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Adsorption Equilibria of Aromatic Compounds on Activated Carbon, Silica Gel, and 13X Zeolite

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The adsorption of volatile organic compounds (VOCs) on the activated carbon, silica gel, and type-13X synthetic zeolite were investigated by a gravimetric adsorption method. The sorbates (VOCs) include benzene, toluene, *o*-xylene, *p*-xylene, and *m*-xylene. The equilibrium isotherm data obtained from this study were fitted by the Freundlich equation. The standard deviations for the predicted adsorption isotherms in the activated carbon bed were from 0.44 to 0.92, and the standard deviations were from 0.25 to 4.79 in the silica gel bed and were from 0.12 to 0.87 in the 13X zeolite bed.

Introduction

Volatile organic compounds (VOCs) are defined as compounds with vapor pressures greater than 133.3 Pa (1 mm Hg) at room temperature. They can be released from fabrics, furniture, and solvents and diffuse to air easily. In this study the selected VOCs, which are generated from the printing, painting, or solvent industries, are benzene, toluene, *o*-xylene, *p*-xylene, and *m*-xylene.

The VOCs removal technologies are classified to the nondestructive and destructive methods. The adsorption method is one of the nondestructive methods. The adsorbed VOCs can be regenerated after this nondestructive process. The activated carbon, silica gel, and zeolite (molecular sieve) are widely used in industry to deal with VOCs. In general, the activated carbon has a pore diameter in the size of nanometers and a specific surface area of 500−1500 $m^2\ g^{-1}$. Silica gel is usually prepared from a sol−gel process,[1] and its surface properties (pore size and specific surface area) are controlled during the hydrolysis and synthesis processes. The surface properties of zeolites are determined by the structure of tetrahedron (SiO_4/AlO_4). The first family of synthetic zeolites was known as type A. Later a type-X zeolite was developed with a larger pore size than type A.[2] The performance of the porous adsorbents is determined by their intrinsic characteristics and the surface porous structure. The amount of the VOCs that can be collected on the external surface of the sorbent is small. Thus a porous sorbent with a large internal surface area is selected to deal with the VOCs. The sorbents that meet these criteria and used in this study are the activated carbon, silica gel, and 13X zeolite.

The equilibrium isotherm is one of the important parameters to design an adsorption separation process. The amount of sorbent needed in an absorber is determined by the equilibrium data, and the selection of an effective sorbent 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. The equilibrium uptake is a function of pressure or concentration of VOCs at a specific temperature.

Table 1. Surface Properties of the Sorbents

sorbent	a^a/m^2·g^{-1}	v^b/cm^3·g^{-1}	d^c/nm
activated carbon	990	0.094	2.7
silica gel	535	0.653	3.6
13X zeolite	440	0.117	9.9

[a] BET surface area. [b] Pore volume. [c] Pore diameter.

A number of isotherm equations have been proposed to describe the adsorption processes. Freundlich and Langmuir equations were the oldest and most frequently used isotherm equations.[3] The semiempirical Freundlich equation was applied in the low−intermediate concentration range.[2] Besides, the adsorption capacity could be expressed by the Langmuir isotherm equation on the uniform adsorption surface and by the Fruendlich isotherm equation on the nonuniform adsorption surface.[4] Since the VOCs were controlled from low to intermediate pressures, the Fruendlich isotherm equation was selected to fit the equilibrium data in this study.

Experimental System

Sorbents. The commercial sorbents including activated carbon (China Activated Carbon Industries Co.), silica gel (Kanto Chemical Co.), and 13X zeolite (Lancaster Synthesis Co.) were selected in this study. Their 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 were carried out at 77 ± 1 K. The specific surface area, pore volume, and average pore diameter were calculated by the BET method.[5]

Chemicals. Studies of VOCs adsorbed by the activated carbon can be found in the open literature; however, discussions of the VOCs adsorbed onto the surfaces of silica gel and 13X zeolite are rare. In this study the purity of

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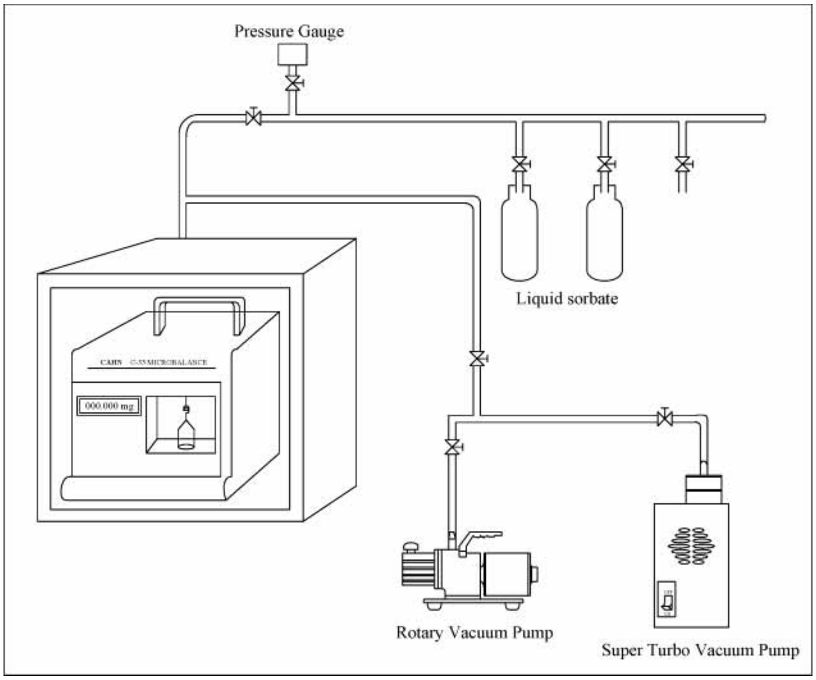

Figure 1. The gravimetric adsorption apparatus of this study (static gravimetric method).

aromatics was chosen in the grade of reagent to generate VOCs in each adsorption process.

Apparatus and Procedure. Figure 1 shows the 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 8.265×10^3 Pa (62 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, 24 h), 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.

Results and Discussion

The test of the adsorption apparatus was performed by comparing the experimental results with the literature data. The studies of the selected sorbate adsorbed onto the sorbent with the same surface properties of the sorbent in this study are rare in the literature. Helminen et al.[6] studied the adsorption of NH_3 by using some organic or inorganic sorbents. One of the sorbents used was the activated carbon. Since the surface area of the activated carbon and the system temperature are similar to this study, the equilibrium uptake of NH_3 on the activated carbon was compared to that of this study. Properties of the activated carbon and equilibrium uptakes of the experiment of Helminen et al.[6] and this work are compared and shown in Table 2. The amount of the sorbate adsorbed onto the sorbent is directly measured by a microbalance in the static gravimetric method, whereas it is calculated by the ideal gas law in the static volumetric method. Both methods are used in the literature widely to get the equilibrium uptakes of gases. 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.

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	ammonia gas
sorbent	activated carbon	activated carbon
a/m^2·g^{-1}	450	530
T^a/K	298.15	298.15
q^b/mg·g^{-1}	13	12.7

[a] Temperature. [b] Uptake.

The organic solvents of aromatics were generally used in the painting, printing, and solvent industries. The vapors of these organic solvents (VOCs) include benzene, toluene, *o*-xylene, *p*-xylene, and *m*-xylene, which were used in this study. The adsorption capacity of the VOCs on the activated carbon, silica gel, and 13X zeolite were listed in Table 3. Adsorption experiments were conducted at 298.15 K for these VOCs adsorbed onto the sorbents. The adsorption capacity vs relative pressure, P/P^0, was recorded as the adsorption isotherm and shown in Figure 2. P^0 represents the vapor pressure of the liquid solvent at 298.15 K. Activated carbon has a great affinity for the aromatics because of the nonpolar nature of its surface.[7] Since benzene has a simple aromatic-ring structure, its adsorption capacity on the activated carbon is larger than the aromatics with side chains. The orientations of methyl

Table 3. Experimental Data of This Work

benzene		toluene		*o*-xylene		*m*-xylene		*p*-xylene	
P/P^0	q/mg·g^{-1}	P/P^0	q/mg·g^{-1}	P/P^0	q/mg·g^{-1}	P/P^0	q/mg·g^{-1}	P/P^0	q/mg·g^{-1}
Sorbent: Activated Carbon									
0.040	130.685	0.045	87.937	0.148	96.696	0.121	22.681	0.111	21.618
0.093	141.244	0.182	97.442	0.296	103.423	0.242	27.823	0.222	24.254
0.147	145.323	0.273	99.692	0.444	106.659	0.364	30.094	0.333	27.915
0.227	149.743	0.364	101.942	0.593	108.573	0.485	30.709	0.444	28.798
0.320	153.426	0.500	104.139	0.741	111.471	0.606	31.088	0.556	29.461
0.387	154.956	0.591	105.705						
0.467	157.128	0.682	107.091						
0.547	158.885	0.727	108.297						
0.600	159.848	0.773	108.981						
0.640	160.528	0.818	109.449						
0.680	161.416								
Sorbent: Silica Gel									
0.160	56.909	0.045	37.470	0.148	58.259	0.148	68.579	0.111	14.553
0.307	81.033	0.182	77.774	0.296	73.733	0.296	79.198	0.222	17.667
0.440	95.025	0.273	100.946	0.444	78.682	0.444	82.048	0.333	19.464
0.560	100.856	0.455	125.607	0.593	89.465	0.593	86.059	0.444	21.852
0.667	103.960	0.545	136.634	0.741	96.538	0.741	87.965	0.556	22.901
0.720	104.914	0.682	143.079						
0.800	106.216								
Sorbent: 13X Zeolite									
0.053	5.416	0.091	7.920	0.148	5.989	0.148	9.555	0.111	14.053
0.160	7.890	0.227	9.504	0.296	9.721	0.296	11.293	0.222	17.567
0.267	9.431	0.364	10.436	0.444	12.455	0.444	13.334	0.333	19.364
0.320	10.318	0.455	11.461	0.593	15.015	0.593	14.550	0.444	21.652
0.400	11.158	0.545	12.160	0.741	17.663	0.741	16.244	0.556	22.101
0.467	11.952	0.636	13.185						
0.547	12.932	0.727	14.583						
0.707	15.547	0.773	15.608						
0.747	16.154	0.818	16.027						
0.773	17.041								
0.813	17.835								
0.827	18.021								

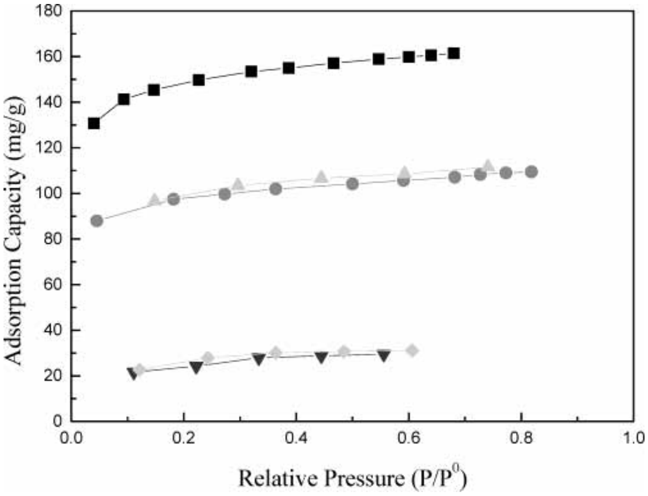

Figure 2. Adsorption capacities for aromatics adsorbed by activated carbon at different pressures: ■, benzene; ●, toluene; ▲, *o*-xylene; ▼, *p*-xylene; ◆, *m*-xylene.

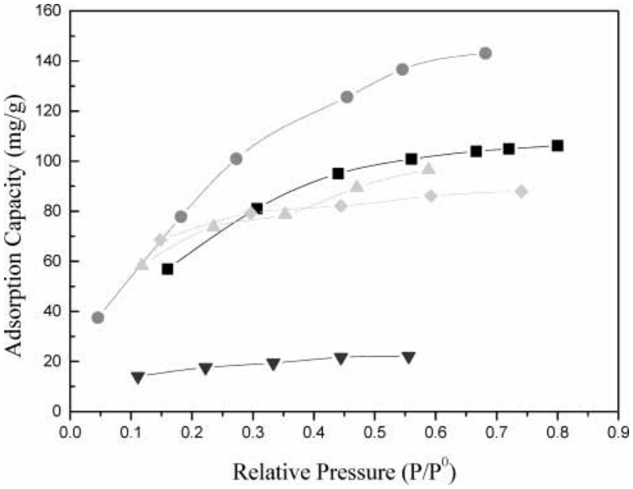

Figure 3. Adsorption capacities for aromatics adsorbed by silica gel at different pressures: ■, benzene; ●, toluene; ▲, *o*-xylene; ▼, *p*-xylene; ◆ *m*-xylene.

group(s) are similar in the structures of toluene and *o*-xylene, and the geometric barrier effect of them is smaller than that of m- and *p*-xylene. Therefore, the adsorption capacities of toluene and *o*-xylene on the activated carbon were almost the same, whereas they were much lower for *m*- and *p*-xylene.

Since the silica gel surface has polarity and the aromatics have weak polarity, the adsorption of aromatics on the silica gel is a polarity-induced phenomenon. The symmetric structure of *p*-xylene has a lower polarity and the adsorption capacity of *p*-xylene on the silica gel is lower than that of other xylenes. The adsorption capacity is also decreased when the geometric barrier effect increases. The adsorption capacity is considered on both polarity and geometric barrier effects of the molecule on the surface of silica gel. Therefore, the order of the adsorption capacity is toluene > benzene > xylene in Figure 3.

The pore size and surface properties of 13X zeolite are uniform and polar, and the aromatics are weak polar molecules. The adsorption of aromatics on the 13X zeolite is also a polarity-induced phenomenon. Since the averaged pore diameters of sorbents in this study were in the range of 2.5−10 nm and the molecular sizes of sorbates were 0.5−0.7 nm only, the adsorption of these sorbates onto the 13X

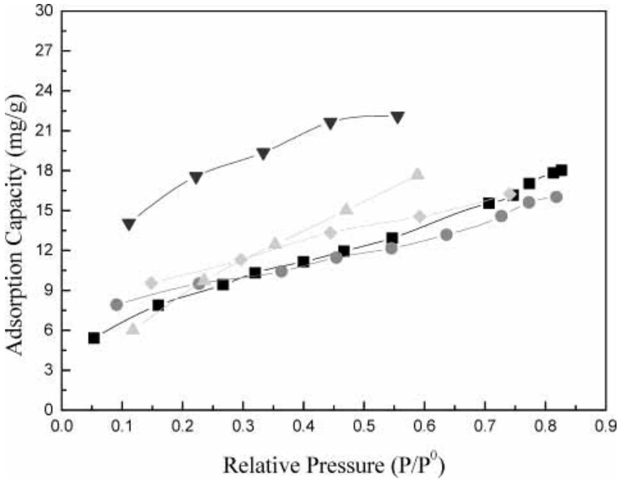

Figure 4. Adsorption capacities for aromatics adsorbed by 13X zeolite at different pressures: ■, benzene; ●, toluene; ▲, *o*-xylene; ▼, *p*-xylene; ◆, *m*-xylene.

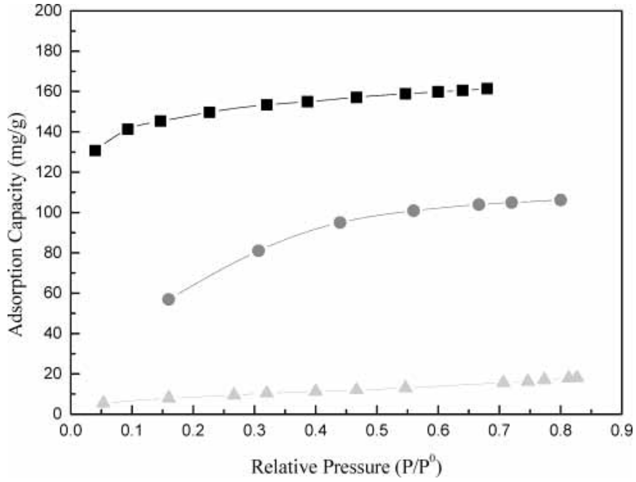

Figure 5. Adsorption capacities for benzene adsorbed by different sorbents at different pressures: ■ activated carbon; ●, silica gel; ▲, 13X zeolite.

zeolite should not be affected by the molecular sieving effect significantly. In this case, the effect of molecular weight is stronger than the geometric barrier. The adsorption capacity is increased as the molecular weights of the aromatics increase. As shown in Figure 4, the adsorption capacity of xylene is greater than that of toluene and benzene.

The greatest amount of aromatics (with and without side chain) adsorbed onto the activated carbon was found in Figures 5 and 6. It may result that the activated carbon has a nonpolar nature of its surface as compared to other solid sorbents and the specific surface area of the selected activated carbon is larger than that of silica gel and 13X zeolite. In Figures 5 and 6, the affinity for armatics on a nonpolar surface of the activated carbon is important. On the basis of this study, the order of the aromatics adsorption performance on different sorbents is activated carbon > silica gel > 13X zeolite.

Adsorption Isotherm. Because the gas pressure was controlled from low to intermediate pressures in this study, the Freundlich isotherm model was applied to fit the equilibrium data. The Freundlich isotherm equation can be expressed as

$$q = Kp^n$$

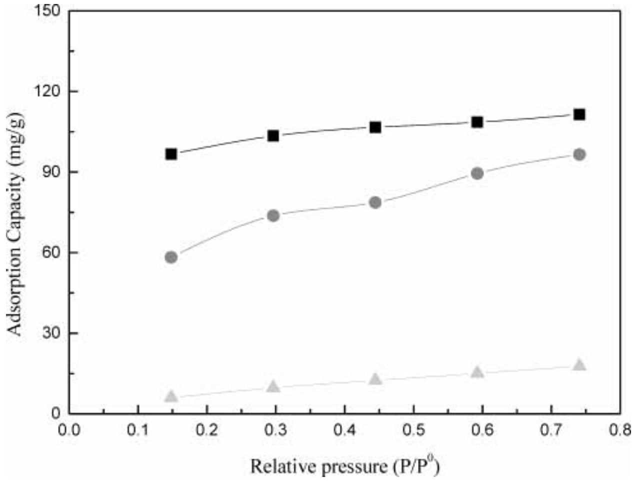

Figure 6. Adsorption capacities for *o*-xylene adsorbed by different sorbents at different pressures: ■ activated carbon; ●, silica gel; ▲, 13X zeolite.

Table 4. Regression Values of *K* and *n* in the Freundlich Equation

sorbent	sorbate	*K*	*n*	std dev
activated carbon	benzene	121.86	0.07	0.60
	toluene	87.64	0.07	0.52
	o-xylene	96.95	0.09	0.44
	p-xylene	23.39	0.2	0.61
	m-xylene	21.57	0.20	0.92
silica gel	benzene	23.02	0.39	4.35
	toluene	38.36	0.51	4.79
	o-xylene	58.35	0.31	1.78
	p-xylene	14.50	0.28	0.25
	m-xylene	69.51	0.15	1.17
13X zeolite	benzene	2.67	0.44	0.87
	toluene	5.88	0.32	0.86
	o-xylene	6.03	0.67	0.12
	p-xylene	9.33	0.33	0.37
	m-xylene	14.18	0.29	0.33

where q is the adsorption capacity (mg sorbate/g sorbent), K is the Freudlich constant, p is the gas pressure of the aromatics (mm Hg), and n is the exponent. The regression constants and exponents for all the aromatics adsorbed by different sorbents at 298.15 K were shown in Table 4. The standard deviations for the predicted adsorption isotherms in the activated carbon bed were from 0.44 to 0.92, and the standard deviations were from 0.25 to 4.79 in the silica gel bed and were from 0.12 to 0.87 in the 13X zeolite bed. It demonstrated the confidence of the Freundlich isotherm on the adsorption of aromatics onto the activated carbon, silica gel, and 13X zeolite.

Conclusions

The static gravimetric apparatus was built and applied to measure the adsorption equilibrium data. The equilibrium isotherms of the adsorption of aromatics onto the activated carbon, silica gel, and 13X zeolite were obtained in this study. The effects of the specific surface area of the sorbent and the molecular weight and structure of the sorbate were used to discuss the change of adsorption capacities in different adsorption systems. On the basis of this study, the adsorption performance for the same aromatic adsorbed to different sorbents was found in the order of activated carbon > silica gel > 13X zeolite. Nonpolar molecules were induced by polar molecules to get the polarity-induced force to attract each other. The standard deviations were small when the Freundlich equation was used to fit these equilibrium isotherms. The adsorption equilibrium data obtained from this static gravimetric apparatus were considered appropriate.

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