Adsorption Isotherms of Benzene and Toluene on Corn Grain-Based Carbon Monolith at (303.15, 313.15, and 323.15) K

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The adsorption isotherms of benzene and toluene on a newly made corn grain-based carbon monolith were measured at (303.15, 315.15, and 323.15) K using a gravimetric method. The Toth isotherm model was adopted to fit the adsorption equilibrium data of benzene and toluene. The Dubinin−Astakhov equation was used to calculate the total micropore volume of carbon monolith. By using the Clausius−Clapeyron equation, the surface energetic character of the carbon monolith was analyzed. The thermal desorption works were carried out to investigate the interaction between the adsorbates and monolith.

Introduction

Organic compounds which evaporate readily to the atmosphere are called volatile organic compounds (VOCs) as defined by the Environment Protection Agency (EPA). The main origins of VOC emissions include the burning of coal and gasoline and also other sources such as solvents, paints, and cleaners. Benzene, toluene, and other secondary petrochemicals from various sources not only pollute our environment but also threaten human health. The recovery of valuable VOCs is an economically and ecologically feasible method rather than their destruction. A nondestructive adsorption process is one of the most appropriate methods for removing VOCs.

Compared to other adsorbents, activated carbon is the most applicable adsorbent for the removal of VOCs because of its high surface area, easy operation, low operation cost, and high efficiency.[1,2] At low pressure, the adsorption of VOCs is fairly good in micropores compared to mesopores because of the interaction between the attractive forces of the pore walls.[3–5] However in a real situation, the existence of mesopores with micropores in most activated carbons is an unavoidable fact.

On the other hand, by making a monolithic form of carbon, the adsorption of VOCs can be increased by a reduction of excess void volumes as well as the level of mesopores, while maintaining a high level of micropores. Other applications of monolith forms are compact size, easy handling, low pressure drop, very comfortable for mobile systems, and the possibility of electrical regeneration.[4–6] However, discussion on the adsorption of VOCs on carbon monolith has been limited.[6,7] Therefore, in this paper, we take advantage of a new corn grain-based carbon monolith for the adsorption of benzene and toluene. The adsorption equilibrium experiments were conducted at three different temperatures (303.15, 313.15, and 323.15) K.

Experimental

Materials. The carbon monolith was made by compressing a mixture of corn grain-based super high surface area activated carbon and sodium derived carboxymethyl cellulose. The prepared carbon monolith was round in shape, and the diameter was about 0.02 m with a width of 0.005 m. The detailed recipe for the preparation of corn grain-based activated carbon is available elsewhere.[8] The surface of the carbon monolith was characterized by a nitrogen adsorption–desorption study at 77 K using a Micrometrics ASAP 2020 analyzer. The monolith sample was dried in a vacuum drier at 423.15 K for 24 h to remove the moisture content and impurities. The adsorbates such as benzene (99.5 % purity) and toluene (99.5 % purity) were purchased from Junsei Chemical Co., Ltd., and used without further treatment.

Gravimetric Apparatus. The schematic diagram of the gravimetric apparatus has been given in our previous papers.[2,9] The adsorbed amount was calculated by measuring the variation of mass in a closed system. At a constant temperature, the solvent vapor was generated in a small chamber and sent into the adsorption part. A given amount of adsorbent was placed into a quartz basket which was connected to the spring balance sensor. The adsorbent sample was weighed with an accuracy of ± 10 μg. At each equilibrium step, the variation in mass was quantified by a digital voltmeter that is connected to the spring sensor. To remove the impurities, the system was evacuated by both a turbomolecular pump (Edward type EXT70) and a rotary vacuum pump (Edward model RV5) for 12 h at 10^{-3} Pa and 523.15 K. Pirani and Penning vacuum gauges (Edward series 1000) were used for the vacuum measurements. The pressure of the system was measured by a Baratron absolute pressure transducer (MKS instruments type 128) with a precision of ± 0.15 %. To overcome the condensation during adsorption, the adsorption cell was placed in a temperature-controlled water bath with a circulator, and the temperature was maintained constant within ± 0.02 K. The adsorption equilibrium studies were performed at three different temperatures (303.15, 313.15, and 323.15) K. The thermal desorptions were carried out for both solvents by heating from (303.15 to 523.15) K with a heating rate of 5 K·min^{-1}.

Results and Discussion

The adsorption and desorption isotherms of nitrogen on the corn grain-based carbon monolith are shown in Figure 1a. This

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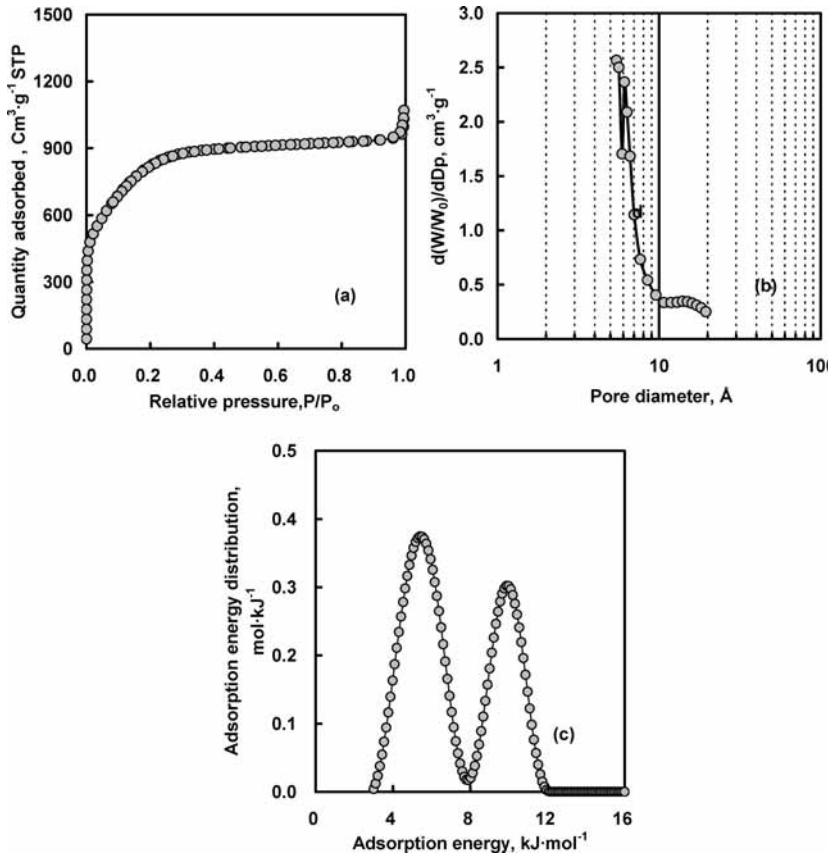

Figure 1. Characterizations of corn grain-based carbon monolith, (a) the adsorption and desorption of nitrogen at 77 K, (b) the HK micropore distribution, and (c) the adsorption energy distribution based on the nitrogen adsorption.

Table 1. Physical Properties of Corn Grain-Based Carbon Monolith

property	value
BET surface area	3065 $m^2 \cdot g^{-1}$
DR micropore volume	1.851 $cm^3 \cdot g^{-1}$
BJH mesopore volume	1.383 $cm^3 \cdot g^{-1}$
HK average pore diameter	7.62 Å
bulk density	0.290 $g \cdot cm^{-3}$

result indicates that the adsorbent has type Ib characteristics according to the IUPAC classification.[10] The Horvath and Kawazoe micropore distribution is shown in Figure 1b. The physical properties of the carbon monolith are listed in Table 1. Usually, the microporous carbons are energetically and structurally heterogeneous solids; therefore, information about these factors is necessary in the adsorption field. The energetic heterogeneity of the corn grain-based carbon monolith was characterized by the adsorption energy distribution (AED).[11] Figure 1c shows the AED for nitrogen on the carbon monolith with two distinct narrow peaks. In the lower energy part, the peak was located in the range between (3.00 and 7.92) $kJ \cdot mol^{-1}$ with a maximum peak value of 5.40 $kJ \cdot mol^{-1}$. A small peak was observed in the higher energy part, compared to the lower energy part, which was located in the range between (7.92 and 12.00) $kJ \cdot mol^{-1}$ with the maximum peak value of 9.99 $kJ \cdot mol^{-1}$.

The adsorption equilibrium data of benzene and toluene on the corn grain-based carbon monolith were obtained at three isotherm temperatures (303.15, 313.15, and 323.15) K, and the data are listed in Tables 2 and 3. As shown in Figures 2a and 2b, the adsorption equilibrium results represent type Ib characteristics according to the IUPAC classification.[10] The maximum benzene adsorption on the carbon monolith

Table 2. Adsorption Isotherm Data for Benzene on Corn Grain-Based Carbon Monolith

303.15 K		313.15 K		323.15 K	
P	*N*	*P*	*N*	*P*	*N*
kPa	$mmol \cdot g^{-1}$	kPa	$mmol \cdot g^{-1}$	kPa	$mmol \cdot g^{-1}$
0.031	1.372	0.123	1.372	0.050	0.529
0.073	2.670	0.310	3.430	0.122	1.132
0.102	3.687	0.614	5.381	0.221	1.835
0.192	4.877	1.131	7.009	0.304	2.298
0.291	6.034	1.712	8.340	0.470	3.207
0.453	7.051	2.480	9.374	0.672	4.133
0.790	8.357	3.453	10.729	0.964	5.075
1.292	10.299	4.481	11.374	1.341	5.985
1.930	11.217	5.424	11.919	1.854	6.852
2.714	12.151			2.413	7.828
3.631	12.391			3.101	8.684
4.653	12.639			3.842	9.428
5.721	12.688			4.804	10.172
				5.650	10.891

was found to be 12.67 $mmol \cdot g^{-1}$ at 303.15 K and 5.721 kPa. For the case of toluene, it was 10.62 $mmol \cdot g^{-1}$ at 303.15 K and 2.391 kPa. Because of the high surface area, benzene and toluene adsorption capacities of the prepared corn grain-based carbon monolith are high compared to other adsorbents such as activated carbons,[12–14] activated carbon fiber,[1] and monoliths.[6,7]

The preliminary adsorption experimental data must be examined using either a theoretical or empirical equation for the analysis and design of an adsorption separation process.[15] The isotherm data were correlated with the Toth isotherm model which is widely known and highly applicable for correlation of adsorption measurements involving heteroge-

Table 3. Adsorption Isotherm Data for Toluene on Corn Grain-Based Carbon Monolith

303.15 K		313.15 K		323.15 K	
P	*N*	*P*	*N*	*P*	*N*
kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}
0.050	1.530	0.064	1.593	0.052	0.477
0.112	2.912	0.133	2.821	0.114	1.193
0.223	4.358	0.271	4.204	0.180	2.456
0.364	5.979	0.423	5.656	0.262	3.425
0.606	7.636	0.682	7.200	0.383	4.660
0.882	9.222	0.974	8.541	0.541	5.846
1.243	10.106	1.408	9.762	0.764	7.060
1.820	10.520	1.912	10.267	1.011	8.000
2.391	10.618	2.453	10.422	1.282	8.709
				1.613	9.404
				1.940	9.797
				2.314	10.204

neous adsorbents. The Toth isotherm is a simple and highly accurate one at both low and high pressures.

$$N = \frac{mP}{(b + P^t)^{1/t}} \tag{1}$$

where P is the equilibrium pressure; N is the moles adsorbed; and m, b, and t are the model parameters. The total micropore volume of the carbon monolith was also evaluated using the Dubinin−Astakhov (DA) equation which is based on potential theory. This isotherm equation is reasonably good in explaining adsorption equilibria of organic vapors onto microporous activated carbon.[15]

$$W = W_0 \exp\left[-\left(\frac{\epsilon}{\beta E^0}\right)^r\right] \tag{2}$$

$$W_0 = NV^0, \quad \epsilon = RT \ln\left(\frac{P^*}{P}\right) \tag{3}$$

where W is the volume of the adsorbate in the micropore; W_0 is the maximum volume that the adsorbate can occupy; T is the temperature; P^*/P is the relative pressure; R is the universal gas constant; β is the affinity coefficient; E^0 is the characteristic adsorption energy for a reference vapor; γ describes the surface heterogeneity; ϵ is the adsorption potential; N is the moles adsorbed at the equilibrium; and V^0 is the liquid molar volume.[1,2,16] Benzene was selected as a reference vapor, and the liquid molar volume was calculated using the modified Rackett equation.[17]

The Nelder−Mead simplex method was used for the calculation of isotherm parameters from the experimental results.[18] The experimental and theoretical result correlations were assessed on the basis of the square of residuals (SOR) method.

$$\mathrm{SOR} = \frac{1}{2}\sum (N_{\mathrm{exptl}} - N_{\mathrm{calcd}})^2 \tag{4}$$

where N_{exptl} and N_{calcd} are the experimental and calculated adsorbed amounts, respectively. The Toth and DA isotherm parameters as well as the SOR values are listed in Tables 4 and 5. The saturation volumes of the carbon monolith for both benzene and toluene at various temperatures were calculated from the DA equation, and the results are shown in Figure 3. From this study, the total micropore volume of the carbon monolith was found to be approximately 1250 cm^3·g^{-1}.

The heat evaluation during the adsorption is well-known. Hence the thermodynamic details are essential along with the adsorption properties for better design of adsorption systems. Also, the isosteric heat of adsorption characterizes the adsorbent surface and explains the adsorbate–adsorbate interaction as well

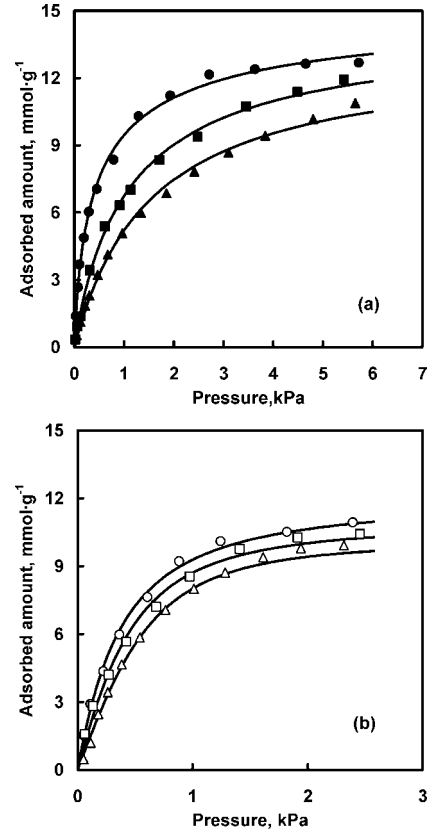

Figure 2. Adsorption isotherms of benzene (●, 303.15 K; ■, 313.15 K; ▲, 323.15 K; -, Toth isotherm) (a) and toluene (○, 303.15 K; ▽, 313.15 K; Δ, 323.15 K; -, Toth isotherm) (b) on corn grain-based carbon monolith.

Table 4. Toth Equation Parameters for Benzene and Toluene

	T	*m*	*b*		
adsorbate	K	mmol·g^{-1}	kPa	*t*	SOR
benzene	303.15	15.505	0.385	0.658	0.350
	313.15	14.452	0.994	0.905	0.260
	323.15	13.132	1.547	1.009	0.331
toluene	303.15	11.997	0.368	1.216	0.201
	313.15	10.891	0.425	1.584	0.407
	323.15	10.119	0.575	1.942	0.288

Table 5. Dubinin−Astakhov Parameters for Benzene and Toluene

	T	W^0	*E*			
adsorbate	K	cm^3·g^{-1}	kJ·mol^{-1}	*r*	β	SOR
benzene	303.15	1211.42	11.056	2.265	1.000	0.270
	313.15	1257.57	9.642	2.108	1.000	0.107
	323.15	1352.57	9.345	1.885	1.000	0.033
toluene	303.15	1226.09	6.895	2.149	1.179	0.314
	313.15	1267.94	7.548	2.185	1.174	0.204
	323.15	1205.02	7.768	2.149	1.176	0.261

as the adsorbate–adsorbent interaction. The Clausius−Clapeyron equation was applied for the evaluation of isosteric heat of adsorption.[19] Using the Toth isotherm parameters, the isosteric enthalpy of adsorption was found for benzene and toluene. A graph relating the isosteric heat of enthalpy and the surface loading is shown in Figure 4. The average isosteric heat of adsorption was found to be (64.3 and 22.6) kJ·mol^{-1} for benzene and toluene, respectively. The isosteric heat of adsorption of toluene turned out to be low compared to the previous study where the carbon monolith was also used as the adsorbent.[6] A higher isosteric heat of adsorption was observed for benzene compared to toluene, because of the higher affinity of the monolith to benzene. The results revealed that the adsorbate–adsorbent interaction highly dominates the system. An

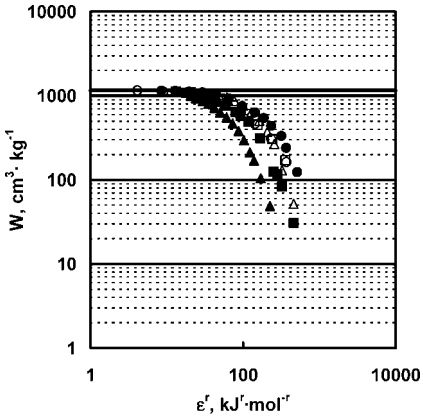

Figure 3. Saturation volume of corn grain-based carbon monolith for benzene (●, 303.15 K; ■, 313.15 K; ▲, 323.15 K) and toluene (○, 303.15 K; □, 313.15 K; △, 323.15 K).

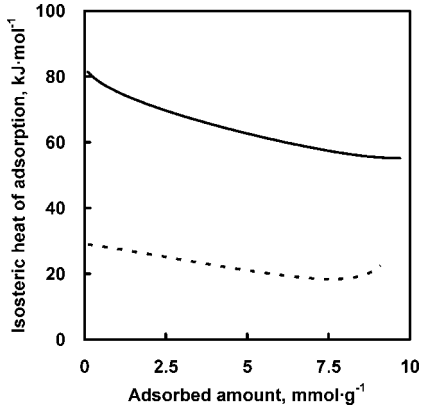

Figure 4. Isosteric heat of adsorption as a function of surface loading (−, benzene; ---, toluene).

energetically heterogeneous surface of microporous carbon monolith was noted from the variation of isosteric heat of adsorption along with the surface loading for each adsorbate.

From the viewpoint of adsorbent regeneration, understanding the thermal desorption behavior of adsorbates from an adsorbent is essential. Thermal gravimetric (TG) desorption is a technique which is used to examine the adsorbate–adsorbent interaction and pore structures. The weight loss curves (Figure 5a) and the differential TG profiles (Figure 5b) of benzene and toluene on the carbon monolith were obtained by the thermal desorption process with a heating rate of 5 K·min^{-1}. At the initial stage, the weight loss of benzene was relatively low compared to toluene, and a reversed trend was observed in the weight loss curve with increasing temperature. According to the relationship between the VOCs and adsorbent, the surface of the adsorbent has been classified into organophilic and organophobic categories, and the type can be established from the difference between the weight loss peak (T_d) and adsorbate boiling point (T_b) as given in Table 6.[20,21] The results revealed that the surface of the carbon monolith is organophilic for benzene and organophobic for toluene.

Conclusions

The carbon monolith was prepared from corn grain-based super high surface area activated carbon, and its surface characteristics were examined in terms of nitrogen adsorption and desorption isotherms as well as the adsorption energy distribution. The adsorption of benzene and toluene on carbon monolith was obtained at three different temperatures (303.15, 313.15, and 323.15) K and pressures up to 5.7 kPa for benzene and 2.4 kPa for toluene. The adsorption results were high compared to previous results and were well correlated by the Toth isotherm model. From the experimental results, the total micropore volume of the carbon monolith was found by applying the Dubinin−Astakhov equation. The isosteric heats of adsorptions calculated from the Clausius−Clapeyron equation revealed the energetically heterogeneous surface nature of the carbon monolith. Based on the thermal desorption test, it was found that the carbon monolith has a higher affinity for benzene compared to its affinity for toluene under comparable experimental conditions.

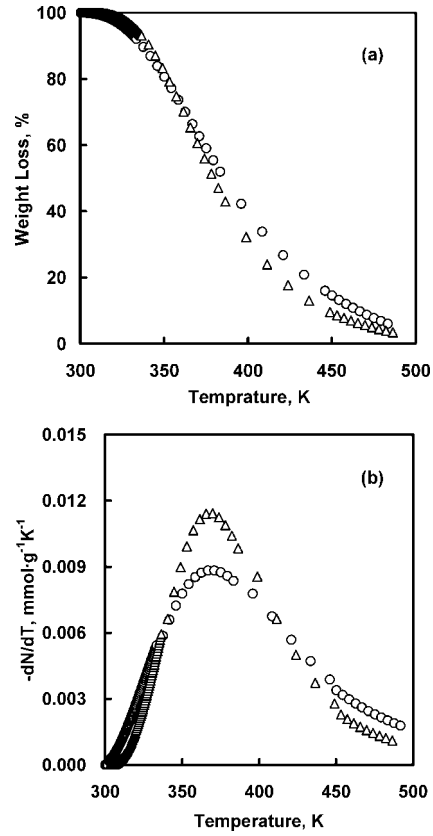

Figure 5. Thermal desorption curves and the differential curves of thermal desorption of ○, benzene and △, toluene on corn grain-based carbon monolith at a heating rate of 5 K·min^{-1}.

Table 6. Weight Loss Peak Position and the Affinity of Corn Grain-Based Carbon Monolith to Adsorbates

	weight loss peak, T_d	adsorbate boiling point, T_b	$T_d - T_b$
adsorbate	K	K	K
benzene	369.82	353.30	16.52
toluene	366.82	383.80	−16.98

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