Internal Correspondence

3500

To R. M. Pieper

From J. A. Kvikstad

Subject Trichloroethylene

Date January 7, 1986

3M

I have attached a copy of an article which appeared in a recent issue of American Industrial Hygiene Association Journal, discussing the effects of relative humidity on adsorption of trichloroethylene onto activated carbon.

Since we have seen increased mention of trichloroethylene in the literature, I would like to suggest that we examine the capacity of the #3500 OVM for this compound, and how that capacity is effected by humidity.

JAK:smt

Attachment

c: A. G. Holcomb
R. E. King
J. B. Palazzotto

D/C

Is this on the list for 1986?

3-3

3M 006547

Am. Ind. Hyg. Assoc. J. 46(10):585-590 (1985)

The Effects of Relative Humidity on the Vapor Phase Adsorption of Trichloroethylene by Activated Carbon

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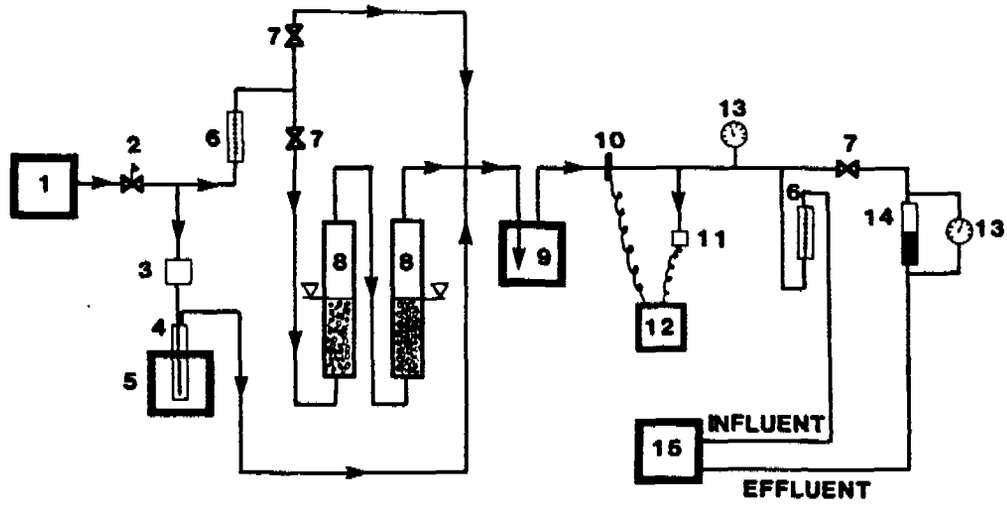
The effect of relative humidity on activated carbon adsorption of trichloroethylene (TCE) was determined. Five levels of relative humidity were tested for each of four TCE influent concentrations. The effect of humidity was greatest at the lowest TCE influent concentration (1 mg/m³) and highest relative humidity involved (85%). Under those conditions the amount of TCE adsorbed was only 9% of the amount adsorbed at the same challenge concentrations and lowest relative humidity (5%). The effect of humidity was negligible at the highest TCE concentrations (1000 and 1300 mg/m³) and moderate level of relative humidity (25%). Under all other conditions tested the effect was intermediate to these extremes. Differences in TCE breakthrough curves caused by the presence of water vapor are presented and discussed. Data sets (grouped by relative humidity) fit the Dubinin - Polanyi equation equally well.

Introduction

Activated carbon adsorption has numerous applications which involve the removal of organic compounds from air, including: (1) occupational respirators,[1-3] (2) air pollution control devices,[4-6] (3) air sampling devices,[7-11] and (4) vapor recovery operations.[12] The use of activated carbon is, in general, relatively expensive and can involve cases for which process failure can lead to direct health risks (*e.g.*, occupational respirators). Therefore, reliable criteria for process design and operation are highly desirable.

Although its impact is poorly understood, relative humidity is an important factor which may adversely affect adsorption processes.[4,5,9,10,13] Since various humidity levels occur during each of the applications of activated carbon mentioned, relative humidity should be considered during design and application of many types of activated carbon systems. Therefore, the purposes of this paper are: (1) to present results which illustrate the degree to which several levels of relative humidity reduced the adsorption capacity of acti-



1. DRY, PURE AIR GENERATOR
2. PRESSURE VALVE
3. AIR FLOW CONTROLLER
4. IMPINGER TUBE FOR TCE GENERATION
5. CONSTANT TEMP BATH
6. ROTOMETER
7. FLOW VALVE
8. HUMIDITY GENERATOR
9. EQUALIZATION VESSEL
10. TEMP PROBE
11. DEWPOINT SENSOR
12. HYGROCOMPUTER
13. PRESSURE GAGE
14. ACTIVATED CARBON COLUMN
15. GAS CHROMATOGRAPH

Figure 1—Diagram of experimental system

mental trials required from one to [illegible] plete, depending on the specific conditions of TCE concentration and humidity.

Determination of adsorption capacity were based on time to 50% TCE breakthrough and the assumption of a symmetric breakthrough curve.[1,2,3]

Results and Discussion

Effects of Humidity on Adsorption Capacity

The quantities of TCE adsorbed per gram of activated carbon are presented in Table I for the individual trials. For similar influent TCE concentrations, the amount of TCE adsorbed decreased with increasing relative humidity. Although other investigators have noted the adverse effect of humidity on gaseous phase adsorption,[4,13,14] data were collected during this research in a systematic manner specifically designed to permit a detailed analysis of the impact of relative humidity.

The effect of increasing relative humidity on the amount of TCE adsorbed for each influent TCE concentration is illustrated in Figure 2. Additionally, an analysis of similar results from other studies is summarized in Table II. The effect of humidity was more pronounced at the lower TCE influent concentrations tested than at higher concentrations. The magnitude of the humidity effect in the present study is comparable to results reported by two investigators,[4,14] but much greater than results reported by another (Table II).[13] At least four factors influence the impact of humidity on gaseous phase adsorption, however, and should therefore be considered when comparing studies. First, the manner in which carbon is preconditioned often differs between studies. For example, one investigator[13] preconditioned the carbon in an atmosphere of 50% relative humidity; in another study[4] preconditioning procedures varied between trials; the third investigator[14] apparently performed no preconditioning; and this author preconditioned the carbon by oven drying for two days. Since the manner in which the

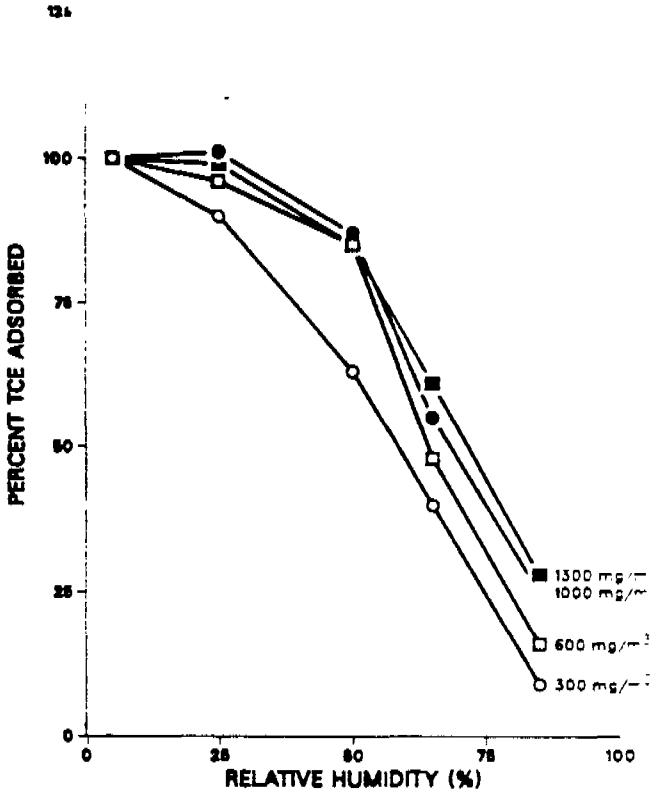


Figure 2—Percent of TCE adsorbed at each level of humidity relative to that adsorbed at the lowest humidity

carbon is preconditioned has significant effects on the adsorption efficiency of carbon,[13] a complete quantitative comparison between the studies (as represented in Table II is tenuous.

The second factor which may influence the impact of humidity is adsorbate concentration. Results of this study indicate that low concentrations of adsorbate are affected by a given level of humidity to a greater extent than higher concentrations. Thus, direct quantitative comparison

TABLE II
Results from Selected Studies on the Effect of Humidity on Carbon Adsorption Under Various Experimental Conditions

Adsorbate	Influent Adsorbate Conc. (ppm)	Reference Humidity %	Test Humidity	% Adsorption Capacity Retained	Reference
Benzene	1000	20	80	86	13
1-Chlorobutane	1000	20	80	79	13
Carbon tetrachloride	1000	20	80	78	13
Ethyl acetate	1000	20	90	77	13
Acetone	1000	20	90	87	13
Hexane	1000	0	90	83	13
Benzene	500	15	80	73	4
Chloroform	500	15	80	67	4
Acrylonitrile	100	15	80	45	4
Chloromethyl methyl ether	1	15	80	30	4
Acrylonitrile	10	7.5	90	17	14
Trichloroethylene	222	5	85	28	Present study
Trichloroethylene	50	5	85	9	Present study

TABLE I
TCE Adsorbed for Individual Trials

Relative Humidity (%)	TCE Influent Concentration mg/m m	ppm	TCE Adsorbed (g TCE/g carbon)
5	303	52	0 286
25	295	50	0 257
50	293	50	0 180
65	295	50	0 114
85	293	50	0.027
5	602	103	0 334
25	605	103	0.320
50	597	102	0 284
65	599	102	0 160
85	593	101	0 054
5	987	168	0 399
25	995	170	0 403
50	978	167	0.342
65	996	170	0 218
85	986	168	0 098
5	1331	227	0.434
25	1306	223	0.431
50	1356	231	0 370
65	1322	226	0 262
85	1304	222	0.121

[1]Calculations were based on time to 50% TCE breakthrough

ated carbon for a single volatile organic compound (VOC) low influent concentrations. (2) to examine the interaction etween VOC concentration and humidity during carbon dsorption and (3) to suggest a potential approach that ay be taken for predicting the degree of impact of relative umidity on the adsorption process.

xperimental Methods and Design

he experimental system employed is illustrated in Figure 1.)ry (5% or less relative humidity) and purified air entered e system through a pressure valve (2) (numbers in paren-eses refer to system components in Figure 1). The air was en immediately split into two streams. One stream (0.2 .5% of the total flow) was directed through a mass flow ansducer (3) to an organic vapor generating apparatus. or these experiments, the vapor generating apparatus con-sted of a 4.5 cm impinger tube (4) partially filled with chloroethylene (TCE) in a temperature controlled water ath (5). The concentration of TCE in the air was controlled all of the following mechanism: regulating air flow to the nerating apparatus, regulating the temperature in the ater bath and setting the distance between the air entry nt in the impinger tube and the surface level of TCE.

The second air stream (10 L/min) flowed through a ometer (6) and into the main portion of the system. This stream also could be split to keep any portion of the total w dry, while the remainder could be humidified by expo-to water. The air humidifying system consisted of two ss tubes connected in series (8). Each tube was 5 cm in ter and was partially filled with water. The tubes con-d plastic pall rings which served to disperse the air and ase air-water contact.

The three portions of air (TCE laden, water vapor laden and pure dry air) were then united and directed through a 20-liter equalization vessel (9) to dampen short-term variations in TCE concentration and air humidity. The total volume of air then passed over a temperature probe (10). A low air flow (25 mL min) entered a dew point sensor (11). Signals from the temperature probe and dew point sensor were continuously relayed to a hygrocomputer (12) to permit monitoring of dew point and relative humidity. The air stream was again divided; 2.3 L min was diverted to a gas chromatograph for influent TCE concentration determination, while the re-maining 7.7 L min was directed through the activated carbon column (14). The effluent from the column was also directed to the gas chromatograph for analysis. A pressure driven solenoid valve mounted on the gas chromatograph permitted alternating samples of the influent and effluent air to be taken on a programmed time schedule. The time interval for a complete sampling cycle during the experiments was 20 minutes.

The flow (7.7 L/ min of test air) through a 2.54 cm diameter activated carbon column resulted in a linear velocity of 25 cm/ sec and an air retention time of 0.5 sec within the carbon. For all experimental trials the mass of activated carbon used (37.5 g of CECA GAC48C Carbonundum) was constant and resulted in a carbon bed depth of approximately 13.5 cm. The carbon was washed with distilled water and oven dried for a minimum of two days.

Experimental trials were performed at four TCE concentrations (approximately 300, 600, 1000 and 1300 mg/ m^3, each at five levels of relative humidity (5, 25, 50, 65 and 85%). Temperature levels were maintained at 23±2° C. Single trials were conducted for each experimental condition. Experi-

TABLE III
Time to Breakthr ugh of 50% of the Influent TCE C ncentration Standardized to that Value at Low Relative Humidity (5%).

TCE Influent Conc. (mg/m')	Relative Humidity 5	25	50	65	85
	Relative Amount Adsorbed				
300	100	90	63	40	9
600	100	96	85	48	16
1000	100	101	87	55	25
1300	100	99	85	61	28

TABLE IV
Time to Breakthrough of 10% f the Influent TCE Concentration Standardized to that Value at Low Relative Humidity (5%).

TCE Influent Conc. (mg/m)	Relative Humidity 5	25	50	65	85
	Relative Amount Adsorbed				
300	100	67	58	32	9
600	100	82	77	38	15
1000	100	93	80	48	24
1300	100	87	83	51	27

etween adsorbate concentrations are invalid. Related to his point, the "multiplier factor" suggested as a tool to ccount for the effect of humidity on activated carbon respirators[13] is probably only reliable within a range of adsorbate concentrations near the concentration tested. Specifically, a "multiplier factor" should not be used directly for challenging adsorbate concentrations that are much lower than concentrations for which the factor was derived.

The third factor which influences the impact of humidity is the type of adsorbate compound. The degree to which humidity affects adsorption is a function of the adsorbate.[4] Specifically, hydrophobic adsorbates are expected to be more adversely affected by humidity than hydrophilic compounds.[5]

The fourth influential factor is the type of activated carbon. The carbon structure can influence the amount of water vapor adsorbed as well as the competitive interaction between water molecules and organic adsorbate molecules for available sites on the carbon. For example, one study demonstrated that for several types of activated carbon the oxygen content of the carbon was positively correlated to the carbon's affinity for water molecules.[15]

Since humidity can have substantially adverse effects on the gaseous phase carbon adsorption process, humidity should be considered during the establishment of design and operational criteria. But, as argued, quantitative statements based solely on laboratory results which investigate the impact of humidity of specific compounds under a given set of conditions can not always be generalized to other situations. The extent to which results of research, such as that reported here, are general for other adsorbates, adsorbate concentrations, and activated carbon types needs to be determined by additional experimentation under similar conditions. Ultimately, research is needed to assess mechanisms by which humidity interferes with adsorption for various classes of organic compounds and adsorbate concentrations. Then predictive equations could be developed to extrapolate experimental results to a large number of combinations of conditions which exist under actual operating conditions.

Shape of the Breakthrough Curve

A recently introduced parameter,[2,3] termed the relative standard deviation (σ_r), describes the shape of an adsorption breakthrough curve.

Where:

σ= Standard deviation of the adsorbate breakthrough curve. (The calculation of σ is based on tabulations of the normal probability distribution and the assumption of a symmetrical adsorbate breakthrough curve about the 50% breakthrough point).[2]

T_{50}= Time to 50% adsorbate breakthrough.

This parameter should be independent of adsorbate challenge concentration. Broader contaminant breakthrough curves have greater values of σ_r than do narrower curves. The mean value of σ_r for the low humidity (5%) trials of this research was 0.126 (range 0.100 to 0.167); for all higher humidity trials σ_r was 0.210 (range 0.156 to 0.298). Thus, the presence of water vapor caused the shape of the TCE breakthrough curve to be broader than would have been predicted by results at the lowest relative humidity tested (5%).

Values in Tables III and IV are length of the time for all experimental trials to 50% and 10% TCE breakthrough, respectively. Each value is standardized to the length of time to breakthrough for the corresponding low humidity trial. (Note, the standardized times at 50% breakthrough are comparable to the standardized quantities of TCE adsorbed, since the midpoint of the breakthrough curve was used to calculate adsorptive capacity).[2] If relative humidity had no effect on the shape of the breakthrough curve, values in Tables III and IV would be identical. Differences in the values reflect the effect of water vapor (*i.e.*, boadening of the TCE breakthrough curve).

Practical implications of the effect of relative humidity on the shape of a breakthrough curve depend upon the application of the adsorption process. Broadening of the curve has little importance for air pollution control processes in which carbon columns are used in series. For those processes the upstream column can remain in service until its carbon is completely exhausted. However, a broadening of the curve would be significant for operations in which a single carbon bed is involved (*e.g.*, occupational respirators). Under conditions of high humidity and when the threshold limit of the contaminant is below 50% of the ambient concentration, the unit may have to be removed from service sooner than would be predicted by the carbon's adsorption capacity and the shape of the breakthrough curve obtained at a lower relative humidity. Research on other compounds at various relative humidities is required to determine if the effect of water vapor on the shape of the TCE breakthrough curve is a common phenomenon.

A Potential Predictive Approach

The Dubinin-Polanyi isotherm equation in its linearized form follows:

$$\ln W = \ln Wo - (\kappa_s \beta^2)(RT \ln(Po/P))^2$$

Where:

W = volume of adsorbate which is adsorbed (mL adsorbate/g adsorbent),
Wo = limiting adsorption volume (mL/g adsorbent),
κ_s = parameter for each adsorbent-adsorbate system,
β = affinity coefficient of adsorbate,
R = gas constant (8.3143 J/K mole),
T = temperature (K),
Po = saturated vapor pressure of adsorbate at a given temperature,
P = actual vapor pressure of adsorbate under the specific operation conditions.

The equation is based on rational chemical and physical principles and was specifically designed to describe adsorption of gaseous compounds on porous surfaces.[16,17] The equation has been shown to accurately fit experimental data and has proven to be a useful predictive equation for adsorption in single adsorbate systems.[18-20] Recent advances have been made in predicting parameter values of the equation

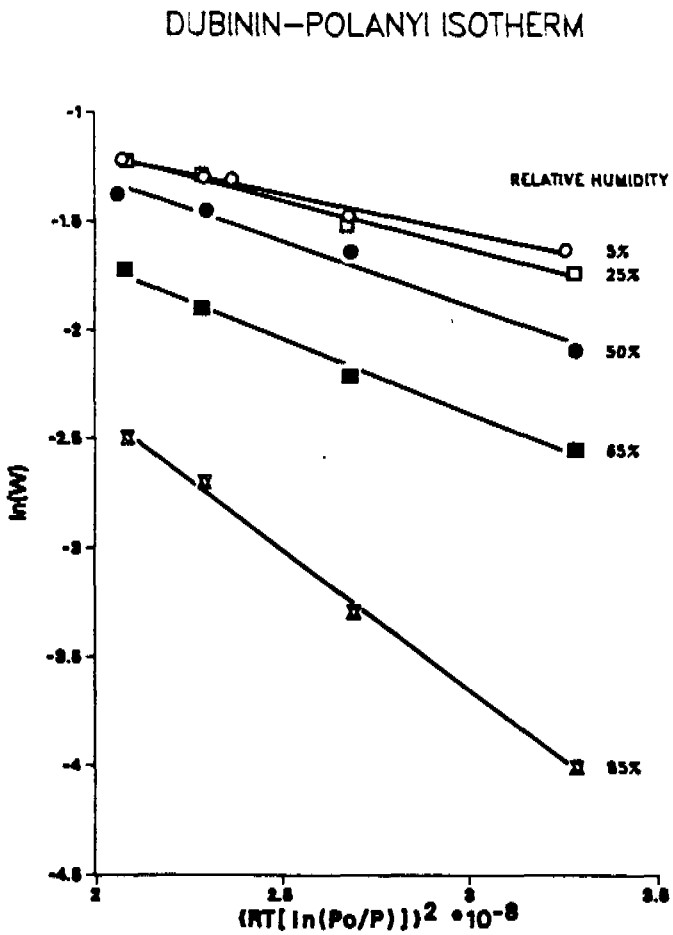


Figure 3—Experimental results fit to the Dubinin-Polanyi isotherm equation

[illegible] tion for actual applications. Parameter predictions [illegible] on physicochemical properties and empirical [illegible]

To further analyze the effect of water vapor on the adsorption process, each set of data corresponding to a specific level of relative humidity was fit to the Dubinin-Polanyi equation. Results are shown in Figure 3. Based on the results, two major points can be made. First, each set of data fits the equation equally well ($r^2 > 0.97$), indicating that for each humidity level the effect of water vapor was consistent with the theoretical basis of the Dubinin-Polanyi equation. Thus, to predict the effect of relative humidity on carbon adsorption, one only needs to determine how the parameter values, β and κ_s, are altered by the presence of water vapor for a given adsorbate-adsorbent system. The solubility of the adsorbate in water, along with other physical chemical properties of the adsorbate and adsorbent, influence the effect of humidity on the adsorption process; these properties may result in predictable changes in the values of β or κ_s, or both. Notice, the lines in Figure 3 converge as values along the abscissa decrease. Thus, the value of Wo (the Y intercept in Figure 3) was not appreciably changed at different relative humidity levels. Apparently, the concentration of water vapor had little effect on the limiting adsorption volume of the carbon for TCE.

Second, the trend seen in Figure 3 clearly illustrates an important interaction between the level of humidity and adsorbate (TCE) concentration. (Influent adsorbate concentrations increase as values along the abscissa decrease.) The deleterious impact of humidity is less at high TCE concentrations than at lower concentrations. In fact, if the adsorbate concentration were extended beyond the experimental range, the lines in Figure 3 would meet. Thus, based on an extrapolation of these data, one could predict that at some high adsorbate concentration the impact of humidity would be negligible. Experimental results substantiate this hypothesis; at the two highest TCE concentrations (1000 and 1300 mg m^3), 25% relative humidity did not reduce the amount of TCE adsorbed (Table I). Based on these results, the relatively small impact of humidity reported in one study[13] (Table II) can largely be explained by the high influent adsorbate concentration used (*i.e.*, four times the highest adsorbate concentration used in this research). If results were extrapolated to very low organic adsorbate concentrations and high relative humidity, carbon adsorption could become impractical, based on the trends demonstrated in Figure 3.

Conclusion

Relative humidity at five different levels affected the adsorption capacity of activated carbon. In general, each increase of humidity level further decreased the carbon's adsorptive capacity at all four TCE concentrations tested. Furthermore, at low TCE concentrations the effect of humidity was greater than at high TCE concentrations.

The results indicate that two assumptions sometimes made concerning the effect of humidity on vapor phase

activated carbon adsorption should be applied only with caution. First, making an assumption that relative humidities below 50% have negligible impact on adsorption may be invalid. All levels of relative humidity had an adverse effect at the low TCE concentrations tested during this experiment. Second, applying a "multiplier factor" determined at one adsorbate concentration to account for a given humidity at other adsorbate concentrations is tenuous. As indicated previously, the effect of humidity on the carbon's adsorption capacity was strongly influenced by the influent TCE concentration. Additional research is required for other adsorbates under similar experimental design to determine how general these results are.

The Dubinin-Polanyi isotherm equation fits data at each humidity level equally well. The basis of the equation may be useful for predicting the effect of humidity on gaseous phase carbon adsorption. Determining the mechanism by which the values of the equation parameters (specifically, β and κs) are influenced by humidity will be critical in applying the predictive power of the equation to the impact caused by humidity.

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