J. Chem. Eng. Data **2002,** *47,* 467−473

Adsorption Isotherms of VOCs onto an Activated Carbon Monolith: Experimental Measurement and Correlation with Different Models

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A new material, activated carbon monolith, can be used as an adsorbent to remove volatile organic compounds (VOCs). Vapor−solid adsorption isotherms of three VOCs (toluene, 1-butanol, and ethyl acetate) on an activated carbon monolith were measured at: 20 °C, 60 °C, 100 °C, and 140 °C using a microbalance. The experimental data were correlated with the following adsorption isotherm models: Langmuir, Freundlich, Langmuir−Freundlich, and Toth equations. The Langmuir−Freundlich and Toth equations provided good fits to the experimental data.

Introduction

Environmental protection regulations for volatile organic compounds (VOCs) emission control have been accelerating the development of VOCs abatement systems. Methods such as condensation, absorption, adsorption, oxidation, and incineration have been used for removal and recovery of VOCs. Among these methods, carbon adsorption is an established technology, widely used in industrial processes for removal and recovery of hydrocarbon vapors from gaseous stream.

The search for a suitable adsorbent is generally the first step to develop an adsorption separation process and adsorption equilibria data of pure components is essential to understand the adsorption process. The most widely used adsorbent for VOCs removal from air is activated charcoal in form either grains or pellets. Desorption of adsorbed molecules usually occurred by means of a temperature increase using steam or hot gas (sometimes, for gasoline vapors, a pressure decrease: vacuum swing adsorption, VSA). These processes have two main drawbacks. The VOCs are condensed with waters after desorption with steam; if VOCs are miscible with water, a distillation step must be required. In addition, some VOCs (halogenated) can be destroyed by hydrolysis, preventing recycling. The concentration of desorbed VOCs is lower, leading to difficulties for condensation with desorption by hot gas. Therefore, a new method of regeneration was proposed:[1] heating of carbon by the Joule effect. Some difficulties arise due to the contacts between grains or pellets for a granular carbon bed:[2] the electric resistance is mainly located in the contacts between grains, and thus the power is dissipated in these contacts. Hot points can appear, which result in decomposition of some molecules such as perchloroethylene or tetrachloroethylene at high temperature. To avoid these inconveniences, a new material activated carbon monolith was introduced in this study; in addition, it also has a low-pressure drop. There is much adsorption equilibria information about granular activated carbon but few on the monolith.[3−5] Adsorption equilibria on activated carbon monolith were studied. Many isotherm models have been developed for describing adsorption equilibria; these models are successful either at lower pressures, prior to monolayer formation or at higher pressure corresponding to the multilayer region in adsorption. Detailed presentations of experimental methods and result analysis of gas−solid adsorption isotherm have been given by Do[6] and, with experimental results on several systems, by Ruthven.[7] In this paper, adsorption equilibria data for VOCs on the activated carbon monolith are reported at four different temperatures. The experimental data obtained were correlated with the Langmuir, Freundlich, Langmuir−Freundlich, and Toth adsorption models. Three VOCs (toluene, 1-butanol, and ethyl acetate) were chosen for their widespread uses in the industries.

Isotherm Models[6]

Langmuir Equation. The minimum number of parameters required to fit a nonlinear isotherm is three, as in the Langmuir isotherm model is

$$q = q_s \frac{bp}{1 + bp}$$

$$b = b_0 \exp\left(\frac{-\Delta_{ads}H}{RT}\right) \tag{1}$$

where the independent parameters are the saturation solid loading, q_s, the enthalpy of adsorption, $\Delta_{ads}H$, and the adsorption equilibrium constant, b_0. The Langmuir isotherm model is applicable for monolayer adsorption on a homogeneous adsorbent surface with negligible intermolecular force.

Freundlich Equation. The Freundlich isotherm is

$$q = kp^n \tag{2}$$

where k and n are empirical constants that are generally temperature dependent. The Freundlich equation is very popularly used in the description of adsorption organics from aqueous streams onto activated carbon and gas phase systems having heterogeneous surfaces. However, it is generally valid in a large but limited range of the adsorption data, for this isotherm equation does not have a proper Henry law behavior at low pressure and a finite limit at sufficiently high pressure.

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10.1021/je010183k CCC: $22.00

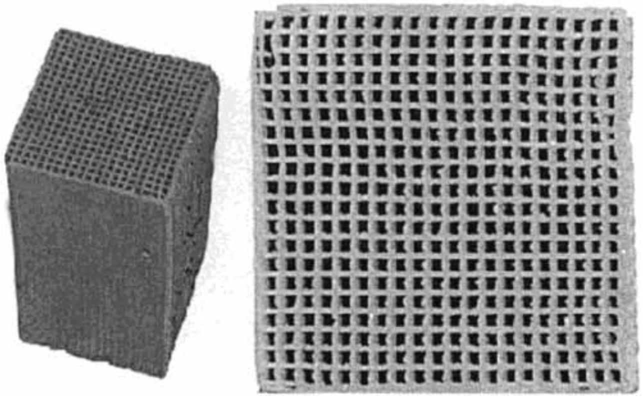

Figure 1. Photos of the activated carbon monolith.

Langmuir−Freundlich Equation. To eliminate the problem of a continuous increase of adsorbed amounts with an increase in pressure (concentration) in the Freundlich equation, the Langmuir−Freundlich equation was proposed:

$$q = q_s \frac{(bp)^n}{1 + (bp)^n}$$

$$b = b_0 \exp\left(\frac{-\Delta_{ads}H}{RT}\right) \tag{3}$$

This equation possesses a finite saturation limit when the pressure is sufficiently high, which cannot be solved by the Freundlich equation. But it still shares the same disadvantage with the Freundlich equation in that neither of them has the right behavior at low pressure.

Toth Equation. Another empirical equation is the Toth equation that is popularly used and satisfies both low- and high-pressure ranges.

$$q = q_s \frac{bp}{[1 + (bp)^t]^{(1/t)}}$$

$$b = b_0 \exp\left(\frac{-\Delta_{ads}H}{RT}\right) \tag{4}$$

Here t is a parameter that is usually less than unity. The parameters b and t are specific for adsorbate−adsorbent pairs. Hence the parameter t only depends on the adsorbent−adsorbate, and it should be constant for the same system at different temperatures.

Experimental Section

The adsorbent used in this study is an activated carbon monolith which was imported from China (Research Institute of Chemical Defence, Beijing). It is obtained by mixing activated charcoal powder with a binder and subsequent extrusion. No information is available on the chemical composition from the provider. The monolith is 10 cm long and has a square section of 5 cm in side that includes 400 channels. Typical channel pitch is 2 mm × 2 mm and wall thickness is about 0.8 mm. The photos and SEM picture of activated carbon monolith are shown in Figures 1 and 2, respectively. The BET surface of activated carbon monolith was measured with N_2 adsorption at 77 K by a Micromeritics ASAP 2000M. Its BET surface is 603 $m^2 \cdot g^{-1}$, which is much less than that of granular adsorbent AMBERSORB572 (1100 $m^2 \cdot g^{-1}$)[2] and pellet activated carbon AC 40 (1300 $m^2 \cdot g^{-1}$).[4]

Adsorption Isotherms Measurements. The experimental setup was shown in Figure 3. A magnetic suspension microbalance RUBOTHERM was used to measure adsorption isotherms with a condenser and a computer. A precision for a measurement was ±0.01 mg.

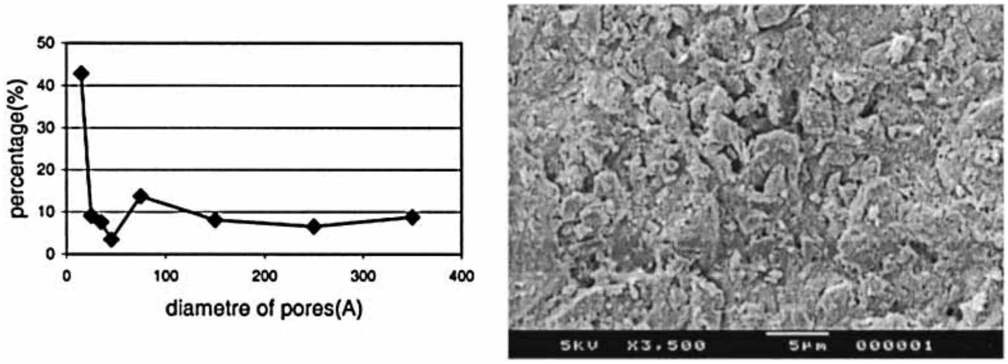

Figure 2. Pores distribution and SEM picture of activated carbon monolith

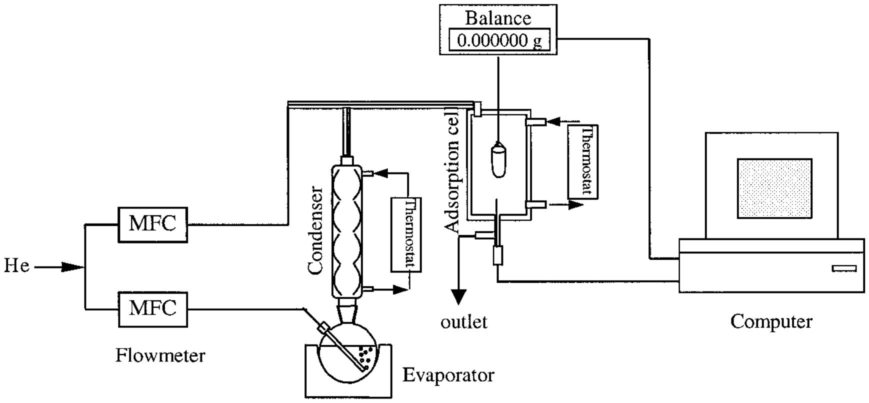

Figure 3. Gravimetric adsorption equilibrium apparatus

Table 1. Experimental Adsorption Equilibria Data of Toluene on the Activated Carbon Monolith Measured with a Microbalance

$t = 20$ °C		$t = 60$ °C		$t = 100$ °C		$t = 140$ °C	
P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}
0	0	0	0	0	0	0	0
50	1.32	100	0.99	50	0.42	50	0.24
150	1.67	200	1.17	150	0.64	150	0.38
250	1.83	300	1.27	250	0.75	250	0.47
350	1.93	450	1.37	300	0.78	300	0.49
450	2.02	600	1.44	350	0.82	350	0.52
603	2.11	1000	1.59	450	0.87	450	0.56
800	2.19	1503	1.72	600	0.93	600	0.61
999	2.24	1998	1.81	1000	1.05	1000	0.71
1503	2.33	2802	1.92	1503	1.14	1500	0.79
1998	2.44	4008	2.04	1998	1.20	2000	0.86
2300	2.53	5991	2.16	2800	1.29	2800	0.94
2499	2.65	8015	2.24	4008	1.37	4008	1.02
2611	2.76	9995	2.27	5991	1.49	5991	1.13
2698	2.92			8015	1.58	8015	1.21
2832	3.40			9995	1.64	9995	1.26
2910	3.98			11999	1.67	11999	1.30
				14993	1.70	14993	1.33
				25012	1.76		

Table 2. Experimental Adsorption Equilibria Data of Butanol on the Activated Carbon Monolith Measured with a Microbalance

$t = 20$ °C		$t = 60$ °C		$t = 100$ °C		$t = 140$ °C	
P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}
0	0	0	0	0	0	0	0
30	1.75	50	0.96	30	0.48	30	0.48
50	1.97	150	1.31	50	0.53	50	0.49
80	2.16	250	1.50	100	0.61	100	0.52
100	2.23	350	1.64	200	0.73	200	0.57
150	2.39	452	1.73	300	0.82	300	0.61
200	2.51	602	1.85	450	0.91	450	0.65
301	2.63	801	1.96	602	0.97	602	0.68
399	2.73	998	2.05	998	1.12	998	0.74
499	2.83	1204	2.13	1505	1.26	1505	0.81
551	2.95	1505	2.22	1996	1.36	1996	0.87
580	3.15	1996	2.29	3004	1.48	3004	0.96
602	3.32	2494	2.37	4009	1.62	4009	1.03
625	3.54	3004	2.37	5000	1.72	5000	1.08
		3496	2.49	5992	1.79	5992	1.18
				6995	1.85	6995	1.22
						11967	1.36

Adsorption equilibria experiments were performed at a pressure range of (0 to 15) kpa at 20 °C, 60 °C, 100 °C, and 140 °C with about (0.5 to 1) g fragments of activated carbon monolith. The gas flowrate is 100 mL/min. Before the measurement, the monolith was put in a dryer at about 180 °C for several days in order to eliminate water. The liquid VOC was first evaporated by heating in a continuous flow of helium, and then contacted with a condenser at the temperature corresponding to the desired partial pressure. Mixing the vapor with an additional helium stream allowed us to obtain a gas stream with a given VOC partial pressure. The resulting VOC-laden gas was continuously fed to adsorption cell. The mass increase of adsorbents as a function of time is continuously recorded. When the mass of cell remains constant (at $\pm 2 \times 10^{-5}$ g) for about 60 min under the operating condition, the equilibrium was regarded to be attained. Isotherm data points were obtained from the mass difference between pure adsorbents and the saturated adsorbents at each vapor concentration. After obtaining one point, the vapor concentration was changed and the system was allowed to reach another equilibrium point. The temperature of the microbalance cell containing adsorbents was taken as the measured isotherm temperature, which was controlled by a thermostatic bath. Depending on VOC concentration, vapor flowrate and adsorbent mass, the equilibrium time can take several or several tens of hours.

Table 3. Experimental Adsorption Equilibria Data of Ethyl Acetate on the Activated Carbon Monolith Measured with a Microbalance

$t = 20$ °C		$t = 60$ °C		$t = 100$ °C		$t = 140$ °C	
P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}	P/Pa	q/mol·kg^{-1}
0	0	0	0	0	0	0	0
100	0.97	100	0.34	100	0.19	100	0.07
200	1.18	300	0.67	300	0.34	300	0.17
300	1.34	500	0.83	500	0.44	500	0.23
400	1.46	800	0.99	800	0.54	800	0.30
600	1.59	1000	1.05	1000	0.60	1000	0.32
800	1.70	2000	1.30	2000	0.76	2000	0.47
1000	1.79	3000	1.41	3000	0.86	3000	0.54
1500	1.94	4987	1.55	4987	1.00	4987	0.65
2000	2.04	5991	1.62	5991	1.05	5991	0.69
2997	2.16	8002	1.72	8002	1.15	8002	0.79
4987	2.29	12007	1.89	12007	1.29	12007	0.89
5991	2.36	14987	1.98	14987	1.36	14987	0.95
7010	2.42	17973	2.07	17973	1.42	17973	1.01
8002	2.52	20043	2.12	20043	1.46	20043	1.04
9017	2.77	24993	2.22	24993	1.53	24993	1.11
9686	5.11	30016	2.26	30016	1.60	30016	1.16
		34972	2.31	34972	1.65	34972	1.21
		40096	2.36	40096	1.70	40096	1.24
				45108	1.74	45108	1.28

Solution of Isotherm Models. Experimental adsorption equilibria data were fitted to the several different isotherm models described in the previous section. The parameter estimation of temperature dependent equations was carried out simultaneously for the equilibria data at some temperatures using the least-squares approach. The parameters of models were estimated with regression by minimizing the square sum of relatively residual squares. Every optimization was repeated several times with different initial estimates of the parameters to avoid local minimum. The objective function Q to be minimized is expressed as the following:

$$Q = \sum \left(\frac{q_{\text{exptl}} - q_{\text{calcd}}}{q_{\text{exptl}}} \right)^2 \tag{5}$$

Note that, just as defined, Q is a relative value that depends on the goodness of fits and the experimental data.

Results and Discussions

The results for three VOCs adsorped on the monolith as a function of the VOCs partial pressures are summarized in Tables 1−3 at four temperatures. Four models were used to correlate the experimental adsorption equilibria data of VOCs. The experimental adsorption equilibrium data for three VOCs on the monolith at four temperatures were correlated along with the Langmuir, Freundlich, Langmuir−Freundlich, and Toth models.

The curves for the different models were used for the selection of the models. The experimental data, Langmuir and Freundlich models were shown in Figures 4−6. All the isotherms for the three VOCs exhibited a classical type-II shape characteristic of adsorbents in which there is a wide range of pore sizes. It is obvious that the Langmuir isotherm fails to correlate the results. The Langmuir isotherm equation contains only three parameters, which is not enough to describe the adsorption equilibria. At the lower pressures, the Langmuir model gives a good fit to the experimental data for the three VOCs at all the

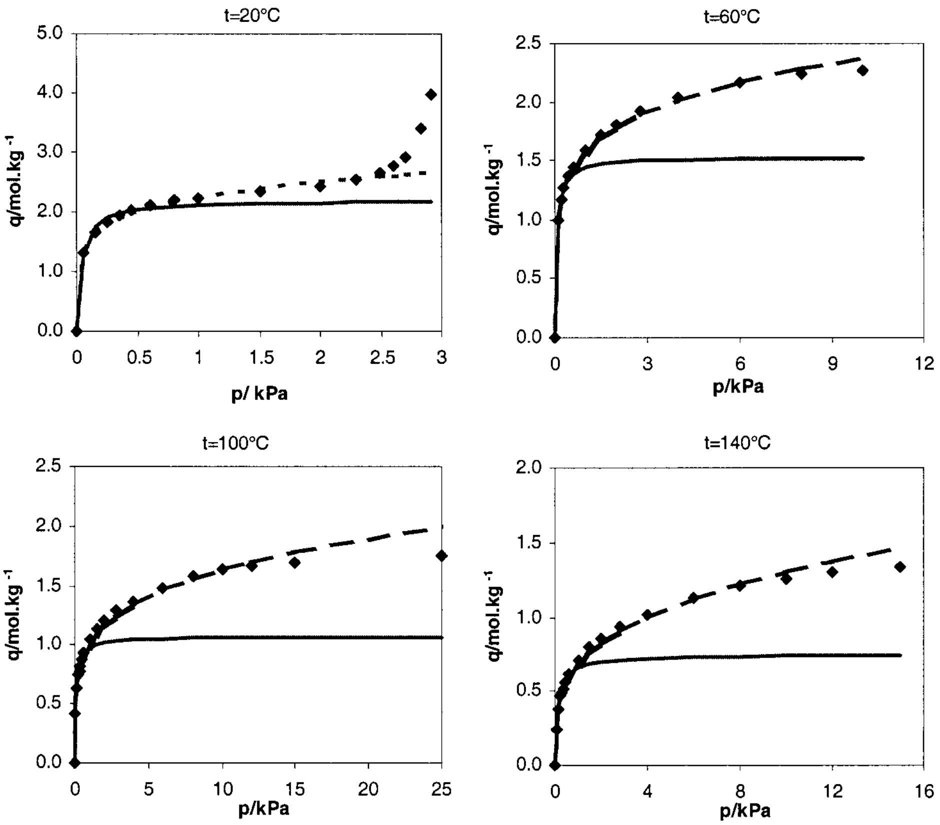

Figure 4. Experimental and predicted toluene adsorped quantities at four temperatures on the activated carbon monolith: —, Langmuir; - - -, Freundlich; ◆, experimental.

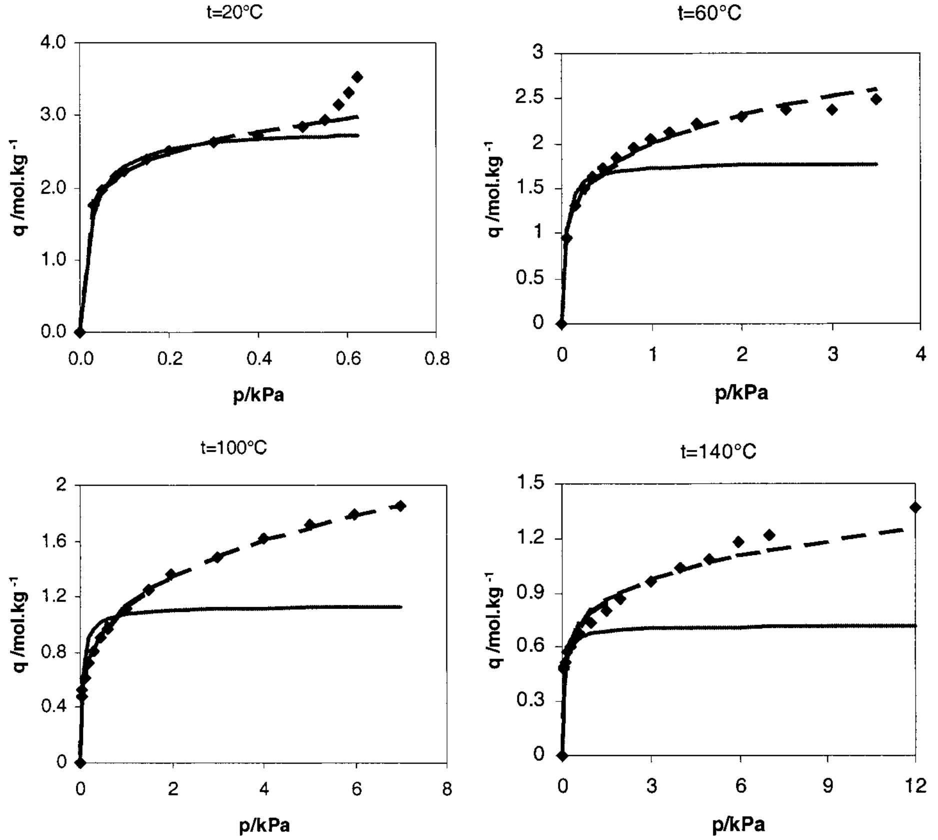

Figure 5. Experimental and predicted butanol adsorped quantities at four temperatures on the activated carbon monolith: —, Langmuir; - - -, Freundlich; ◆, experimental.

temperatures. That is because at low pressure there is less coverage on the surface, there is few interaction between the molecules. The Freundlich model provided better fits to the experimental data than the Langmuir equation, but it has large deviations at the higher pressures because of its limitations.

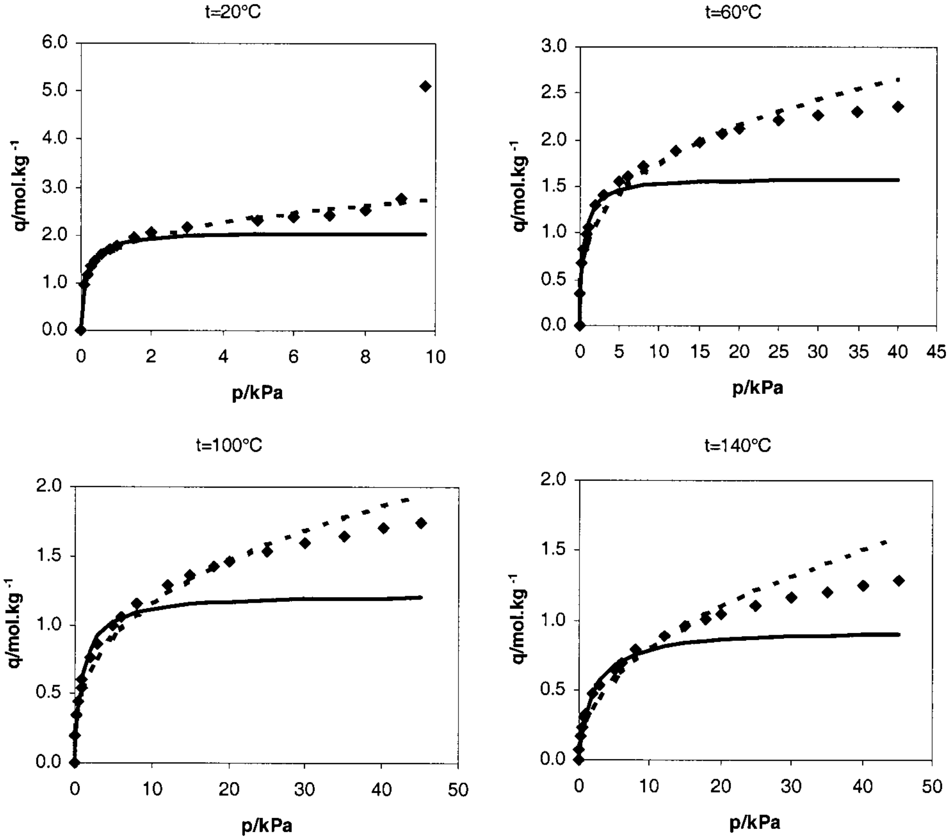

Figure 6. Experimental and predicted ethyl acetate adsorped quantities at four temperatures on the activated carbon monolith: —, Langmuir; - - -, Freundlich; ◆, experimental.

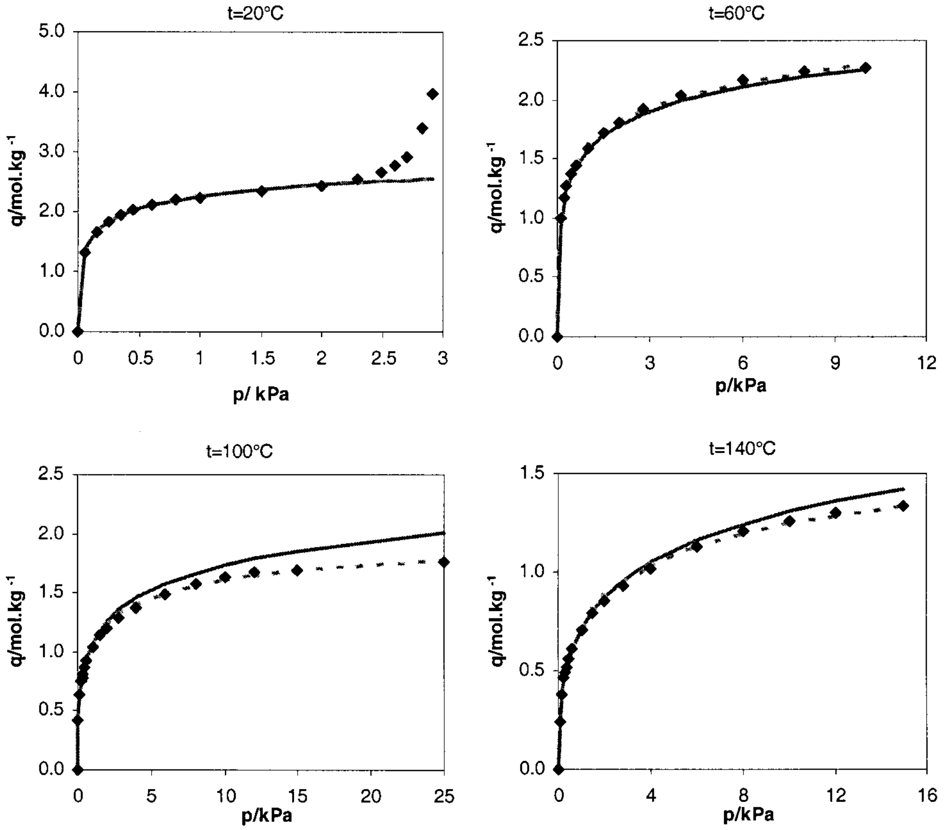

Figure 7. Experimental and predicted toluene adsorped quantities at four temperatures on the activated carbon monolith: - - -, Langmuir–Freundlich; —, Toth; ◆, experimental.

The regression results of Langmuir–Freundlich and Toth equations were shown in Figures 7–9. Both equations provided good fits to the experimental data. However at 20 °C when the VOCs pressures are higher than some

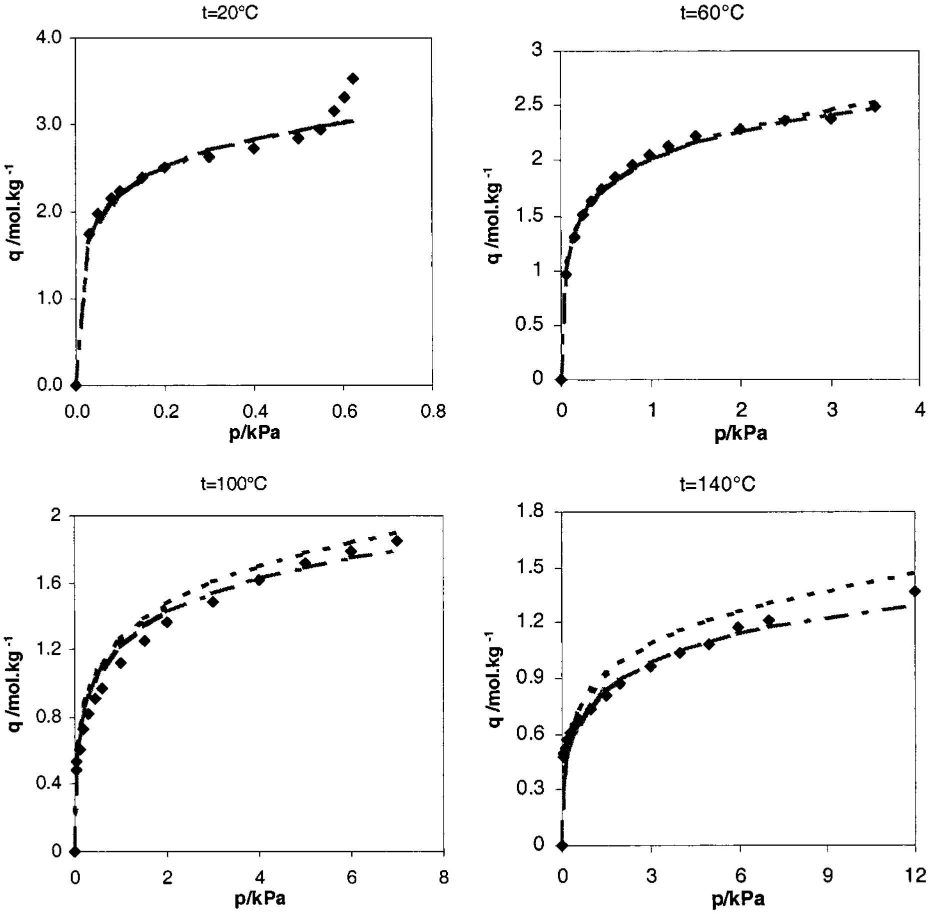

Figure 8. Experimental and predicted butanol adsorped quantities at four temperatures on the activated carbon monolith: - - -, Langmuir–Freundlich; — - —, Toth; ◆, experimental.

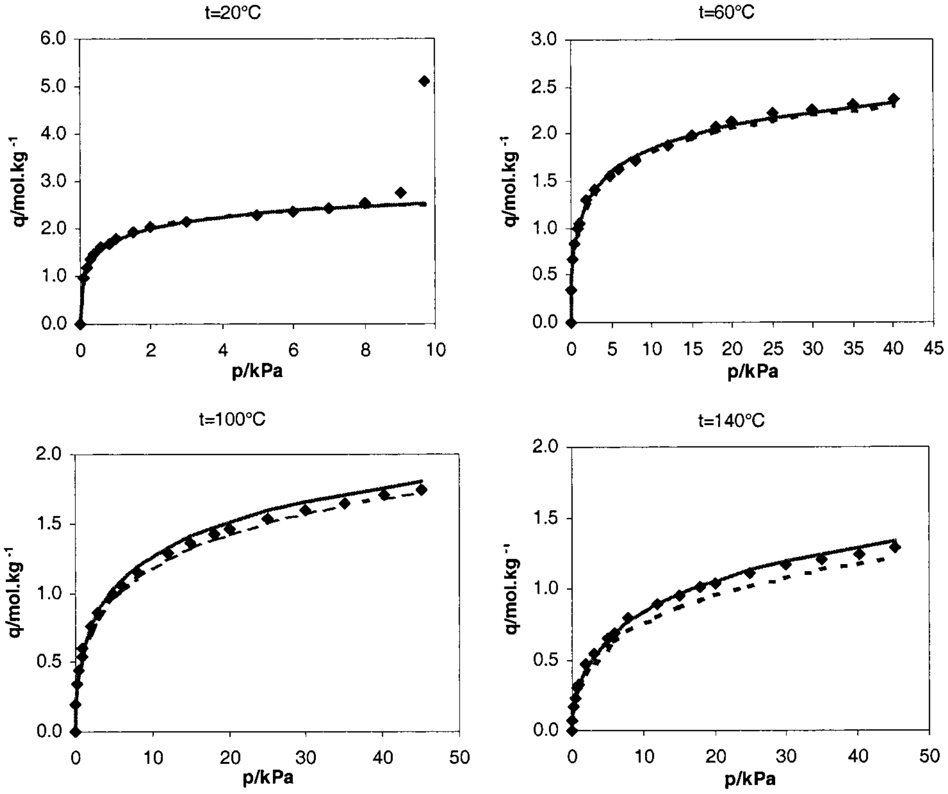

Figure 9. Experimental and predicted ethyl acetate adsorped quantities at four temperatures on the activated carbon monolith: - - -, Langmuir–Freundlich; —, Toth; ◆, experimental.

Table 4. Estimated Parameter Values of the Langmuir−Freundlich and Toth Equations for the Activated Carbon Monolith

		toluene	butanol	ethyl acetate
Langmuir−Freundlich	q_s/mol kg^{-1}	3.3	3.84	3.25
	b_0/Pa^{-1}	6.8×10^{-11}	4.46×10^{-12}	1.40×10^{-11}
	$-\Delta_{ads}H$/kJ mol^{-1}	45.1	54.25	45.1
	n	0.3912	0.4179	0.4555
Toth	q_s/mol kg^{-1}	4.35	4.04	3.94
	b_0/Pa^{-1}	6.9×10^{-8}	5.62×10^{-10}	3.88×10^{-9}
	$-\Delta_{ads}H$/kJ mol^{-1}	46.14	60.29	42.08
	t	0.2061	0.2332	0.2837

value (varying with the component), none of these models can describe the adsorption isotherms. This is because the adsorption mechanism goes from multilayer adsorption to capillary condensation as the VOCs partial pressures of gas phase in the adsorption system approaches the saturation pressure of the solvent at that temperature, and the smaller pores become completely filled with liquid sorbates. At 60 °C, 100 °C, and 140 °C, the highest measured VOCs pressures are much lower than the respective saturated pressures. Therefore the capillary condensation does not appear. The fits of Langmuir−Freundlich model and Toth model are accurate on the three VOCs sorbates. Their parameters are given in Table 4. VOC adsorption on the monolith showed the same characteristics as the granular adsorbent AMSORB572 and AC 40, but its adsorption capacity is only about 0.5−0.8 of that of AMSORB572[2] and AC 40;[4] this is because some adhesives and additives were added to form it into such a shape.

Conclusion

Adsorption isotherms of toluene, 1-butanol, and ethyl acetate onto an activated carbon monolith were measured at four different temperatures ranging from 20 °C to 140 °C. The results were correlated with the Langmuir, Freundlich, Langmuir−Freundlich, and Toth models. The isotherms of three VOCs exhibit a classical type-II shape characteristic of adsorbents in which there is a wide range of pore sizes from this study. It was concluded that the Langmuir−Freundlich equation and the Toth equation give a good correlation of VOCs adsorption data on activated carbon monolith at all four temperatures.

Acknowledgment

The present work is performed in the framework of a PRA project in environmental protection (French−Chinese cooperation program).

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Received for review June 21, 2001. Accepted January 23, 2002. F.D.Y. is deeply indebted to the ADEME in France for providing the scholarship.

JE010183K