The effect of fixed adsorption bed height on adsorption of gaseous mixture of volatile organic compounds

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Abstract
The influence of a fixed adsorption bed height on the adsorption process was studied using acetone, ethyl acetate, toluene, and n-butyl acetate as a gaseous adsorbate mixture. All experiments were conducted under the same gas flow and temperature conditions. Concentrations of adsorbates were monitored using gas chromatography with a flame ionization detector. Activated carbon WG-12 (Grand Activated Sp. z o.o) was selected as the adsorbent, and the following heights of the fixed adsorption bed were used: 0.8, 1.6, 3.2, and 4.8 cm. The results of the study allowed to deduce that as the height of the fixed adsorption bed increased, the degree of displacement of adsorbate molecules from the bed strengthened. In addition, it was found that both the bed breakthrough time increased linearly with a height rise of the fixed adsorption bed. The process carried out on a fixed adsorption bed with a height of 0.8 cm was characterized by an undeveloped mass transfer zone, as well as the complete displacement of the most volatile components (acetone and ethyl acetate). The utilization rate of the fixed adsorption bed also increased as the height of the adsorption bed went up. However, at a certain bed height, the bed breakthrough curves were formed and the adsorption capacity did not change significantly, solely the bed breakthrough time increased.

Keywords
volatile organic compounds, adsorption bed height, breakthrough curves, breakthrough time

1. INTRODUCTION

Air pollution is a topic that has gained significant attention from both researchers and journalists. While the impact of carbon dioxide on the climate is frequently discussed, there is a noticeable lack of attention regarding the presence and harmful effects of volatile organic compounds (VOCs) in the air (Abd et al., 2021; Marć et al., 2018). Due to certain properties, volatile organic compounds can be selected among numerous organic compounds (Yang et al., 2019). Under normal conditions, they have a relatively high vapour pressure and high saturated vapour concentration. Therefore, they are distinguished from other compounds by their considerable volatility, so they easily pass from the liquid to the vapor state. Due to their characteristic, often irritating smell, they are unpleasant to the human sense of smell and comfort. Their boiling point does not exceed 250 °C (Ding et al., 2020; Li et al., 2021). Most VOCs dissolve poorly in water (Mahmoodlu et al., 2017). The harmful effects of VOCs on human health have long been known. Most of these compounds have irritating effects on mucous membranes, causing coughing, headaches and dizziness. Contact with VOC vapours can result in asthma, cardiovascular disease, kidney disease, concentration problems, cancer, etc (Cruz et al., 2014; Cui et al., 2020; Helen et al., 2020). On the other hand, some VOCs are released by humans through the skin or breath, both by healthy and sick people (Wang et al., 2022a).

There are many methods to purify the gas stream of volatile organic compounds. The choice of treatment method is influenced by the character of the VOCs, their concentration, and the source of emission (He et al., 2019). In industry, a popular, effective, and relatively economical method is the adsorption process. Adsorption involves the accumulation of adsorbate molecules in the pores of the adsorbent. The effect of this spontaneous phenomenon is a change in the concentration of adsorbate in the bulk phase compared to the surface phase. The system in which adsorption takes place strives for a state of equilibrium, which is established when the rates of adsorption and desorption are balanced (Li et al., 2017; Lim et al., 2020). Adsorption process provides the ability to effectively clean the gas stream of VOCs even at low concentrations (El Mohajir et al., 2021; Yang et al., 2019). Many literature reports discuss the adsorption of single components, although interest in the adsorption of mixtures of VOCs is growing (Jurkiewicz et al., 2022; Wang et al., 2022b).

Gupta et al. (2013) studied the effect of bed height on the adsorption of one component (xylene) from the gas phase. They found that the bed breakthrough time increased with increasing adsorption bed height. They reached similar conclusions when studying the adsorption of toluene (Gupta et al., 2011; 2015). Analogous trends were also noted for adsorption from the aqueous phase (Pełech et al., 2006; Yagub et al., 2015). The objective of this paper was to investigate the influence of the height of the adsorption bed on the adsorption process of a gaseous mixture of four volatile organic compounds.

2. EXPERIMENTAL

In the study of the effect of bed height on the adsorption of vapours of acetone (Stanlab, pure, p.a.), ethyl acetate (Chempur, pure, p.a.), toluene (POCH, pure, p.a.), and n-butyl acetate (Stanlab, pure, p.a.), activated carbon WG-12 (Grand Activated, Sp. z o.o.) was used as an adsorbent. The following fixed adsorption bed heights were used to study the adsorption of vapours of VOCs: 0.8, 1.6, 3.2 and 4.8 cm.

Adsorption beds were given names as indicated by the *WG-12-bed height* (in cm) scheme, such as WG-12-0.8. The process was conducted according to the procedure and conditions described in our previous publication. Figure 1 shows a schematic of the experimental apparatus.
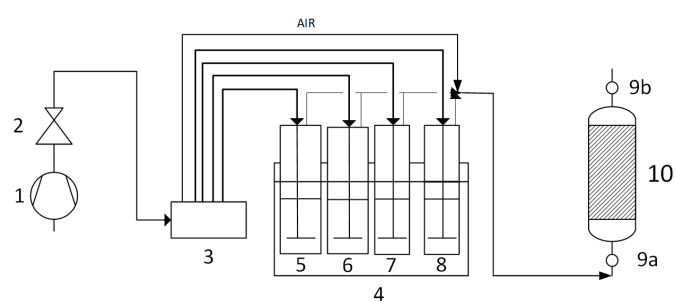

Figure 1. Scheme of the experimental setup:
1 – air compressor; 2 – pressure regulator;
3 – mass flow controller; 4 – thermostat; 5, 6, 7, and 8 – scrubbers with VOCs; 9a – inlet sampling point; 9b – outlet sampling point; 10 – fixed bed adsorber with the inside diameter of 3.2 cm (Jurkiewicz et al., 2023).

The temperature in the thermostat was $15\,^{\circ}$C, while the adsorption process was carried out at $20\,^{\circ}$C. The flow rates of the individual components were (mL/min): acetone 20, ethyl acetate 45, toluene 130, n-butyl acetate 275, air 50. Initial concentrations of adsorbates were (mg/L): acetone 30; ethyl acetate 25; toluene 29; n-butyl acetate 25. The adsorption capacities a for each component of the mixture were calculated according to Equation (1) (Jurkiewicz et al., 2023).

$$a = \frac{q}{m_a}\left(C_0 \cdot t - \int_0^t C\mathrm{d}t\right) \qquad (1)$$

To compare the processes carried out on different adsorbent masses, a value for the volume of purified gas, V_{pg}, was introduced. The value of V_{pg} was expressed by Equation (2).

$$V_{pg} = \frac{q \cdot t}{m_a} \qquad (2)$$

Table 1 shows the properties of the WG-12 activated carbon, based on the producer's information.

3. RESULTS AND DISCUSSION

Changes in the ratio of outlet to initial concentrations of adsorbates are shown as a function of the volume of purified gas V_{pg} in Figure 2. For all the adsorption processes carried out, an exceedance of the initial concentration value at the outlet was observed. As we already know, this is related to the mutual displacement of adsorbate molecules from the pores of the adsorbent (Jurkiewicz et al., 2023). The degree of displacement of adsorbates from the fixed adsorption bed is lowest for the height of the bed $h = 0.8$ cm (by about 30% exceeded the outlet concentration value relative to the inlet concentration value for each component) and increases with the height of the fixed adsorption bed. For a value of $h = 4.8$ cm, the C/C_0 ratio is 2.0 for acetone, 1.8 for ethyl acetate and 1.4 for toluene. The increase in the degree of displacement with increasing bed height is related to the fact that a larger volume of activated carbon results in a larger number of available adsorption sites. Consequently, more adsorbate molecules can be adsorbed and thereby more molecules can be displaced by other components.

As the height of the fixed adsorption bed increases, the shape of the breakthrough curves is steeper. Similar observations are presented for single-component (CCl_4) adsorption studies on fixed adsorption beds of different heights (Milchert et al., 2000).

The increase in the degree of displacement of adsorbate molecules with increasing bed height is particularly evident for acetone and ethyl acetate. In the studied system, these two compounds are the most volatile.

In the case of $h = 0.8$ cm, the shape of the curves makes it possible to conclude that the mass transfer zone did not develop. For adsorption bed heights of 3.2 and 4.8 cm, the

Table 1. Properties of WG-12 activated carbon (Grand Activated Sp. z o.o.).

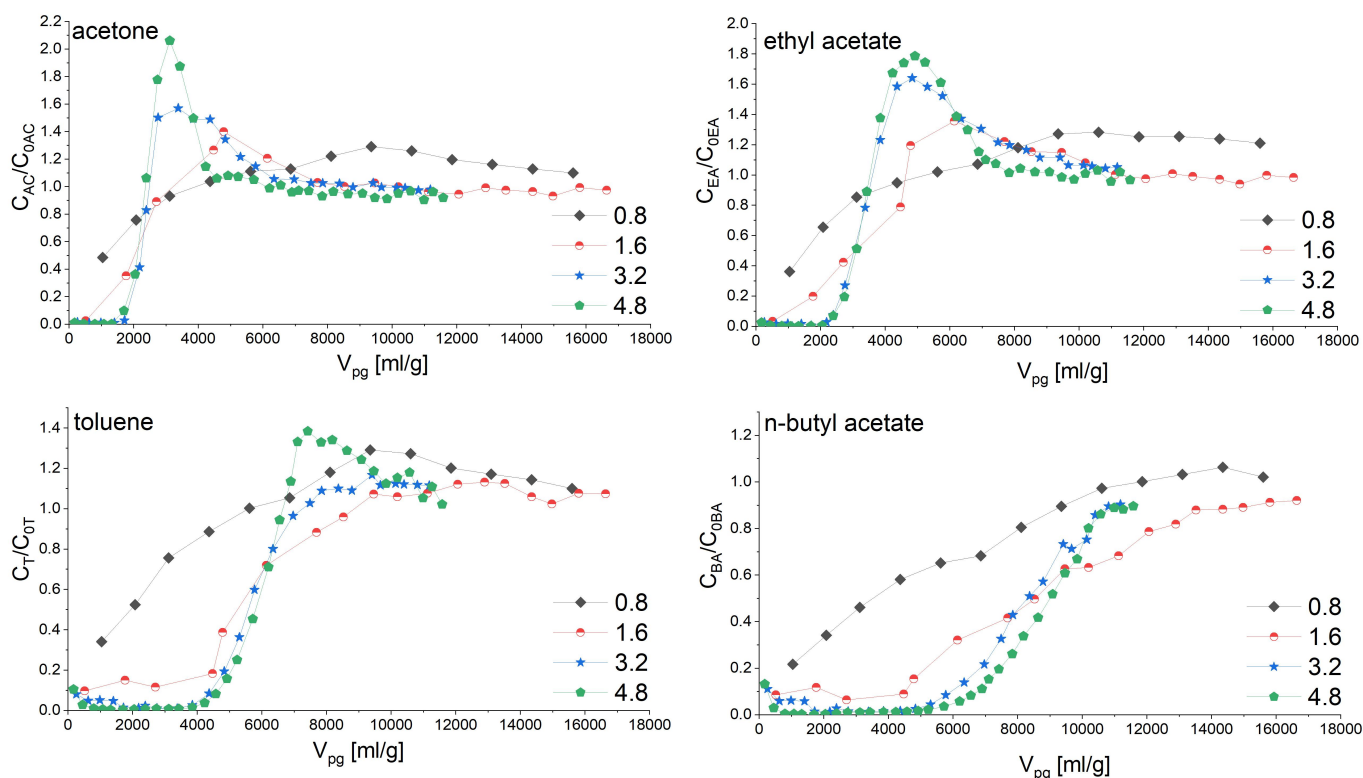| Property	Value
iodine number [mg/g]	1025
bulk density [g/L]	398
mechanical strength [%]	97.5
moisture content [%]	0.6
ash content [%]	16.8
grain size [%]:	
> 2.0 mm	0.2
2.0–1.5 mm	20.8
1.5–1.25 mm	69.8
1.25–1.0 mm	8.2
1.0–0.75 mm	0.8
0.75–0.5 mm	0.1
< 0.5 mm	0.1

Figure 2. Comparison of the breakthrough curves of each adsorbate for adsorption processes carried out on fixed adsorption beds of different heights (0.8, 1.6, 3.2, and 4.8 cm).

concentration points move along the adsorption bed at a constant speed. The narrowing effect of the curves is related to the shortening of the mass transfer zone as the height of the bed increases.

Figure 3 shows the changes in the C/C_0 ratio of the mixture components as a function of time. In each of the processes carried out, the order of appearance of the component at the outlet is as follows: acetone, ethyl acetate, toluene, and n-butyl acetate. We have taken as the breakthrough time the time at which the value of outlet concentration $C = 0.05C_0$. The exception is the process carried out on a bed with $h = 0.8$ cm. In this process, the breakthrough of the fixed adsorption bed occurred practically immediately. As the height of the adsorption bed increases, the bed breakthrough time grows. Figure 4 presents the dependence of bed breakthrough time for each mixture component as a function of bed height. The graphs show that the breakthrough time linearly goes up $(0.97 \leq R^2 \leq 0.99)$ as the height of the bed increases.

For each of the processes carried out, adsorption capacities were calculated for each component of the mixture, based on Equation (1). The results are summarized in Table 2. For the process carried out on the fixed adsorption bed with a height of $h = 0.8$ cm, the adsorption capacities for acetone and ethyl acetate were 0 mg/g. This is due to the complete displacement of these compounds from the fixed adsorption bed by toluene and n-butyl acetate. This also indicates that adsorption on WG-12 activated carbon is not specific to individual adsorbates. That is the molecules of individual adsorbates compete for the same adsorption sites. In addition, it can be concluded that the adsorption potential to the surface of the applied activated carbon is related to the boiling point of the adsorbed component (Jurkiewicz et al., 2023). As its boiling point increases, the displacement force (and thus the adsorption potential) of a given adsorbate rises.

At certain heights of the adsorption bed, the breakthrough curves are fully formed for given gas flow rates. Then the adsorption volume does not change significantly. This is mainly the case for the least volatile and thus best adsorbing compounds – toluene and n-butyl acetate.

The relationship between bed height and adsorption capacity is shown in Figure 5.

Table 2. The adsorption capacities in processes carried out at different heights of the fixed adsorption bed.

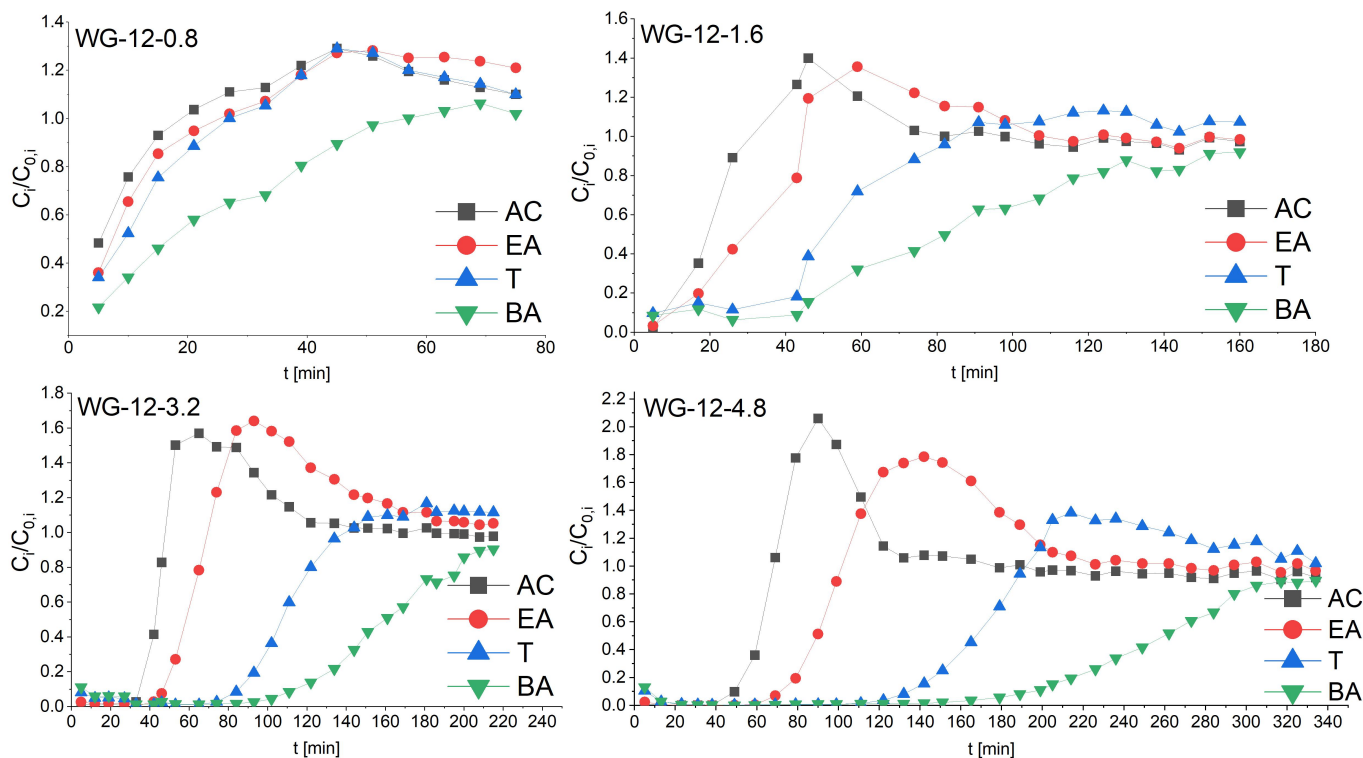| h [cm]	a [mg/g]			
	acetone	ethyl acetate	toluene	n-butyl acetate
0.8	0	0	110	101
1.6	39	48	130	189
3.2	22	22	150	199
4.8	32	29	127	191

Figure 3. Breakthrough curves of volatile organic compounds for adsorption processes carried out at different bed heights.
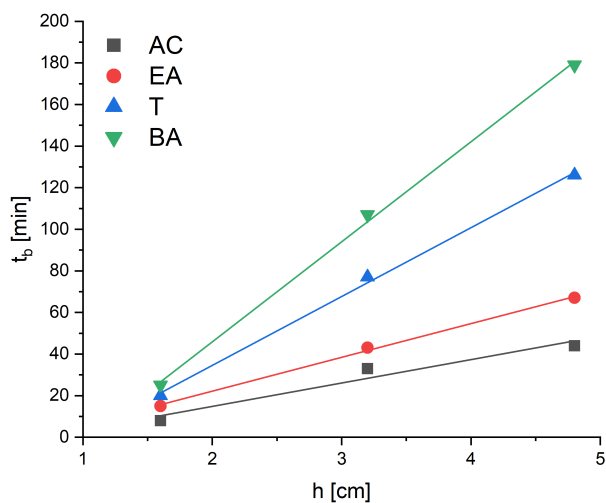

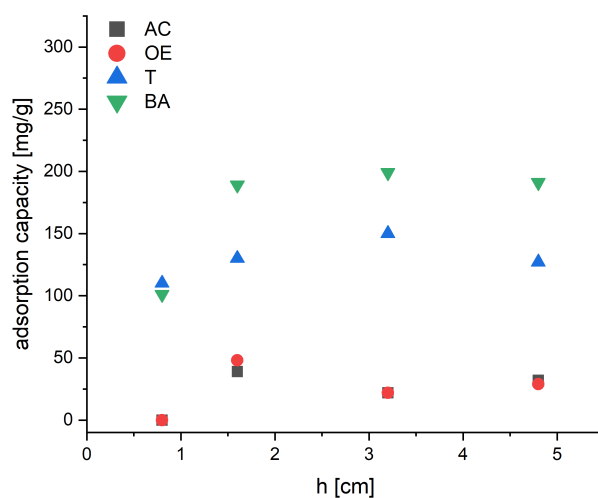Figure 4. Dependence of bed breakthrough time on fixed adsorption bed height.

Figure 5. Correlation of the adsorption capacity with the height of the adsorption bed.

4. CONCLUSIONS

As the height of the fixed adsorption bed is raised, the utilization degree of the fixed adsorption bed increases. At the same time, it was found that the higher the fixed adsorption bed, the smaller the mass transfer zone. This enhances the adsorption capacities of the gaseous volatile organic compounds. Expanding the volume of adsorbent in the bed intensifies the phenomenon of competitive adsorption. Under the same gas flow conditions, at certain bed heights, the adsorption capacity does not change, solely the intensity of competitive adsorption changes. In addition, the breakthrough time of the adsorption bed increases with increasing the fixed adsorption bed height. What is more, regardless of the height of the fixed adsorption bed, the adsorption capacities of VOC vapours are determined by the presence of other components. In the presented study, the effective utilization of the fixed adsorption bed occurs at bed heights equal to and above 3.2 cm.

SYMBOLS

AC	acetone
OE	ethyl acetate
T	toluene
BA	n-butyl acetate
a	adsorption capacity, mg/g
C	outlet concentration, mg/L
C_0	inlet concentration, mg/L
h	adsorption bed height, cm
m_a	mass of the adsorption bed, g
t	time, min
t_b	breakthrough time, min
q	gas flow, mL/min
V_{pg}	volume of purified gas per mass of adsorbent, mL/g

Subscripts

i	component

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