu 14C Gas Chromatograph with a flame ionization detector was used to analyze the effluents of the adsorber.

## 3. Results and discussion

Fig. 2 shows breakthrough curves of MEK under different concentrations in ACF6, ACF14 and ACF16 beds with the same bed mass, 0.20 g. There were good breakthrough curve shapes for ACF14 and ACF16. However, the concentration of effluent increased gradually with time in the case of ACF6 at all inlet concentrations, suggesting a larger mass transfer resistance for ACF6. This may be due to ACF6's narrow pore entrance leading to a

low adsorption rate. Hence, a long time was required to reach equilibrium. It was obvious that the breakthrough times decreased with increasing inlet concentration for all samples. Moreover, the breakthrough curves became steep with increasing inlet concentrations. For a given concentration, the longer breakthrough time indicated a greater adsorption capacity.

Comparing the MEK breakthrough curves of ACF samples at three concentrations, it was found that lower specific surface area resulted in longer breakthrough times at a concentration of approximately 50 ppm. However, it was the reverse when the concentration increased

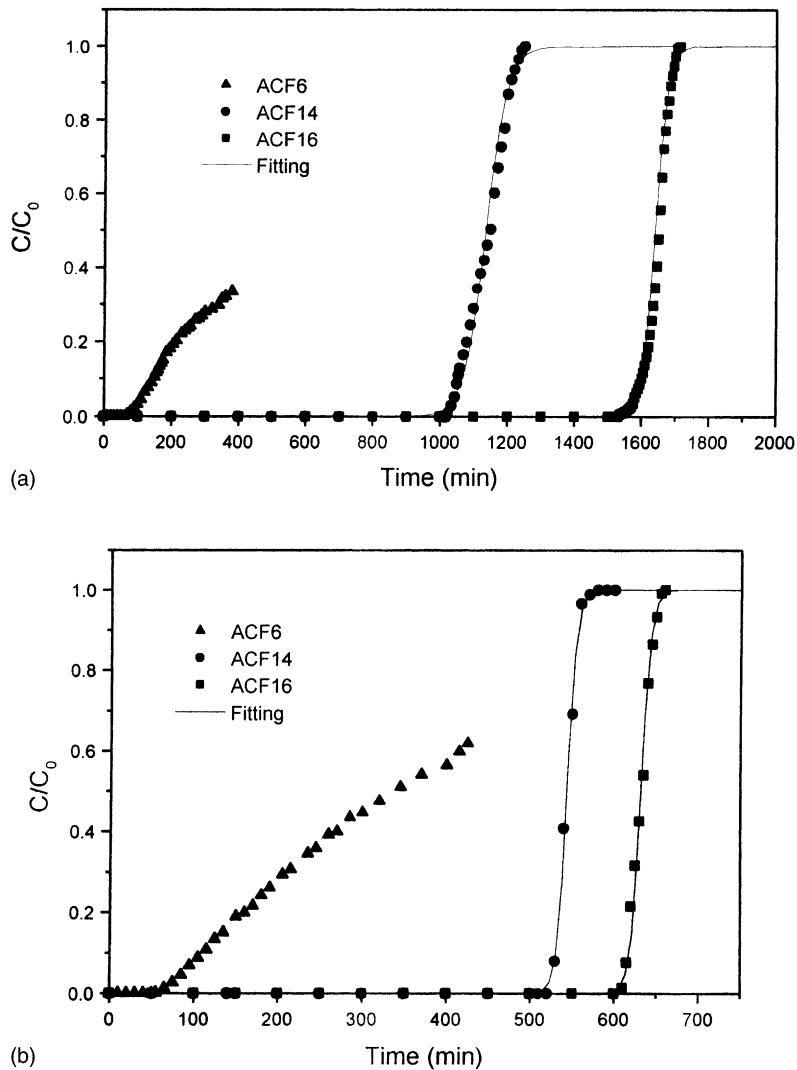


Fig. 3. Comparison of breakthrough curves of ACFs for benzene with (a) 50 ppm, (b) 250 ppm, and (c) 1000 ppm at 30 °C.

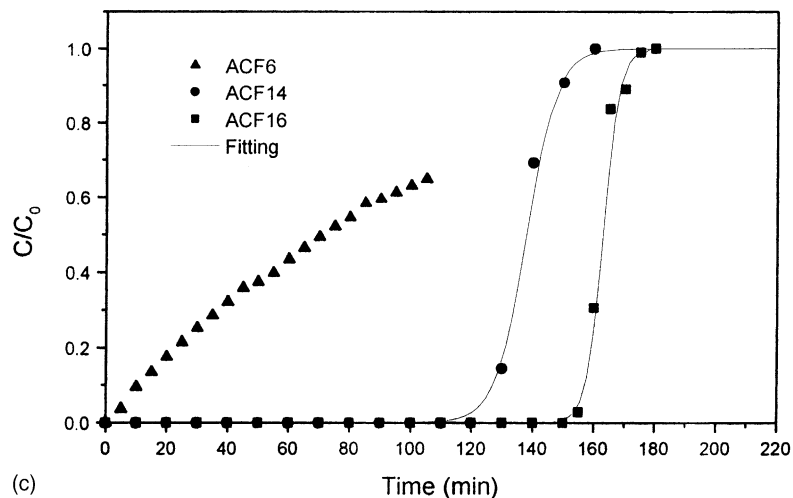


Fig. 3. (Continued).

to approximately 250 and 1000 ppm, that is, the higher the specific surface area, the longer the breakthrough time. These results are consistent with gravimetric adsorption isotherm data [13]. Higher specific area resulted in higher adsorption capacity when the concentration was higher than 100 ppm. However, it was the inverse case when the concentration was below 100 ppm [13]. Similar results have been reported elsewhere [15]. It should be noted that at a concentration of approximately 50 ppm, the time to begin breakthrough for ACF6 was shorter than that for two other samples. Moreover, the time difference became larger with increasing inlet concentration.

Fig. 3 illustrates breakthrough curves of benzene under different concentrations in ACF6, ACF14 and ACF16 beds with the same bed mass, 0.20 g. There were good breakthrough curve shapes for ACF14 and ACF16 but not for ACF6. However, due to considerable oxygen complexes on the ACF surface, leading to an enhancement of adsorption for polar adsorbate, benzene adsorption capacity for ACF6 was lower than for MEK, resulting in shorter breakthrough time of benzene. It was previously found [13] that the equilibrium adsorption capacity of benzene was higher than that of MEK for both ACF14 and ACF16. Consequently, the breakthrough times for benzene were longer than those of MEK for both ACF14 and ACF16. Eq. (1) was applied to fit all breakthrough curves, and it fit the curves of both ACF14 and ACF16 very well.

The effect of temperature on the breakthrough curve of MEK and benzene in ACF14 bed is shown in Fig. 4. The column temperatures were set to 30, 45 and 60 °C, respectively. Apparently, the breakthrough time decreased with increasing bed temperature. This result is ascribed to VOC physical adsorption onto ACF [16]. Increasing temperature resulted in decreasing capacity, corresponding to decreasing breakthrough time. We found that the breakthrough times of benzene were slightly higher than those of MEK at the three temperatures.

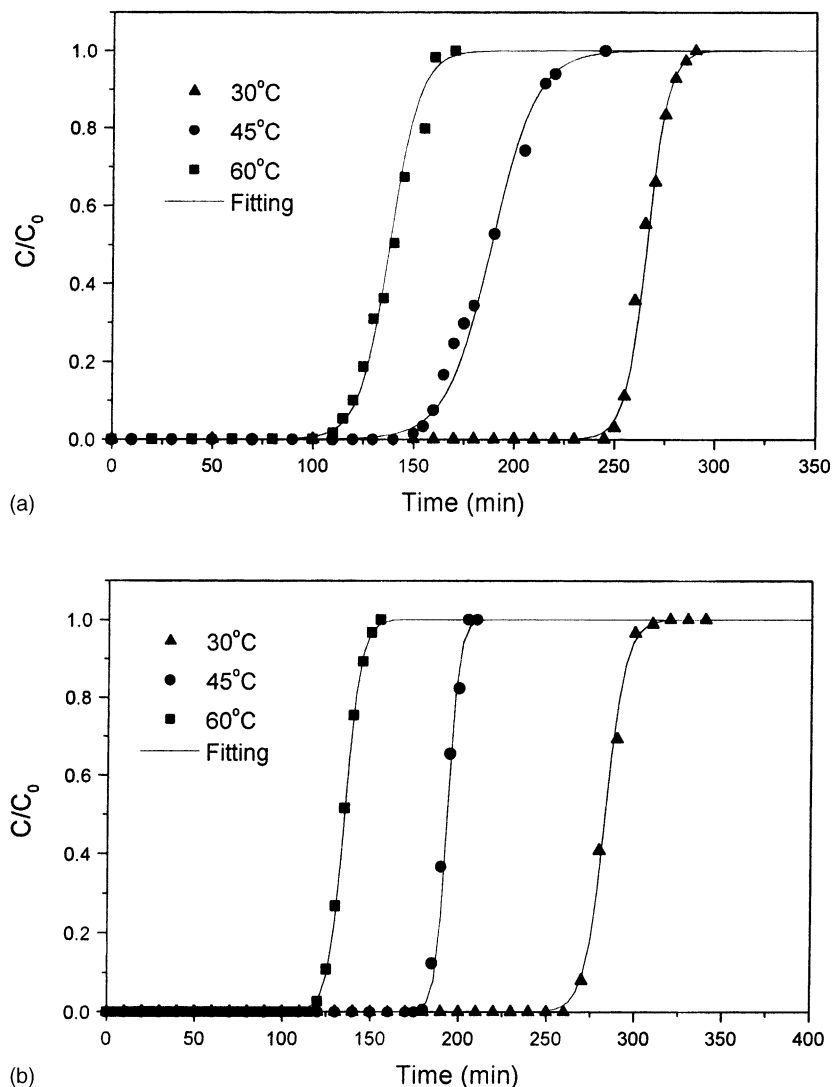


Fig. 4. Effect of temperature on breakthrough curve of (a) MEK and (b) benzene in ACF14 bed.  $C_0 = 250$  ppm, bed mass = 0.10 g.

For the same concentration, the breakthrough time in high humidity is less than that in low humidity (see Fig. 5). Because the active sites of ACF may have been occupied by water molecules in higher humidity conditions, the entire mass transfer zone (MTZ) velocity increased, and consequently, the breakthrough time decreased with increasing relative humidity. Similar results have been reported previously [17]. In fact, the adsorption of vapors from a humid fluid is a complex process. The influence of humidity may depend on other adsorbates, and on the adsorption procedure [18]. If the measurements are started

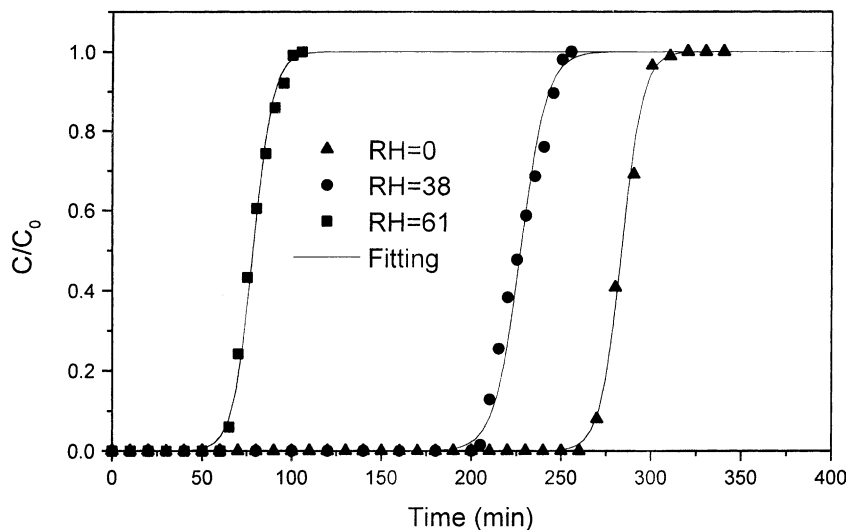


Fig. 5. Effect of relative humidity on breakthrough curve of benzene in ACF14 bed at 30 °C.  $C_0 = 250$  ppm, bed mass = 0.10 g.

with carbon in equilibrium with the air at the onset of adsorbate vapor, the results could be quite different from measurements starting with dry carbon, as was done used in the procedure presented here. In the former case, the humidity would have very little influence on the breakthrough time of water soluble vapor, however, the influence on insoluble vapor would be significant [18]. Other researchers [19] have found that solubility is not a major factor. Molecules with high affinity for the carbon surface, whether soluble or not, were less influenced by the presence of water.

#### 4. Conclusions

The breakthrough characteristics of organic vapors in packed beds of ACF depended on the properties of both the ACF and the vapors, as well as on the adsorption conditions. The results of dynamic adsorption of MEK and benzene in packed beds of ACF were consistent with those of equilibrium adsorption by gravimetric methods. Higher equilibrium adsorption capacity corresponds to longer breakthrough times at different concentrations. ACF with a low surface area (just as ACF6 in the present study) does not possess good dynamic breakthrough adsorption characteristics even though it has a higher equilibrium adsorption capacity at low concentrations. This finding suggests that ACF with appropriate surface area could be employed in controlling VOCs in indoor air.

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