ISOTHERM EQUATION FOR WATER VAPOR ADSORPTION ONTO ACTIVATED CARBON

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ABSTRACT: A simple isotherm model has been developed for the type-5 equilibrium adsorption systems by considering the effects of both primary and secondary adsorptive sites. The model was applied to interpret experimental data describing water vapor adsorption capacities of four activated carbon adsorbents for relative vapor pressures from 0.0 to 0.95 and temperatures between 288 and 308 K. Good agreement was observed between the model and experimental results. The isotherm parameters were found to either correlate well to the Brunauer, Emmett, and Teller specific surface area or have limited effect on describing the adsorption onto adsorbents made from the same precursor but activated with different degrees of burnout. The limiting pore volumes of the adsorbents obtained from the model based on water vapor adsorption compared favorably with those measured using volatile organic compounds.

INTRODUCTION

Equilibrium adsorption of water vapor onto microporous activated carbon adsorbents generally exhibits a type-5 isotherm according to Brunauer's classification (Adamson 1976; Basmadjian 1997). Because of the sigmoidal shape of this type of isotherm, only a few of many available isotherm models may be applied to water vapor adsorption, such as the well-known Dubinin-Serpinski (DS) equation (Dubinin 1980; Baron et al. 1991). The original DS equation describes water vapor adsorption for the relative vapor pressure range (P/P_0, where P is the actual partial pressure and P_0 is the saturation partial pressure of water vapor) from 0.0 to 0.6 (Cal 1995). A recent modification by Barton et al. (1992) extended the DS equation to describe the entire water vapor adsorption isotherm (Cal et al. 1997). This modified DS equation relates P/P_0 to the adsorption capacity of the adsorbent by an empirical four-parameter nonlinear equation. Because the adsorption capacity cannot be expressed explicitly, it is inconvenient to use the modified DS equation to determine the adsorption capacity of adsorbent for water vapor at a given P/P_0.

MODEL DEVELOPMENT

Water vapor adsorption onto activated carbon involves primary and secondary adsorptive sites (Dubinin 1980). The primary adsorptive sites consist of oxygenated surface compounds capable of forming hydrogen bonds with water molecules. The secondary adsorptive sites are the previously adsorbed water molecules, which can form hydrogen bonds with the adsorbing water molecules. At low relative pressures of water vapor, adsorption occurs mainly on the primary sites. The number of available primary sites contributing to water vapor adsorption decreases with increasing water vapor pressure as water vapor adsorbs onto those sites. With further increase in water vapor pressure, adsorption occurs mainly on the secondary sites of the previously adsorbed water molecules. Therefore, it is the combination of the primary and secondary adsorptive sites that determines the change in adsorption capacity with the change in water vapor pressure. It is assumed that (1) the number of secondary adsorptive sites is proportional to the amount of water adsorbed or the adsorption capacity q at a specified P/P_0; (2) the number of primary adsorptive sites is proportional to the remaining adsorption capacity, $(q_0 - q)$, where q_0 is the limiting adsorption capacity at P/P_0 approaching 1.0; and (3) the driving force for the change in adsorption capacity with the change in vapor pressure is proportional to the product of $(q_0 - q)$ and q. These assumptions result in a simple isotherm model in dimensionless form that follows:

$$\frac{d\left(\frac{q}{q_0}\right)}{d\left(\frac{P}{P_0}\right)} = k\left[1 - \left(\frac{q}{q_0}\right)\right]\left(\frac{q}{q_0}\right) \tag{1}$$

where k = a proportionality constant. Mathematically, (1) is a logistic function (Beltrami 1987). Although nonlinear, it can be integrated by separating variables to yield

$$q = \frac{q_0}{1 + \exp[k(P_{50}/P_0 - P/P_0)]} \tag{2}$$

where P_{50} = an isotherm constant; and $P = P_{50}$ at $q/q_0 = 0.5$. The plot of (2) exhibits a characteristic S shape with P_{50} at $q/q_0 = 0.5$ as an inflection point. Comparing with the modified DS equation (Barton et al. 1992), the simple isotherm model of (2) has the advantages of expressing q explicitly as a function of P/P_0 and containing three instead of four isotherm parameters.

RESULTS AND ANALYSIS

The experimental data of Cal (1995) for adsorption of water vapor at room temperature (25°C) onto three activated carbon–fiber cloth (ACFC) adsorbents were used to verify the isotherm model of (2). The three ACFCs, made from a cross-

TABLE 1. Water Vapor Adsorption Isotherm Parameters for Activated Carbon–Fiber Cloths

Adsorbent[a] (1)	Surface area[b] A (m^2/g) (2)	Slit-pore half-width[c], x_0 (nm) (3)	k (4)	P_{50}/P_0 at q/q_0 = 0.5 (5)	q_0 (g/g) (6)
ACF-15	900	0.492	20.0	0.451	0.351
ACF-20	1,610	0.637	27.9	0.542	0.571
ACF-25	2,420	0.915	23.3	0.650	0.788

[a] Manufactured by American Kynol, Inc., New York.
[b] Foster et al. (1992).
[c] Cal et al. (1994).

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linked phenol-aldehyde fiber precursor, differ in adsorption properties (Table 1), which was achieved by adjusting the degree of burnout or the duration of activation. Fig. 1 shows that (2) compares favorably with the experimental data for all three ACFCs over the entire P/P_0 range. The best-fit isotherm parameters q_0, P_{50}/P_0, and k are presented in Table 1. Those parameters were determined by fitting (2) to the experimental data using a nonlinear least-squares optimization program written in Fortran, which includes a subroutine obtained from the International Mathematical and Statistical Library (1994). Both q_0 and P_{50}/P_0 increase with increasing the Brunauer, Emmett, and Teller (BET) specific surface area (A). However, the dependence of k on A is inconclusive. Parameter P_{50}/P_0 may relate to A linearly with a regression coefficient of 1.000 (Fig. 2). The limiting adsorption capacity q_0 also may relate to A linearly with a regression coefficient of 0.996 (Fig. 3). Among the three isotherm parameters, q_0 and P_{50}/P_0 play a more important role than k in (2) in describing the experimental data. Thus, with $k = 23.7$ (the average of the three values for k in Table 1) and values for P_{50}/P_0 and q_0 calculated using the correlations in Figs. 2 and 3, (2) is able to approximate the water vapor adsorption onto all three ACFCs (Fig. 4).

The linear dependence of q_0 on A comes as no surprise because the BET specific surface area is a measure of micropore filling rather than actual surface area for a microporous adsorbent. The limiting adsorption capacity q_0 relates to the limiting pore volume V_0 by the simple relation that follows:

$$V_0 = \frac{q_0}{\rho} \tag{3}$$

where ρ = density of condensed adsorbate in the adsorbent pores. It is assumed that ρ is equal to the normal liquid density at atmosphere pressure for temperatures below its normal boil-

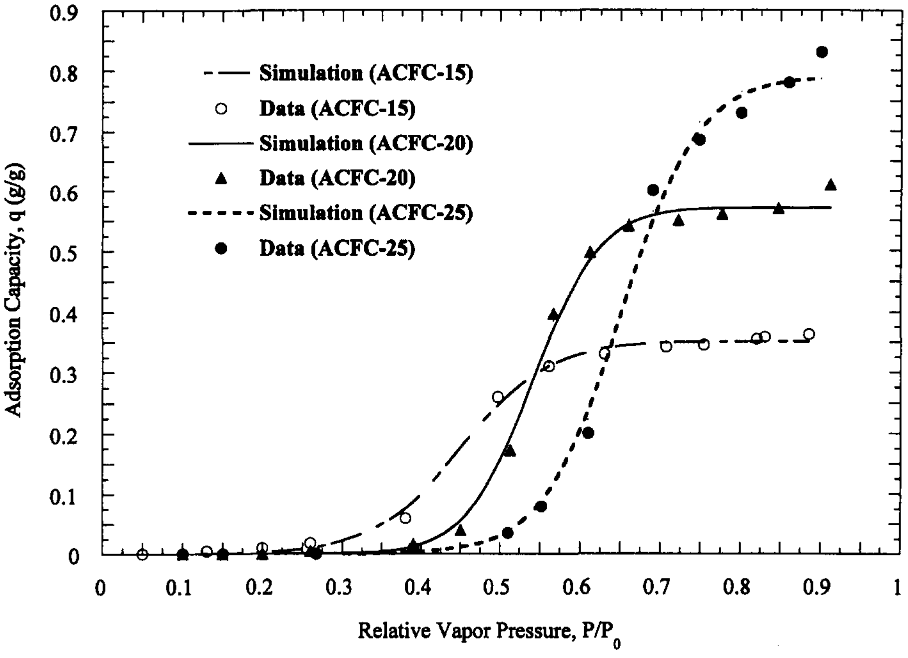

FIG. 1. Equilibrium Adsorption of Water Vapor onto ACFC with Different Degrees of Burnout; Data of Cai (1995) Compared with (2) with Best-Fit Parameters

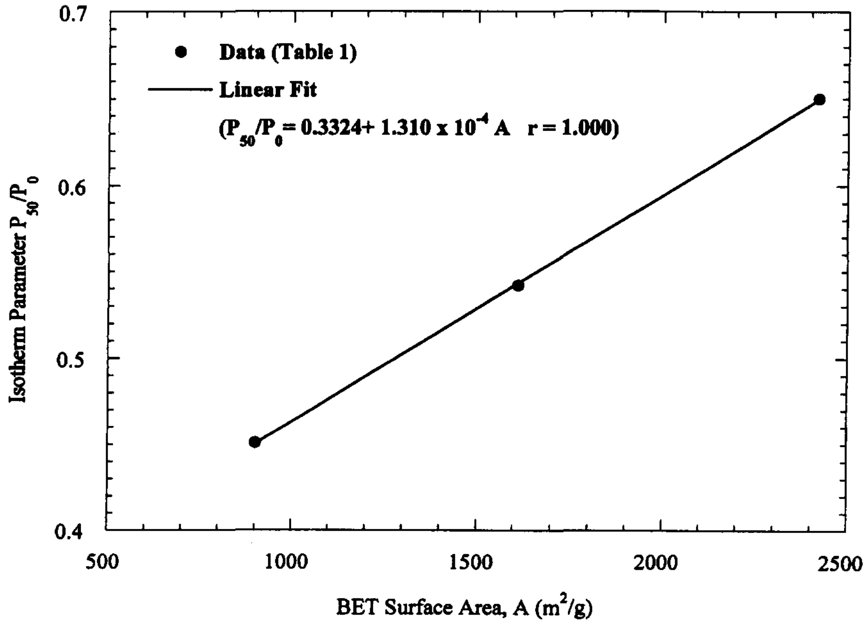

FIG. 2. Relation between Isotherm Parameter P_{50}/P_0 and N_2 BET Surface Area of ACFCs

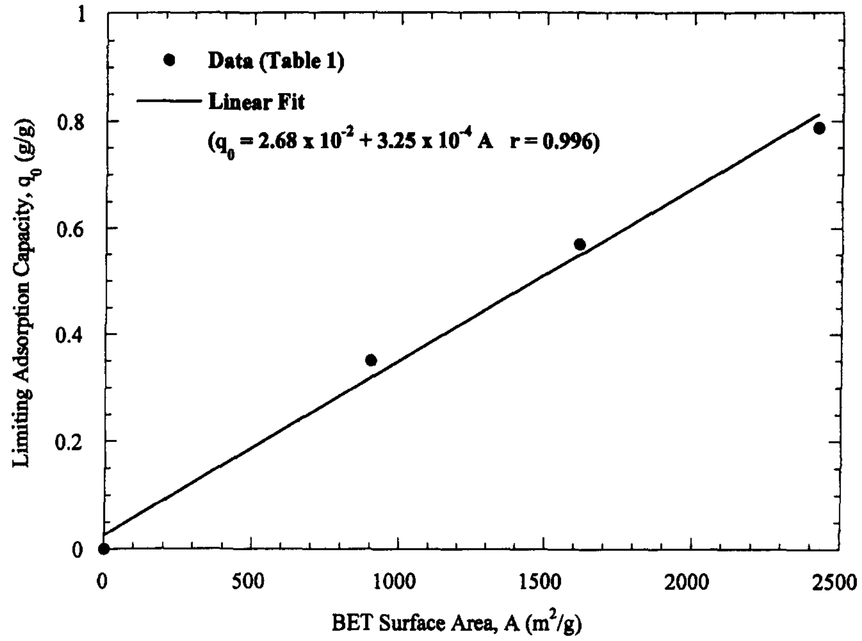

FIG. 3. Relation between Limiting Adsorption Capacity and N_2 BET Surface Area of ACFCs

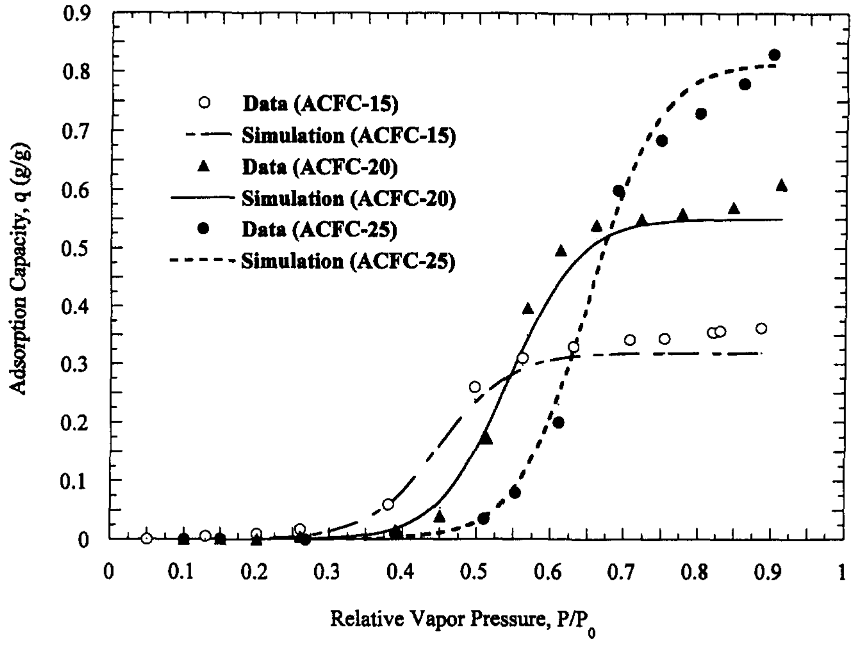

FIG. 4. Equilibrium Adsorption of Water Vapor on ACFCs with Different Degrees of Burnout; Data of Cal (1995) Compared with (2) with Parameters Calculated from Correlations

TABLE 2. Limiting Pore Volumes of Activated Carbon-Fiber Adsorbents

Adsorbent (1)	Average V_0 (cm^3/g) (VOCs as adsorbates) range of |difference %|[a] (2)	V_0 (cm^3/g) from (3) (H_2O as adsorbate) (3)	Difference (%) (4)
ACF-15	0.325 (0.6–6.2%)	0.352	+7.7
ACF-20	0.636 (0.3–2.7%)	0.573	−9.9
ACF-25	0.845 (0.5–4.7%)	0.791	−6.4

[a] Foster et al. (1992).

ing point. For temperatures higher than the normal boiling point, an adjustment similar to the one made by Dubinin (1975) may be necessary. The limiting pore volumes for the three ACFCs calculated using (3) are presented in Table 2. The value of V_0 for each of the ACFCs is slightly dependent on the adsorbate used to perform the adsorption test (Foster et al. 1992). Thus, the comparison is made only between the value of V_0 based on water vapor adsorption and the average V_0 for a given ACFC. The average V_0 was determined using a series of volatile organic compounds (VOCs) including acetone, toluene, and benzene as adsorbates (Foster et al. 1992). Our results and those from Foster et al. (1992) are within a relative difference of <10%. Thus, the determination of V_0 for the microporous activated carbon adsorbents may be achieved using low cost, safe, and readily available water vapor as an adsorbate with tests conducted at ambient temperature and pressure.

Eq. (2) was further verified using the experimental data of Hassan et al. (1991) for water vapor adsorption onto type BPL activated carbon at temperatures between 288 and 308 K. Type BPL activated carbon is a microporous adsorbent commercially available from Calgon Carbon Corporation. Fig. 5 shows

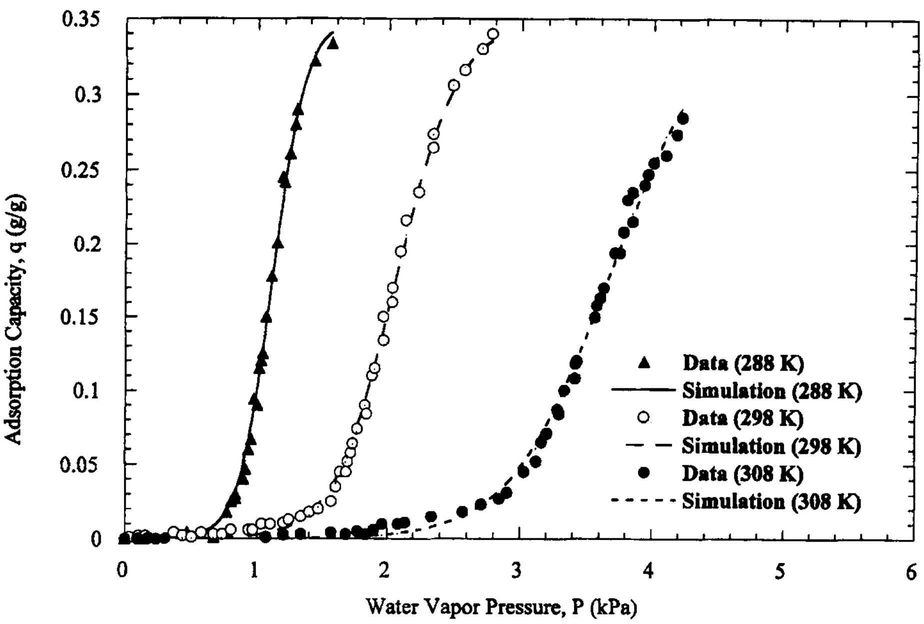

FIG. 5. Equilibrium Adsorption of Water Vapor onto BPL Activated at Different Temperatures; Data of Hassan et al. (1991) Compared with (2) with Best-Fit Parameters

TABLE 3. Water Vapor Adsorption Isotherm Parameters on BPL Activated Carbon

Temperature (K) (1)	V_0 (cm^3/g) (2)	P_{50} (kPa) (3)	P_{50}/P_0 (4)	k (5)
288	0.347	1.104	0.648	14.95
298	0.347	2.054	0.648	14.88
308	0.347	3.645	0.648	16.57
Average (Difference %)[a]	0.347	—	0.648 (0%)	15.47 (4.7%)

[a] Difference % = $[(\Sigma|\text{data}_i - \text{average}|/\text{data}_i)/3]\%$ (i from 1 to 3).

that (2) provides good description of the experimental data at all three temperatures. The best-fit isotherm parameters are summarized in Table 3. The value for V_0 was determined simultaneously with k and P_{50} for the adsorption at 298 K. This V_0 was then kept constant when determining k and P_{50} at 288 and 308 K. The results demonstrate that V_0 is mainly an adsorbent structure parameter and the thermal expansion of adsorbent has a small effect on V_0 in this temperature range.

Additional conclusions may be obtained about the isotherm parameters for the water vapor adsorption onto BPL activated carbon. At temperatures between 288 and 308 K, parameter P_{50} increases dramatically with increasing temperature. However, P_{50}/P_0 remains constant, and k also is insensitive to changes in temperature. This suggests that the isotherms shown in Fig. 5 may be represented by one isotherm curve if V_0 is plotted against P/P_0. Good agreement is observed for the results between 288 and 308 K as shown in Fig. 6.

Coadsorption of water vapor may limit the uptake of a variety of VOCs by an activated carbon adsorbent. The foregoing analysis shows that P/P_0 controls the amount of water vapor adsorbed at typical ambient conditions near 298 K and atmospheric pressure. A simple way to reduce the competitive adsorption of water vapor is to reduce P/P_0 by elevating the

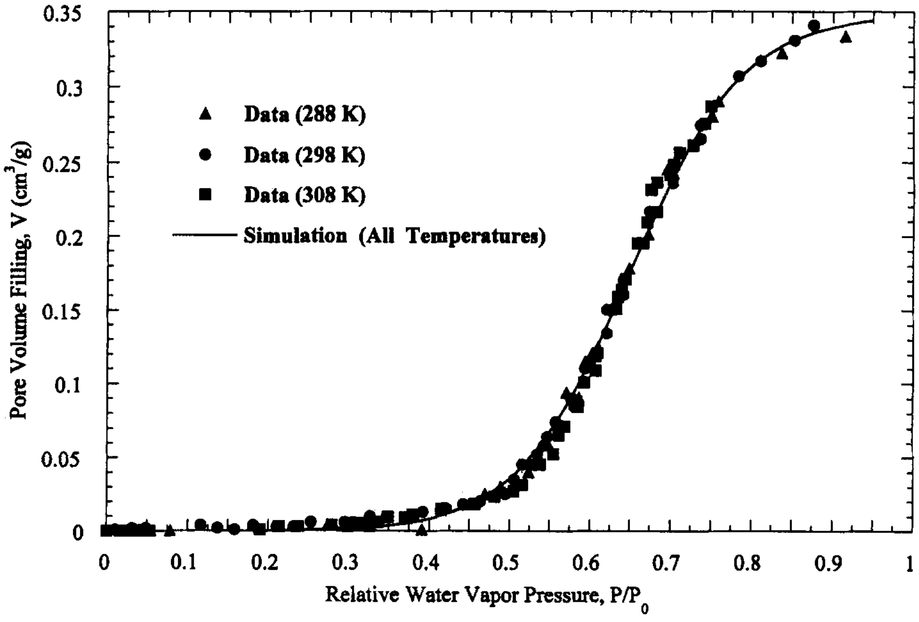

FIG. 6. Equilibrium Adsorption of Water Vapor onto BPL Activated Carbon at Different Temperatures; Data of Hassan et al. (1991) Compared with (2) with Average Parameters

adsorption temperature. Suzuki (1994) demonstrated that for removal of trichloroethylene from the off-gas of an air stripping process, the service life of a fixed-bed activated carbon adsorber was almost doubled when P/P_0 was controlled at a level of 0.3 by heating the influent gas stream. If a cryogenic condenser is used to recover VOCs downstream of a regenerating adsorption bed, then a reduction in water vapor adsorption with increasing the adsorption temperature would limit ice formation in the condenser.

SUMMARY AND CONCLUSIONS

A simple isotherm model has been developed for the type-5 equilibrium adsorption systems by considering the effects of both primary and secondary adsorptive sites. The model compares favorably with the experimental data for water vapor adsorption onto four different activated carbon adsorbents for relative vapor pressures from 0.0 to 0.95 and for temperatures between 288 and 308 K. The isotherm parameters were found to either correlate well to the BET specific surface area or have limited effect on describing the adsorption onto adsorbents made from the same precursor but activated with different degrees of burnout. The limiting pore volume of an adsorbent obtained from the model based on water vapor adsorption compares favorably with the one measured using VOCs.

Future studies will focus on the investigation of the model over a broad temperature range and the application of the model to describe competitive adsorption between water vapor and organic chemicals in gas streams.

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APPENDIX II. NOTATION

The following symbols are used in this paper:

A = BET surface/area (m^2/g);
k = isotherm constant;
q = adsorption capacity (g/g);
q_0 = limiting adsorption capacity (g/g);
P = equilibrium partial vapor pressure (kPa);
P_0 = saturated partial vapor pressure (kPa);
P_{50} = isotherm constant and $P = P_{50}$ at $q/q_0 = 0.5$ (mmHg);
r = linear regression coefficient;
V_0 = limiting pore volume (cm^3/g);
x_0 = slit-pore half-width (nm); and
ρ = density of condensed liquid in adsorbent pores (g/cm^3).