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A REVIEW AND COMPARISON OF ADSORPTION ISOTHERM EQUATIONS USED TO CORRELATE AND PREDICT ORGANIC VAPOR CARTRIDGE CAPACITIES

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Four adsorption isotherm equations for describing measured capacities of organic vapor air-purifying cartridges were compared. Experimental breakthrough curves were measured for five organic vapors: ethanol, carbon tetrachloride, acetone, chloroform, and hexane. Plots of service life at 1% breakthrough versus bed weight (stacked cartridges) yielded capacities over concentration ranges for three brands of cartridges. The Freundlich, Langmuir, Dubinin/Radushkevich, and Hacskaylo/LeVan isotherm equations fit the capacity versus vapor concentration data equally well, except in the case of ethanol. The ethanol fit was worse for the Freundlich equation. Other characteristics of these equations were related to their usefulness for correlating service life.

One of the most important considerations in selecting and using an organic vapor air-purifying respirator cartridge is its service life (also called breakthrough time), i.e., how long it will provide respiratory protection. The service life of such a cartridge is determined by the equilibrium sorbent bed capacity and the kinetics of transfer of air contaminant(s) to the sorbent bed. These factors are, in turn, determined by the vapor the cartridge is used against, the vapor concentration, the cartridge design, its contents, the user's breathing rate, the environmental conditions, and the allowable penetration. Kinetic effects on breakthrough curve shape can be very important but have been reviewed elsewhere.(1)

This paper addresses the effects of vapor concentration and type and, to a lesser extent, the effects of cartridge design (brand and bed size) and average airflow (breathing) rate on bed capacity and service life. This is done by correlating experimental results of extensive cartridge breakthrough studies(2) by using four mathematically distinct two-parameter adsorption isotherm models.

BACKGROUND

Service life of a cartridge has been described by various equations.(1) One of these is the modified Wheeler equation(3):

$$t_b = \left(\frac{W_e W}{C_0 Q}\right) - \left(\frac{W_e \rho_\beta}{k_v C_0}\right) \ln(C_0/C_x) \qquad (1)$$

t_b = breakthrough time (min) at selected penetration fraction, C_x/C_0
C_x = exit concentration (g/cm^3)
C_0 = inlet concentration (g/cm^3)
Q = volumetric flow rate (cm^3/min)
W = weight of carbon adsorbent (g$_c$)
ρ_β = bulk density of the packed bed (g$_c$/cm^3)
W_e = adsorption capacity (g/g$_c$)
k_v = mass transfer rate coefficient (min^{-1})

Other breakthrough curve equations usually differ from the Wheeler only in the form of the second (kinetic) term, a function (usually logarithmic) of C_x/C_0. The first term contains the absolute (versus relative) equilibrium capacity, W_eW, of the bed in equilibrium with vapor at C_0. This term represents the breakthrough time if the transfer kinetics were infinitely fast, i.e., k_v infinitely large. Note that this equilibrium bed capacity is distinct from what is sometimes referred to as the bed capacity (or loading) at breakthrough, C_0Qt_b. To avoid confusion, only the former (equilibrium bed capacity) will be called capacity in this paper. Also, in unusual cases W_e may be a "pseudoequilibrium capacity," because of hindrances (e.g., macropore blocking or preadsorbed vapor displacement) in reaching equilibrium during the time scale of breakthrough curve measurements.

Various applications of the Wheeler equation lead to consistent values for the equilibrium adsorption capacity, but often differing values are obtained for the kinetic rate coefficient.(1) One of these applications, the bed weight variation at constant penetration fraction approach, avoids the uncertainty in the form and magnitude of the second term of Equation 1.

For this approach at constant C_x/C_0, C_0, W_e, k_v, and ρ_β, this second term can be considered a constant. Adsorption capacity, W_e, can be obtained from the slope, $S = W_e/C_0Q$, of plots of breakthrough time, t_b, versus bed weight, W, when the experimental values of C_0 and Q are known. The linearity of such plots has been demonstrated,(1,4,5) confirming the validity of this approach. This also confirms the "constant pattern assumption," fundamental to the derivation of breakthrough curve equations,(6) which says that the adsorption wavefront forms quickly in the sorbent bed and moves at a constant shape and rate through it. By conservation of mass the rate at which such a constant shape wavefront moves is proportional to C_0Q/W_e, i.e., the inverse of S. Because of this constant shape of the wavefront, S is independent of the penetration fraction (1%, 10%, etc.) selected for measuring t_b. Although the modified Wheeler equation (Equation 1) was used above to demonstrate that $S = W_e/C_0Q$, this relationship is independent of the other (kinetic) assumptions on which the Wheeler equation is based.

Adsorption equilibrium capacities are themselves determined by other factors, including sorbent type and condition, competing vapors, temperature, and, most importantly, vapor type and concentration. The dependence of equilibrium adsorption capacity on vapor concentration with all other factors held constant is usually described by an adsorption isotherm plot, such as Figure 1. Except for very polar methanol, all organic vapors on activated carbon exhibit Type I isotherms (as in Figure 1), according to the Brunauer classification scheme.(7) This is another fundamental assumption in the derivation of breakthrough curve equations.(6)

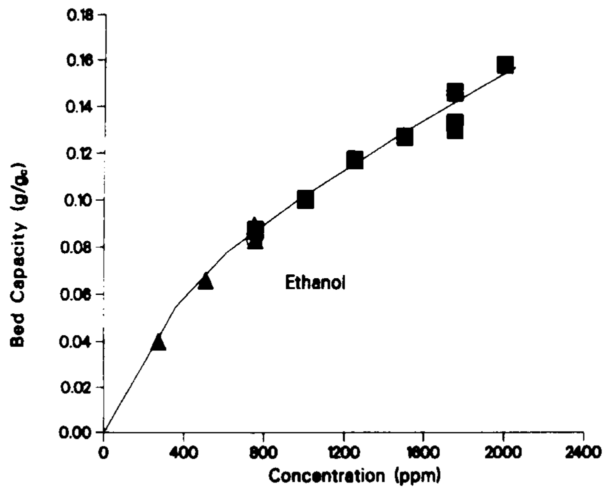

FIGURE 1. Adsorption isotherm plot of ethanol capacities from breakthrough curves for Willson (○), Pulmosan (△), and Norton (□) cartridges. Open symbols = dried; solid = as received.

The negative curvature of the adsorption isotherm explains why doubling the vapor concentration decreases the breakthrough time (cartridge service life) to less than half. According to Equation 1, t_b is proportional to W_e/C_0, the capacity/concentration ratio, not merely $1/C_0$. Figure 1 shows that this ratio (the slope from the origin to a point on the isotherm curve) decreases at higher concentrations, even though W_e also increases. Therefore, t_b decreases faster than $1/C_0$.

Many equations have been proposed and fit to Type I equilibrium adsorption isotherm data and data from breakthrough studies. The simplest ones of these contain only two adjustable curve fit parameters. In this paper, four of these equations will be discussed and their usefulness in correlating data from breakthrough studies will be compared.

The Freundlich isotherm equation(8) is

$$W_e = aC_0^{1/n} \tag{2}$$

where a and n are the two adjustable curve fit parameters. In practice, the logarithm of W_e is plotted against the logarithm of C_0 in hopes of getting a straight line with slope of 1/n and intercept of $\log a = \log (W_{sat}C_{sat}^{-1/n})$ where W_{sat} is the adsorption capacity at vapor saturation concentration, C_{sat}. Breakthrough times have also been correlated with concentrations by using such a relationship.(9,10) Equation 1 shows that t_b is proportional to W_e/C_0, all other parameters being kept constant. Therefore, according to the Freundlich equation, the slope of log t_b versus log C_0 should be a constant, $(1/n) - 1$, differing from the slope of log W_e versus log C_0 by 1.0.(11)

The Langmuir adsorption isotherm equation(12) is

$$W_e = \frac{W_{max}K_HC_0}{1 + K_HC_0} \tag{3}$$

where W_{max} is the upper limit to capacity at very high vapor concentrations and K_H is Henry's law constant. This equation is often used in a linearized form by plotting C_0/W_e versus C_0.

The Dubinin/Radushkevich (D/R) isotherm equation(13) can be expressed as:

$$\ln W_v = \ln W_{vsat} - \left(\frac{KR^2T^2}{\beta^2}\right)\left[\ln\left(\frac{P}{P_{sat}}\right)\right]^2 \tag{4}$$

W_v = volume capacity = W_e/ρ_L
ρ_L = density of condensed liquid in micropores
W_{vsat} = volume capacity at saturation vapor pressure, P_{sat}
T = absolute temperature
P/P_{sat} = relative vapor pressure = C_0/C_{sat}
R = ideal gas constant ($P = C_0RT$)
K = carbon structural constant
β = affinity (similarity) coefficient

The D/R equation is based on the micropore volume filling theory and the Polanyi concept of adsorption potential and characteristic curves.

Hacskaylo and LeVan (H/L) developed an adsorption isotherm equation based on analogy with the well-established Antoine equation for vapor pressures(14):

$$\ln P = A' + \ln \theta - \frac{B' + b'(1 - \theta)}{C' + T} \tag{5}$$

A′, B′, C′ = Antoine constants(15)
θ = fraction of saturation capacity = W_e/W_{sat}

P = equilibrium pressure = C_0RT
b' = constant of linear variation of heat of adsorption with loading

Although these isotherm equations have been compared for equilibrium data, no study of their relative usefulness in correlating breakthrough curve data has been reported.

EXPERIMENTAL MATERIALS AND METHODS

The experimental apparatus and procedures used to measure breakthrough curves of organic vapors have been described in detail elsewhere.(1,2,5) Briefly, dried air at controlled flow (70–190 L/min) was mixed with vapor of the chemical of interest. The vapor was produced by evaporation of liquid fed from a syringe pump or liquid pump at a rate predetermined to give the desired concentration. A portion of this mixture in a buffer tank was then drawn by vacuum through a cell housing containing one to four cartridges in series.(5) MIRAN 1A infrared analyzers (Foxboro Co., Foxboro, Mass.) with variable pathlength gas cells were used to monitor vapor concentrations both upstream of the housing and downstream of the individual cartridges. Analytical wavelengths used were acetone, 8.2 μm; carbon tetrachloride, 12.6 μm; chloroform, 13.0 μm; ethanol, 9.5 μm; and hexane, 3.4 μm. The analyzers were calibrated daily in the appropriate concentration ranges by using a closed loop of recirculating air with aliquots of liquid chemical injected by syringe, as recommended by the manufacturer. Data were collected, stored, and analyzed by computer.

Air-purifying organic vapor cartridges from three manufacturers were used. The carbon weight characteristics are listed in Table I; no other information is available on the carbons used in these commercial cartridges. Pretreatments were either none (as received, AR) or drying in a vacuum oven at about 100°C for at least 24 hr before testing (dried, D). Carbon bed weights for each cartridge were determined by cartridge weight just before use minus the case weight determined after removing the carbon. Airflow rate was 64 L/min, except for acetone, for which it varied from 32 to 115 L/min to examine flow rate effects.

Five vapors were studied at the following concentration ranges: ethanol (275–2000 ppm), chloroform (525–1000 ppm), carbon tetrachloride (550–1000 ppm), hexane (500–1040 ppm), and acetone (500–1745 ppm).

One to three (usually two) experiments were run at each set of conditions. Three or four breakthrough curves (0.2–20% penetration measured at 0.5- or 1-min intervals) were obtained for each experiment from measurements downstream of one to four stacked cartridges. These correspond to different total bed weights of the stacked cartridges.(5) Upstream (challenge) vapor concentration was also monitored during the experiments to obtain a mean value (±20 ppm). Experimental temperatures averaged 23°C at 0.97 atmospheric pressure.

Data Analysis

Breakthrough curve data (penetration fraction versus time) for each experiment and bed depth were interpolated to obtain breakthrough times at 1% penetration. These 7 to 12 such breakthrough times versus their corresponding total carbon bed weights for replicate experiments (at each set of vapor, concentration, cartridge lot, pretreatment, and flow) were analyzed by linear regression to obtain each value of the slope, S. Thus, for each vapor a matrix of concentrations and S was obtained (Table II). Linear correlation coefficients (R^2) were almost always above 0.99.(2) Capacities were calculated from these slopes (Table II).

In a separate report, values of W_e obtained from these slopes were used to calculate W_{vsat} and K/β^2 by using the linear form of the D/R equation (Equation 4).(2) However, linear least squares curve fitting is not always the best approach because it may bias the curve fit inappropriately.(16) Nonlinear least squares (NLLS) data fitting to equations is preferable and just as easily performed on today's desktop computers. Another reason NLLS was chosen for these analyses is that one of the equations (H/L) cannot be linearized. Because the number of experiments included in the data from which each S was obtained (Table II) varied (1–3), the data used in NLLS was weighted by this number. A two-parameter, weighted nonlinear least squares (WNLLS) program was written in BASIC by using the linearization (or Taylor series) approach.(17) The program was confirmed by comparing best fit results with those obtained by using a commercial nonlinear curve fitting program, SYSTAT (SYSTAT, Evanston, Ill.).

TABLE I. Organic Vapor Cartridge Characteristics

Cartridge		*Dried Carbon Bed Weight (g)*			*Weight Loss on Drying (%)*	
Brand	*Lot*	*Average*	*SD*	*N*	*Average*	*SD*
Willson	5C-121-3-40	46.6	1.6	38	1.5	0.5
	4K-271-68-60	47.3	2.0	88	0.4	0.4
	5C-111-3-27	51.2	0.9	16	1.9	0.5
Pulmosan	42-2-85	63.2	1.5	24	2.6	0.6
	49-4-84	63.5	1.2	63	0.8	0.3
Norton	27-F-4	36.8	1.4	81	(not dried)	

The next step, therefore, was to fit these slopes, related to W_e by $S = W_e/C_0Q$, to the four adsorption isotherm equations (2–5). These equations were rearranged as follows:

$$\text{Freundlich:} \quad S = \frac{A}{Q} C_0^{-B} \tag{6}$$

where $A = W_{sat}C_{sat}^{-1/n}$ and $B = 1 - 1/n$.

$$\text{Langmuir:} \quad S = \frac{AB/Q}{1 + BC_0} \tag{7}$$

where $A = W_{max}$ and $B = K_H$.

$$\text{D/R:} \quad S = \frac{A}{C_0Q} \exp\{-B[\ln(C_0/C_{sat})]^2\} \tag{8}$$

where $A = W_{vsat}\rho_L$, $B = KR^2T^2/\beta^2$, and ρ_L = liquid density.

TABLE II. Slopes of Linear 1% Breakthrough Time vs. Bed Weight Fits^A

Compound	Cartridges			Number of Exp.	Average Vapor Conc. (ppm)^D	Slope (min/g_c)	Capacity (g/g_c)
	Type^B	Condition^C	Number				
Acetone	W5C-12	D	8	2	1060	0.715	0.116
		AR	8	2	1060	0.739	0.120
		D	8	2	750	0.889	0.102
		AR	8	2	750	0.929	0.107
		D	8	2	530	1.075	0.087
		AR	8	2	530	1.134	0.092
	W4X-271	D	7	2	1060	0.743	0.121
		AR	8	2	1060	0.762	0.124
		D	8	2	750	0.978	0.112
		D	8	2	530	1.031	0.084
	P42-2	D	8	2	1050	0.721	0.116
		D	4	1	700	0.818	0.086
		D	4	1	700	0.785	0.082
		D	4	1	500	0.995	0.075
		D	4	1	500	0.985	0.074
		AR	8	2	1745	0.485	0.130
		AR	8	2	1500	0.538	0.124
		AR	11	3	1260	0.588	0.113
		AR	4	1	1060	0.612	0.099
		AR	8	2	1050	0.649	0.104
		AR	8	2	1000	0.660	0.101
		AR	4	1	790	0.726	0.088
		AR	8	2	745	0.803	0.092
		AR	8	2	500	1.005	0.077
	P49-4	D	8	2	1060	0.606	0.098
		AR	8	2	1060	0.643	0.104
Chloroform	W4K-271	D	8	2	1000	1.038	0.327
		D	8	2	825	1.155	0.300
		D	8	2	525	1.631	0.269
	P49-4	D	8	2	1000	1.191	0.375
		D	8	2	825	1.290	0.335
		D	8	2	525	1.721	0.284
Hexane	W4K-271	D	4	1	1040	0.970	0.229
		D	7	2	750	1.154	0.197
	W5C-121	D	8	2	1040	0.933	0.220
		AR	8	2	1040	0.928	0.219
		D	4	1	750	1.312	0.223
		D	2	1	500	1.810	0.205
	W5C-111	D	8	2	750	1.159	0.197
		AR	8	2	750	1.108	0.189
		D	8	2	500	1.505	0.171
		AR	8	2	500	1.521	0.173
	N27-F	AR	4	1	1000	1.073	0.244
		AR	4	1	1000	0.912	0.207
		AR	4	1	750	1.331	0.227
		AR	4	1	750	1.278	0.218
		AR	4	1	500	1.861	0.211
		AR	4	1	500	2.004	0.228
	P49-4	D	9	3^E	750	1.260	0.396
Carbon Tetrachloride	W4K-271	D	8	2	1000	1.017	0.412
		D	11	3	800	1.355	0.439
		D	8	2	550	1.649	0.368
	P49-4	D	8	2	1000	1.155	0.486
		D	9	3^E	770	1.385	0.432
		D	10	3	550	1.861	0.415

TABLE II: (Cont.)

Compound	Cartridges			Number of Exp.	Average Vapor Conc. (ppm)^D	Slope (min/g$_c$)	Capacity (g/g$_c$)
	Type^B	Condition^C	Number				
Ethanol	W4K-271	D	8	2	750	0.912	0.083
	P49-4	D	8	2	750	0.979	0.089
	P42-2	AR	8	2	275	1.204	0.040
		AR	11	3	510	1.060	0.066
		AR	8	2	755	0.906	0.083
	N27-F	AR	8	2	755	0.951	0.087
		AR	8	2	1005	0.821	0.100
		AR	10	3	1250	0.774	0.117
		AR	8	2	1500	0.695	0.127
		AR	4	1	1750	0.624	0.133
		AR	4	1	1750	0.609	0.130
		AR	4	1	1750	0.689	0.146
		AR	8	2	2000	0.650	0.158

^{A}64 L/min experiments only.

^{B}See Table I.

^{C}D = dried; AR = as received.

^{D} ±15 ppm range.

^{E}The ninth data point was not weighted as a full experiment in calculations.

$$\text{H/L:}\quad S = \frac{A}{QC_{sat}} \exp\left[B\left(1 - \frac{SQC_0}{A}\right)\right] \qquad \textbf{(9)}$$

where $A = W_{sat}$ and $B = b'/(c' + T)$.

The values of C_{sat} required for the D/R and H/L equations were calculated from vapor pressures by using the Antoine equation and Antoine parameters.(15) When acetone data for different flow rates, Q, were combined, SQ, rather than S, was used as the dependent variable in all four models. In each of the four equations above A and B are the curve fit parameters.

The criterion selected for comparing the "goodness of fit" of each of the four isotherm equations to the experimental capacities was an estimate of the standard deviation (SD), the residual root mean square error (RMSE)(16):

$$\text{RMSE} = \left(\frac{\text{WRSS}}{m - 2}\right)^{1/2} \qquad \textbf{(10)}$$

where m is the number of experiments, 2 is the number of adjustable parameters, and WRSS is the sum of the squares of the residuals with normalized weighting by the number of experiments w_i included in each data point S_i:

$$\text{WRSS} = \sum_i w_i(S_i - S)^2 \Big/ \sum_i w_i \qquad \textbf{(11)}$$

where S_i is an experimental slope value and S is the corresponding point on the best fit curve of a selected equation at the experimental concentration. The residual sum of the squares is the quantity that is minimized in performing the regression analysis.(17) Using the RMSE allows comparison of data sets with different numbers of data points.

RESULTS AND DISCUSSION

Tables II and III list the compounds, cartridges (type, condition, and number), vapor concentrations, and slopes obtained from 1% breakthrough time versus bed weight plots. Calculated values of relative equilibrium capacities, $W_e = C_0QS$, are also given. Figure 1 shows an adsorption isotherm plot of the ethanol capacities versus vapor concentrations. Figures 2 and 3 show linearized Langmuir plots (C_0/W_e versus C_0 from rearranged Equation 1) of the experimental results for four compounds. These four Langmuir plots, taken together, show (within experimental scatter of the data) no differences in relative adsorption capacities, W_e, among the three brands of cartridges and various lots tested. However, because the carbon bed sizes (weights) varied among the brands, the absolute adsorption capacities, W_eW, differed. This agreement among cartridge brands is not too surprising because the manufacturers may have obtained their carbon from the same source. On the basis of this agreement, all the data for each compound were combined in testing the fits of the equations. Acetone data at varied airflow rates (Table III) were considered separately.

Table IV lists the compounds, the equations fit to the capacity data, the number of experiments included, the WNLLS best fit parameters A and B defined in Equations 6–9, and the standard deviations estimated by Equation 10. Units of A were converted from volumetric (L-ppm) to gravimetric (g) by the conversion factor 25.1 L/mol at 23°C, 0.97 atm.

The first comparison that can be made is among the four adsorption isotherm equations for each vapor. With chloroform, carbon tetrachloride, hexane, and acetone the fits of the capacity data S versus C_0 to the four equations were essentially equal. Only with ethanol was the Freundlich equation fit significantly worse than with the other three (RMSE 0.035 versus 0.022).

Comparing fits (of the four equations to data) among the five compounds is less certain because the numbers of experiments and ranges of concentrations varied. However, Figures 2 and 3

TABLE III. Effect of Flow Rate on Capacities of Pulmosan 42-2-85 Cartridges for 1050 ppm Acetone

Flow Rate (L/min)	Cartridges Condition^A	Cartridges Number	Slope (min/gc)	Capacities (g/gc)
31.9	D	4	1.322	0.106
32.4	D	4	1.285	0.105
40.0	D	4	1.069	0.107
40.8	D	4	1.132	0.116
63.9	D	8	0.721	0.116
83.0	D	8	0.551	0.115
94.3	D	4	0.466	0.110
94.6	D	4	0.482	0.114
110.3	D	4	0.384	0.106
114.8	D	4	0.380	0.110
			Average:	0.110
			Est. SD:	0.004
35.1	AR	4	1.135	0.100
35.2	AR	4	1.250	0.110
45.5	AR	4	0.979	0.112
46.3	AR	4	1.022	0.119
64.0	AR	8	0.649	0.104
67.8	AR	4	0.680	0.116
67.3	AR	4	0.766	0.129
67.3	AR	4	0.662	0.112
66.7	AR	4	0.617	0.103
80.3	AR	4	0.551	0.111
81.0	AR	4	0.520	0.106
81.0	AR	4	0.554	0.113
94.6	AR	4	0.498	0.118
95.6	AR	4	0.449	0.108
113.2	AR	4	0.416	0.118
115.0	AR	4	0.369	0.106
			Average:	0.111
			Est. SD:	0.007
			Grand Average:	0.111
			Est. SD:	0.006

^{A}D = dried; AR = as received.

and Table IV indicate that the ethanol data were tighter (smaller RMSE) than for the other four compounds. One possible explanation for this is that most of the cartridges used in the ethanol studies were used as received, not dried. This explanation was strengthened when the subset of acetone data for 15 experiments with as-received Pulmosan cartridges yielded a Langmuir equation RMSE of 0.026 versus 0.054 for 6 with dried Pulmosan cartridges and 0.040 for 12 with dried Willson canisters. Contrary to first assumptions, the drying process seems to produce a less consistent starting point than the original cartridges.

The differences between capacities of dried and as-received cartridges could not be detected by differences in the data plotted in Figures 2 and 3; however, this may not always be the case. There were also no significant differences in capacities between the as-received and dried Pulmosan cartridges used in the varied flow rate studies (Table III) at the 99% confidence level.

The lack of flow rate effects on W_e reported previously$^{(1)}$ was confirmed in the study (Table III). Data for 79 acetone experiments at all flow rates (32–115 L/min) yielded the same RMSE value (0.068) as data including a subset of 47 experiments at 64 L/min only (Table IV). Again, there were no significant differences in goodness of fit among the four isotherm equations when all 79 acetone experiments were included.

CONCLUSIONS

According to the selected criterion of goodness of fit of capacity data, three of the four equations studied are equally satisfactory in describing all the measured concentration effects. The fourth, the Freundlich equation, did not fit ethanol data as well as the other three. Whether this is because of the wider concentration range of the ethanol data, the higher polarity and/or hydrogen bonding of ethanol, or some other factor, is unknown.

The equal data fitting of these equations has only been demonstrated for a limited range of concentrations (275–2000 ppm) over which organic vapor cartridges are frequently used for common solvents. Equal fitting is not likely at much lower or higher concentrations because some of these isotherm equations have different (or no) asymptotic limits. Therefore, until applicability over wider ranges is demonstrated, these equations are most useful for data interpolating and smoothing. Extrapolating beyond an experimental concentration range is less certain.

Other criteria should also be considered in the selection of an isotherm equation for correlating capacities. Table V lists five desirable characteristics of such an equation in addition to goodness of fit of data.

As just mentioned, an equation with the proper (theoretical) asymptotic limit has a better chance of describing capacities beyond the range of data. One such theoretical limit for adsorption isotherms occurs at low concentrations where, according to Henry's law, capacity should become proportional to vapor concentration: $W_e = K_H C_0$, where K_H is the Henry's law "constant" for a particular system. Although Henry's law assumes homogeneous surfaces and low adsorbed amounts at which the adsorbate molecules do not interact with each other, it is often a good approximation for low concentration data. Of these four adsorption isotherm equations, only the Langmuir and H/L reduce to Henry's law at low vapor concentrations.

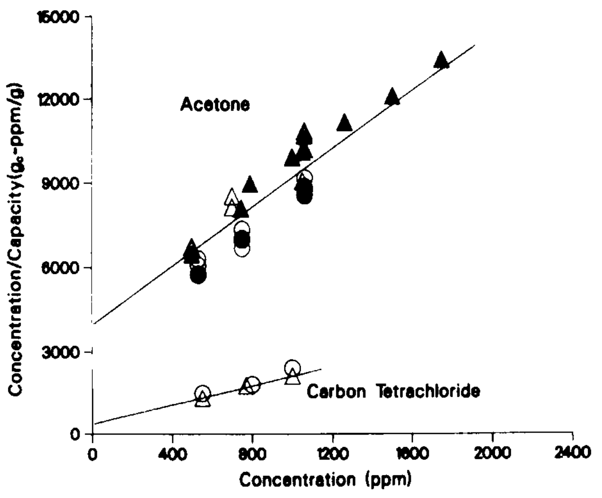

FIGURE 2. Linearized Langmuir isotherm plots for Willson (○) and Pulmosan (Δ) cartridges with acetone and carbon tetrachloride. Open symbols = dried; solid = as received.

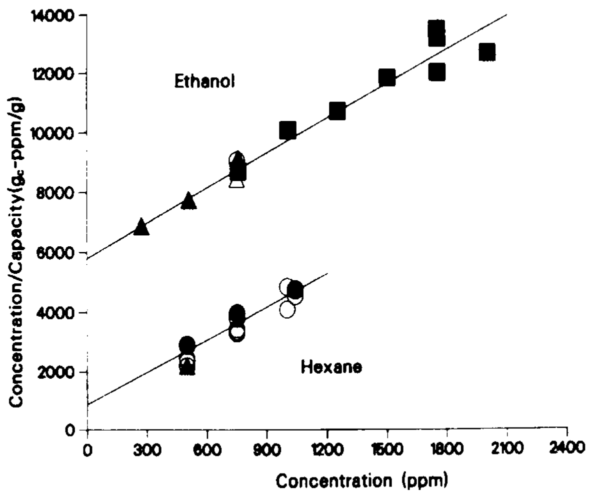

FIGURE 3. Linearized Langmuir isotherm plots for Willson (○), Pulmosan (Δ), and Norton (□) cartridges. Open symbols = dried; solid = as received.

The adsorption isotherm equation should include temperature as a parameter so that measurements made at one temperature can be extrapolated to other temperatures. The D/R and H/L explicitly include temperature as a parameter. Because K_H in the Langmuir equation represents an equilibrium coefficient, it may have the expected exponential inverse temperature dependence, but this has not been demonstrated. Temperature dependencies of the Freundlich parameters have been derived theoretically(18) but not demonstrated experimentally for organic vapors.

If the data fit parameters can be assigned physical significance, correlations and predictions from independently determined physical or chemical properties may be possible. According to Equations 6–9, the curve fit A parameters are proportional to capacities at vapor-in-air saturation concentrations (Freundlich, D/R, or H/L) or at theoretical infinite concentration (Langmuir). The B parameters also have physical meaning, except for the Freundlich equation, where B is purely empirical. Comparisons of the magnitudes of the A and B parameters among the chemicals are beyond the scope of this paper.

The usefulness of an equation for describing experimental data also depends on how easy it is to apply. The H/L equation cannot be put in the mathematical forms of $\theta = f(C_0)$ or $W_e = f(C_0)$; therefore, a cumbersome iterative process is required to derive the data fit parameters.

Another factor in ease of application is whether an equation requires independent input data. The Freundlich and Langmuir equations can be used empirically with only C_0 and W_e (or S) data. The D/R equation requires having the vapor saturation

TABLE IV. Results of Weighted Nonlinear Least Squares Fitting of Capacity Data at 64 L/min Flow Rate to Isotherm Equations

Compound	Isotherm Equation	Number of Exp.	Best Fit Parameters^A A	Best Fit Parameters^A B	RMSE SD Est.
Acetone	Freundlich	47	0.00671	0.6016	0.0697
	Langmuir	47	0.1613	0.001915	0.0661
	D/R	47	0.3106	0.03414	0.0672
	H/L	47	0.3538	6.248	0.0674
Chloroform	Freundlich	12	0.03043	0.6529	0.0727
	Langmuir	12	0.4558	0.002704	0.0744
	D/R	12	0.8126	0.02982	0.0731
	H/L	12	1.1357	6.060	0.0751
Hexane	Freundlich	25	0.04978	0.7896	0.1437
	Langmuir	25	0.2491	0.005632	0.1442
	D/R	25	0.3539	0.01880	0.1438
	H/L	25	0.4425	8.581	0.1438
Carbon Tetrachloride	Freundlich	14	0.1051	0.7940	0.0751
	Langmuir	14	0.5158	0.005356	0.0741
	D/R	14	0.7018	0.01968	0.0749
	H/L	14	0.8732	8.410	0.0746
Ethanol	Freundlich	25	0.000942	0.3285	0.0349
	Langmuir	25	0.2481	0.000672	0.0225
	D/R	25	0.3666	0.07306	0.0215
	H/L	25	0.5137	3.204	0.0214

^A Units of A's are converted to g/g_c except for the Freundlich where the units are $(g/g_c)\ (ppm)^{B-1}$. Units of B's are $(ppm)^{-1}$ for Langmuir and no units for the others.

TABLE V. Adsorption Isotherm Equation Selection Criteria

	Isotherm Equation			
Desirable Characteristics	*Freundlich*	*Langmuir*	*D/R*	*H/L*
Good fit of data (this paper)	?[A]	+[B]	+	+
Henry's law limit	–[C]	+	–	+
Includes temperature effect	?	?	+	+
Parameters have physical meaning	–	+	+	+
Ease of application to data	+	+	+	–
Does not require independently determined parameters	+	+	–	–

[A] ? = May meet requirement with reservations (see text).

[B] + = Meets requirement.

[C] – = Does not meet requirement.

pressure (or concentration), which may not be known for some gases and vapors and which has its own temperature dependence. In the H/L equation, the saturation pressure and three Antoine constants are required as input. Although extensive compilations of Antoine parameters exist,(15,19) they are by no means all-inclusive.

Considering the comparisons in Tables IV and V, there is no clear "winner" among the four adsorption isotherm equations. The choice for correlating organic vapor respirator cartridge breakthrough data may depend on which equation characteristics are most important to the user of the equation. There does seem to be one equation that has the fewest desirable characteristics: the Freundlich.

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