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Adsorption characteristics of binary vapors among acetone, MEK, benzene, and toluene

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Abstract−Adsorption dynamics of single and binary vapor systems on the activated carbon bed were studied by using acetone, methylethyketone (MEK), benzene, and toluene. Relationships between the equilibrium adsorption capacity and the characteristics of vapors such as molecular weight, density, boiling point, vapor pressure, molecular diameter, and polarity index were also investigated. From breakthrough experiments, toluene had the strongest affinity with activated carbon in the single and binary vapor systems. The shape of the breakthrough curves of vapor with higher affinity in the binary system was similar to that of the single vapor. On the other hand, the vapor with lower affinity showed a roll-up phenomenon, but the level of roll-up became lower and wider with the increase in fraction in the binary system.

Key words: Adsorption, Activated Carbon, Binary Vapor, Fraction, Acetone, MEK, Benzene, Toluene, Breakthrough Curve

INTRODUCTION

Volatile organic compounds (VOCs) are critical toxic gases that are significantly higher in indoor air than in outdoor air [1]. These contaminants may have significant effects on the eyes and nose, and long-term exposure may even cause cancer. The usual way to diminish the harmful effects of these compounds is to reduce the concentration of VOCs. Many methods to treat these VOCs have been developed. Among these methods, the adsorption method by activated carbon is considered as the most effective technology [2,3]. Many researchers [4-8] have studied the adsorption characteristics of VOCs on various activated carbons using dynamic adsorption method. These studies are mainly limited to a single vapor among various VOCs [9-11]. But most VOCs are composed of multi-components and mixed with each other. Also, it is thought that the adsorption characteristics of a multi-component vapor system are different from that of single vapor system. Knowledge of the interaction and competition of different gases in adsorption process design is necessary. However, most researches for multicomponent have focused on the model studies [12-15], because multi-component vapor is difficult to treat and analyze the concentrations. And there are few studies [16-18] concerning the breakthrough characteristics for binary and ternary vapors according to the fraction of each component among VOCs. Yun et al. [19] studied the equilibria and dynamics for mixed vapors of BTX in an activated carbon bed. However, the purpose of this study is to compare the breakthrough curves according to fractions of each binary vapor to understand the competitive adsorption behavior of mixtures. For these purposes, binary vapors composed of two components among acetone, MEK, benzene, and toluene were used, and breakthrough experiments were carried out using dynamic adsorption.

EXPERIMENTAL

Coconut-based granular activated carbon obtained from Calgon, U.S.A. in the particle size of 8-12 mesh was used as adsorbent. Characteristics of the activated carbon calculated by BET analyzer (Micromeritics, ASAP-2010) are listed in Table 1. BET specific surface area was compared with total pore volume and average pore diameter. Pore size distribution of the activated carbon measured by BET analyzer is illustrated in Fig. 1. The activated carbon has micropores under 30 Å mainly and the pores in the range of 30-2,000 Å. This activated carbon was used in this experiment after drying at 120 °C for 5 hrs. Acetone, methylethylketone (MEK), benzene, and toluene of 99.9% grade obtained from Samchun Chemical Co., Ltd., Korea were used as adsorbate without purification. And characteristics of the adsorbates are listed in Table 2.

Table 1. Characteristics of activated carbon used as adsorbent

Properties	Values
Raw material	Coconut shell
BET specific surface area (m^2/g)	1,241
Total pore volume (cm^3/g)	0.61
Average pore diameter (Å)	19.80

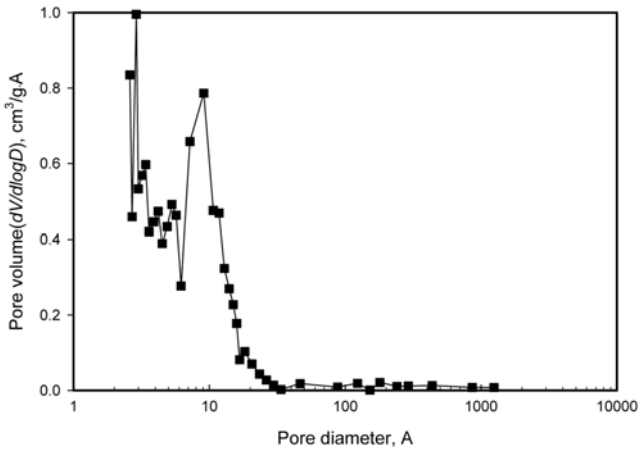

Fig. 1. Pore size distribution measured by BET analysis for coconut-based granular activated carbon.

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Table 2. Characteristics of adsorbates

Adsorbate	Formula	Molecular weight (g/mol)	Density at 25 °C (g/ml)	Boiling point at 760 mmHg (°C)	Vapor pressure at 20 °C (mmHg)	Molecular diameter [22] (Å)	Polarity index [23]
Acetone	CH_3COCH_3	58.08	0.791	56	184	4.82	5.1
MEK	$CH_3COC_2H_5$	72.11	0.805	80	71	5.25	4.7
Benzene	C_6H_6	78.11	0.874	80	74.6	5.26	2.7
Toluene	$C_6H_5CH_3$	92.14	0.865	110.5	22	5.68	2.4

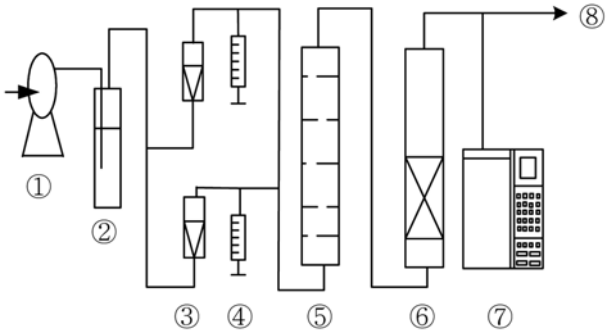

Fig. 2. Schematic diagram of experimental apparatus.
① Air pump
② Drying bottle
③ Flowmeter
④ Syringe pump
⑤ Mixing chamber
⑥ Adsorption bed
⑦ GC
⑧ Vent

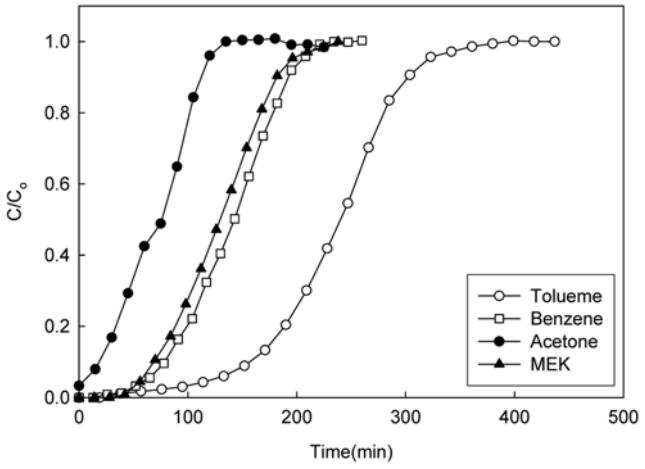

Fig. 3. Comparison of breakthrough curves of single vapor composed of acetone, MEK, benzene, and toluene on activated carbon, respectively (inlet concentration: 200 ppmv, flow rate: 4 *l*/min, activated carbon: 2 g) [8].

Adsorption experiments were performed in a laboratory controlled at 20 °C by using the apparatus shown in Fig. 2, and a fixed-bed prepared by Pyrex tube of 16 mm inside diameter was used. Air from an air pump (Young Nam Yasunaga Co. Ltd. LP-40A) was fed to the bottle packed with silica gel in order to minimize the effect of moisture during adsorption. The single vapors were prepared by vaporizing the adsorbates, acetone, MEK, benzene, and toluene that flowed out from the syringe pump (Cole Parmer International, U.S.A p-74901-10) with the dried air. The concentration of binary vapor was controlled by regulation of each flowmeter of single vapor. The single vapor was combined into a binary vapor according to mole fraction, and the binary vapor flowed into the bottom side of the reactor and flowed out from the upside. The upside of the reactor was connected to the injection port of the gas chromatograph (GC, Donam DS-6200), and the vapor concentration was analyzed at interval of 10 minutes. The equilibrium adsorption capacity was calculated by the area of breakthrough curve and confirmed by measuring the weight difference before and after the adsorption.

RESULTS AND DISCUSSION

1. Relations between Equilibrium Adsorption Capacity and Characteristics of Single Vapor

To compare breakthrough characteristics of single vapor composed of acetone, MEK, benzene, and toluene, a breakthrough experiment was carried out at 20 °C in the following conditions: inlet concentration 200 ppmv, flow rate 4 *l*/min, activated carbon 2 g. Breakthrough curves are compared in Fig. 3 [8]. Breakthrough time was defined as the time when the outlet concentration was 10% of inlet concentration. The breakthrough times of single vapor of acetone, MEK, benzene, and toluene were 20 min, 70 min, 80 min, and 160 min, respectively. The times needed to reach at equilibrium with acetone, MEK, benzene, and toluene vapor were 135 min, 240 min, 250 min, and 400 min, and the equilibrium adsorption capacities of acetone, MEK, benzene, and toluene vapor were 71 mg/g, 170 mg/g, 200 mg/g, and 320 mg/g, respectively. The breakthrough time of acetone vapor among these vapors was the fastest, and breakthrough time of toluene vapor was the latest. MEK and benzene had similar breakthrough characteristics on activated carbon. At the same condition, the equilibrium adsorption capacity of toluene vapor was 4.5 times that of acetone vapor. This result can be explained by the difference of affinity between adsorbate and absorbent, and the differences in characteristics of adsorbates--molecular weight, density, boiling point, and vapor pressure, molecular diameter, polarity index-are shown in Table 2 [10].

To investigate relations between equilibrium adsorption capacity and characteristics of adsorbates (molecular weight, density, boiling point, and vapor pressure, molecular diameter, and polarity index), the relations are illustrated in Fig. 4-Fig. 9. The relation between equilibrium adsorption capacity and density of adsorbate was poor, as illustrated in Fig. 4. And the equilibrium adsorption capacity according to increment of vapor pressure and polarity index showed falling tendency as illustrated in Fig. 5 and Fig. 6. But the correlation coefficients (r^2) between equilibrium adsorption capacity and boiling point, molecular diameter, and molecular weight were over 0.98, as illustrated in Fig. 7-Fig. 9, that is, the higher the boiling point, molecular diameter, and molecular weight were, the greater the equi-

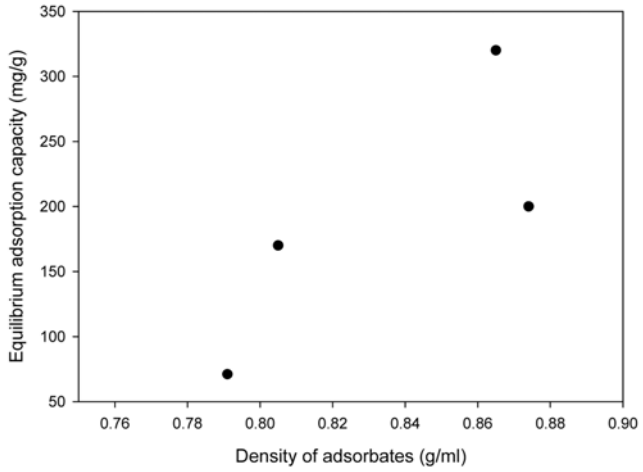

Fig. 4. Relation between equilibrium adsorption capacity and density of adsorbates: acetone, MEK, benzene, and toluene.

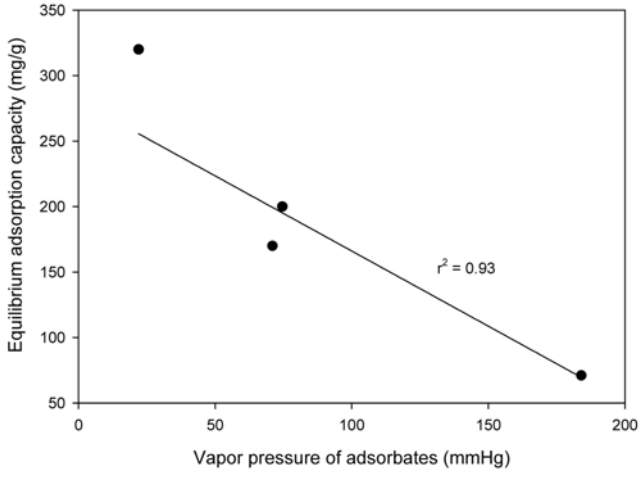

Fig. 5. Correlation between equilibrium adsorption capacity and vapor pressure of adsorbates: acetone, MEK, benzene, and toluene.

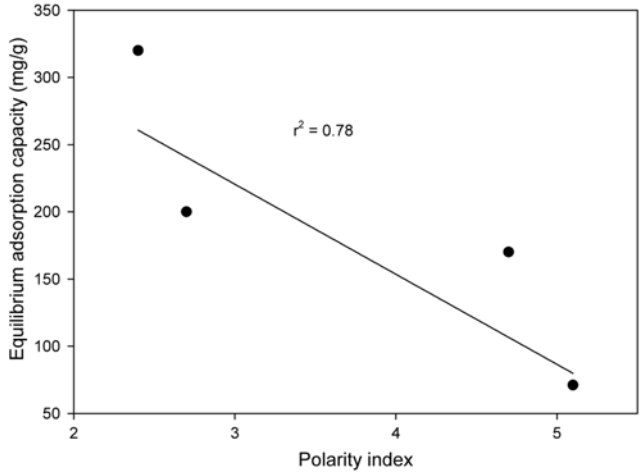

Fig. 6. Correlation between equilibrium adsorption capacity and polarity index of adsorbates: acetone, MEK, benzene, and toluene.

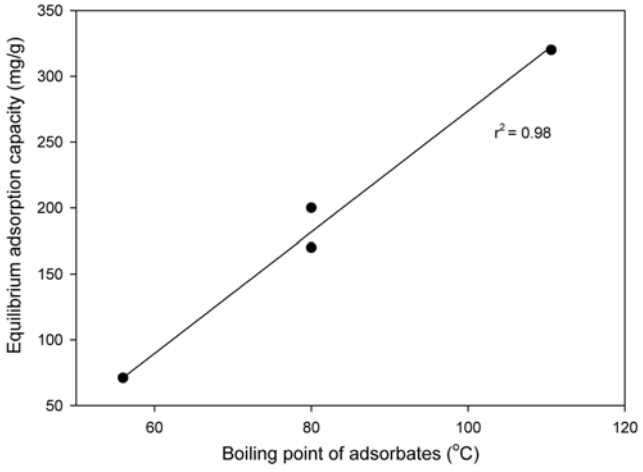

Fig. 7. Correlation between equilibrium adsorption capacity and boiling point of adsorbates: acetone, MEK, benzene, and toluene.

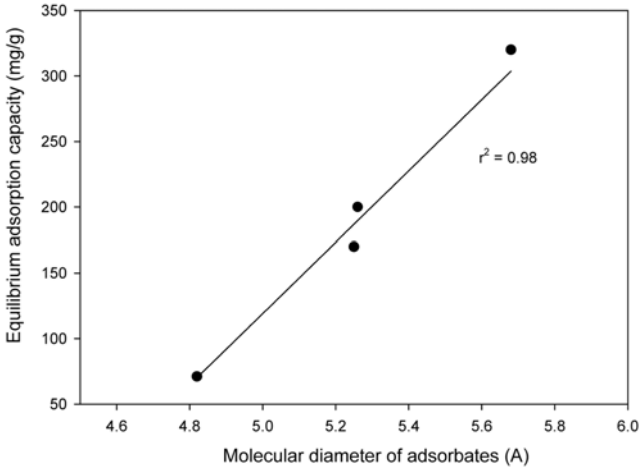

Fig. 8. Correlation between equilibrium adsorption capacity and molecular diameter of adsorbates: acetone, MEK, benzene, and toluene.

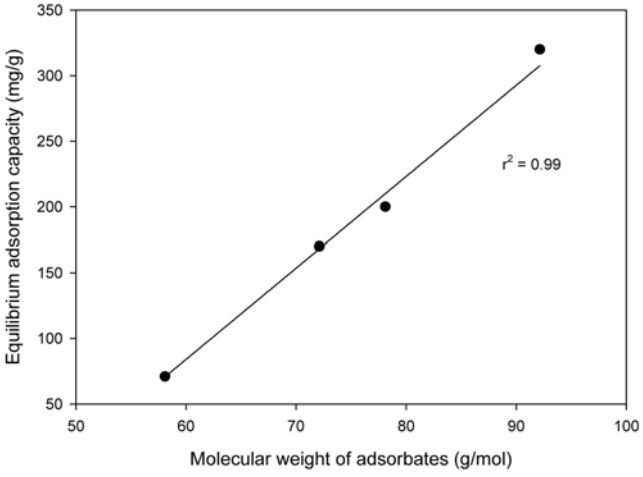

Fig. 9. Correlation between equilibrium adsorption capacity and molecular weight of adsorbates: acetone, MEK, benzene, and toluene.

librium adsorption capacity was. And there was the highest correlation coefficient 0.99 between equilibrium adsorption capacity and molecular weight. When silica-alumina was used as adsorbent, there was a very poor linear relationship between equilibrium adsorption capacity and characteristics of adsorbates [20]. But when activated carbon was used as adsorbent, there was good linear relationship between equilibrium adsorption capacity and characteristics of adsorbates. The non-polar nature of activated carbon showed a high affinity toward non-polar organic compounds. The results showed non-polar and larger molecules adsorbed better than polar and smaller molecules.

2. Effects of Fraction of Binary Vapors on Breakthrough Curves

To investigate the effect of fraction of binary vapor on breakthrough curves, breakthrough experiments were carried out at 20 °C in the following conditions: total inlet concentration of binary vapor 200 ppmv, fraction of each vapor in binary vapor 0.2, 0.5, and 0.8, flow rate 4 l/min, activated carbon 2 g. Polar organic compounds, acetone and MEK, and non-polar organic compounds, benzene and toluene were used as adsorbate to investigate breakthrough characteristics based on polarity of binary vapor on activated carbon. Binary vapors with the same polarity as each other and binary vapors with different polarity from each other were used as adsorbate in this study, respectively. Breakthrough curves according to fraction of binary vapor composed of acetone and MEK are compared in Fig. 10, breakthrough curves of binary vapor composed of benzene and toluene are compared in Fig. 11, and breakthrough curves of binary vapor composed of acetone and benzene are compared in Fig. 12. Breakthrough curves of binary vapor composed of MEK and benzene are compared in Fig. 13, breakthrough curves of binary vapor composed of acetone and toluene are compared in Fig. 14, and breakthrough curves of binary vapor composed of MEK and toluene are compared in Fig. 15. The roll-up phenomena were observed at all of the breakthrough curves. Those roll-up phenomena were thought due to the difference of adsorption force of each vapor on the surface of activated carbon. Vapor with weaker adsorption ability between two vapors on the surface of activated carbon was displaced

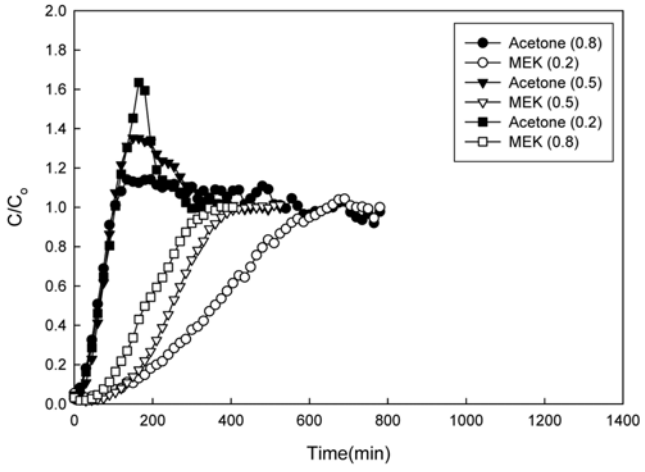

Fig. 10. Effect of fraction of binary vapor composed of acetone and MEK on breakthrough curve: acetone (●)/MEK (○)= 0.8/0.2, acetone (▼)/MEK (▽)=0.5/0.5, acetone (■)/MEK (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 l/ min, activated carbon: 2 g).

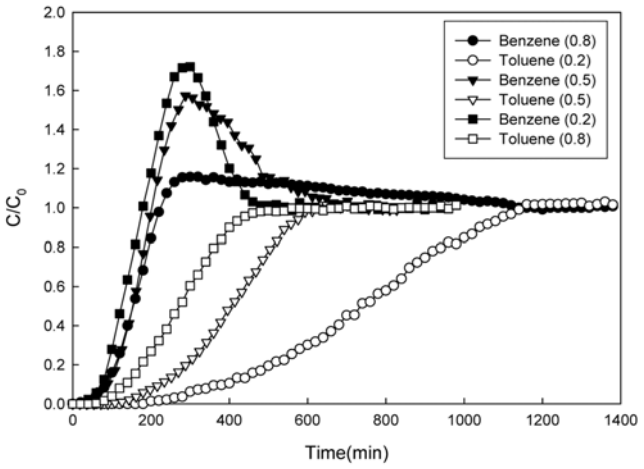

Fig. 11. Effect of fraction of binary vapor composed of benzene and toluene on breakthrough curve: benzene (●)/toluene (○) =0.8/0.2, benzene (▼)/toluene (▽)=0.5/0.5, benzene (■)/ toluene (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 l/min, activated carbon: 2 g).

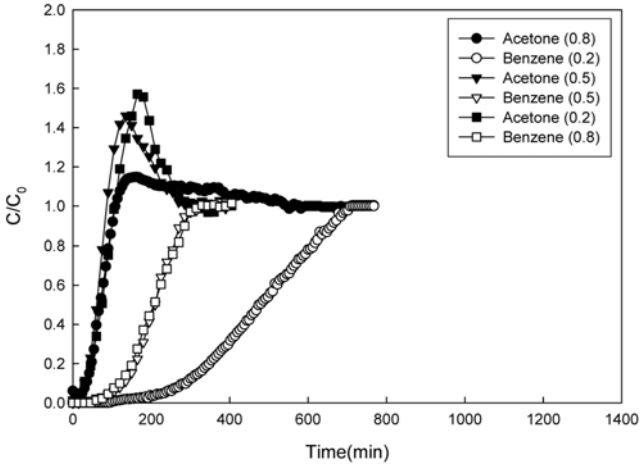

Fig. 12. Effect of fraction of binary vapor composed of acetone and benzene on breakthrough curve: acetone (●)/benzene (○) =0.8/0.2, acetone (▼)/benzene (▽)=0.5/0.5, acetone (■)/ benzene (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 l/min, activated carbon: 2 g).

by vapor with stronger adsorption ability during adsorption process and discharged. This is due to an affinity difference between adsorbate and adsorbent. On the basis of higher affinity vapor, the breakthrough curves were similar to the single vapor. The higher fraction was, the faster breakthrough time was, and the slope of breakthrough curve was gradually increased [21]. Because of lower affinity vapor, the higher the fraction was, the lower the level of roll-up was, and the time needed to reach equilibrium was increased. Therefore, displacement in higher fraction progressed more slowly than that in lower fraction. The breakthrough curves of binary vapor composed of the same polarity were compared in Fig. 10 and Fig. 11. Fig. 10 is the breakthrough curves of polar vapors, acetone and MEK, and Fig. 11 is breakthrough curves of non-polar vapors, benzene and toluene. As shown in Fig. 10, MEK vapor has stronger affinity with

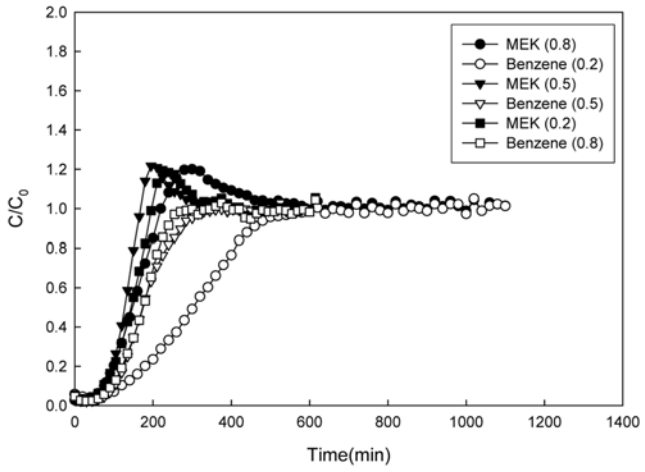

Fig. 13. Effect of fraction of binary vapor composed of MEK and benzene on breakthrough curve: MEK (●)/benzene (○) =0.8/0.2, MEK (▼)/benzene (▽)=0.5/0.5, MEK (■)/benzene (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 *l*/min, activated carbon: 2 g).

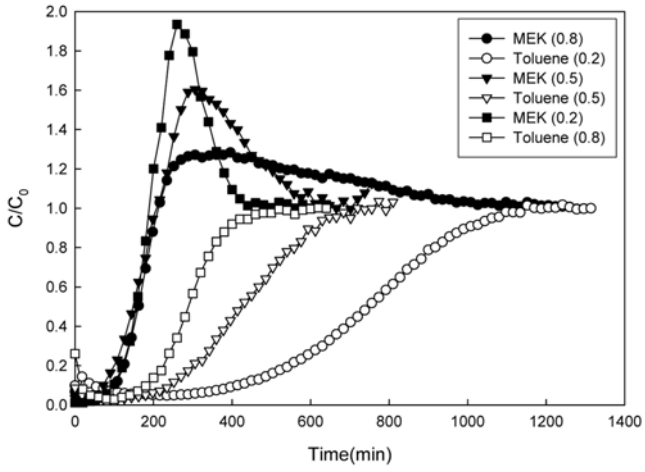

Fig. 15. Effect of fraction of binary vapor composed of MEK and toluene on breakthrough curve: MEK (●)/toluene (○) =0.8/0.2, MEK (▼)/toluene (▽)=0.5/0.5, MEK (■)/toluene (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 *l*/min, activated carbon: 2 g).

activated carbon than that of acetone vapor. And as shown in Fig. 11, toluene vapor has stronger affinity with activated carbon than that of benzene vapor. The breakthrough time and the time needed to reach at equilibrium of non-polar toluene vapor were relatively longer than that of polar MEK vapor. The breakthrough curves of binary vapor composed of different polarity vapors are compared in Fig. 12, Fig. 13, Fig. 14, and Fig. 15. As shown in Fig. 12, non-polar benzene vapor has stronger affinity with activated carbon than that of polar acetone vapor. Also as shown in Fig. 13, non-polar benzene vapor has stronger affinity with activated carbon than that of polar MEK vapor. The breakthrough curves in Fig. 12 are similar to the breakthrough curves in Fig. 10. The level of roll-up in Fig. 13 is lowest among breakthrough curves of binary vapor in this study.

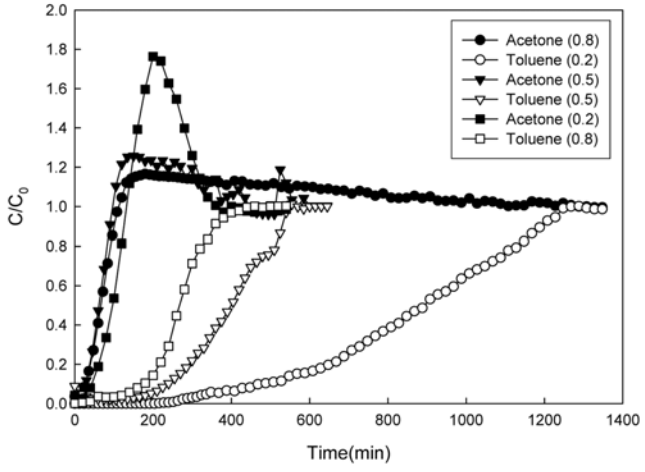

Fig. 14. Effect of fraction of binary vapor composed of acetone and toluene on breakthrough curve: acetone (●)/toluene (○) =0.8/0.2, acetone (▼)/toluene (▽)=0.5/0.5, acetone (■)/toluene (□)=0.2/0.8 (inlet concentration: 200 ppmv, flow rate: 4 *l*/min, activated carbon: 2 g).

It was thought that MEK and benzene had similar characteristics except polarity as shown in Table 2. As shown in Fig. 14, non-polar toluene vapor has stronger affinity with activated carbon than that of polar acetone vapor. Also as shown in Fig. 15, non-polar toluene vapor has stronger affinity with activated carbon than that of polar MEK vapor. The breakthrough curves in Fig. 14 are similar to the breakthrough curves in Fig. 15. The level of roll-up in Fig. 15 is highest among breakthrough curves of binary vapor in this study. It was thought that toluene had the strongest affinity with activated carbon among the compared non-polar and polar vapors. So the lower the polarity index value of adsorbate was, the higher the adsorption affinity with activated carbon was. The adsorption amount of adsorbate in binary component systems was lower than that in its single component system, due to the competitive adsorption.

CONCLUSIONS

Single and binary adsorption experiments composed of acetone, MEK, benzene, and toluene on activated carbon were carried out in activated carbon fixed-bed reactor. In the relationship between equilibrium adsorption capacity and characteristics of adsorbates, the highest correlation coefficient (r^2) was in the relation between equilibrium adsorption capacity and molecular weight. The adsorption amount of adsorbate in the binary component system was lower than that in its single component system, due to the competitive adsorption. The non-polar nature of activated carbon showed a high affinity toward non-polar organic compounds. The results showed non-polar and larger molecules adsorbed better than polar and smaller molecules.

Breakthrough characteristics of binary vapor were compared to study the effect of fraction and polarity difference of binary vapor. Vapor with weaker adsorption ability on activated carbon between two vapors was displaced by vapor with stronger adsorption ability during adsorption process and discharged. Toluene had the strongest affinity with activated carbon among the compared non-polar

and polar vapors. The shape of the breakthrough curves of vapor with higher affinity in the binary system was similar to that of the single vapor. On the other hand, the vapor with lower affinity showed a roll-up phenomenon, but the level of roll-up becomes lower and wider with the increase in fraction in the binary system.

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