Experimental and Modeled Results Describing the Adsorption of Toluene onto Activated Carbon

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Adsorption isotherms of toluene on activated carbon were measured by time integration of the breakthrough curves at 298.15 K and 308.15 K using an apparatus developed for this purpose. Isotherms were also measured at 318.15 K and 333.15 K using a microbalance. Activated carbon was used as the adsorbent because it typically exhibits high adsorption capacities and shows potential as an adsorbent to effectively remove volatile organic compounds (VOCs) such as toluene. The experimental data were correlated with the following adsorption isotherms: Langmuir, Freundlich, Toth, and Dubinin. All these models except the Langmuir model were able to correlate our data.

Introduction

Control of air emissions of organic vapors is one of the primary objectives of the stringent regulations introduced under the 1990 Clean Air Act amendments. Several chemical process industries and other sources are seriously impacted by this act. There are several methods such as condensation, absorption, adsorption, contact oxidation, and incineration for removal and/or recovery of organic vapors. Among the alternatives available, carbon adsorption has received increased attention in the past few years. It is an established technology, widely used in industrial processes for the removal and recovery of hydrocarbon vapors from gaseous streams. Moreover, it offers some advantages over the others: the possibility of pure product recovery for reuse; high removal efficiency at low inlet concentrations; and low fuel/energy costs.

To design the adsorption facilities, thermodynamic data on the adsorption equilibria must be known over a broad range of temperature. Because of the trace level concentrations and the analytical limitations, there appears to be relatively little information in the literature concerning adsorption of aromatic compounds. This lack of data is also due to the elaborate instrumentation and high degree of precision required. Nevertheless, the adsorption on activated carbon of some very common aromatic compounds such as benzene, *m*-xylene, and toluene has been measured by a few authors.[1−9] This means that the adsorption of toluene on activated carbon was previously measured, but as each type of coal presents different forces of interaction, it is necessary to measure the adsorption isotherm for various adsorbate−adsorbent couples. This is the reason, in this paper, the adsorption equilibrium data of toluene on activated carbon are reported at $T = (298.15, 308.15, 318.15, \text{and } 333.15)$ K. The experimental data obtained are correlated with different existing adsorption isotherms such as the Langmuir model, the Freundlich model, the Toth model, and the Dubinin equation.

Products and Material

The toluene (mass fraction 0.99 purity) was purchased from Carlo Erba, and nitrogen (volume fraction 0.99995) was supplied from Air Liquide. The AC 40 activated carbon evaluated in this research was obtained from the supplier CECA S.A. (La Défense 5, 92062 Paris La Défense, France). The BET surface area and macropore volume of the granular activated carbon sample used were measured and are summarized in Table 1. The BET surface area was measured with liquid nitrogen at $T = 77$ K using a Carlo Erba Sorptomatic 1900 apparatus. The macropore volume was determined by porosimetry using a porosimeter 2000 from Carlo Erba.

Experimental Section

Dynamic Method. Adsorption experiments were performed with the homemade apparatus shown in Figure 1. Nitrogen was used as a carrier gas for the organic pollutant. The nitrogen flow rate equal to 4×10^{-4} $m^3 \cdot h^{-1}$ at $P = 0.1$ MPa and $T = 293.15$ K was regulated with an uncertainty of ±0.5% using a GFC 17 mass flow controller supplied by Aalborg. The adsorption column height and internal diameter are respectively 290 mm and 19 mm. For each experiment, 3 g of activated carbon was introduced into the column. The activated carbon was located in the middle of the column, and the top and the bottom of the column were filled with glass beads. The toluene was introduced into the system using a syringe pump (model 200 from KDScientific) allowing the selection of flow rate in the range 10^{-12} $m^3 \cdot h^{-1}$ to 4.649×10^{-5} $m^3 \cdot min^{-1}$. Different concentrations in nitrogen were obtained by changing the flow rate of toluene. However, to avoid any condensation of toluene in the gas phase, the partial pressure of toluene (P_{tol}) was kept lower than the toluene vapor pressure (P^s) at the column temperature. Attention was paid always to maintain $P_{tol} < 0.8P^s$.

During each experiment, the adsorption column temperature is kept constant by means of a thermostated bath

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Table 1. Adsorbent Properties

type	supplier	geometry	total macropore volume	surface area
AC 40 carbon bed	CECA	pellets diameter: 2 mm length: from 2 to 3 mm	$\approx 5.6 \times 10^{-4}\ m^3 \cdot kg^{-1}$	$1.3 \times 10^6\ m^2 \cdot kg^{-1}$

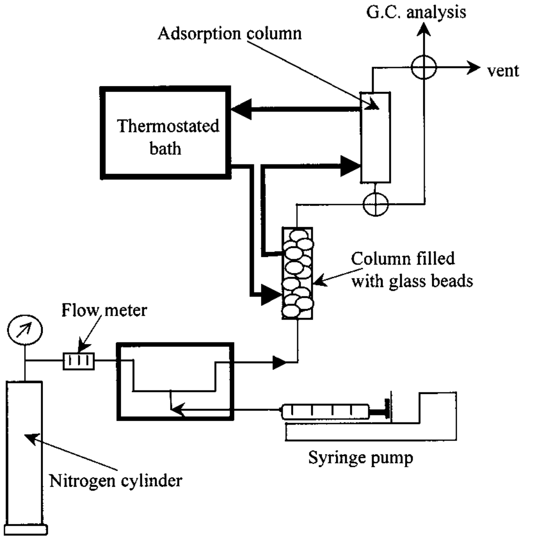

Figure 1. Schematic flow sheet of the apparatus allowing the measurement of adsorption isotherms.

Table 2. Experimental Adsorption Isotherms of Toluene on Activated Carbon Measured Either with a Specific Apparatus Developed for This Purpose or with a Microbalance

homemade apparatus				microbalance			
$T = 298.15$ K		$T = 308.15$ K		$T = 318.15$ K		$T = 333.15$ K	
P[a]	q[b]	P	q	P	q	P	q
Pa	$mol \cdot kg^{-1}$	Pa	$mol \cdot kg^{-1}$	Pa	$mol \cdot kg^{-1}$	Pa	$mol \cdot kg^{-1}$
105	4.23 ± 0.17	105	3.78 ± 0.15	227	3.94	416	3.52
209	4.64 ± 0.19	209	4.03 ± 0.16	466	4.10	857	3.75
313	4.83 ± 0.19	313	4.17 ± 0.17	806	4.25	1484	3.92
418	5.00 ± 0.20	418	4.40 ± 0.18	1129	4.33	2080	4.00
522	5.09 ± 0.20	522	4.64 ± 0.19	1808	4.41	3335	4.12
626	5.29 ± 0.21	626	4.73 ± 0.19	2503	4.46	4621	4.19
730	5.36 ± 0.21	730	4.75 ± 0.19	3198	4.52	5908	4.23
833	5.44 ± 0.22	833	4.82 ± 0.19	3859	4.57	7131	4.27
		937	4.87 ± 0.19	4554	4.62	8418	4.33
				5199	4.66	9610	4.35
				5911	4.69		
				6573	4.71		
				7268	4.73		
				7947	4.74		
				8591	4.75		
				9270	4.76		

[a] *P* is the partial pressure of toluene in the gas mixture entering the adsorption column. [b] *q* is the toluene mole number adsorbed at equilibrium per kilogram of activated carbon.

having a temperature uncertainty of ±0.1 K. The column pressure is controlled by the manometer located at the exit of the nitrogen cylinder. To render homogeneous the mixture of nitrogen and toluene, a preliminary column, thermostated at the same temperature as that of the adsorption column and filled with glass beads was introduced in our apparatus.

In this study, two temperatures were selected (298.15 K and 308.15 K) whereas the column pressure was maintained constant and equal to 0.17 MPa. To avoid any pressure drop inside the column, the gas mixture was added at low speed ($0.023\ m \cdot s^{-1}$). Before an adsorption experiment is started, the gas entering the adsorption column is analyzed by gas chromatography (GC) via the three-way valves located at the top and at the bottom of the column. Once the gas composition is constant, the adsorption experiment may start; that is, the gas is sent into the adsorption column and is periodically analyzed at the top with an on-line gas chromatograph. Consequently, a calibration curve giving the toluene concentration as a function of its area peak was first determined using mixtures of nitrogen and toluene the composition of which were known. Typically, an experiment ends when the outlet concentration equals the inlet concentration, meaning that equilibrium has been achieved (the activated carbon is saturated with toluene).

The plot of outlet toluene concentration versus time (breakthrough curve) yields the equilibrium data and information on the adsorption dynamics. The adsorption loading is obtained by numerical integration of the area behind the breakthrough curve.[10]

To know the precision of the proposed dynamic method, each experiment (breakthrough curve) was performed four times. Some dispersion was observed on such curves, resulting in an average error of the adsorption loading close to 4%.

Adsorption by Microbalance. A SARTORIUS 4201 electromagnetic suspension microbalance was installed for an accurate measurement of diffusion rates of vapors in activated carbon. It has a ±0.01 mg resolution and a ±0.02 mg precision, for a measuring full scale of 100.00 mg. In a typical experiment, the system is evacuated by vacuum pumping, and then the toluene vapor source is connected to the sorption chamber. The mass is digitized and monitored as a function of time with a personal computer. The mass value at every moment was obtained by averaging five mass values acquisitioned at 0.2 s intervals around the time point (one point every 1 s). The background noise, averaged by means of a statistical function in the software, was subtracted from the measured values. In this way, smooth, reproducible sorption curves were obtained. The sorption experiments were carried out below atmospheric pressure, and the sample weight was measured in a large range of vapor pressures. In this study two new temperatures higher than the previous ones were selected: $T = 318.15$ K and $T = 333.15$ K.

Results and Discussion

The experimentally determined quantities for toluene adsorbed on activated carbon as a function of the toluene pressure in the bulk phase are summarized in Table 2 at four different temperatures. Each experiment was performed four times. In Table 2, an average value with the corresponding experimental uncertainty is given.

The Langmuir, Toth, and Freundlich models and the Dubinin equation were used to correlate the experimental toluene adsorption data.

Langmuir Equation. The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir[11] isotherm, usually written as

$$\frac{q}{q_s} = \frac{bP}{1 + bP} \tag{1}$$

where q is the adsorbed quantity and P is the pressure of the adsorbate in the bulk gas phase. The two parameters q_s and b are respectively the saturation limit and the Langmuir constant.

In this study, a nonlinear curve-fitting procedure was used to determine b and q_s. The parameters obtained and the corresponding percent deviations are summarized for each temperature in Table 3. Such deviations were calculated by

$$\Delta q/\% = \frac{100}{N_{PT}} \sum_{k=1}^{N_{PT}} \left| \frac{q_k^{exp} - q_k^{cal}}{q_k^{exp}} \right|$$

with N_{PT} being the number of data points at a given temperature. q^{exp} and q^{cal} are respectively the experimental and the calculated adsorbed quantity. The mean deviation is obtained with the same formula with N_{PT} being equal to the total number of data points.

From the mean deviation given in Table 3, it is possible to conclude that the Langmuir model is not good for description of toluene adsorption on activated carbon.

Toth Isotherm. The Toth[12] isotherm is a semiempirical expression used to describe a monolayer adsorption. The parameters of this equation characterize the heterogeneity of the surface and the interactions of molecules adsorbed. It is a three-parameter model usually written as

$$\frac{q}{q_s} = \frac{P}{(b + P^{\tau})^{1/\tau}} \tag{2}$$

The parameters (q_s, b, and τ) in eq 2 were numerically determined. The parameters obtained and the percent deviations are summarized for each temperature in Table 4. The average deviation being lower than 1%, it is possible to conclude that such a model is able to correlate the data very well. Because the τ value is very different from unity, it can be concluded once more that the Langmuir model is not adequate.

Freundlich Isotherm. The Freundlich[13] isotherm is an empirical expression used to describe adsorption isotherms. It is represented as

$$q = KP^{1/n} \tag{3}$$

K and n are empirical constants which were determined with a classical nonlinear curve-fitting routine. The parameters and the percent deviations are summarized in Table 5. The deviations between measured and calculated adsorbed quantities are shown in Figure 2 whereas the corresponding calculated adsorption isotherms are shown in Figure 3. It is possible here to conclude that the Freundlich model is perfectly adapted to the description of toluene adsorption on activated carbon.

Dubinin Equation. On the basis of the potential theory, Dubinin and co-workers[14,15] have shown that the adsorption isotherms of various organic compounds could be represented by one of the following Dubinin−Radushkevich equations:

$$W = W_0 \exp\left[-\left(A\frac{\epsilon}{\beta}\right)^2\right] \tag{4}$$

$$W = W_0 \exp\left[-A\frac{\epsilon}{\beta}\right] \tag{5}$$

Table 3. Langmuir Parameters for Toluene Adsorption onto Activated Carbon

T	q_s	$10^3 b$	percent deviation (Δq)
K	mol·kg^{-1}	Pa^{-1}	%
298.15	5.54	28.45	1.94
308.15	5.04	24.52	2.48
318.15	4.66	20.48	2.06
333.15	4.39	8.572	2.15
		mean deviation/%:	2.15

Table 4. Toth Parameters for Toluene Adsorption onto Activated Carbon

T	q_s	b		percent deviation (Δq)
K	mol·kg^{-1}	Pa	τ	%
298.15	6.92	1.28	0.38	0.79
308.15	5.66	1.27	0.42	1.88
318.15	5.25	0.36	0.275	0.63
333.15	5.13	0.56	0.274	0.36
			mean deviation/%:	0.80

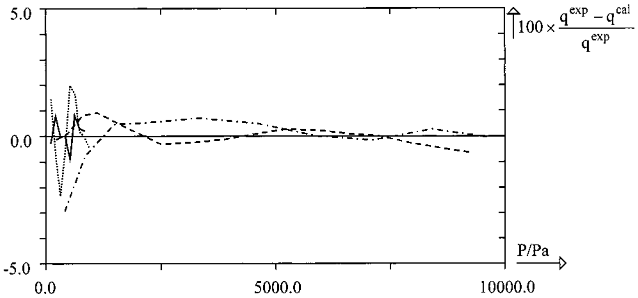

Figure 2. Plot of the percent deviations between measured and calculated adsorbed quantities using the Freundlich model: —, $T = 298.15$ K; ···, $T = 308.15$ K; - - -, $T = 318.15$ K; − - −, $T = 333.15$ K.

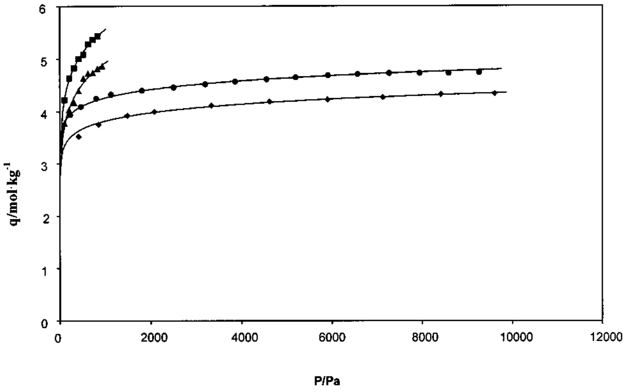

Figure 3. Plot of toluene adsorbed against relative pressure for the Freundlich model (solid lines) and for the experimental results: ■, $T = 298.15$ K; ▲, $T = 308.15$ K; ●, $T = 318.15$ K; ◆, $T = 333.15$ K.

W is the volume of liquidlike adsorbate within the pore structure, and W_0 is the micropore volume. W is simply calculated by $W = qv$, where q is the number of moles adsorbed per unit mass of sorbent and v is the liquid molar volume of toluene. In this study, v was estimated at temperature T by the Rackett[16] equation. $\epsilon = RT \ln(P^s/P)$ is the thermodynamic adsorption potential required to bring 1 mol of adsorbate to the state of the bulk liquid at absolute temperature T. In this study, the saturated vapor pressure of toluene was calculated with the accurate Wagner[16] equation. A is the characteristic adsorption energy, which is a function of the adsorbent, and β is an affinity coefficient that permits the comparison of the

Table 5. Freundlich Parameters for Toluene Adsorption onto Activated Carbon

T			percent deviation (Δq)
K	K	n	%
298.15	2.43	8.38	0.41
308.15	2.09	8.03	1.03
318.15	2.97	19.10	0.31
333.15	2.48	17.12	0.63
		mean deviation/%:	0.55

Table 6. Dubinin Parameters for Toluene Adsorption onto Activated Carbon

T	$10^3 W_0$	$10^5 A$	percent deviation (Δw)
K	$m^3 \cdot kg^{-1}$	$mol \cdot J^{-1}$	%
298.15	7.09	4.75	2.37
308.15	6.67	4.49	1.05
318.15	5.35	1.97	0.30
333.15	5.13	2.10	0.45
		mean deviation/%:	0.82

adsorption potential of the test adsorbate to that of a reference adsorbate. Choosing toluene as the reference adsorbate results in $\beta = 1$.

According to their authors, eqs 4 and 5 are respectively more suitable for micropore (type I) and large-pore (type II) carbon sorbents. In a first step it was decided to correlate our data with eq 4 because activated carbon was classified by Radushkevich as a micropore sorbent (type I). It was, however, impossible to obtain an accurate correlation, especially at high toluene pressure. Equation 5 was thus considered. The parameters A and W_0 were assumed to be temperature dependent and were determined at each temperature. The corresponding parameters and the percent deviations are summarized in Table 6. From this table, it is possible to conclude that the Dubinin equation is well adapted to the description of toluene adsorption on activated carbon.

Conclusion

The adsorption isotherms of toluene onto activated carbon were measured at four different temperatures ranging from 298.15 K to 333.15 K. The data obtained were correlated with several models described in the literature. From this study, it can be concluded that the Toth model, the Freundlich model, and the Dubinin equation lead to a good correlation of the data.

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