American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

Calculation of the Performance of Activated Carbon at High Relative Humidities

DWIGHT W. UNDERHILL

To cite this article: DWIGHT W. UNDERHILL (1987) Calculation of the Performance of Activated Carbon at High Relative Humidities, American Industrial Hygiene Association Journal, 48:11, 909-913, DOI: 10.1080/15298668791385796

To link to this article: https://doi.org/10.1080/15298668791385796

Am. Ind. Hyg. Assoc. J. 48(11):909-913 (1987)

Calculation of the Performance of Activated Carbon at High Relative Humidities

DWIGHT W. UNDERHILL
Graduate School of Public Health, University of Pittsburgh, 130 DeSoto Street, Pittsburgh, PA 15261

The Dubinin-Radushkevich potential theory was extended to include a term giving the effect of relative humidity on the uptake of adsorbate. This extended equation permits the adsorptive capacity of the activated charcoal in a respirator cartridge to be estimated for any combination of temperature, relative humidity, and concentration of contaminant. Application of this theory to previously published data of Werner showed a good correlation between theory and experiment. This equation is consistent with the experimental observations that 1) below a certain value, the relative humidity has little effect on the uptake of adsorbate, and 2) the effect of relative humidity, if observed, is more severe for lower than for higher concentrations of contaminant.

Introduction

Because the uptake of water by activated charcoal increases rapidly as the relative humidity increases above 40%, the performance of a respirator cartridge in humid atmospheres may be quite unsatisfactory. In a highly humid environment, a worker may be at risk by using a respirator cartridge tested for 1) dry conditions; or 2) for a shorter period of time at the same relative humidity: or 3) for some other organic compound at a high relative humidity. This problem is compounded by the fact that the interfering compound, water vapor, is colorless, odorless and present at much higher concentrations than various air contaminants. A simple procedure is needed to calculate the effect of relative humidity on respirator performance. In this paper, the author uses ideas of Polanyi,(1) Dubinin and Radushkevich,(2) and Manes(3) to develop a simple mathematical model for the effect of relative humidity on the adsorption of water-immiscible compounds. The predictions of this theoretical model and its accuracy when applied to previously published data are examined.

The Polanyi Potential Theory

The basic concept of the Polanyi potential theory(1) is that an adsorbent can be characterized by an attractive force field over the microporous surfaces of the adsorbent (see Figure 1(4)). Polanyi has described these forces of attraction by the adsorption potential, which is defined for a point near the surface of the adsorbent, as the work done by the attractive forces in bringing a molecule of a gas to that given point. The adsorption potential has its maximum value at the surface of the adsorbent and it decreases to zero at some limiting distance. The broken lines in Figure 1 represent planes of equal adsorption potential.

Because the adsorption potential increases as the distance from the surface decreases, the density of the compressed adsorbate is not constant throughout the adsorption space. The adsorption potential may be defined in terms of ϵ, the isothermal work of compression per unit volume of adsorbed adsorbate:

$$\epsilon = RT/V \ln(C_o/C) \tag{1}$$

where: T = absolute temperature, °K;
R = ideal gas constant (8.3143 joule/M/°K);
V = molar volume of liquefied adsorbate, cc/M;
C = ambient concentration of adsorbate, g/cc;
C_o = concentration of adsorbate on a given equipotential surface, g/cc.

In the adsorption of vapors, if the isothermal work of compression causes C_o (the concentration of adsorbate on a given equipotential surface) to be equal or greater than C_s (the concentration of the vapor of the pure adsorbate at the temperature of adsorption) then the adsorbate will condense to form a liquid phase held within this equipotential plane.

For the adsorption of vapors, it is usually sufficiently accurate to associate all of the adsorption that is observed with this liquefaction. This volume is calculated with the assumption that the adsorbate has the density of the saturated liquid phase. The relationship between the volume of adsorbate enclosed in the adsorption space and the adsorption potential is described by a characteristic curve. On a characteristic curve (so named because it should be the same for a given vapor and adsorbent at all temperatures below the critical temperature) the volume (V_t) of an adsorbed film is expressed as a function of $RT/V \ln(C_s/C)$. This characteristic curve takes the place of the more familiar plot of the adsorption isotherm, which gives the amount adsorbed as a function of pressure at a constant temperature.

A limitation of the Polanyi potential theory is that it does not provide an analytical expression for the adsorption isotherm. Such relationships must be found experimentally. For example, Grant *et al.*(5) derived a fifth order polynomial for determining the adsorption space from the adsorption potential for one activated carbon (30/100 mesh BPL activated carbon Audit Sample 104). To calculate the inverse (*i.e.*, the adsorption potential from the adsorbate volume), they use an eighth order polynomial.

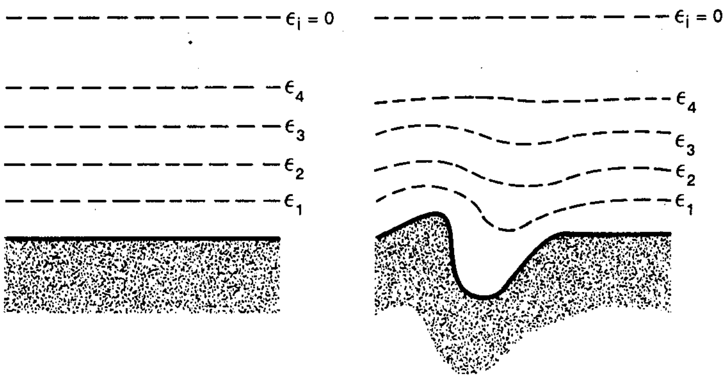

Figure 1 — Schematic representation of the force field at the surface of solid adsorbents according to the potential theory a) idealized case of a plane homogeneous surface, b) real surface.

The Dubinin-Radushkevich Model

Dubinin and Radushkevich(2) noted that in many cases it is not necessary to use high order polynomials to describe the adsorption potential. Very often the relationship between the adsorption potential and the adsorbed adsorbate is Gaussian:

$$W_t = W_o \rho \exp[-k\epsilon^2] \tag{2}$$

where: W_t = weight of adsorbed adsorbate/gm adsorbent;
W_o = total (limiting) volume of the adsorption space/gm adsorbent;
ρ = density of liquid adsorbate at temperature of adsorption; and
k = constant.

Golovoy and Braslaw(6) demonstrated the high accuracy possible with the Dubinin-Radushkevich approximation. They found a mean error of 1.9% when the Dubinin-Radushkevich equation was used to predict the uptake of 14 solvents on activated charcoal. Given this high accuracy possible with the use of the Dubinin-Radushkevich isotherm, the problem that is addressed here is the modification of this equation so that it can be applied to the adsorption of solvents in the presence of water vapor. Before this is done, examination of how Manes has developed a graphical procedure using the Polanyi potential theory to describe the effect of adsorbed water on water-immiscible solvents was made.

Manes Treatment of the Polanyi Potential Theory

Manes(3) and Manes and Greenbank(7) have shown how, by simple geometric constructions, the Polanyi adsorption potential theory can be extended to the adsorption of water-immiscible adsorbates in the presence of water vapor. The basic concepts are shown graphically in Figure 2, which describes the effect of relative humidity on the adsorption of butane from air. In Figure 2, the curve on the far right represents the Polanyi potential curve for butane alone, and the curve marked H_2O represents the Polanyi potential curve for water vapor. In the presence of water vapor at 100% RH, the Polanyi potential curve for butane is shifted to the left by an amount that is equal to the potential energy for the adsorption of the water vapor. The lower set of horizontal arrows shows how this shift is made in order to determine the adsorption of butane from air saturated with water vapor.

If the air is saturated only partially with water vapor, the Polanyi potential for adsorption in the presence of water vapor is shifted to the left by an amount determined by the change in the free energy of the water vapor. This shift is proportional to $RT \cdot \ln(RH/100)$, where R and T have their usual values, and RH is the relative humidity. In Figure 2, the upper set of horizontal arrows shows the determination of the adsorption of butane at 60% RH. The result of this shift is an increase in the amount of adsorbed butane from what was adsorbed from air saturated with water vapor.

Figure 2 can be used to determine how the combined concentrations of water vapor and organic adsorbate on the adsorption of the organic adsorbate interact. At the higher adsorption potentials (*i.e.*, in pore spaces that may be filled at low concentrations of either water vapor or of the organic adsorbate), the filled pore volume changes very rapidly with

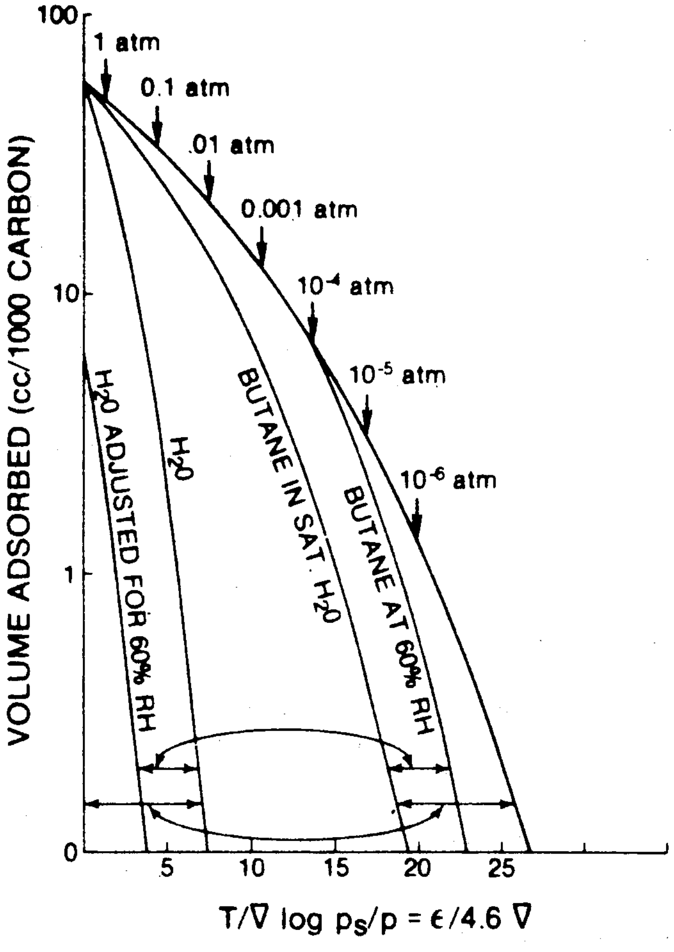

Figure 2 — Illustrative graphic calculation for adsorption of butane and water at 60% and 100% RH. Reprinted with permission from Manes.(3)

small changes in the adsorption potential, and thus it would be expected that at low concentrations of organic adsorbate, the relative humidity has its strongest effect. Figure 2 shows that, in fact, at low uptakes of organic adsorbate, the uptake of organic adsorbate changes very rapidly with the relative humidity.

A complementary effect is that at a sufficiently high concentration of an organic vapor, relative humidities below a certain value cause a negligible reduction in the adsorption coefficient of the organic component. The physical explanation for this effect is that at less than 100% RH, many pores are filled only partially with water. If the vapor pressure of the organic adsorbate causes the organic adsorbate to fill the pores beyond the level occupied by the water, displacing all the water, then the presence of water vapor has no effect on the adsorption of the organic vapor. This is seen in Figure 2, in which at pressures of butane over 10^{-4} atm and at 60% RH, the butane uptake is the same as from dry air.

Calculation of the Uptake of Adsorbate

Rather than depend on graphical analysis, an equation that permits a rapid calculation of the effect of water vapor on the adsorption of water-immiscible organic compounds was developed. These equations use the three assumptions implicit in the geometrical analysis developed in Figure 2. The first is that the adsorption potential in the presence of completely saturated air is some multiple of the adsorption potential from dry air; that is,

$$\epsilon'_{100\%\,\mathrm{RH}} = \epsilon(1 + k_1)_{\mathrm{dry\ air}}. \qquad \textbf{(3)}$$

The second assumption is that the adsorption potential decreases linearly with a decrease in the free energy of the water vapor. Thus, to calculate the adsorption of organic vapors from air partially saturated with water vapor, a correction factor proportional to $RT/V_h \cdot \ln(RH/100)$, where V_h is the molar volume for water and RH is the percent relative humidity, should be applied. Based on these two assumptions, the adsorption potential for a water-immiscible organic compound in the presence of water vapor is as follows:

$$\epsilon' = (1 + k_1) + k_2RT/V_h \cdot \ln(RH/100) \qquad \textbf{(4)}$$

where: k_1 = factor defined in Equation 2 to describe the change in the adsorption potential of a water-immiscible compound brought about by replacing air with water in the micropores;

k_2 = factor giving the change in the adsorption potential of a water-immiscible compound as a function of the relative humidity; and

V_h = molar volume of water, (18.0 cm^3/M).

The symbols ϵ, R, T, V, C, and C_s are as defined previously.

The third assumption is that if $|k_2RT/V_h \cdot \ln(RH/100)|$ is greater than $k_1RT/V \cdot \ln(C_s/C)$, then the organic adsorbate will displace all the water from the micropores. When this is the case, the adsorption potential for the organic solvent is given by Equation 1, which does not contain any factors for the effect of coadsorbed water.

After the adsorption potential for the organic solvent has been determined using Equation 1 or 4, depending on whether $|k_2RT/V_h \cdot \ln(RH/100)|$ is greater than $k_1RT/V \cdot \ln(C_s/C)$, the uptake of organic adsorbate is calculated from Equation 2.

Experimental Studies

Realistic tests on the effect of relative humidity on the adsorption of a water-immiscible organic compound were reported recently by Werner,(8) who challenged small beds (containing 37.5 gm) of activated charcoal to input concentrations of 300 to 1300 $\mathrm{mg/m^3}$ of trichloroethylene (TCE) at relative humidities ranging from 5% to 85%. Werner found that the lower the concentration of adsorbate (trichloroethylene), the stronger the effect of relative humidity. In Werner's paper this effect was shown in a series of empirical curves in which the uptake was plotted against the square of the logarithm of the concentration. Next, Werner's data in terms of the procedure developed above was reexamined.

Table 1 gives Werner's measurements of the uptake of trichloroethylene on activated carbon, as a function of the input concentration and relative humidity. The first step in this analysis was to determine the appropriate values for k and W_o from Werner's data. The authors assumed that at 5% RH, the results were equivalent to the adsorption of trichloroethylene on dry charcoal and using Equation 2, derived values of $W_0 = 0.62\ \mathrm{cm^3/gm}$ and $k = 2.89 \times 10^{-5}\ \mathrm{cm^6/joule^2}$ from these data. The first row in Table 1 shows the fit of Werner's data to the Dubinin-Radushkevich equation with the values of k and W_0 given above. The next step was to use trial and error to find the best values for k_1 and k_2 to fit Equation 4 to the measurements of adsorption of trichloroethylene at higher relative humidities (*i.e.,* 25% - 85% RH). For k_1 and k_2, the values found by a trial and error procedure were 0.86 and 1.54, respectively. The mean error between the calculated values and Werner's experimental values was 11%, in the same range as the experimental error in Werner's measurements. Figure 3 shows a plot of the adsorption potential calculated from Equation 4 along with the measured uptake of trichloroethylene. All the data points fall close to the Dubinin-Radushkevich curve originally derived for the adsorption of trichloroethylene from dry air.

Thus the effect of relative humidity on adsorption can be found by the addition of two new parameters, one of which, k_1, gives the maximum effect of adsorbed water on the adsorption of the immiscible compound, and the other parameter, k_2, describes the increase in the adsorption of the immiscible compound as the partial pressure of the water vapor is reduced. This gives a quantitative way of representing the basic findings of Werner; *i.e.,* 1) below a certain value, the relative humidity has little effect on adsorption and 2) the effect of relative humidity, if observed, is more severe for lower than for higher concentrations of contaminant.

TABLE I
Measured *vs.* Calculated Uptake of Trichloroethylene in the Presence of Water Vapor[A,B,C]

	Uptake at 300 mg/m^3		Uptake at 600 mg/m^3		Uptake at 1000 mg/m^3		Uptake at 1300 mg/m^3	
R.H.	**Calc.**	**Meas.**	**Calc.**	**Meas.**	**Calc.**	**Meas.**	**Calc.**	**Meas.**
5%	0.281	0.286	0.345	0.334	0.396	0.399	0.428	0.434
25%	0.278	0.257	0.346	0.320	0.397	0.403	0.426	0.431
50%	0.189	0.180	0.296	0.284	0.387	0.342	0.430	0.370
65%	0.083	0.114	0.146	0.160	0.208	0.218	0.250	0.262
85%	0.030	0.027	0.089	0.054	0.091	0.098	0.114	0.121

[A] In using Equations 2 and 4 to make the calculations given in Table I, the following parameters were used: $\rho = 1.455$ gm/cm^3; $C_s = 500{,}500$ mg/M^3; $W_0 = 0.62$ cm^3/gm; $k = 2.89 \times 10^{-5}$ cm^6/joule^2; $k_1 = 0.86$ (dimensionless); $k_2 = 1.54$ (dimensionless); V = molar volume of adsorbate (= 90.3 cc/mole for trichloroethylene); and V_h = molar volume of water, 18 cc/M.

[B] If $k_1RT/V \cdot \ln(C_s/C) > |k_2RT/V_h \cdot \ln(RH/100)|$, the uptake, W_t, of trichloroethylene per gram of adsorbent was calculated as:

$$W_t = W_o \exp[-k\{(1 + k_1)RT/V \cdot \ln(C_s/C) + k_2RT/V_h \cdot \ln(RH/100)\}^2];$$

otherwise:

$$W_t = W_o \exp[-k\{RT/V \cdot \ln(C_s/C)\}^2].$$

[C] Experimental data from Werner.[8]

Discussion

Aside from its accuracy, one of the advantages of the Dubinin-Radushkevich equation is that it gives a clear meaning to each of the factors going into calculating the uptake of adsorbate. In the simplest form of the Dubinin-Radushkevich equation, there are four factors. Two of these factors, C_s and ρ, depend only on the adsorbate; the other two factors, W_0 and k, depend on the pore volume and pore size distribution of the adsorbent. The modification that has been presented here attempts to keep the spirit of the earlier forms of this equation, by retaining these factors and adding two additional factors that describe the interaction between the organic adsorbate and the moisture in the pores of the adsorbent. The physical meanings for k_1 and k_2 have been given above. What should be noted here is that if k_1 (and therefore also k_2) is equal to zero, then the energy of attraction of the organic adsorbent to the pores is so strong that the presence of water vapor has no effect on the uptake of adsorbent. If k_1 is in the range of unity (what the authors observed for the adsorption of trichloroethylene in the presence of water vapor), then the organic adsorbate is attracted into the pores with about the same energy as is the competing water vapor. With k_1 significantly greater than unity, the organic adsorbate is significantly displaced by adsorbed water. From Figure 2, judging by the tripling of the adsorption potential as the humidity passes from 0 to 100% RH, the k_1 value for butane should be in the range of 2 to 3, which is to be expected for a light, nonpolar molecule. This result is in keeping with the underlying purpose of this paper: to extend the Dubinin-Radushkevich equation to take into account, in a natural way, the effect of relative humidity on adsorption.

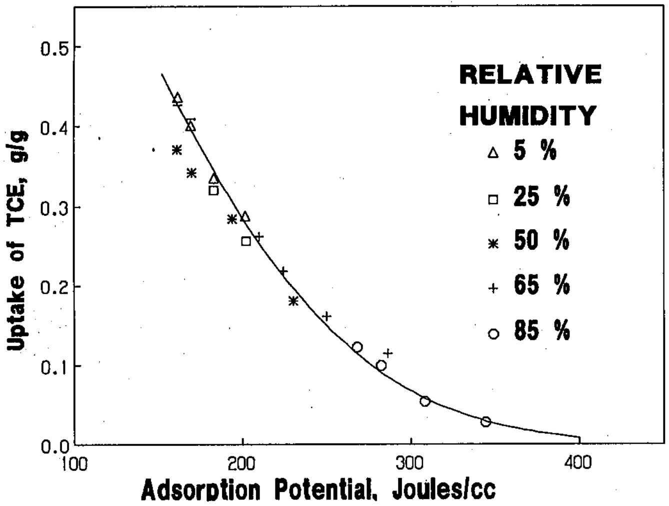

Figure 3 — Werner's results plotted as adsorption potential *vs.* uptake. X Axis: Adsorption potential, joule/cm^3; Y Axis: Uptake of trichloroethylene, gm/gm adsorbent.

Acknowledgment

This research was supported by NIOSH Grant 1 RO1 OHO1644-01.

References

1. **Polanyi, M.:** Adsorption of Gases (Vapors) by a Solid Non-volatile Adsorbent. *Verh. Dtsch. Phys. Ges. 18*:55 (1916). [In German].
2. **Dubinin, M.M. and L.V. Radushkevich:** Equation of the Characteristic Curve of Activated Charcoal. *Dokl. Akad. Nauk. SSSR 55*:327-329 (1947). [In Russian].

3. **Manes, M.:** Estimation of the Effects of Humidity on the Adsorption Onto Activated Carbon of the Vapors of Water-Immiscible Organic Liquids. In *Proceedings of the Engineering Foundation Conference Held at Schloss Elmau, Bavaria, West Germany, May 1983,* edited by A.L. Myers and G. Belfort. New York: Engineering Foundation, 1984. pp. 335-344.
4. **Smisek, M. and S. Cerny:** *Active Carbon, Manufacture, Properties and Applications.* Amsterdam: Elsevier Publishing Co., 1970. p. 104.
5. **Grant, R.J., R.S. Joyce and J.E. Urbanic:** The Effect of Relative Humidity on the Adsorption of Water Immiscible Organic Vapors on Activated Carbon. In *Proceedings of the Engineering Foundation Conference Held at Schloss Elmau, Bavaria, West Germany, May 1983,* edited by A.L. Myers and G. Belfort. New York: Engineering Foundation, 1984. pp. 219-227.
6. **Golovy, A. and J. Braslaw:** Adsorption of Automotive Paint Solvents On Activated Carbon. *J. Air Pollut. Control 31*:861-865 (1981).
7. **Manes, M. and M. Greenbank:** Adsorption of Multicomponent Liquids from Water Onto Activated Carbon: Convenient Estimation of Methods. In *Advances in Chemistry Series, No. 202: Treatment of Water by Granular Activated Carbon,* edited by M.J. McGuire and I.H. Suffet. Washington, D.C.: American Chemical Society, 1963.
8. **Werner, M.D.:** The Effects of Relative Humidity on the Vapor Phase Adsorption of Trichloroethylene by Activated Charcoal. *Am. Ind. Hyg. Assoc. J. 46*:585-590 (1985).

16 June 1986; Revised 15 June 1987