Adsorption−Desorption Rate of Nonpolar Volatile Organic Compounds onto Activated Carbon Exemplified by C_6H_6 and CCl_4

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Abstract: This investigation was to evaluate the performance of a thermodynamic model using nonlinear driving force in conjunction with the Langmuir model exemplified by the adsorption of benzene and carbon tetrachloride onto activated carbon in mono- and binary-adsorbate systems. Results show that model-fitted adsorption and desorption rate constants could well predict the adsorption isotherms and breakthrough curves under various conditions. This numerical model can provide adsorption and desorption rate constants. The kinetic parameters are of the same order of magnitude as reported in several studies. Under high reaction temperatures, both the adsorption and desorption rate constants increased while equilibrium constants decreased. A dimensionless valuable C_0/K can be used to describe the relationship between adsorbate and adsorbent, and predict the service cycle during the adsorption process. For adsorption in binary mixtures, a high inlet concentration or a low temperature, the weak adsorbate, C_6H_6, will have a high breakthrough concentration when the strong adsorbate, CCl_4, began to break through.

CE Database subject headings: Activated carbon; Adsorption; Desorption; Kinetics.

Introduction

Activated carbon has been used extensively as an adsorbate for the removal of hazardous air pollutants. Major parameters affecting the adsorption process include the surface properties of the activated carbon, the characteristics and concentration of volatile organic compounds (VOCs), temperature, and humidity. King and Do (1996) used the Fourier transfer infrared technique to evaluate the effect of temperature on the adsorption capability of ethane, propane, and *n*-butane on activated carbon. They reported that the equilibrium time at high temperatures was shorter than that at low temperatures. Wood (1992) observed good correlation between molar polarization of adsorbent and adsorption capacity using the Dubinin/Radushkevich model. Other researchers (Jonas and Rehmann 1972; Vahdat et al. 1995) considered the activated carbon bed adsorption process as a first-order reaction and found the Wheeler equation to be successful for application to several organic gases.

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Most adsorption studies were conducted at a specific temperature. Major adsorption models used include the linear driving force (LDF) approximation (Crittenden and Weber 1978; Malek et al. 1995; Malek and Farooq 1996, 1997; Vahdat 1997), the empirical method (Yoon and Nelson 1984); and the thermodynamic equilibrium approach (Myers and Prausnitz 1965) (Table 1). The LDF method considers the adsorption process as an irreversible reaction, and the reaction rate is governed by the difference between the temporal and the equilibrium concentrations of the gas adsorbate. The LDF method is based on an isothermal plug-flow system with a linear equilibrium adsorption isotherm (Malek et al. 1995; Malek and Farooq 1996, 1997). Yoon and Nelson (1984) developed an empirical model to predict the breakthrough curve of activated carbon beds. Based on the thermodynamic characteristic of each solute at equilibrium, an ideal adsorbed solution theory was developed by Myers and Prausnitz (1965). The adsorption equilibrium of the gas mixture can be predicted from the individual single-gas isotherm using the Toch equation (Myers and Valenzuela 1986) and/or the Dubinin/Radushkevich equation (Dubinin 1989). The desorption behavior of carbon films was also observed based on the Arrhenius equation and thermal desorption spectroscopy (Pigram et al. 1994).

There are problems with the above methods. For example, the thermodynamic method considers the adsorption process only under equilibrium conditions. The LDF method accounts for the adsorption step only. The empirical method lacks theoretical validity. In essence, the adsorption is not truly equilibrium; both adsorption and desorption occur at the same time. The objectives of this investigation were to evaluate the performance of the thermodynamic model using nonlinear driving force exemplified by the adsorption of benzene and carbon tetrachloride onto activated carbon in mono- and binary-adsorbate systems, and to predict the adsorption isotherm and adsorption breakthrough curves under different operational conditions, such as temperature and gas concentration, as a means to determine the system service time.

Table 1. Adsorption Models

| Column adsorption model	Typical model equation
Linear driving force (LDF) approximation	$-D_L\dfrac{\partial^2 C}{\partial^2 L}+U\dfrac{\partial C}{\partial L}+\dfrac{\partial C}{\partial t}+\dfrac{1-\varepsilon}{\varepsilon}\rho_p\dfrac{\partial q}{\partial t}=0$
	$\dfrac{\partial q}{\partial t}=k(q^*-q)$
Empirical method	$t=t_{1/2}+\dfrac{1}{k'}\ln\left(\dfrac{C}{C_0-C}\right)$
	$k'=\dfrac{kCQ}{W_e}$
	$t_{1/2}=t$ when $C=C_0/2$
Ideal adsorbed solution theory	$t=\dfrac{W_e}{CQ}\left[W-\dfrac{\rho_B Q}{k}\ln\left(\dfrac{C_0}{C}\right)\right]$

Experimental Method

Materials

The VOCs selected were benzene (C_6H_6) and carbon tetrachloride (CCl_4), and the activated carbon studied was Sorbonorit 3 (Norit, the Netherlands). The activated carbon sample was of pellet form with a diameter of 3 mm and a density of 880 kg/m^3. The activated carbon was ground and sieved to size between 0.35 and 0.50 mm (35–45 mesh) to prevent the wall effects. Then it was heated to 573 K in a N_2 atmosphere (purity 99.99%) over 24 h to desorb contaminants. The treated activated carbon was stored in a N_2-filling chamber (300 K) before experiments.

Volatile organic compounds were generated by passing a stream of water and hydrocarbon-free N_2 gas over a series of diffusion tubes containing the pure liquid. The VOC concentrations were controlled by the number of diffusion tubes and temperature. The carrier gas flow rate was controlled at 1.2 L/min (298 K) by a mass flow meter (Instrument Inc., Sierra). The temperature of the VOC vapor was controlled by a thermostat (283–363 K) before entering the reaction column (Fig. 1). The concentrations of C_6H_6 and CCl_4 studied were 8–150 and 6–300 mmol/m^3, respectively.

Adsorption in Activated Carbon Bed

For mono-VOC adsorption experiments, about 600 mg of treated activated carbon was packed in a small glass column (height=9
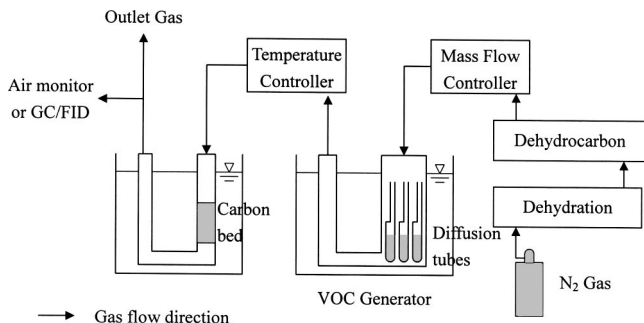
Fig. 1. Experimental apparatus

mm and cross-section area=1.76 cm^2), whereas for bi-VOC experiments, the amount of treated activated carbon used was about 4,000 mg (height=60 mm and cross-section area=1.76 cm^2). The column temperature was maintained at the range from 283 to 363 K for 3 h before testing. For single-component experiments, the outlet gas was continuously monitored with a portable photoionization air monitor (Perkinelmer, Photovac Model 2020). The measurements were calibrated by gas chromatography (GC) (HP 5890A; column: Supel Co., VOCOL™, No. 9354-04A) with a flame ionization detector (FID). For two-component experiments, the outlet gas was collected about 1 mL every 15 min and injected into the GC/FID for the analysis of residual organics. The detection limits of C_6H_6 and CCl_4 were 100 and 30 ppm V, respectively.

Mathematical Model

Numerical Model Development

The following dynamic equation was used to describe the temporal mass balance of containment in question:

$$\frac{\partial C}{\partial t}-D_L\frac{\partial^2 C}{\partial^2 L}+u\frac{\partial C}{\partial L}+\frac{1-\varepsilon}{\varepsilon}\rho_p\frac{\partial q}{\partial t}=0 \qquad (1)$$

where D_L, C, L, u, ε, ρ, and q=dispersion coefficient (m^2/s); concentration of VOC in the gas phase (mol/m^3); length of activated carbon bed (m); gas velocity (m/s); bed void fraction; a density of activated carbon (g/m^3); and adsorption capacity (g/g), respectively. By assuming the process as a nonequilibrium surface reaction and since the column is relatively short, the diffusion term can be negligible, the surface reaction rate is equal to the adsorption rate minus the desorption rate, i.e.

$$\frac{\partial \theta}{\partial t}=k_a(1-\theta)C-k_d\theta \qquad (2)$$

where θ (q/q_0)=degree of surface coverage of VOC on activated carbon surface; k_a=adsorption rate constant (m^3/(s mol)); and k_d=desorption rate constant (L/s). Eq. (1) can be rewritten as

$$\frac{\partial C}{\partial t}=-U\frac{\partial C}{\partial L}-\frac{\partial \theta}{\partial t}S \qquad (3)$$

where S (g/m^3)=conversion factor between solid and gas phase can be further expressed by the following relation:

$$S=\frac{q_0 W}{LA-W/\rho} \qquad (4)$$

It is known that the flow rate, Q (m^3/s), has the following form:

$$Q=UA\left(1-\frac{\dfrac{W}{\rho}}{LA}\right) \qquad (5)$$

where W=weight of activated carbon (g); A=cross-sectional area of the adsorption bed (m^2); and q_0=maximum adsorptive capacity at the monolayer level (g/g).

Considering the activated carbon bed as an entity of n series ($n=50$) of constant volume units, i.e., the physicochemical conditions within each unit are identical, and the adsorption/desorption process follows the Langmuir model. Let Δt (s) and ΔV (m^3) be the reaction time and the gas volume in each unit. At
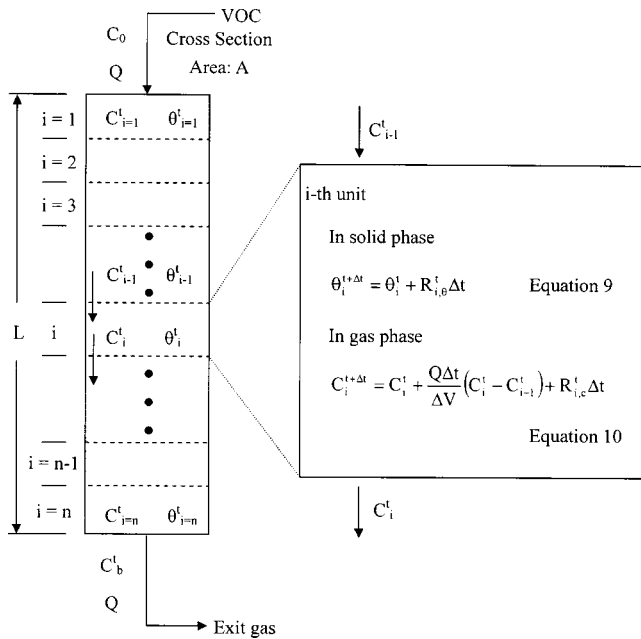
Fig. 2. Conceptual presentation of modeling approach

the ith unit and experimental time, t, the concentration change in the solid phase and the gas phase can be determined by a finite difference method.

In solid phase from Eq. (2) one has

$$\theta_i^{t+\Delta t} = \theta_i^t + [k_a(1-\theta_i^t)C_i^t - k_d\theta_i^t]\Delta t \qquad (6)$$

In the gas phase from Eq. (3), it yields

$$C_i^{t+\Delta t} = C_i^t + \frac{Q\Delta t}{\Delta V}(C_i^t - C_{i-1}^t) + [-k_a(1-\theta_i^t)C_i^t + k_d\theta_i^t]S\Delta t \qquad (7)$$

Accordingly, ΔV can be expressed by the following equation:

$$\Delta V = \frac{LA - \dfrac{W}{\rho}}{n} \qquad (8)$$

In the case when both VOCs are present, it is assumed that both prefer the same adsorption sites, and that a competitive adsorption process takes place.

In the solid phase, Eq. (6) becomes

$$\theta_i^{t+\Delta t, Z} = \theta_i^{t,Z} + \left[k_a\left(1 - \sum_Z \theta_i^{t,Z}\right)C_i^{t,Z} - k_d\theta_i^{t,Z}\right]\Delta t \qquad (9)$$

In the gas phase, Eq. (7) becomes

$$C_i^{t+\Delta t, Z} = C_i^{t,Z} + \frac{Q\Delta t}{\Delta V}(C_i^{t,Z} - C_{i-1}^{t,Z}) + \left[-k_a\left(1 - \sum_Z \theta_i^{t,Z}\right)C_i^{t,Z} \right.$$
$$\left. + k_d\theta_i^{t,Z}\right]S\Delta t \qquad (10)$$

where $Z = Z$th adsorbate. Fig. 2 is the conceptual presentation of the modeling approach.

Calculation

By definition, the equilibrium adsorption mass, W_e, and the equilibrium adsorption capacity, q, can be calculated by the following

equation:

$$q = \int_0^\infty (C_0 - C_b)Q\,dt/W = W_e/W \qquad (11)$$

where C_0 and C_b=inlet and outlet organic vapor concentrations, respectively; and W_e=equilibrium adsorption mass. With q obtained, the parameters of Langmuir (q_0, K_L), Freundlich (K_F, n), and Redlich–Peterson (K_R, B, m) adsorption isotherms can be computed using the *SYSTAT* software package.

In numerical modeling, a series of knowns (ρ, A, C_0, W, L, Q, and T) and estimated parameters (k_a and k_d) were input into Eqs. (6) and (7) followed by iterative computations. The breakthrough curves were then resulted. The best fit was verified evaluating by the root mean square error method, δ, i.e.

$$\delta = \frac{1}{C_0}\sqrt{\frac{1}{N}\sum_{n=1}^N (C_b - C')^2} \qquad (12)$$

where C_b, C', and N=observed breakthrough concentration, calculated breakthrough concentration, and measured number in each test, respectively.

Results and Discussion

Determination of Reaction Parameters (k_a, k_d, E_a, and E_d)

Table 2 shows the experimental conditions and results of a single contaminant column adsorption process, where retention time, τ, is defined as $(LA - W/\rho)/Q$. The breakthrough time (t_b at $C_b = 0.01\,C_0$) and the exhaustion time (t_e at $C_b = 0.99\,C_0$) deceased significantly as temperature increased. Clearly, the model developed for the present study can reasonably predict the effluent concentration ($\delta = 0.02$–0.07). Although both k_a and k_d increased with temperature, the equilibrium adsorption constant ($K = k_a/k_d$) actually decreased. For example, the desorption rate constant of C_6H_6 increased from 1.0×10^{-4} to 1.1×10^{-2} L/s as the temperature increased from 283 to 363 K; the increase in the desorption rate constant was greater than that of the adsorption rate constant [1.3×10^{-2}–6.0×10^{-2} m^3/(s mol)]. The equilibrium constant, however, decreased by 2 orders of magnitude (130–5.4 m^3/mol) when the temperature increased from 283 to 363 K. Results also show that the equilibrium adsorption constant of CCl_4 was greater than that of C_6H_6.

Based on the Arrhenius equation, the adsorption activation energy (E_a), desorption activation energy (E_d), adsorption frequency coefficient (a_a), and desorption frequency coefficient (a_d) can be calculated from the corresponding k_a and k_d values (Fig. 3). For C_6H_6, the E_a and E_d were determined to be 4.0 and 12.2 kcal/mol, respectively; the corresponding a_a and a_d values were 13 m^3/(s mol) and 2.6×10^5 L/s, individually. For CCl_4, the E_a and E_d values were 4.8 and 15.3 kcal/mol, respectively; the respective a_a and a_d values were 340 m^3/(s mol) and 4.6×10^7 L/s. Consequently, the heat of adsorption of C_6H_6 and CCl_4 can be determined; the values are -8.2 and -10.4 kcal/mol, respectively, for C_6H_6 and CCl_4. In comparison, C_6H_6 has a larger adsorption rate constant, desorption rate constant, equilibrium adsorption constant, adsorption activation energy, and desorption activation energy but a lower heat of adsorption and adsorption capacity than that of CCl_4.

Table 2. Adsorption Conditions, Parameters, and Statistics

VOC	Adsorption conditions and parameters		Unit Temp. (K)	Run 1 283	Run 2 303	Run 3 323	Run 4 343	Run 5 363
C_6H_6	Reaction conditions	Weight of carbon, W	g	2.001	2.005	2.001	2.002	2.001
		Length of carbon bed, L	cm	3	3.1	3	3	3
		Influent concentration, C_0	mmol/m^3	116	132	108	103	88
		Saturation concentration, C_{sat}	mol/m^3	2.6	6.3	13.5	25.8	45.1
		Flow rate, Q	L/min	1.14	1.2	1.3	1.38	1.46
		Breakthrough time, t_b	min	39	27	25	22	20
		Exhaustion time, t_e	min	130	100	90	56	38
		Retention time, τ	s	1.60×10^{-1}	1.59×10^{-1}	1.41×10^{-1}	1.33×10^{-1}	1.25×10^{-1}
	Reaction parameters	Adsorption rate constant, k_a	m^3/(s mol)	1.3×10^{-2}	1.6×10^{-2}	1.9×10^{-2}	4.0×10^{-2}	6.0×10^{-2}
		Desorption rate constant, k_d	L/s	1.0×10^{-4}	4.4×10^{-4}	1.6×10^{-3}	5.0×10^{-3}	1.1×10^{-2}
		Equilibrium constant, K	m^3/mol	130	36.6	11.7	8	5.4
	Statistics	Measured number in each test, N	—	27	29	41	32	26
		Root mean square error, δ	—	0.02	0.03	0.03	0.05	0.04
CCl_4	Reaction conditions	Weight of carbon, W	g	0.600	0.600	0.600	0.600	0.600
		Length of carbon bed, L	cm	0.9	0.9	0.9	0.9	0.9
		Influent concentration, C_0	mmol/m^3	26.8	23.7	22.5	22.2	20.6
		Saturation concentration, C_{sat}	mol/m^3	3.2	7.5	15.5	28.9	49.5
		Flow rate, Q	L/min	1.15	1.21	1.31	1.39	1.47
		Breakthrough time, t_b	min	44	42	30	26	16
		Exhaustion time, t_e	min	100	68	54	50	45
		Retention time, τ	s	4.70×10^{-2}	4.46×10^{-2}	4.14×10^{-2}	3.89×10^{-2}	3.68×10^{-2}
	Reaction parameters	Adsorption rate constant, k_a	m^3/(s mol)	7.5×10^{-2}	1.0×10^{-1}	1.5×10^{-1}	2.0×10^{-1}	6.0×10^{-1}
		Desorption rate constant, k_d	L/s	4.0×10^{-5}	1.1×10^{-3}	3.0×10^{-3}	4.8×10^{-3}	3.1×10^{-2}
		Equilibrium constant, K	m^3/mol	1,875	90.0	50.0	41.7	19.4
	Statistics	Measured number in each test, N	—	41	29	24	22	19
		Root mean square error, δ	—	0.04	0.07	0.02	0.02	0.03

Note: Experimental conditions: density=880 kg/m^3, bed cross-section area=1.76 cm^2 and q_0 460 mg/g for C_6H_6, and 600 mg/g for CCl_4 at 303 K.

Adsorption Isotherm

In this study, both C_6H_6 and CCl_4 are nonpolar molecules; i.e., dipole moments are zero. Table 3 summarizes the results of the equilibrium adsorption capacity under various C_6H_6 and CCl_4 concentrations. As expected, the equilibrium capacity increased
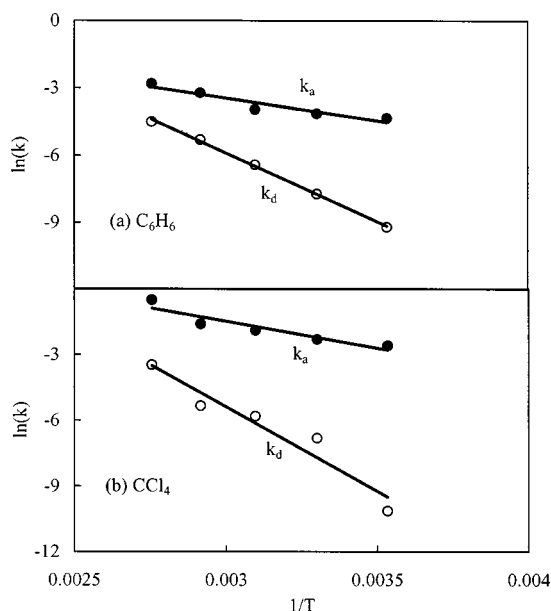
Fig. 3. Relationship between rate constants (k_a and k_d) and temperature

with the VOC concentration. The C_6H_6 or CCl_4 saturation concentration (C_{sat}) at a given temperature was calculated from its vapor pressure, and the adsorption capacity was plotted versus the "relative concentration" (C_0/C_{sat}) as shown in Fig. 4. All three models (Langmuir, Freundlich, and Redlich–Peterson) can reasonably describe the experimental data ($R^2=0.89-0.99$). Table 4 summarizes the model parameters. The results indicate that CCl_4 has both high maximum adsorptive capacity and Langmuir adsorption constant ($K_L=k_a/k_d$), which implies that CCl_4 is a stronger adsorbate than C_6H_6 toward activated carbon. For the sake of convenience, the Langmuir model was chosen in subsequent numerical model analysis of the adsorption/desorption process.

Many researchers have reported that the adsorbed VOC molecules behave as a liquid phase. In this study, both C_6H_6 and CCl_4 are nonpolar molecules with a liquid density of 0.885 and 1.584 g/cm^3, respectively.

In principle, both the breakthrough (t_b) and exhaustion (t_e) time of the activated carbon decreased as the influent concentration (C_0) and/or the reciprocal adsorption constant (K) increases. These phenomena were clearly demonstrated in Fig. 5, which shows that t_b and t_e decrease exponentially with increasing C_0/K. Meanwhile, the breakthrough time of C_6H_6 (or CCl_4) will approach the exhaustion time when the C_0/K reaches 1.6×10^{-2} (or 4.0×10^{-3}). That is at exhaustion condition, influent concentration (C_0) increases while the reaction constant (K) decreases and vice versa. Therefore, the dimensionless quantity C_0/K not only reflects the relationship between adsorbent (C_0)

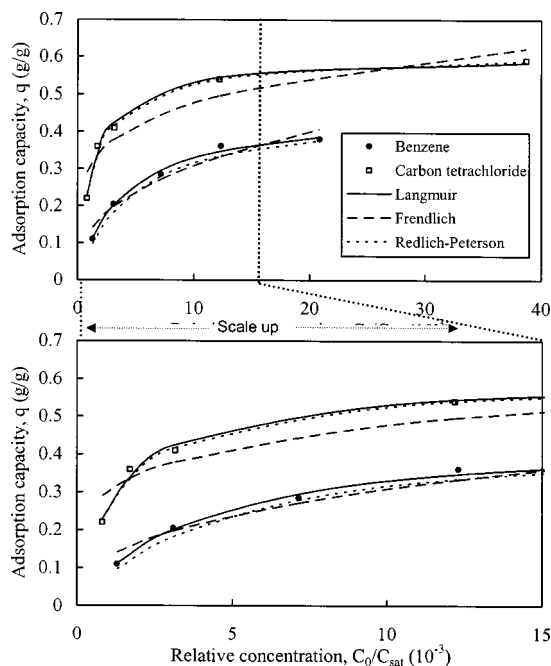**Table 3.** Adsorption Capacity of C_6H_6 and CCl_4 onto Activated Carbon

VOC	Conditions and result	Unit	Run 1	Run 2	Run 3	Run 4	Run 5
C_6H_6	Concentration, C_0	mmol/m³	8.1	19.5	45.1	77.7	131.6
	Activated carbon weight, W	g	2.002	2.005	2.002	2.011	2.005
	Equilibrium adsorption weight, W_e	mmol	2.82	5.26	7.31	9.32	9.79
	Equilibrium adsorption capacity, q	mg/g	110	205	285	362	381
CCl_4	Concentration, C_0	mmol/m³	6.1	12.8	23.7	91.7	291.1
	Activated carbon weight, W	g	0.601	0.600	0.600	1.000	2.000
	Equilibrium adsorption weight, W_e	mmol	0.86	1.40	1.60	3.50	7.66
	Equilibrium adsorption capacity, q	mg/g	220	360	410	539	590

Note: Experimental condition: $T = 303$ K and $Q = 1.2$ L/min.

and adsorbate ($1/K$), but also provides a guideline for predicting the service time during the adsorption cycle.

Table 5 and Fig. 6 compare the equilibrium adsorption constants obtained from the Langmuir adsorption isotherm and model calculations. Results show that the average relative percentage difference (RPD) value is about 6%, which indicates that the model predicates well the adsorption and desorption rate constants.

Vahdat (1997) reported Langmuir constants between 27 VOCs and 11 activated carbons and suggested that both the VOCs and activated carbon can affect the Langmuir constants (q_0 and K_L). For benzene, the average q_0 is 0.353 g/g; the average K_L is 60.1 m³/mol; the maximum K_L is 120.2 m³/mol; and the minimum K_L is 34.5 m³/mol at 298 K. For carbon tetrachloride, the average q_0 is 0.738 g/g; the average K_L is 61.3 m³/mol; the maximum K_L is 163.7 m³/mol; and the minimum K_L is 43.3 m³/mol in the temperature range of 296–298 K. In a previous study, Chiang et al. (2001) reported a q_0 of 0.43 and 0.62 g/g for benzene and carbon tetrachloride, individually, and a K_L of 29 and 90 m³/mol for benzene and carbon tetrachloride, respectively, at 300 K for the same activated carbon sample (Fig. 6). Our results of Langmuir constants were of the same order of magnitude as those reported by Vahdat (1997) and Chiang et al. (2001).

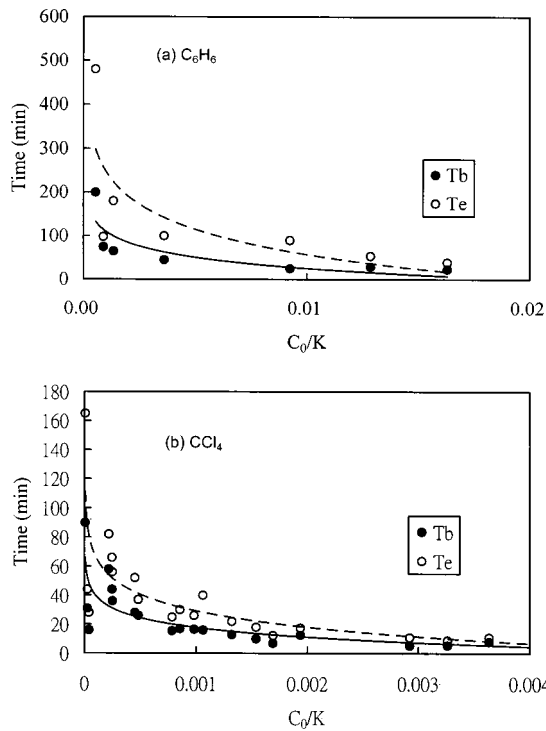### Effect of Temperature and Concentration

Fig. 7 illustrates the effect of temperature on the adsorption of VOCs. Results indicate that the adsorption of C_6H_6 was not temperature dependent, especially in the low VOC concentration range. As relative concentration increased, the effect of temperature on VOC adsorption diminished.

Fig. 8 shows predicted single-contaminant breakthrough curve as a function of temperature. For the single contaminant system, the model predicts well the adsorption breakthrough curves of both C_6H_6 and CCl_4. At high reaction temperatures, the adsorption capacity decreased due in part to small equilibrium constants and an early breakthrough time. The breakthrough curves were steeper at high temperatures than at low temperatures, due in part to the effects of k_a and k_d. Furthermore, CCl_4 has a longer relative breakthrough time, due to low inlet CCl_4 concentrations.

Fig. 9 shows the predicted breakthrough curves of the binary contaminant system at four temperatures. The inlet concentrations of CCl_4 at 303, 323, 343, and 363 K were 1.26×10^{-2}, 1.45×10^{-2}, 1.54×10^{-2}, and 3.07×10^{-2} mol/m³, respectively;

Fig. 4. Adsorption isotherms of C_6H_6 and CCl_4 at 303 K

Table 4. Pertinent Parameters of Various Adsorption Isotherm Equations

VOC	Isotherm	Parameter	Unit	Value
C_6H_6 ($N=5$)	Langmuir $q = \dfrac{q_0 K_L C}{1 + K_L C}$	q_0	g/g	0.46
		K_L	m³/mol	39.8
		R^2	—	0.99
	Freundlich $q = K_F C^n$	K_F	g/g	0.88
		n	—	0.38
		R^2	—	0.97
	Redlich–Peterson $q = \dfrac{K_R C}{B + C^m}$	K_R	mol/m³	0.44
		B	—	0.03
		m	—	1.03
		R^2	—	0.99
CCl_4 ($N=5$)	Langmuir	q_0	g/g	0.60
		K_L	m³/mol	99.8
		R^2	—	0.99
	Freundlich	K_F	g/g	0.80
		n	—	0.20
		R^2	—	0.89
	Redlich–Peterson	K_R	mol/m³	0.62
		B	—	0.01
		m	—	0.98
		R^2	—	0.99

Fig. 5. Relationship of inlet concentration with equilibrium constant and breakthrough time or equilibrium time ($W = 2.0$ and 0.6 g for C_6H_6 and CCl_4, respectively)

Fig. 6. Relationship of equilibrium constants of Langmuir and adsorption/desorption models

whereas the inlet concentrations of C_6H_6 were 6.38×10^{-2}, 6.86×10^{-2}, 7.84×10^{-2}, and 1.64×10^{-1} mol/m³, individually. In general, the predicted results agree well with what were observed. Again, high temperatures exhibited a steeper breakthrough curve and an earlier breakthrough time. At high temperatures, the adsorption and desorption rate constants were large, whereas the equilibrium constants were small. Both high adsorption and desorption rate constants were typically related to steeper breakthrough curves, whereas low equilibrium constants cause low adsorption density and early breakthrough time.

Fig. 10 shows the predicted results at three concentration level of VOC, i.e., high ($[C_6H_6]_0 = 309$ mmol/m³, $[CCl_4]_0 = 90$ mmol/m³); medium ($[C_6H_6]_0 = 164$ mmol/m³, $[CCl_4]_0 = 31$ mmol/m³); and low ($[C_6H_6]_0 = 84$ mmol/m³, $[CCl_4]_0 = 16$ mmol/m³) concentrations. At the high (or medium) inlet concentration, the effluent concentration ratio (C/C_0) of the weak adsorbate (C_6H_6) presents a high C/C_0 value 1.20 (versus 1.06 for CCl_4) when the breakthrough time approaches 30 min (versus 55 min for CCl_4). At a high inlet concentration, the strong adsorbate competed with the weak adsorbate, and caused the desorption rate of the weak adsorbate to be higher than the adsorption rate. It caused the outlet concentration to be higher than the inlet concentration (C_0). However, the effluent concentration ratio of C_6H_6 did not exhibit a value higher than 1.0 at the low concentration level. The total adsorption capacity of C_6H_6 and CCl_4 was found to decrease as the inlet concentration decreased.
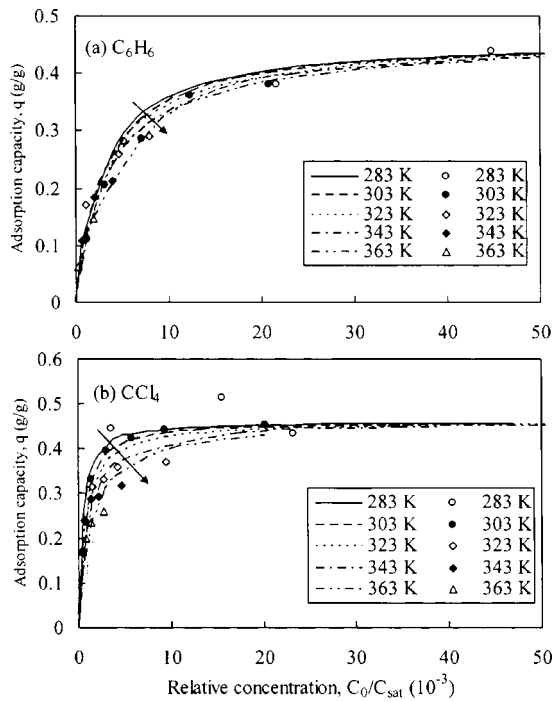
It was thus concluded that, at high temperature and/or high inlet concentration, there was significant adsorptive breakthrough. For both high-inlet concentration (Fig. 10) and low-temperature conditions (Fig. 9), the weak adsorbate, C_6H_6, exhibited a high adsorption density at the beginning of the experiment.

Table 5. Relationships of Equilibrium Constants of Both Langmuir and Adsorption/Desorption Models

VOC	Parameter	Unit	Unit Temp. (K)	Temperature 283	303	323	343	363
C_6H_6	Number of test	N	—	3	5	3	3	3
	Langmuir	q_0	g/g	0.46[a]	0.46	0.46[a]	0.46[a]	0.46[a]
		K_L	m³/mol	111.5	39.8	22.5	11.2	6.3
		R^2	—	0.97	0.99	0.54	0.68	0.72
	Ads./Des.	K	m³/mol	130.0	36.6	11.7	8.0	5.4
	Statistics	RPD[b]	%	3.8	2.1	15.8	8.3	3.7
CCl_4	Number of test	N	—	3	5	5	5	4
	Langmuir	q_0	g/g	0.60[a]	0.60	0.60[a]	0.60[a]	0.60[a]
		K_L	m³/mol	2,212	99.8	78.0	40.4	16.7
		R^2	—	0.72	0.99	0.79	0.57	0.60
	Ads./Des.	K	m³/mol	1,875	90.0	50.0	41.7	19.4
	Statistics	RPD[b]	%	4.1	2.6	11.0	0.8	3.7

[a]Fixed at the same value of 303 K.

[b]$RPD = |K_L - K| / 2(K_L + K)$.

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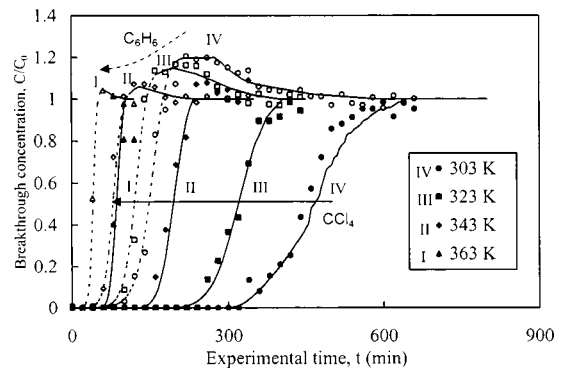
Fig. 7. Prediction of adsorption isotherms under different concentration and temperature conditions (points are experimental data and lines are model predicted)
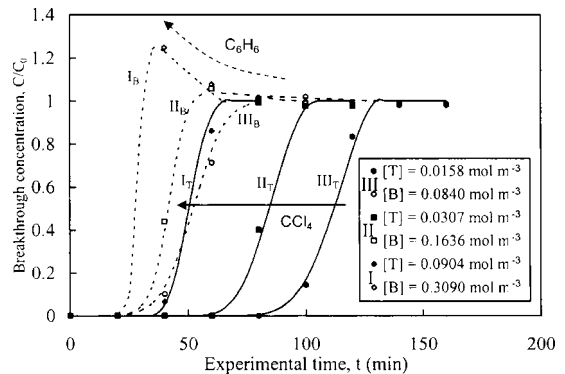

Fig. 9. Prediction of binary adsorption breakthrough curves under different temperature conditions (solid points are experimental CCl_4 data, air-corn points are experimental C_6H_6 data, solid lines are predicted CCl_4 value, and broken lines are predicted C_6H_6 value, $W = 4.0$ g)

contaminant adsorption, the adsorption capacities are smaller than that of a single contaminant adsorption.

Conclusion

The activated carbon adsorption process was affected by several factors, such as temperature, adsorbent and adsorbate characteristics, and VOC concentration. In this study, a numerical model was developed. Results show that model-fitted adsorption and desorption rate constants could predict well the adsorption isotherms and breakthrough curves under various conditions. Both experimental and model-predicted data indicate that under high reaction temperatures, both the adsorption and desorption rate constants increase, whereas equilibrium adsorption constants decreased. The adsorption capacity was also affected by temperature. For binary contaminants adsorption, a high inlet concentration or a low temperature will cause a high breakthrough concentration of weak adsorbate (C_6H_6) when contaminant (CCl_4), a strong adsorbate, began to break through.

Binary contaminant breakthrough shows a competitive adsorption. For example, at 303 K, with CCl_4 and C_6H_6 inlet concentrations of 1.26×10^{-2} and 6.38×10^{-2} mol/m^3, the experimental adsorption capacities are about 1.8 and 2.0 mol/kg, respectively. For a single contaminant adsorption, the adsorption of CCl_4 and C_6H_6 are 2.9 and 4.2 mol/kg, respectively. As expected, at binary

Fig. 8. Prediction of volatile organic compound breakthrough as function of temperature (points are experimental data and lines are model predicted, influent concentrations of C_6H_6 and CCl_4 are 88–132 and 20–27 mmol/m^3, respectively)

Fig. 10. Prediction of binary adsorption breakthrough curves under different concentration conditions (363 K, $W = 4.0$ g, solid points are experimental CCl_4 data, air-corn points are experimental C_6H_6 data, [T] and [B] are concentration (mol/m^3) of carbon tetrachloride and benzene)

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