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Adsorption of Benzene and Toluene from Aqueous Solution onto Granular Activated Carbon

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The liquid-phase adsorption of benzene and toluene on granular activated carbon TOG 20 \times 50 has been studied at (303.15, 313.15, and 323.15) K. The temperature dependent forms of the Toth and Sips equations were used to correlate the experimental data. Excellent agreement between the experimental data and those two equations are observed.

Introduction

Benzene and toluene are important materials in the chemical industry. They are starting materials in chemical manufacture, and they are usually used as solvent in a wide variety of manufacturing processes. Since these chemicals are classed as flammable and toxic materials, their presence in the environment, usually in wastewater at low concentration, is of major concern. Hence, removal of these compounds from an aqueous waste stream is required.

Adsorption onto activated carbon provides a feasible technique and is one of the most extensively used technologies for removal of organic pollutants from industrial wastewater. As one of the most important pieces of information in analysis and design of adsorption separation processes, liquid-phase adsorption isotherm data of various organic compounds in several systems have been obtained by various investigators and have been reported in different places over the years.^{1–11}

There have been few experimental liquid-phase adsorptions on activated carbon for benzene and toluene.^{12–15} Adsorption in the liquid phase is more complex than gas-phase adsorption, as it is influenced by many factors, such as pH, type of adsorbent, solubility of adsorbate in the solvent, and temperature as well as adsorptive concentration. In adsorption on activated carbon, the type of activated carbon plays an important role, since the carbon has a complex porous structure, with associated energetic as well as chemical inhomogeneities. The energetic and chemical heterogeneities are determined by the variety of surface functional groups, irregularities, and strongly bound impurities, as well as structural nonuniformity. This heterogeneity considerably influences the process of physical adsorption. Different types of activated carbons have been used for the liquid-phase adsorption of benzene and toluene, and different types of isotherms have been reported. Dobbs and Cohen¹⁵ investigated the adsorption of toxic organic compounds (including benzene and toluene) at low concentration (4 to 15 mg·L⁻¹) using granular activated carbon F-300. The adsorption isotherm for these compounds is reported to follow the Freundlich equation. The liquid-phase adsorption of benzene on activated carbon

F-200, CAL, GW, MI, PC, RIAA, RIB, and RIC¹³ is reported to follow the Dubinin–Radushkevich and the Dubinin–Astakhov equations. Chatzopolous et al.¹² also reported that the adsorption of toluene on F-300 at 298.15 K with low to moderate concentration (0.7 to 50 mg·L⁻¹) follows the Fritz–Schlunder and Toth isotherms. Therefore, the availability of adsorption isotherms on different activated carbons as a function of concentration and temperature would be very useful in the design of adsorption separation processes.

This paper presents the liquid-phase adsorption equilibrium data of benzene and toluene on industrial granular activated carbon at three different temperatures (303.15 K, 313.15 K, and 323.15) K. Since activated carbon is a heterogeneous adsorbent, the Toth and Sips equations with their temperature dependence forms are employed to correlate the adsorption experimental data. Both of those equations have a parameter characterizing the heterogeneity of the system.

Experimental Section

Materials. The granular activated carbon TOG 20 \times 50 was chosen as adsorbent. This activated carbon is manufactured using a metallurgical grade of bituminous coal combined with a suitable binder and was purchased from Calgon Carbon, Pittsburgh, PA. The specifications and physical properties of the carbon are summarized in Table 1. These properties were obtained from the supplier. Prior to use, the activated carbon was washed to remove impurities and fine particles. Then, it was degassed using a vacuum-drying oven at 473.15 K for 24 h.

The benzene and toluene used in this study were purchased as analytical grade from Merck KgaA with purity > 99%. These chemicals were used without further purification.

Procedure. Adsorption experiments were carried out by adding a known mass of activated carbon (0.2 to 0.8 g) to a series of 250 mL glass-stoppered flasks filled with 250 mL of solution. The glass-stoppered flasks were then placed in a thermostatic shaker water bath (Thermoline) with temperature control to within ± 0.05 K, and shaken at maximum speed for 48 h. Measurements were made at (303.15, 313.15, and 323.15) K. Preliminary experiments indicated that the adsorption equilibrium was reached about 12 h for both benzene and toluene with no ap-

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Table 1. Specifications and Physical Properties of TOG 20 × 50 Activated Carbon

mesh size, U.S. sieve series	20 × 50
larger than 20 mesh, max %	3
smaller than 50 mesh, max %	1
iodine number, minimum	850
ash, max %	8
total surface area (N ₂ BET method)/m ² ·g ⁻¹	800–900
bulk density packing/g·cm ³	0.54
particle density (Hg displacement)/g·cm ⁻³	0.78

Table 2. Experimental Adsorption Isotherm Data for Aqueous Solutions of Benzene on Granular Activated Carbon TOG 20 × 50

T = 303.15 K		T = 313.15 K		T = 323.5 K	
C _e /mg·L ⁻¹	q _e /mg·g ⁻¹	C _e /mg·L ⁻¹	q _e /mg·g ⁻¹	C _e /mg·L ⁻¹	q _e /mg·g ⁻¹
3.87	93.9	4.83	89.6	1.89	53.1
9.55	122.9	8.65	107.4	7.65	94.4
16.89	142.6	18.49	132.0	19.19	122.4
23.56	150.9	28.16	142.1	26.19	130.1
37.11	163.5	36.15	152.9	39.52	143.3
48.67	172.6	42.61	158.9	52.36	154.3
62.53	177.8	68.43	173.2	64.39	162.2
73.45	183.6	78.91	176.4	75.21	165.0
91.56	191.7	98.56	182.1	91.51	171.9
122.76	197.9	112.73	188.7	119.37	178.8
142.57	204.7	132.78	190.4	147.78	186.1
168.93	207.1	171.35	198.4	161.37	187.6
189.73	211.1	189.13	202.0	195.18	193.0
211.56	210.8	218.76	203.9	228.77	195.4
245.68	217.5	251.89	208.6	253.81	200.9
261.22	220.0	273.21	210.7	277.71	203.7
281.56	218.6	289.59	212.2	286.51	203.5
302.53	221.5	307.13	213.1	311.15	205.7

preciable decrease in adsorbate bulk concentration for time periods up to 1 week. The concentration range of solutions used in this study was (100 to 550) mg·L⁻¹ and (50 to 450) mg·L⁻¹ for benzene and toluene in water, respectively. The adsorbate solutions were prepared by mixing a known amount of adsorbate with distilled water to yield various desired concentrations. The uncertainty of the initial solution concentrations was ±0.0001 g/L. Each experiment was repeated three times under identical conditions.

The initial and equilibrium concentrations of adsorbate solutions were determined by means of a Shimadzu UV/visible spectrophotometer (UV-1201) at a wavelength of 206 nm for toluene and 254 nm for benzene, by comparing the light absorbances of the sample solutions against a calibration curve in an appropriate range of concentrations. The accuracy of this method is ±0.1 mg·L⁻¹. The amount adsorbed on the activated carbon was determined from the initial liquid-phase concentration and equilibrium concentration:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

here C_0 and C_e are the initial and equilibrium concentrations respectively, V is the volume of solution, and m is the mass of activated carbon. On the basis of the estimated calibration error, the adsorbed amount of data was reproducible within 5% at low concentrations (<10 mg·L⁻¹) and better at higher concentrations.

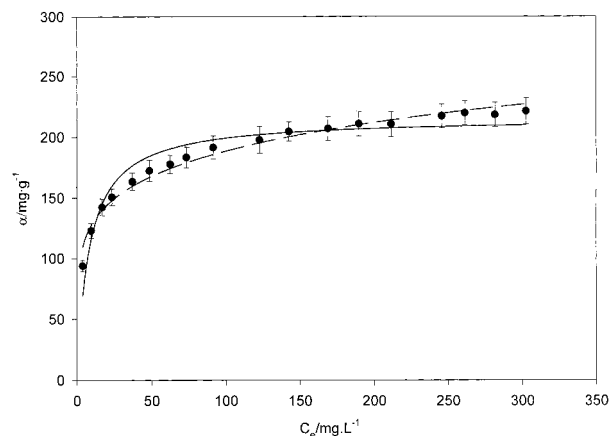
Results and Discussion

The experimental adsorption equilibrium data of benzene and toluene on granular activated carbon at (303.15, 313.15, and 323.15) K were obtained in this study, and the results are presented in Tables 2 and 3.

For the correlation of the liquid-phase adsorption equilibria of a single component, several isotherm equations for gas-phase adsorption can in principle be extended to

Table 3. Experimental Adsorption Isotherm Data for Aqueous Solutions of Toluene on Granular Activated Carbon TOG 20 × 50

T = 303.15 K		T = 313.15 K		T = 323.5 K	
C _e /mg·L ⁻¹	q _e /mg·g ⁻¹	C _e /mg·L ⁻¹	q _e /mg·g ⁻¹	C _e /mg·L ⁻¹	q _e /mg·g ⁻¹
1.07	109.4	1.17	94.3	2.39	105.3
3.56	157.5	2.56	126.5	5.76	141.9
11.23	203.3	4.52	150.7	8.92	163.1
19.27	223.3	10.72	183.1	16.34	186.1
28.54	237.0	18.24	203.1	19.21	190.7
39.19	247.4	27.12	222.0	25.12	203.3
46.78	253.0	35.71	230.9	39.76	220.1
56.77	258.9	44.65	238.6	44.61	223.1
59.66	260.4	51.72	243.5	58.89	235.0
68.91	264.6	63.47	251.2	67.49	239.8
77.54	267.9	67.52	251.9	69.57	240.8
84.24	270.2	83.29	258.6	75.28	243.5
99.23	274.6	91.27	263.4	83.31	246.8
102.55	275.4	108.95	266.5	98.63	252.3
115.37	278.5	113.37	267.7	119.32	258.3
126.77	280.9	121.32	268.6	126.81	260.1
141.32	283.6	129.37	270.3	128.32	260.5
147.88	284.7	131.56	271.8	137.96	263.3

**Figure 1.** Plot of equilibrium concentration C_e as a function of amount adsorbed α for the Langmuir and Freundlich isotherms of benzene at 303.15 K on granular activated carbon TOG 20 × 50: ●, experimental data; —, Langmuir; - - -, Freundlich.

liquid-phase adsorption by the simple replacement of adsorbate pressure by its concentration.¹ These equations are the Langmuir, Freundlich, Sips, Toth, and Dubinin–Radushkevich equations.^{1,16} The Langmuir isotherm equation is

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

and the Freundlich isotherm is

$$q_e = A C_e^{1/n} \quad (3)$$

where q_e is the amount adsorbed, q_m and b are Langmuir's parameters, A and n are the Freundlich parameters, and C_e is the equilibrium concentration. Those equations are the most widely used to correlate liquid-phase adsorption data.^{2–11,15,17–19} In a number of studies, these two equations failed to describe the liquid-phase adsorption data.^{1,11,20,21} Both of these equations also give unsatisfactory result for correlation of our experimental data, as indicated in Figure 1. The Langmuir and Freundlich parameter values for benzene and toluene obtained from our adsorption experiment are summarized in Table 4. From Figure 1 it is obvious that the Freundlich equation fails to represent the adsorption data at low concentrations (since the Freundlich

Table 4. Langmuir and Freundlich Parameters for the Adsorption of Benzene and Toluene from Aqueous Solution at 303.15 K on Activated Carbon TOG 20 × 50

compound	Langmuir equation			Freundlich equation		
	$q_m/\text{mg}\cdot\text{g}^{-1}$	$b/\text{L}\cdot\text{mg}^{-1}$	DP	$A/\text{mg}\cdot\text{g}^{-1}$	$1/n$	DP
benzene	215.71	0.1216	0.1374	86.98	0.1682	0.0781
toluene	275.74	0.3743	0.1413	132.91	0.1594	0.0897

equation does not incorporate Henry's law), and the Langmuir equation gave a poor fit, with positive deviation at high liquid concentration. This phenomenon has also been observed by Chatzopoulos et al.¹²

The Sips and Toth equations were fitted to the adsorption equilibrium data of benzene and toluene. These two equations are often found to be superior to either the Langmuir or Freundlich equation in correlations,¹ as they were developed for adsorption on heterogeneous solids such as activated carbon.

The Sips equation is also known as the Langmuir–Freundlich equation and has the following form:¹⁶

$$q_e = q_0 \frac{(dC_e)^{1/S}}{1 + (dC_e)^{1/S}} \quad (4)$$

where q_0 , d , and S are parameters. The system heterogeneity is allowed for by the parameter S . To describe adsorption equilibrium data over a temperature range, it is important to have a temperature dependence form of an isotherm equation. The temperature dependence is introduced through the parameters d and S by¹⁶

$$d = d_0 \exp \left(\frac{\Delta H}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right) \quad (5)$$

and

$$1/S = 1/S_0 + \frac{\beta}{T} (T - T_0) \quad (6)$$

where T_0 is the reference temperature and was taken as 303.15 K, d_0 and S_0 are the parameters d and S at that reference temperature, respectively, ΔH is the enthalpy of adsorption, and β is a constant.¹⁶ The five constants q_0 , d_0 , S_0 , ΔH , and β have to be determined from the experimental data.

The other three-parameter isotherm equation is the Toth isotherm,¹⁶ which has the following form

$$q_e = q_0 \frac{bC_e}{(1 + (bC_e)^{1/t})} \quad (7)$$

The temperature dependence of the Toth equation is introduced through b and t by

$$b = b_0 \exp \left[\frac{\Delta H}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right] \quad (8)$$

and

$$t = t_0 + \alpha \left[1 - \frac{T_0}{T} \right] \quad (9)$$

where q_0 , b_0 , t_0 , ΔH , and α are the parameters to be determined. $T = 303.15$ K was chosen as the reference temperature.

The unknown parameters for both equations were solved by nonlinear regression analysis using a quasi-Newton

Table 5. Optimal Parameters for the Temperature Dependence of the Sips and Toth Equations

Benzene			
Sips		Toth	
$q_0/\text{mg}\cdot\text{g}^{-1}$	268.82	$q_0/\text{mg}\cdot\text{g}^{-1}$	305.18
$d_0/\text{L}\cdot\text{mg}^{-1}$	0.0721	$b_0/\text{L}\cdot\text{mg}^{-1}$	2.5069
S_0	2.076	t_0	0.3293
$\Delta H/RT$	11.975	$\Delta H/RT$	14.290
β	0.295	α	0.1307
DP	0.0053	DP	0.0027

Toluene			
Sips		Toth	
$q_0/\text{mg}\cdot\text{g}^{-1}$	332.08	$q_0/\text{mg}\cdot\text{g}^{-1}$	361.14
$d_0/\text{L}\cdot\text{mg}^{-1}$	0.2230	$b_0/\text{L}\cdot\text{mg}^{-1}$	4.934
S_0	1.997	t_0	0.3638
$\Delta H/RT$	13.661	$\Delta H/RT$	17.165
β	0.202	α	0.2123
DP	0.0031	DP	0.0012

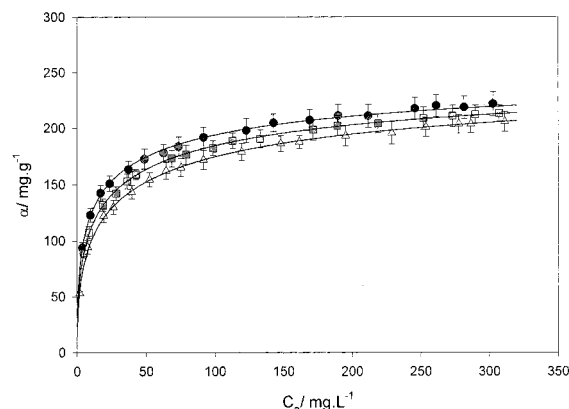


Figure 2. Plot of equilibrium concentration C_e as a function of amount adsorbed α for benzene on granular activated carbon TOG 20 × 50: ●, 303.15 K; ■, 313.15 K; ▲, 323.15 K; —, Sips equation; ···, Toth equation.

optimization method to minimize the root-mean-square of the normalized residuals DP implemented in the subroutine VA10A of the Harwell library,²² and the results are summarized in Table 5.

$$\text{DP} = \left(\frac{1}{n} \sum_{i=1}^n \left[\frac{q_{ei}^{\text{exp}} - q_{ei}^{\text{cal}}}{q_{ei}^{\text{exp}}} \right]^2 \right)^{1/2} \quad (10)$$

Here n is the number of data points. From the results of the fitting procedure for the Freundlich and Langmuir equations presented in Table 4 and the Toth and Sips equations in Table 5, it is clear that the root-mean-square of the normalized residuals DP of Freundlich and Langmuir is higher than the value for the other two equations. High values of the root-mean-square of the normalized residuals DP will give a significantly worse correlation.

The same data in Tables 2 and 3 are replotted in Figures 2 and 3, illustrating the comparison between the experimental data with the two correlations. The correlation obtained by these two equations (Sips and Toth) was in excellent agreement with the experimental data. From these figures, it is clearly seen that the Sips and Toth equations are applicable for a wide range of concentrations and also reduce to Henry's law at very low concentration. The parameters b and t in the Toth equation and d and S in the Sips equation are specific for adsorbate–adsorbent pairs.¹⁶ As indicated above, the liquid-phase adsorption of toluene on F-300 at 298.15 K in the liquid concentration

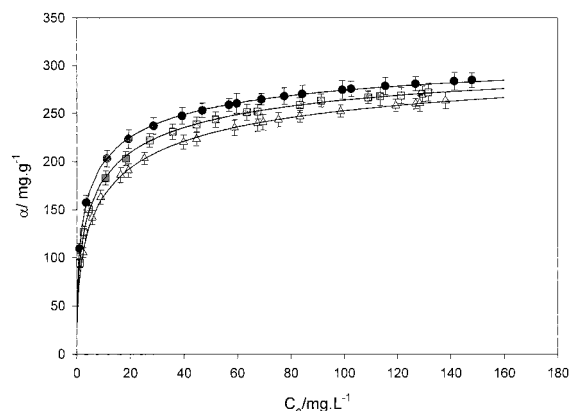


Figure 3. Plot of equilibrium concentration D_e as a function of amount adsorbed α for toluene on granular activated carbon TOG 20 \times 50: \bullet , 303.15 K; \blacksquare , 313.15 K; \blacktriangle , 323.15 K; —, Sips equation; \cdots , Toth equation.

range 0.7 to 50 $\text{mg}\cdot\text{L}^{-1}$ also follows the Toth isotherm,¹² with parameters $q_0 = 380.5 \text{ mg}\cdot\text{g}^{-1}$, $b_0 = 1.519 \text{ L}\cdot\text{mg}^{-1}$, and $t_0 = 0.422$. It is obvious that the parameters b_0 and t_0 are significantly different from those listed in Table 5. The difference between the parameters b_0 and t_0 in the Toth equation obtained by Chatzopolous et al.¹² and our fitted parameters is due to the difference in heterogeneity of the system.

Conclusions

Adsorption of benzene and toluene from aqueous solutions onto granular activated carbon TOG 20 \times 50 has been carried out at three different temperatures: 303.15, 313.15, and 323.15 K. Three-parameter empirical equations, by Sips and Toth, which are generally used for heterogeneous adsorbents such as activated carbon, were employed to correlate the experimental data. An excellent agreement between experimental data and both of these equations is observed.

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