固定床吸附塔中使用活性碳對於不同形狀烷類有機物之吸附效能分析

吳宏達[1*]　黃秀株[2]　鍾財王[2]

[1]崇右技術學院時尚造型設計系

[2]中原大學化學工程系

[1]基隆市義七路 40 號

[2]桃園縣中壢市中北路 200 號

摘　要

本實驗中採用重力吸附法且於活性碳吸附床中對於揮發性有機物質進行吸附作用，吸附平衡實驗之溫度控制於298.15 K，被吸附物質包括n-hexane, cyclohexane, 2-methylpentane, and 3-methylpentane等。由實驗結果分析由於最小立體障礙之因素，活性碳對於直鏈型n-hexane的吸附能力高於環狀與具支鏈的已烷。此外，就分子間的吸引力而言，其通常正比於其沸點。沸點愈高，分子間的吸引力愈大，其於氣相中的擴散速率自然較慢，因而導致活性碳對其吸附效果差。對於C6烷類而言，其沸點高低依序為n-hexane ＞ 3-methylpentane ＞ 2-methylpentane，因此，活性碳對於2-methylpentane的吸附量低於n-hexane與3-methylpentane的吸附量。研究中亦以Langmuir及Freundlich等溫吸附模式對於平衡吸附量進行修正，結果顯示，由Langmuir等溫吸附模式預測吸附量所得之的標準偏差約介於0.0202與0.0251之間，而由Freundlich等溫吸附模式預測吸附量所得之的標準偏差則約介於0.0048與0.0098之間。由等溫吸附曲線觀之，活性碳於低壓狀態下對於C6烷類之吸附作用屬於良性吸附，使得由Freundlich等溫吸附模式對吸附量預測所造成之偏差較低。因此，Freundlich等溫吸附模式較Langmuir等溫吸附模式更適於進行活性碳對於C6烷量吸附量之預測。

關鍵詞： 吸附、活性碳、Langmuir等溫吸附曲線、Freundlich等溫吸附曲線、揮發性有機物質

Performance Analysis for Various Kinds of Alkanes Adsorbed by Activated Carbon in Fixed Adsorber

HONDA WU[1], SHOW-CHU HUANG[2], AND TSAIR-WANG CHUNG[2]

[1]Department of Fashion Styling & Design, Chungyu Institute of Technology
No. 40, Yi-7th Rd., Keelung 20103, Taiwan R.O.C.

[2]Department of Chemical Engineering, Chung Yuan Christian University,
No. 200, Chung Pei Rd., Chung Li, Taiwan 32023, R.O.C

ABSTRACT

The gravimetric adsorption method was used to conduct adsorption of volatile organic compounds (VOCs) on activated carbon. The equilibrium experiments were controlled at 298.15 K. The sorbates (VOCs) included n-hexane, cyclohexane, 2-methylpentane, and 3-methylpentane. The experimental results showed that adsorption capacity for n-hexane is higher than that of cyclohexane and C_6 alkanes with side chain due to the least geometric barrier. In addition, the attractive force between molecules is increased with the increased boiling point, and then the order of adsorption capacity in the ascent is n-hexane, 3-methylpentane, 2-methylpentane. The equilibrium adsorption capacities were correlated by the Langmuir and the Freundlich isotherm models in this study. The average deviations for the Langmuir and the Freundlich isotherm models predicting the adsorption capacities were from 0.0202 to 0.0251 and from 0.0048 to 0.0098 respectively. Since the favorite isotherm and the higher adsorption capacity for C_6 alkanes adsorbed onto activated carbon in low pressure, the derivation was smaller for the Freundlich isotherm model. Therefore, the Freundlich model was more suitable than the Langmuir model to fit the C_6 alkanes adsorbed by the activated carbon.

Key Words: Adsorption, activated carbon, isotherm model, VOCs

1、Introduction

Volatile organic compounds (VOCs) are the main air pollutants for the chemical, painting, and printing industries. They are harmful for the human body and the environment. There are many cautions suggested to reduce the concentration of VOCs. For example, the use of the cement with the additive of formaldehyde is diminished, and the environments of human life are ventilated excellently. Since n-hexane, cyclohexane, 2-metthyl- pentane, and 3-methylpentane were emitted from gasoline storage, petrochemical or solvent industries, the linear, cyclo- and branched C6 alkanes were used as sorbates in this study.

The VOCs removal technologies can be categorized into the nondestructive and the destructive methods. Generally speaking, the chemical reaction does not occur in the nondestructive process, and the VOCs can be desorbed from adsorbent. The common nondestructive methods include adsorption, absorption, condensation and membrane separation etc. On the other hand, the adsorbed VOCs are usually translated into water and carbon dioxide in the destructive process. The common destructive methods include oxidation, and bio-filtration etc.[1] Not only removing VOCs economically but also reusing VOCs desorbed from adsorbent are the advantages for the method of adsorption.

The internal surface area is larger than the external surface area for the activated carbon, and the amount of VOCs adsorbed on the porous adsorbent is determined by the internal surface area. Besides, the specific surface area is 500-1500 m^2g^{-1} for the activated carbon, whose pore diameter is in the scale of nanometer. Therefore, the porous activated carbon with larger internal surface area is selected to remove VOCs in this study.

The design of adsorption apparatus requires some equilibrium data, and they are usually acquired from conducting the adsorption experiment.[2] One of the equilibrium data is the equilibrium adsorption isotherm, and it is often referred to design an adsorber. The amount of adsorbent needed in an adsorber is determined by the equilibrium data, and the selection of an effective adsorbent is dependent on the equilibrium isotherm also. In this study, the equilibrium isotherm data were obtained by using a static gravimetric method in which the amount of VOCs adsorbed onto a solid surface was measured by a microbalance, and the equilibrium adsorption capacity was a function of pressure or concentration of VOCs at a specific temperature.

Many isotherm models had been proposed to describe the adsorption performance and mechanism. The Freundlich and the Langmuir models were the oldest and most frequently used

isotherm models. The Langmuir model was usually used to fit the data operated in the low-intermediate concentration range, and the Freundlich model was used for describing the adsorbent with nonuniform adsorbent surface and the higher pressure. As mentioned from above, the factors included system pressure, the characteristic of adsorbent and adsorption mechanism etc. must be considered for selection of the adsorption isotherm. Therefore, the adsorption equilibrium data for VOCs adsorbed onto the activated carbon were correlated by the Freundlich and the Langmuir isotherm models in this study.

2、Experimental Section

2.1 Sorbents

The commercial activated carbon in granular type, which was supplied from China Activated Carbon Industries Co., was selected in this study. The specific surface of activated carbon was usually higher than that of silica gel and zeolite. The surface properties were measured by a BET sorptometer (Micromeritics ASAP 2000) and shown in Table 1. The sorbent was degassed at 473.15 ±1 K under vacuum before the adsorption measurements of nitrogen were carried out at 77 ± 1 K. The specific surface area, pore volume, and average pore diameter were calculated by the BET method.[3]

Table 1 Physical Properties of Activated Carbon

Property	Value
BET surface area/$m^2 \cdot g^{-1}$	1000
Pore volume/$cm^3 \cdot g^{-1}$	0.145
Pore diameter/nm	2.6

2.2 Chemicals

In this study the purity of C6 alkanes were chosen in the grade of reagent to generate VOCs in each adsorption process. N-hexane and cyclohexane were purchased from Tedia Company Inc, and their purities were beyond 99%. 2-methylpentane and 3-methyl- pentane were purchased from Lancaster Synthesis and their purities were beyond 97%.

2.3 Apparatus and Procedure

Figure 1 shows the adsorption equipment used in this study. The mass change during adsorption was measured by the electronic microbalance (Cahn C-33). The uncertainty of the microbalance is ± 0.1 μg. The pressure of this system was controlled from 1.333×10^2 Pa (1 mm-Hg) to 14.399×10^3 Pa (108 mm-Hg) and measured with a pressure gauge (Cole Parmer U-68700, uncertainty =±0.1333 Pa).

The step-by-step operating procedure for measuring the adsorption capacity (uptake) of VOCs on the sorbent by using the static adsorption system is provided below:

(1) After regeneration in a vacuum dryer (373.15 K, 24h), place 50 mg granular sorbent on a pan of the electric microbalance (Cahn C-33).

(2) Put the liquid sorbate into the glass bottles in Figure 1. Repeat the degassing procedure at least three times (thawing then freezing).

(3) Bring the vapor of the liquid sorbate (VOCs) into the adsorption system.

(4) After equilibrium, record the amounts of the sorbent and sorbate and the pressure of the adsorption system.

(5) Bring the vapor of the liquid sorbate into the adsorption system again to change the pressure of the VOCs.

(6) After equilibrium, record the amounts of the sorbent and sorbate and the pressure of the adsorption system again.

(7) Repeat steps 5 and 6 until saturated pressure is attained.

3、Results and Dissusion

3.1 Adsorption Capacity

The test of the adsorption apparatus was performed by comparing the experimental results with the literature data. The studies related to the different geometric structure of the selected sorbates adsorbed onto the activated carbon were rare in the open literature. Helminen et al.[4] studied the adsorption of NH3 by using some organic or inorganic sorbents. One of the sorbents used was the activated carbon. Since the surface properties of the activated carbon and the operating conditions set by Helminen et al. (2001) were similar to this study, the equilibrium adsorption capacity of NH3 on the activated carbon was compared to that of this study. The properties of the activated carbon and equilibrium uptakes of Helminen et al.[4] and this work were compared in Table 2. The amounts of the

sorbate adsorbed onto the sorbent were directly measured by a electronic microbalance in the static gravimetric method in this study, whereas they were calculated by the ideal gas law in the static volumetric method in the study of Helminen *et al.*[4] Both methods were used in the literature to get the equilibrium uptakes of gases. However, the mass change for the microanalysis was trended to measure by the electronic microbalance recently. Since a good agreement of the equilibrium data in the literature and this work was obtained, the adsorption apparatus of this study was considered adequate. Volatile organic compounds (VOCs) used in this study include n-hexane, cyclohexane, 2-methylpentane, and 3-methyl-pentane. The adsorption capacities of the VOCs on the activated carbon were listed in Table 3. Adsorption experiments were conducted at 298.15K for these VOCs adsorbed onto the activated carbon. The relationship between adsorption capacity and relative pressure, p/p_0, was depicted as the adsorption isotherm and shown in Figure 2. The p_0 represents the vapor pressure of the liquid solvent at 298.15 K. Due to the stronger attractive forces between C6 alkanes and activated carbon and the pore diameter in the scale of nanometer, the adsorption isotherm of vapor of C6 alkanes onto the activated carbon were tended toward the type Ⅰ, which was based on the classification of adsorption isotherm by Brunauer *et al.*[5] and IUPAC.
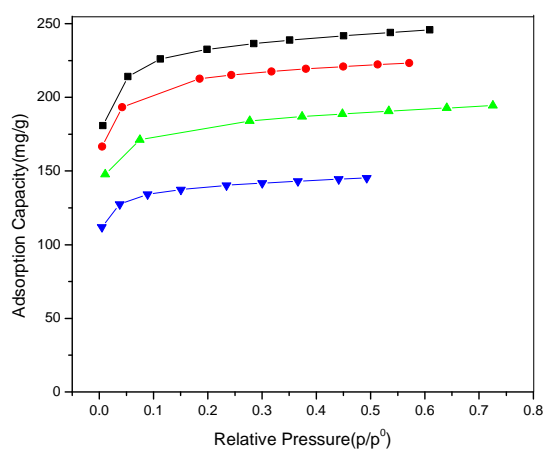

Figure 2 Adsorption capacities for C_6 alkanes adsorbed by activated carbon at different pressures: ■, n-hexane; ●, 3-methylpentane;▲, cyclohexane;▼, 2-methylpentane

Table 2 Comparisons of the Adsorption System and THE Equilibrium Uptake of Helminen *et al.* and This work

	Helminen *et al.* (2001)	this work
apparatus	static volumetric apparatus	static gravimetric apparatus
sorbate	ammonia gas	C6 alkanes
sorbent	activated carbon	activated carbon
a/m²g⁻¹	455	545
T^a/K	298	298
q^b/mg · g⁻¹	13	12.7

a: Temperature
b: Uptake

Table 3 Experimental Data of This Work

n-hexane		cyclohexane		2-methylpentane		3-methylpentane	
P/P⁰	q/mg.g⁻¹	P/P⁰	q/mg.g⁻¹	P/P⁰	q/mg.g⁻¹	P/P⁰	q/mg.g⁻¹
0.007	180.742	0.005	111.930	0.005	166.578	0.005	166.578
0.053	214.025	0.038	127.535	0.042	193.320	0.042	193.320
0.113	226.068	0.089	134.242	0.185	212.755	0.185	212.755
0.199	232.647	0.150	137.344	0.243	215.230	0.243	215.230
0.285	236.522	0.235	140.248	0.317	217.627	0.317	217.627
0.351	238.843	0.300	141.811	0.381	219.359	0.381	219.359
0.450	241.775	0.366	143.140	0.450	220.896	0.450	220.896
0.536	244.044	0.441	144.469	0.513	222.290	0.513	222.290
0.609	245.789	0.493	145.355	0.571	223.319	0.571	223.319

Table 4 Regressed Values of q_0 and b in the Langmuir Isotherm Model

sorbent	sorbate	q_0	b	D
Activated carbon	n-hexane	237.53	3.096	0.024
	cyclohexane	189.04	3.458	0.020
	2-methylpentane	140.45	3.787	0.025
	3-methylpentane	217.39	3.172	0.022

Table 5 Regressed Values of K and n in the Freundlich Isotherm Model

sorbent	sorbate	K	n	D
Activated carbon	n-hexane	183.72	0.067	0.010
	cyclohexane	148.99	0.064	0.005
	2-methylpentane	112.89	0.055	0.005
	3-methylpentane	168.16	0.063	0.007

Since the pore size of the activated carbon is larger than molecular diameter of the C6 alkanes slightly, the adsorption capacity will be affected by the geometric structure of the adsorbates. Because of the least geometric barrier, the adsorption capacity for n-hexane with straight chain is higher than that of cyclohexane and C6 alkanes with side chain, as shown in Figure 2. In addition to effect of geometric barrier, the boiling point of C6 alkanes must be taken into account. The lower is the boiling point, the weaker the attractive force between molecules is. In other words, the weaker attractive force may lead VOCs to diffuse or vaporize to the gas phase easily, and the adsorption capacity will be decreased along with the lower boiling point. Since the sequence of boiling point for

C6 alkanes is n-hexane > 3-methylpentane > 2-methylpentane, the adsorption capacity of 2-methylpentane onto activated carbon is smaller than others.

3.2 Adsorption Isotherm Model

In order to offer the effective information to design the adsorber, the equilibrium datashould be correlated by the adsorption isotherm model. Although the Langmuir isotherm model[6] was suitable for fitting in the low to intermediate pressure, the higher pressure and nonuniform surface of adsorbent were usually ascribed to the field of Freundlich isotherm model[7]. Therefore, both of the Langmuir and Freundlich isotherm models were adopted to correlate the equilibrium adsorption capacity of this study to elucidate the adsorption mechanism of vapor of C6 alkanes onto the activated carbon. The mathematical forms of these models are as follows:

Langmuir model：$\quad q = \dfrac{q_0 bp}{1 + bp}$ (1)

Freundlich model: $\quad q = Kp^n$ (2)

where q is the adsorption capacity (mg sorbate/g sorbent), q_0 is the saturated adsorption capacity (mg sorbate/g sorbent), b is the adsorption equilibrium constant, K is the Freudlich constant, p is the vapor pressure of the alkanes (mm Hg), and n is the Freudlich exponent. Linearizing the Langmuir isotherm model, Figure 3 was obtained to show the relationship between p/q and p. From Figure 3, the q_0 was calculated by the formula of 1/intercept, and the constant b was estimated as the value of intercept divided by slope. The regressed values of q_0 and b were shown in Table 4. Similarly, the Freundlich isotherm model was linearized to get the Figure 4, ln q vs. ln p. From the slope and intercept of Figure 4, the values of K and n can be acquired, as shown in Table 5. Figure 5 shows the experimental adsorption capacity and the regressed curve for the Langmuir isotherm model. Figure 6 shows the experimental adsorption

capacity and the regressed curve for the Freundlich isotherm model. The average deviations, D, were calculated by the eq. (3),

$$D = \frac{1}{N} \sum_{i=1}^{n} \left| \frac{q_i^{\exp} - q_i^{cal}}{q_i^{\exp}} \right|$$ (3)

where N is the number of data points at a given temperature and $q$exp and $q$cal are the experimental and calculated adsorption capacities respectively. The average deviations predicted by the Langmuir and the Freundlich isotherm models are from 0.0202 to 0.0251 and from 0.0048 to 0.0098 respectively. The deviation in the Freundlich modelis smaller than that in the Langmuirmodel to predict the adsorption capacities for vapor of C6alkanes adsorbed onto the activated carbon. By means of deviations, the results can be deduced that the Freundlich modelis thebetter adsorption isotherm to fit the data of this study than the Langmuirmodel.In general, the Langmuir isotherm model is usually applied in the low to intermediate pressure, and the adsorption capacity levels off along with the increased pressure. However, from Figures 5 and 6, the adsorption capacitiesincreased gradually, and resulted in the higher deviation by the prediction of the Langmuir isotherm model. Oppositely, the adsorption isotherms for vapor of C6 alkanes adsorbed onto the activated carbon belong to the favorite isotherm by analyzing from Figure 2 and the regressed data. Generally speaking, the lower adsorption capacity produces the higher deviation in the low pressure, as the Freundlich isotherm model is used to correlate the adsorption capacity. However, the favorite isotherm and the higher adsorption capacity in the low pressure for vapor of C6 alkanes adsorbed onto the activated carbon would result in the better fit for the Freundlich isotherm model. Therefore, the Freundlich isotherm model offers the better description for equilibrium adsorption capacities of vapor of C6 alkanes onto the activated carbon in this study.
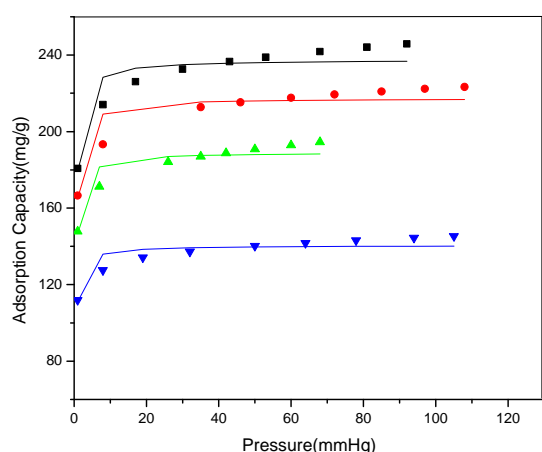
Figure 3 Experimental and correlated isotherms for C_6 alkanes adsorbed onto activated carbon: ■, n-hexane; ●, 3-methyl-pentane; ▲, cyclohexane; ▼, 2-methylpentane; —, Langmuir model
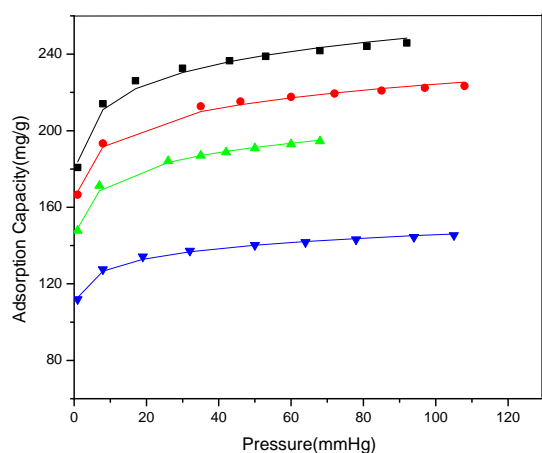

Figure 4 Experimental and correlated isotherms for C_6 alkanes adsorbed onto activated carbon: ■, n-hexane; ●, 3-methyl-pentane; ▲, cyclohexane; ▼, 2-methylpentane; —, Freundlich model

4、Conclusion

The static gravimetric apparatus was applied to measure the equilibrium adsorption capacity. The adsorption isotherms of C6 alkanes onto the activated carbon were obtained at 298.15K in this study. Not only the molecular structure but also the boiling points for the sorbates were used to discuss the adsorption performance. Based on the system pressure and adsorption mechanism, the Langmuir and the Frenudlich models were adopted to fit the experimental data. Since the favorite isotherm and the higher adsorption capacity in the low

pressure were found in the vapor of C6 alkanes adsorbed by the activated carbon, the average deviation for the Freundlich model was smaller than that for the Langmuir model.

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