A Model for Adsorption Capacities of Charcoal Beds
I. Relative Humidity Effects

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Water vapor is the major interferent in the adsorption of other vapors from air when that air is passed through an activated charcoal bed. A limited amount of data (published and unpublished) is available on the magnitudes of capacity (or service life) reduction as a function of relative humidity (water vapor concentration) and preadsorbed water. A simple equilibrium model has been developed that quantitatively explains observed humidity effects and allows extrapolation of data to untested conditions.

Introduction

Water is the most common interferent in adsorption of vapors on air-purifying beds of charcoal. Water vapor is present in most atmospheres at high concentrations (50% relative humidity = 15 700 ppmv at 1 atm and 25°C). It is also present in the beds as adsorbed molecules or condensed water.[1] Water also can enhance the removal of some vapors by acting as a catalyst, a reactant or a solvent. A limited amount of data on the effects of water vapor is available. No model or theory, however, has been proposed to explain these data quantitatively or to use them for predictive purposes.

The objective of some recent work has been to develop a simple model for humidity effects on adsorption and to test it against published and unpublished data. In this first report only adsorption of water-immiscible organic vapors is considered. Two common situations are the following: 1) charcoal beds (canisters) preconditioned at the humidity at which they are tested; and 2) charcoal beds dried before testing or used as received.

Relative Humidity Effects Data

Preconditioned Beds

For the worst case situation and for simplicity, test beds or canisters often are preconditioned at the same relative humidity (RH) at which they subsequently are tested. Nelson et al.[2] examined humidity effects for seven organic vapors on two canisters with two types of charcoal. They varied both preconditioning humidity and use humidity. Breakthrough times (at 10% of challenge vapor concentration) were normalized to the breakthrough time measured at 50% RH preconditioning and 50% RH testing conditions for each vapor. These relative breakthrough times were averaged and presented in their Table 1. Their data of initial interest are those for equal preconditioning and testing relative humidities (0 to 90%). Jonas et al.[3] published similar data for chloroform vapor on an activated carbon. In a laboratory study, the author recently examined chloroform adsorption on an activated charcoal and an ASC-impregnated charcoal, preconditioned and run at three relative

humidities (unpublished data by author). The data from all three sources are plotted in Figure 1 as log-log plots of relative (normalized) breakthrough times (as defined above) for each set vs. relative humidity.

Dry Beds

Nelson et al.[2] also presented averaged data for canisters preconditioned at 0% RH and run at 0 to 90% RH. Werner[4] published extensive data for trichloroethylene breakthrough times on dried beds run at several relative humidities. He also varied the trichloroethylene vapor concentration 300 to 1300 mg/m³. Dry bed data from Nelson[2] and from Werner[4] (at two of four trichloroethylene concentrations) are plotted in Figure 2.

Comparisons

Data for both preconditioned and dry beds (Figures 1 and 2) indicate relative humidity effects that differ. All the data are quite different above 50% RH. It is also difficult to extrapo-
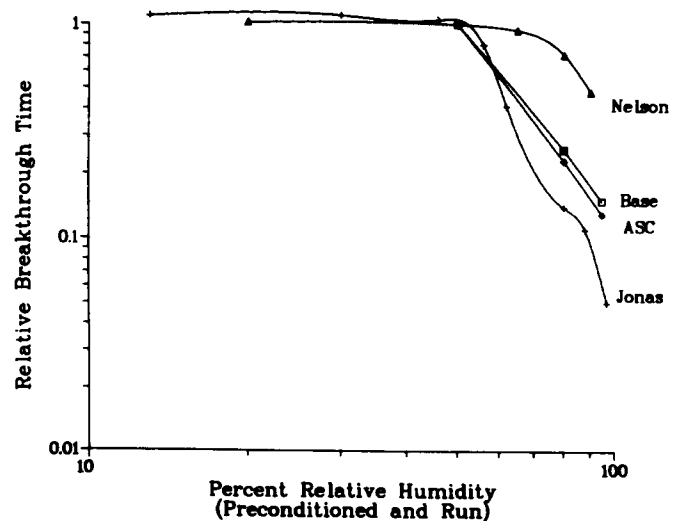

Figure 1 — Effects of humidity on relative breakthrough times of preconditioned charcoal beds. Nelson,[2] Jonas,[3] and author's unpublished data.

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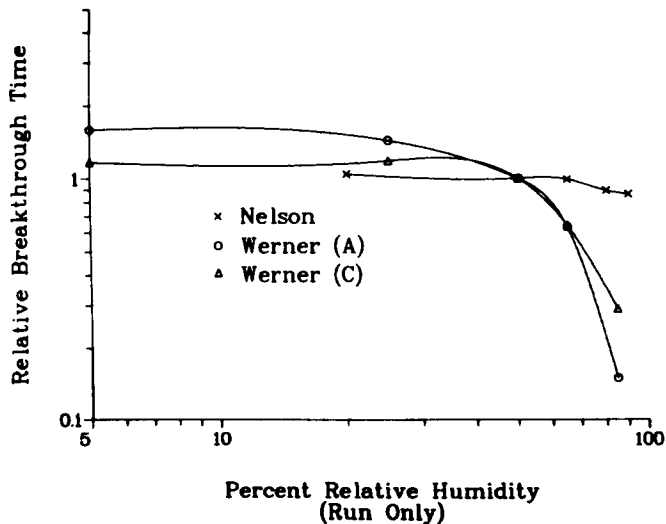Am. Ind. Hyg. Assoc. J. (48)   July, 1987

Figure 2 — Effects of humidity on relative breakthrough times of dry charcoal beds. Nelson[2] and Werner[4] data.

late any of these data to untested or difficult-to-test (e.g., 100% RH) conditions. The meaning of the data is also unknown. What do they reveal about the charcoals? What do they indicate about the removal mechanisms?

Proposed Model

Dubinin[1] has described quite successfully the equilibrium adsorption capacity of vapors on charcoal as due to condensation in the micropores. Yoon and Nelson[5] have described adsorption breakthrough curves by equations of the form:

$$t_B = g + h \ln\left(\frac{C_B}{C_0 - C_B}\right) \quad (1)$$

where t_B is the breakthrough time for the selected penetration fraction C_B/C_0 (ratio of effluent vapor concentration to challenge concentration). The details of the parameters comprising g and h can be found in References 2, 4-7. For the purpose of this study, it is only necessary to note that there is an equilibrium capacity term, g, and there is a kinetic term, $h \ln C_B/(C_0-C_B)$, which considers the spread of the vapor wavefront exiting the bed.

Assumptions that are made for the model are as follows:

1. Only adsorbed (or condensed) water molecules, not water vapor molecules in the air (W), affect the capacity for adsorption of adsorbate molecules in air (A).
2. Only the capacity term g of Equation 1 is affected by this adsorbed water.
3. Equilibria between gas, solid and liquid phases can be assumed for both water and adsorbate at breakthrough.
4. There exists a fixed concentration $[P]_0$ of homogeneous condensation micropores, which can contain either n molecules of water (W_nP) or m molecules of adsorbate (A_mP).

Equilibria and equilibrium constants (K_A and K_W) can be expressed as:

$$mA + P \rightleftharpoons A_mP \qquad nW + P \rightleftharpoons W_nP \quad (2)$$
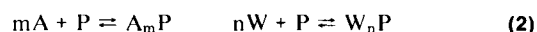
$$K_A = \frac{[A_mP]}{[P][A]^m} \qquad K_W = \frac{[W_nP]}{[P][W]^n} \quad (3)$$

for the challenge vapor and water vapor concentrations (mg/m^3), [A] and [W], respectively. The concentration of pores available for condensed water or adsorbate is:

$$[P] = [P]_0 - [W_nP] - [A_mP] \quad (4)$$

The fraction of pores filled with adsorbate is:

$$F_A = \frac{[A_mP]}{[P]_0} = \frac{K_A[A]^m}{1 + K_W[W]^n + K_A[A]^m} \quad (5)$$

The bed capacity X_A at the preselected breakthrough point is:

$$X_A = bmF_A \quad (6)$$

for $b = [P]_0(MW_A)/A_0$ (where A_0 is Avogadro's number and MW_A is the molecular weight of the adsorbate). Combining the above equations leads to:

$$X_A = \frac{bm K_A[A]^m}{1 + K_W[W]^n + K_A[A]^m} \quad (7)$$

$$\frac{1}{X_A} = \left(\frac{1 + K_A[A]^m}{m\,b\,K_A[A]^m}\right) + \left(\frac{K_W}{m\,b\,K_A[A]^m}\right)[W]^n \quad (8)$$

TABLE I
Parameters Obtained for Preconditioned Bed Data

Data Source	Adsorbates Tested	Adsorbate Concentration	Penetration Fraction	% RH Range	Number of Points	Best Linear Fit Values			
						n	R	Intercept	Slope
Nelson et al.[2]	Seven organics	1000 ppm	0.10	0 - 90	6	8.4	0.9999	0.99	2.65
Jonas et al.[3]	Chloroform	108 000 mg/m³ (22 500 ppm)	0.01	13 - 95	5	7.1	0.9936	1.00	20.94
Wood (ASC)ᴬ	Chloroform	450 mg/m³ (110 ppm)	0.50	50 - 95	3	3.7	1.0000	0.30	9.07
Wood (Base)ᴬ	Chloroform	450 mg/m³ (110 ppm)	0.50	50 - 95	3	3.6	1.0000	0.36	7.82

ᴬAuthor's unpublished data.

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Test of the Model with Data

Equation 8 relates the inverse of the bed capacity to a power of the water vapor concentration. At the assumed equilibrium conditions where the second term of Equation 1 is zero, the inverse of the breakthrough time (min) at constant challenge concentration, $1/t_B = [A]V/X_A M_c$ [where V is the volumetric airflow (m^3/min) and M_c is the weight of charcoal (mg)].[6] Thus, $1/t_B$ is similarly a function of [W].

The inverse of the ratio of a capacity (X_A) or breakthrough time (t_B) relative to that (X_A' or t_B') at a reference water vapor concentration [W'] can be expressed as follows:

$$\frac{X_A'}{X_A} = \frac{t_B'}{t_B} = \left(\frac{1 + K_A[A]^m}{1 + K_A[A]^m + K_W[W']^n}\right) + \left(\frac{K_W[W]_{SAT}^n}{1 + K_A[A]^m + K_W[W']^n}\right)(RH)^n \quad (9)$$

for [W] = [W]$_{sat}$(RH) [where [W]$_{sat}$ is the concentration of water vapor at saturation (100% RH) and RH is expressed as a decimal fraction]. Note that the intercept of Equation 9 must be less than or equal to unity.

In order to test this equation against data previously mentioned, the first step was to normalize breakthrough times (or adsorbate capacities) for each data set to values at 50% RH. This reference humidity was selected since this is the way Nelson[2] reported his data; any other reference could have been chosen. The reciprocals of these, $t_B'/t_B (= X_A'/X_A)$ were fit vs. $(RH)^n$ by least squares to the value of n that gave the best straight line and an intercept ≤ 1, as determined by the correlation coefficient R closest to 1.0000. Generally, there was a maximum in R for n values within ± 0.2. The values of n and R and the slope/intercept ratios obtained by this procedure are independent of the reference humidity selected.

Preconditioned Beds

The results of fitting this model to the data and some experimental parameters obtained for preconditioned beds are given in Table 1 and in Figure 3. Although the charcoals, adsorbates, challenge concentrations, selected penetration fractions and relative humidity ranges varied widely, the data sets were all well fit (R > 0.99) to straight lines. The lowest value of R was for the data of Jonas,[3] which represented rather short breakthrough times (1 to 25 min). Values of n ranged from 3.6 to 8.4.
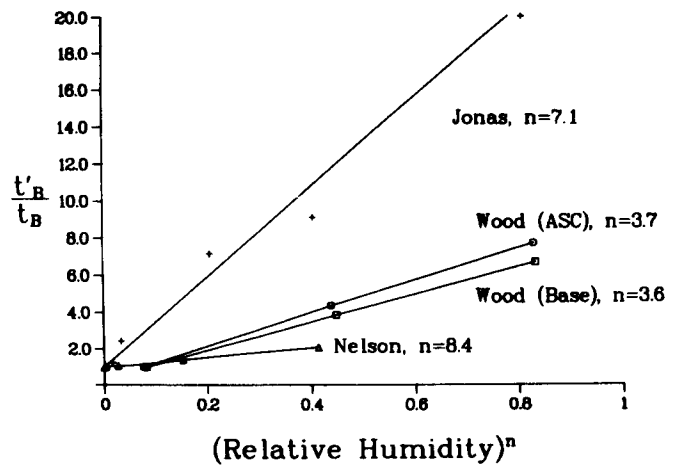

(Relative Humidity)^n

Figure 3 — Plots of preconditioned bed data according to the proposed model. Nelson,[2] Jonas,[3] and unpublished data.

Dry Beds

Results of similar calculations for originally dried or untreated beds are given in Table II and Figure 4. Again, good linear correlations (R > 0.98) were obtained with n ranging from 3.4 to 7.0.

Discussion

A comparison of the results in Table II for Werner's data[4] at 0.1 and 0.5 penetration fraction reveals that there are small but significant differences in the parameters calculated. Higher n and slope values at 0.5 penetration would be expected for initially dry beds, since there was more time to approach water adsorption equilibrium (or pseudoequilibrium) than at the earlier 0.1 penetration point. Also, the assumption that only the capacity term of Equation 1 is affected by the adsorbed water (Assumption 2 above) may be only approximate except for 0.5 penetration fraction, where the second term of Equation 1 is zero.

The model interprets the values of n as the average number of water molecules that fill the charcoal micropores. This is one parameter determining the capacity of the charcoal for water and perhaps other condensable vapors (pore concentration, related to b, is the other parameter).

TABLE II
Parameters Obtained for Dry Bed Data

Data Source	Adsorbates Tested	Adsorbate Concentration	Penetration Fraction	% RH Range	Number of Points	Best Linear Fit Values			
						n	R	Intercept	Slope
Nelson et al.[2]	Seven organics	1000 ppm	0.10	0 - 90	6	3.4	0.9821	0.98	0.31
Werner[1] (A)	Trichloro-ethylene	300 mg/m³ (50 ppm)	0.50	5 - 85	5	7.0	0.9995	0.72	18.56
			0.10	5 - 85	5	6.0	0.9991	0.73	14.63
Werner[1] (B)	Trichloro-ethylene	600 mg/m³ (100 ppm)	0.50	5 - 85	5	5.8	0.9999	0.84	11.34
			0.10	5 - 85	5	5.0	0.9987	0.81	10.04
Werner[1] (C)	Trichloro-ethylene	1000 mg/m³ (170 ppm)	0.50	5 - 85	5	4.9	0.9998	0.84	5.79
			0.10	5 - 85	5	4.2	0.9989	0.80	5.02
Werner[1] (D)	Trichloro-ethylene	1300 mg/m³ (220 ppm)	0.50	5 - 85	5	5.1	1.0000	0.86	4.98
			0.10	5 - 85	5	4.2	0.9968	0.87	4.31

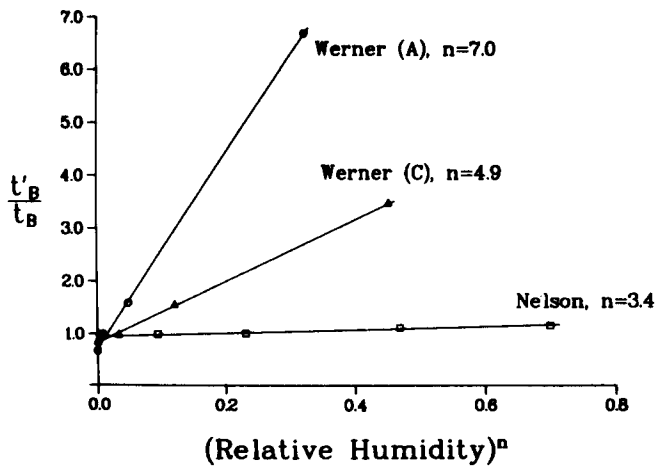$$\frac{t'_B}{t_B}$$

(Relative Humidity)^n

Figure 4 — Plots of dry bed data according to the proposed model. Nelson[2] and Werner[4] data.

The plots in Figures 3 and 4 show widely ranging effects of relative humidity on adsorption. For some unknown reason Nelson's data[2] show much smaller changes (slopes) — particularly for dry beds. Jonas' data[3] showed the greatest change (slope) with relative humidity for preconditioned beds, but reported no effect of relative humidity for dried beds.

Nelson's data[2] showed a big difference in n between preconditioned beds (n = 8.4) and dry beds (n = 3.4). This is not surprising since with the former there was more time and no competition (during the preconditioning process) for water adsorption and condensation, and there was no heating of the beds because of such processes during testing.[8] It is somewhat surprising that the model fits the data so well for unconditioned beds. A pseudoequilibrium must exist to account for this.

Wood's preconditioned bed data (unpublished data) gave similar values of n and slopes for a base charcoal and an ASC charcoal prepared from that base. This can be interpreted as the treatment not changing pore sizes, number or affinity for water.

It would be better to use Equation 8 rather than Equation 9 if the absolute (rather than relative) capacity data are available. There would be less dependence on the data point used for reference. It also might be possible to extract values for other parameters (m, K_W, K_A).

Conclusions

This simple equilibrium model:

1) Successfully describes the effects of testing (or use of) relative humidity on decreasing breakthrough times of water-immiscible adsorbates on charcoals.

2) Also describes humidity effects for dry charcoal beds, although nonequilibrium conditions surely exist because of released heat of water adsorption.

3) Allows interpolation and extrapolation of humidity effect data to untested conditions; and

4) Gives a parameter n of each charcoal that is interpreted as the average number of water molecules filling a micropore.

Obviously, much has been made of very limited data. More data are needed to confirm this model and to discover its limitations (e.g., water-soluble vapors). The calculated parameters of this model need to be correlated with physical properties of charcoals. This model should be expanded to take into account other removal mechanisms: reactions with the condensed water, chemisorption with impregnants, catalytic decomposition, etc.

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