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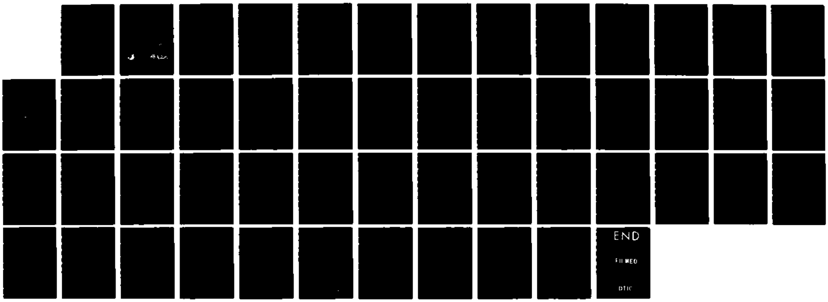
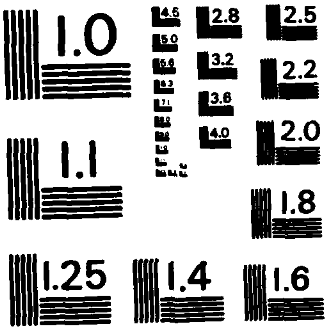
UNCLASSIFIED M D WERNER ET AL. AUG 85 AFESC/SSL-TR-85-29 F/G 7/1 NL





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ESL-TR-85-29

Predictive Models for Gaseous–Phase Carbon Adsorption and Humidity Effects on Trichloroethylene Adsorption

M. D. WERNER
R. L. GROSS
E. C. HEYSE

AUGUST 1985

FINAL REPORT

JUNE 1984 - AUGUST 1984

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD - A159167

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for Public Release;
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
ESL-TR-85-29

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Air Force Engineering
and Services Center

6b. OFFICE SYMBOL *(If applicable)*
RDVW

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State and ZIP Code)*
HQ AFESC/RDVW
Tyndall AFB, FL 32403

7b. ADDRESS *(City, State and ZIP Code)*

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Air Force Office of
Scientific Research

8b. OFFICE SYMBOL *(If applicable)*
N/A

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract # F49620-82-C-0035

8c. ADDRESS *(City, State and ZIP Code)*
AFOSR
Bolling AFB
Washington, D.C. 20332

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
62601F	1900	20	66

11. TITLE *(Include Security Classification)*
Predictive Models for Gaseous-Phase

12. PERSONAL AUTHOR(S)
WERNER, M.D., GROSS, R.L., HEYSE, E.C.

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM Jun 84 TO Aug 84

14. DATE OF REPORT *(Yr., Mo., Day)*
August 1985

15. PAGE COUNT
52

16. SUPPLEMENTARY NOTATION
Keywords Cum
Availability of this report is specified on reverse of front cover

17. COSATI CODES

FIELD	GROUP	SUB. GR.
07	01	
13	08	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Freundich Isotherm, Trichloroethylene,
Langmuir Isotherm, Carbon adsorption,
Dubinin-Polanyi Isotherm, Activated Carbon,

Keywords Cont'd

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Theoretical models were applied to the adsorption of trichloroethylene (TCE) at influent concentrations ranging from 300 to 1350 mg/m^3 in air on granular activated carbon at low relative humidity. The models were shown to predict both the adsorptive capacity of activated carbon (maximum error compared to actual data < 25 percent), and the shape of the breakthrough curve (maximum error < 8 percent). These low humidity data were then compared to TCE adsorption by the same carbon at 25, 50, 65, and 85 percent relative humidities. Increasing levels of humidity had increasingly deleterious effects on the adsorptive capacity of activated carbon at all TCE concentrations tested. The adverse effect caused by the presence of water vapor was more significant at the lower TCE concentrations than at the higher concentrations.

The presence of water vapor not only decreased the carbon's adsorptive capacity but also reduced its efficiency by increasing the dispersion of the breakthrough curve. Data

Cont'd

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
RANDY L. GROSS, Capt, USAF, BSC

22b. TELEPHONE NUMBER *(Include Area Code)*
904-283-4628

22c. OFFICE SYMBOL
HQ AFESC/RDVW

DD FORM 1473, 83 APR   EDITION OF 1 JAN 73 IS OBSOLETE.

Abstract cont'd

Keywords Cont'd

BLK 11. Carbon Adsorption and Humidity Effects on Trichloroethylene Adsorption (U).

BLK 18. Air Pollution Control, Air Stripping Emissions Control.

BLK 19. at all humidity levels fit the Dubinin-Polanyi Isotherm equation equally well, indicating that the impact of water vapor on the adsorptive capacity of carbon for TCE is predictable and could be accurately modeled. Originator supplied Keywords include:)

<— See DD 1473 i

PREFACE

This research was sponsored by the Air Force Office of Scientific Research through a contract with the Southeastern Center for Electrical Engineering Education, as part of the USAF Summer Faculty Research Program. The main author and principal investigator was Dr. Martin D. Werner, School of Public Health, University of Texas (San Antonio) under Contract F49620-82-C-0035. The research was performed at the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RDVW), Tyndall AFB, Florida 32403-6001 between June and August 1984. The AFESC Project Officers and coauthors were Captain Randy L. Gross and First Lieutenant Edward Heyse.

This report presents the effects of humidity and concentration on the adsorption of trichloroethylene on activated carbon. Experimental data were also compared to several adsorption theories.

The mention of trade names and trademarks in this report does not constitute endorsement by the Air Force, nor can it be used for advertising those products.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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SECTION I

INTRODUCTION

A. OBJECTIVE

This study investigated carbon adsorption of trichloroethylene (TCE) from air to determine if adsorption would be a viable option to limit TCE discharges from packed-tower air strippers. Two specific objectives were addressed. First, existing theory on carbon adsorption was applied to experimental data to assess agreement between predictions and the actual data. A short review of the development and assumptions of the relevant theory was also done. Second, an assessment was made on the impact of water vapor, at five relative humidity levels, on the the effectiveness of trichloroethylene adsorption by activated carbon.

B. BACKGROUND

Adsorption of organic contaminants from air streams by activated carbon is a control process which has a variety of uses and potential for future development. Among its applications are contaminant removal from point sources of air pollution, use as a filter in gas masks to prevent inhalation of potentially dangerous organic compounds by industrial workers, and organic solvent recovery or sampling (References 1,2, 3). To take full advantage of any pollution control technology, reliable criteria are needed to determine its design and operation. Reliable design criteria are particularly important for activated carbon adsorption since, upon saturation (or exhaustion), the treatment process can immediately become ineffective for contaminant removal. Additionally, since carbon adsorption is a relatively expensive treatment process, exhaustion of the carbon to the greatest extent possible is desirable, while still meeting standards for effluent quality. Accurate models that predict when the adsorptive capacity of activated carbon would be reached will aid in assuring requirements for effluent quality are met while the treatment operation is as cost-effective as possible.

Models which predict several critical aspects of gaseous-phase carbon adsorption currently exist. Among the aspects that the models attempt to predict are: the carbon's total adsorptive capacity (References 4 and 5) shape of contaminant breakthrough curve (Reference 6), and time to a critical level of contaminant breakthrough (Reference 7). The models cited have been established to predict the adsorption of a single adsorbate from dry air, but most gaseous-phase applications of activated carbon involve mixtures of adsorbates from air with a significant level of relative humidity. Although the models are theoretically sound, further development is required to extend them to more realistic conditions of actual process application.

An application of gaseous-phase carbon adsorption of primary interest to the Air Force concerns removal of volatile organic compounds (VOCs) from air-stripping discharge air. Air stripping of VOCs from contaminated groundwater is generally considered superior to other treatment options by the Air Force for treating polluted groundwater. Air stripping is not only very effective for removing VOCs from water, but is also much less costly than other reliable processes such as aqueous-phase carbon adsorption. Recently, however, some state and federal agencies are considering the air-stripped VOCs as point sources of air pollution which may require additional cleanup efforts. Gaseous-phase carbon adsorption is a logical treatment process for this application.

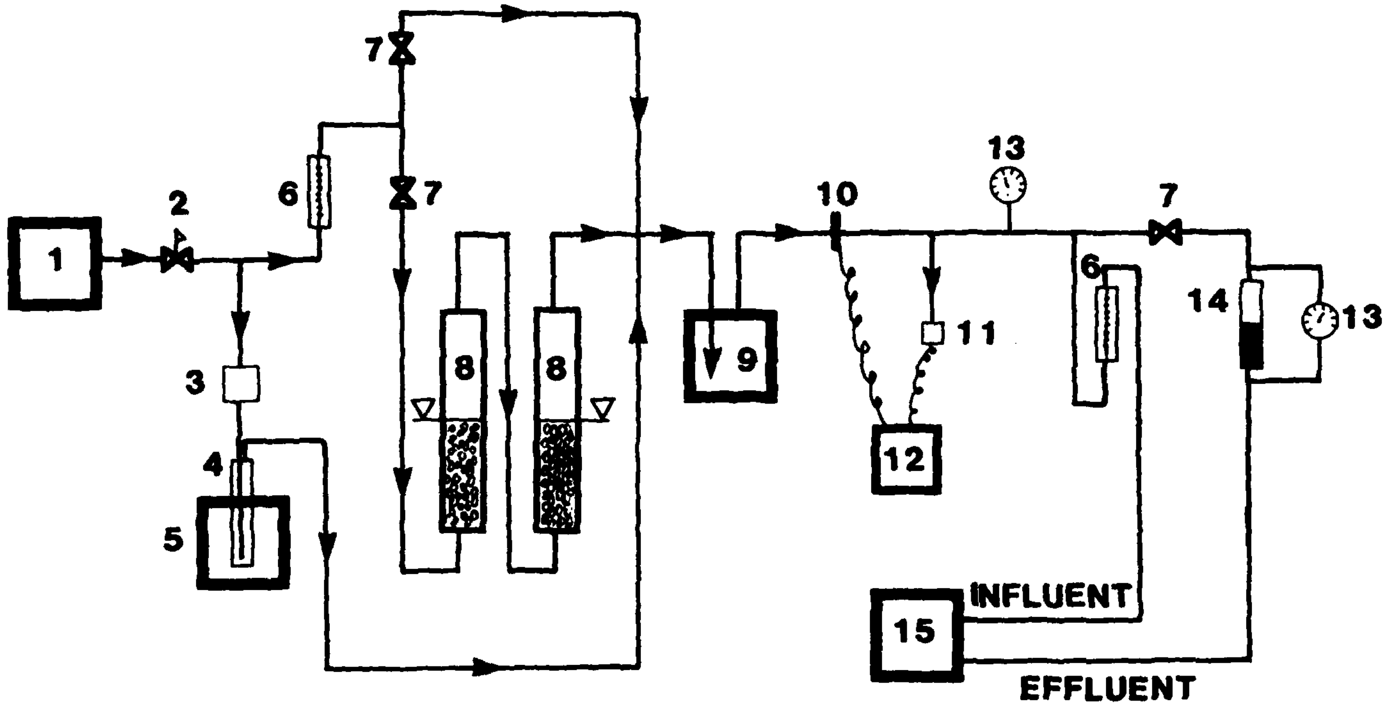
Two important characteristics of the discharged air must be considered if carbon is to be used. First, the VOC concentration in the air is likely to be low because of the advantage of a high air-to-water ratio during a typical stripping operation. Unfortunately, the capacity of activated carbon for an adsorbate decreases with decreasing adsorbate concentration. Most research on gaseous phase carbon adsorption has been performed at higher VOC concentrations than that which would be encountered from a stripping operation; thus, theoretical models to predict adsorption efficiency have been developed for, and verified by, adsorption at high VOC concentrations. It is necessary to determine whether these theoretical models are valid predictors at VOC concentrations within the range produced during an air-stripping operation. Second, the air streams containing the VOC would also have a high water vapor concentration. Numerous reports written on the subject of gaseous phase carbon adsorption mention the detrimental effect of humidity on the adsorption process (References 8, 9, 10), but few studies exist which have quantified the magnitude of the impact. Furthermore, no study has been located which has systematically tested the effect of several levels of humidity on adsorptive efficiency at various concentrations of a VOC. If there is an interaction between the relative adsorption efficiency at different humidity levels and VOC concentration, it would be desirable to take measures to optimize adsorption effectiveness in an overall air stripping/carbon adsorption process. For example, if a given level of humidity has a greater deleterious effect at lower VOC concentration than at higher concentration, it may be desirable to reduce the air-to-water ratio in the stripping operation to increase the VOC concentration in the air and, thereby, increase the effectiveness of subsequent carbon adsorption.

SECTION II

EXPERIMENTAL METHODS

The experimental system used in this research is illustrated in Figure 1. Compressed air was passed through a Zeks NCA 35 Air Dryer which reduced the air's relative humidity to below 5 percent and then purified by an Aadco Model 737-116 Pure Air Generator (1). The air entered the system through a pressure valve (2) and was split immediately into two streams. A small portion (0.2 to 0.5 percent) of the total flow was directed to a TCE-generating apparatus. Air flow to the apparatus was controlled by a Matheson Model 8141 Transducer (calibrated for flows up to 100 mL/min) connected to a Matheson Model 8249 Multi-Flow Controller (3). The TCE-generating apparatus consisted of a 4.5 cm cm diameter impinger tube partially filled with TCE (4) submerged in a constant temperature water bath (5). The concentration of TCE vapor in the air was controlled by a combination of three factors: regulating the quantity of air directed through the impinger tube, regulating the temperature of the water bath, and setting the distance between the air entry point in the impinger tube and the surface level of TCE. As an experimental trial progressed, the TCE level decreased in the impinger resulting in a greater gap between the air entry point and TCE level. Thus, the kinetic energy resulting from air impinging on the TCE surface decreased; to compensate, it was necessary to increase the temperature of the water bath slightly during an experimental trial and thereby maintain a constant TCE concentration in the air stream.

The bulk of the air (10 L/min) flowed through a rotometer (6) and into the main portion of the experimental system. Two flow valves (7) permitted the main air stream to be divided. Any portion of the total could be directed through two 5 cm diameter glass tubes (8) connected in series and partially filled with water and plastic Pall rings. By directing air through these tubes its relative humidity was increased. The Pall rings distributed the air flow to increase air-water contact and heating tape was wrapped around the first tub in series to increase the transfer of water to the air stream. Depending on the portion of air directed through the water, a constant air humidity (up to 85 percent relative humidity) was achieved during the various experimental trials.



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 the Experimental System.

The three portions of air (TCE laden, water vapor laden, and pure dry air) were united and directed through a 20-liter equalization vessel (9) to dampen short-term variation in TCE concentration and air humidity. The total air stream then passed over a temperature probe (10) and a low air flow (25 mL/min) was directed to a dew point sensor (11). Signals from the temperature probe and dew point sensor were relayed to a General Eastern Model 1500 Hygrocomputer (12). Thus, air temperature and water vapor concentration were continuously measured during an experimental trial. Air pressure in the system was measured by a Magnehelic® pressure gage (13). Pressure readings were used to diagnose the system for proper operation. For example, an abnormally high reading may mean a kinked air line, or a low reading may mean an air leak.

The main air stream was again divided. Approximately 25 percent of the flow was diverted to a Perkin-Elmer Sigma 2000 gas chromatograph (15) for determination of TCE concentration. The remaining air (7.7 L/min) was directed through the activated carbon column (14) and then to the gas chromatograph for analysis. Both, the concentration of TCE in the influent and carbon column's effluent air was measured during a experimental trial. A pressure-driven solenoid valve mounted on the gas chromatograph permitted the influent air, then the effluent air, to be analysed on a programmed time schedule. The solenoid valve was controlled by programming an attached Perkin-Elmer Sigma 15 Chromatography Data Station. The interval between a complete sampling cycle was 20 minutes (except for one trial at the lowest TCE influent concentration, which was 60 minutes). An experimental trial was complete after the TCE concentration in the effluent air stabilized at the influent level.

A pressure gage (13) connected across the carbon column was used to measure pressure drop through the activated carbon bed. The air flow (7.7 L/min) through the 2.54 cm diameter column resulted in a linear velocity within the column of 25 cm/s, and an air retention time within the carbon of 0.5 seconds. Air flow and mass of carbon (37.5 grams) were held constant among experimental trials. The carbon bed depth was about 13.5 cm in the column. CECA GAC48C Carborundum® activated carbon was used in all cases. The carbon was washed with distilled water and dried at least two days in a 105 ^{o}C oven prior to use. The carbon was then placed in the glass column, supported on a thin layer of glass wool.

Experimental trials were performed at four TCE concentrations (roughly 300, 600, 900, and 1300 mg/m^3) each at 5 levels of relative humidity (< 5, 25, 50, 65 and 85 percent). An additional trial was performed at 53 mg TCE/m^3 and less than 5 percent relative humidity.

Standardizations of the gas chromatograph were performed by dissolving TCE in quinoline and injecting measured volumes of the liquid mixture into the instrument. Standard concentrations of TCE included the range of all experimental trial concentrations. Calibration of the rotometers was done with a wet test meter.

SECTION III

PREDICTIVE METHODS

A. ISOTHERM EQUATIONS

A number of isotherm equations have been used to describe the adsorption of contaminants from air onto porous adsorbate such as activated carbon. A short description of three isotherm equations, including a review of their advantages and disadvantages, follows.

1. Freundlich Equation

The Freundlich Isotherm equation is of the form:

$$Q = k(C_e)^{1/n} \tag{1}$$

where

Q = quantity of adsorbate sorbed per unit adsorbent
C_e = equilibrium adsorbate concentration
k = coefficient which depends on temperature, characteristics of adsorbent, etc.
n = coefficient which depends on temperature

In the following linearized form the coefficients can be determined graphically from experimental data:

$$\log_e Q = \log_e k + \frac{1}{n} \log_e C_e \tag{2}$$

Although the Freundlich equation often fits experimental data quite well, its usefulness is limited due to its lack of predictability to other conditions of adsorption and for other adsorbates. Fundamentally, fit of experimental data to the Freundlich equation is empirical; the coefficients, k and n, must be determined for each adsorbate/adsorbent system and a given set of external conditions. The primary usefulness of the Freundlich equation for gaseous phase adsorption involves comparisons of the coefficients obtained under controlled conditions to analyze the adsorption process. For example, the relative adsorption affinity of different adsorbates, or the effect of temperature on the adsorption of a single adsorbate, could be determined by comparing coefficients resulting from controlled experiments.

TCE adsorption data obtained at the lowest humidity level during this study were fit to the Freundlich Isotherm equation; results are presented in Figure 2. The correlation coefficient of the data fit to this equation is 0.993.

2. Langmuir Equation

The Langmuir equation, unlike the Freundlich equation, is based on theoretical considerations. However, during its development, several assumptions were made which may invalidate the equation for gaseous phase adsorption. Three critical assumptions are: adsorption on the adsorbent surface is one molecule thick; the adsorption surface is energetically homogeneous; and forces of attraction between adsorbed molecules are negligible. The first two assumptions have been demonstrated to be invalid; there is evidence that the layer of adsorbate covering an adsorbent's surface is multimolecular and energetic heterogeneity at the surface of porous adsorbates has been shown (Reference 11). As with the Freundlich equation, coefficients determined for the Langmuir equation are unique for a set of conditions and are not readily applied to other conditions or adsorbates without additional experimental verification.

The Langmuir equation is of the form:

$$Q = \frac{Q_1 \kappa C_e}{1 + \kappa C_e} \tag{3}$$

where

Q and C_e are as defined in the Freundlich equation

Q_1 = amount adsorbed for a total monomolecular covering of the adsorbent surface (i.e. the limiting adsorption capacity)

κ = coefficient unique for the conditions of adsorption

The linearized form of the equation is:

$$\frac{1}{Q} = \frac{1}{Q_1 \kappa C_e} + \frac{1}{Q_1} \tag{4}$$

In the above form, the values of the coefficients Q_1 and κ can be graphically determined.

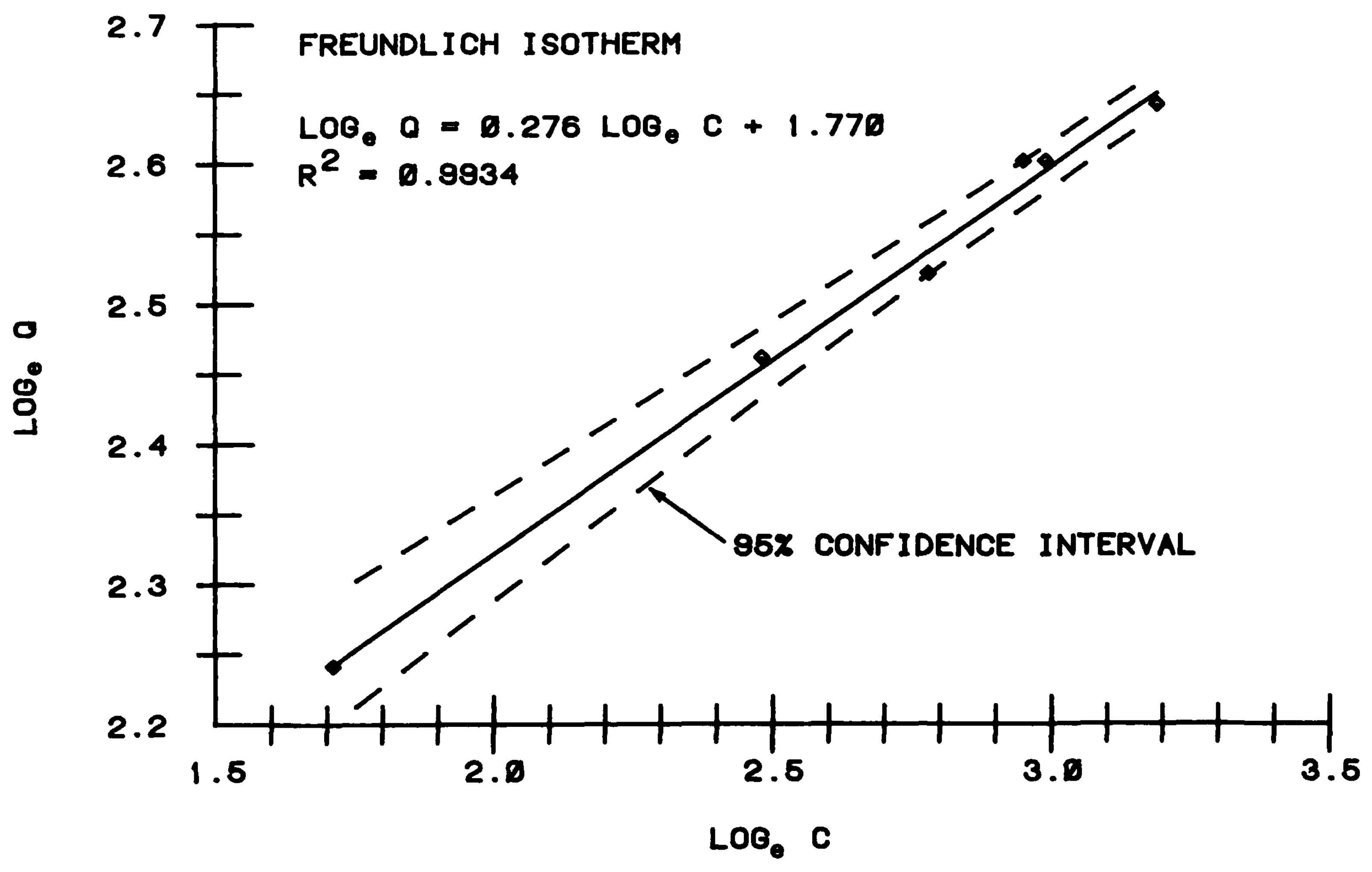


Figure 2. Experimental TCE Adsorption Data Fit to the Freundlich Isotherm Equation.

TCE adsorption data fit to the Langmuir equation arc presented in Figure 3. Two lines were fit to these data (A and B). Line A includes all data while B excludes the point in the upper right-hand corner of the graph. The correlation coefficient for both lines is 0.952. Cerny (Reference 11) states that a discontinuity in a line fit to the Langmuir equation (such as that displayed by Figure 3) indicates energetic heterogeneity at the adsorbate surface (indicating the invalidity of the second critical assumption).

3. Dubinin-Polanyi Equation

The Dubinin-Polanyi isotherm equation was specifically developed for gaseous phase adsorption on porous surfaces, such as activated carbon. The equation is based on theoretical concepts of adsorption with the goal of developing a predictive equation. The predicitve power of the equation is manifested in two major ways. First, the adsorption isotherm can be predicted for an adsorbate at any temperature if the isotherm is known for that adsorbate at another temperature (assuming all temperatures of concern are below the critical temperature of the adsorbate). Second, the adsorption isotherm of a potential adsorbate on a specified adsorbent can be calculated if the adsorption isotherm of a reference adsorbate is known, along with the relative adsorptive affinity of the adsorbate in question and the reference adsorbate. An abbreviated review of the development of the Dubinin-Polanyi equation will enumerate assumptions made and demonstrate the basis for its predictive capacity.

The equation builds on the ideas of the potential theory of adsorpton, which assumes that molecules of gaseous adsorbate are compressed by forces of attraction (designated by the symbol "ε") acting from the adsorbent's surface through a certain distance into the surrounding space (Reference 11). The forces of attraction are greatest near the adsorbent surface and decrease in magnitude with distance from the surface, until reaching zero. The total space included within the force field is considered to be the limiting adsorption volume (designated by "W_o"). A significant assumption of the isotherm equation, and one which permits extrapolation of adsorption results to other temperatures, is that the magnitude of W_o is independent of temperature (References 11, 12). With the restriction that the operating temperature be below the critical temperature of the adsorbate, the maximum adsorption space (W_o) is assumed to be constant over all temperatures.

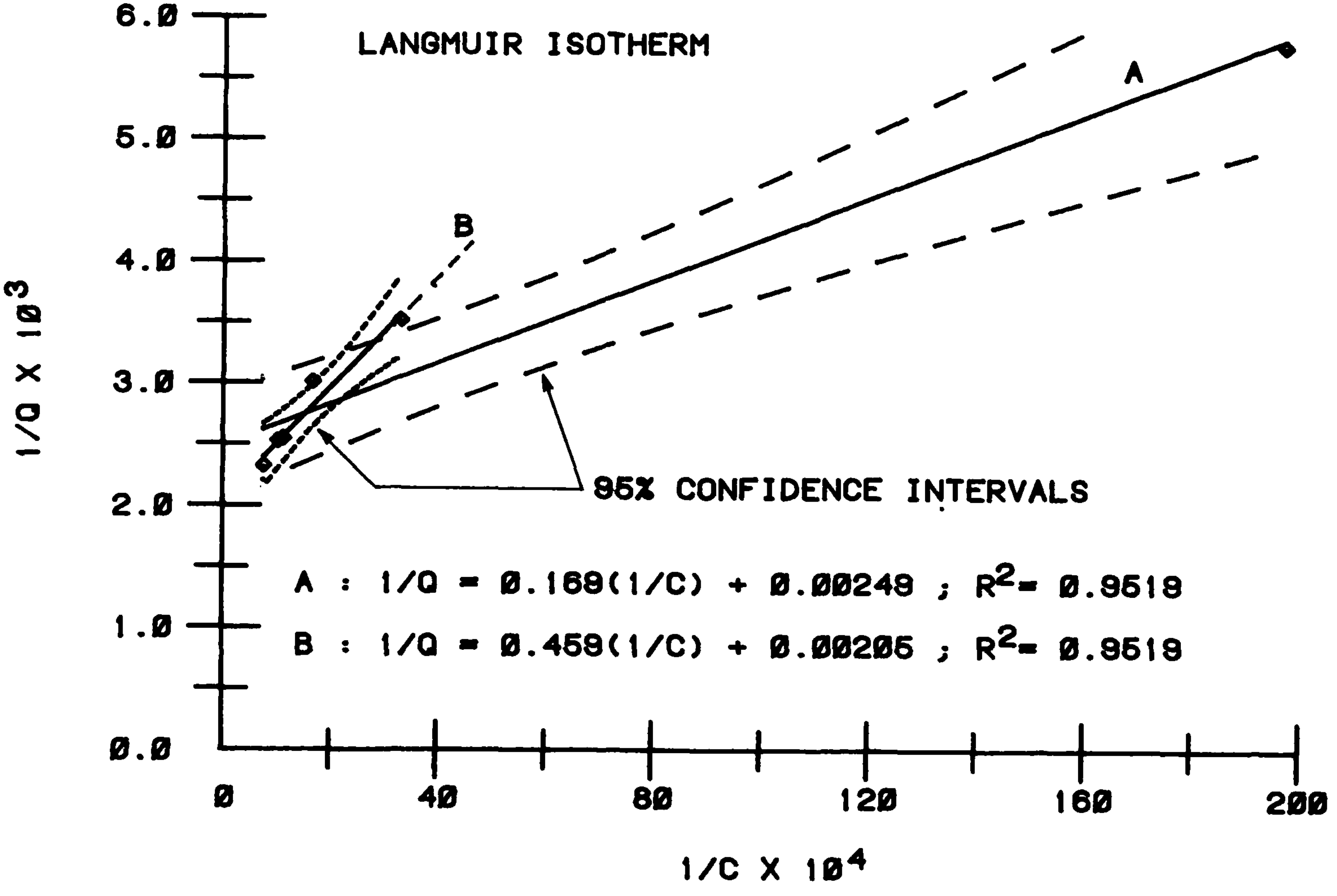


Figure 3. Experimental TCE Adsorption Data Fit to the Langmuir Isotherm Equation.

Two other assumptions concerning the adsorption potential (ε) are: first, it is independent of the presence of adsorbate molecules within the adsorption space (W_o) and, second, interactions between adsorbed molecules within the space are the same as that between nonadsorbed molecules (Reference 11). The assumption that the adsorbate is condensed to the density of its liquid form is also made (References 11, 12). In consideration of these assumptions, the adsorption potential is defined as

$$\varepsilon = RT \log_e(P_o/P) \tag{5}$$

where

R = the universal gas constant (8.3143 J K^{-1} mol^{-1})

T = the absolute temperature (Kelvin)

P_o = the saturated vapor pressure of the adsorbate at the operating temperature, and

P = the equilibrium adsorbate vapor pressure under the conditions of the adsorption process.

Thus, the adsorption potential is considered comparable to the isothermal work of compression (Reference 11).

The quantity of adsorbate actually adsorbed (W) was put into the following general form by researchers who initially developed the Dubinin-Polanyi equation (Reference 11).

$$W = W_o e^{-K_d \varepsilon^2} \tag{6}$$

where K_d is a constant. The rationale for the above equation was that the observation of the the relationship between W and ε is consistently similar to the Gaussian distribution curve. Therefore, the filling of adsorption space on a porous medium could be expressed by the preceding exponential equation (Reference 11). Combining Equations (5) and (6) leads to the following:

$$W = W_o e^{-K_d [RT \log_e(P_o/P)]^2} \tag{7}$$

Assuming the density of adsorbate in the adsorption space equals its liquid form (as stated previously) leads to the following relationship:

$$W = a\nu \tag{8}$$

where a is the quantity of adsorbate adsorbed (moles) and ν is the liquid molar volume of the adsorbate. Combining Equations (7) and (8) results in

$$a = \frac{W_o}{\nu} e^{-K_d[RT \log_e(P_o/P)]^2} \tag{9}$$

Thus, the quantity of adsorbate adsorbed (in moles) can be determined from Equation (9) if the constant K_d is known.

In the form of Equation (9), K_d is a function of both adsorbate and adsorbent. Thus, K_d could have an infinite number of values depending on the combination of adsorbates and adsorbents of concern. It would be desirable to give the equation greater predictive power by separating the effect of adsorbates and adsorbents on the value of K_d. As described by Cerny (Reference 11) an attempt to do this by early researchers was encouraged by the "affine" nature of different adsorbates on porous adsorbing surfaces. (The property of being "affine" means that the adsorption potential (ϵ) of an adsorbent, sufficient to cause the adsorption of a specific adsorbate, is a constant fraction of that same value for any other adsorbate over a wide range of equilibrium vapor pressures). The affine nature relevant to the adsorption process is expressed in equation form as:

$$\epsilon = \epsilon_r \beta \tag{10}$$

where ϵ and ϵ_r are adsorption potentials for any adsorbate and a reference adsorbate, respectively, and β is the affinity coefficient relating the pair of adsorbates. The affinity coefficient can be determined experimentally, or approximated by physico-chemical properties of the adsorbates (e.g., by taking ratios of the adsorbate's molar volumes, parachlors, etc. (References 5, 11, 12, 13).

Returning to Equation (6) and solving for ϵ yields:

$$\epsilon = \sqrt{\frac{\log_e (W_o/W)}{-K_d}} \tag{11}$$

For two vapors filling equal volumes of adsorption space (W), and dropping the "d" subscript on K for clarity, the following is true:

$$\frac{\varepsilon_r}{\varepsilon_1} = \sqrt{\frac{K_1}{K_r}} \qquad (12)$$

Assuming $\varepsilon_1 = \varepsilon_r\beta$ (Equation (10)) makes the following equation possible:

$$K_1 = K_r/\beta^2 \qquad (13)$$

Now Equation (9) can be written

$$a = \frac{W_o}{\nu} e^{-\frac{K_r}{\beta}[RT \log_e(P_o/P)]^2} \qquad (14)$$

or

$$W = W_o e^{-\frac{K_r}{\beta}[RT \log_e(P_o/P)]^2} \qquad (15)$$

Ideally, the affinity coefficient (β) depends on the absorbate and is independent of the adsorbent. Urano et al. (Reference 5) state that this has not been *conclusively confirmed*, but those authors tested 13 organic solvents on 7 granular activated carbons and found β values to be only slightly different for the various activated carbons. The authors concluded that the differences in β for different carbons were negligible when considering actual adsorption processes of vapor on activated carbon (Reference 5). Based on their evidence, β might be considered constant over adsorbent (e.g., activated carbon) types for practical purposes.

The degree to which the value of K_r depends on adsorbate and adsorbent is also not clearly understood. Urano et al. (Reference 5) determined that the K_r value was very nearly constant for their reference adsorbate (benzene) for all carbons tested (except one carbon which was made by a specific process for control of surface oxides). The authors suggest that their value for K_r ($2.8 \pm 0.2 \times 10^{-9}$ Mol^2 J^{-2}) can be used for predicting the adsorption of other adsorbates on porous adsorbents when benzene is used as the reference adsorbate.

If the values of W_o, K_r, and β are known, it is possible to predict the adsorption capacity of any combination of adsorbate and adsorbent on many types of activated carbon. The values of the parameters may be determined experimentally by putting Equation (15) in its linearized form:

$$\log_e W = \log_e W_o - \frac{K_r}{\beta^2} (RT \log_e \frac{P_o}{P})^2 \qquad (16)$$

When $\log_e W$ is plotted against $[RT \log_e(P_o/P)]^2$, $\log_e W_o$ is the y-intercept and K_r/β^2 is the slope. Assuming a value for β (as discussed previously) permits the value of K_r to be calculated. The values obtained in this way could then be applied to prediction of adsorption capacities for different adsorbates on the same adsorbent.

Experimental data taken at the lowest humidity reading were fit to the Dubinin-Polanyi Isotherm equation in Figure 4. The correlation coefficient for this isotherm equation is 0.983.

During their study, Urano et al. (Reference 5) found the following relationship to hold for the 13 organic solvents and 7 different activated carbons:

$$W_o = 0.055 + V_{3.2nm} \qquad (17)$$

where W_o is in mL/g, 0.055 is an empirically derived constant, and $V_{3.2nm}$ is the volume of pores with diameters less than 3.2 nm in the activated carbon.

Dubinin (Reference 12) also stated the value of W_o should be related to the volume of the micropores (pores smaller than 3.2 nm in diameter). The reason the micropores are critical to the value of W_o is that the distance between opposite sides of the pores is sufficiently small to permit the adsorption potential from each side to overlap. Thus, the entire volume of the micropore can be filled by liquid adsorbate, leading to capillary condensation (Reference 11). The $V_{3.2nm}$ values for many commercial carbons are available from their manufacturer, or they can be calculated from the pore size distribution obtained by nitrogen adsorption.

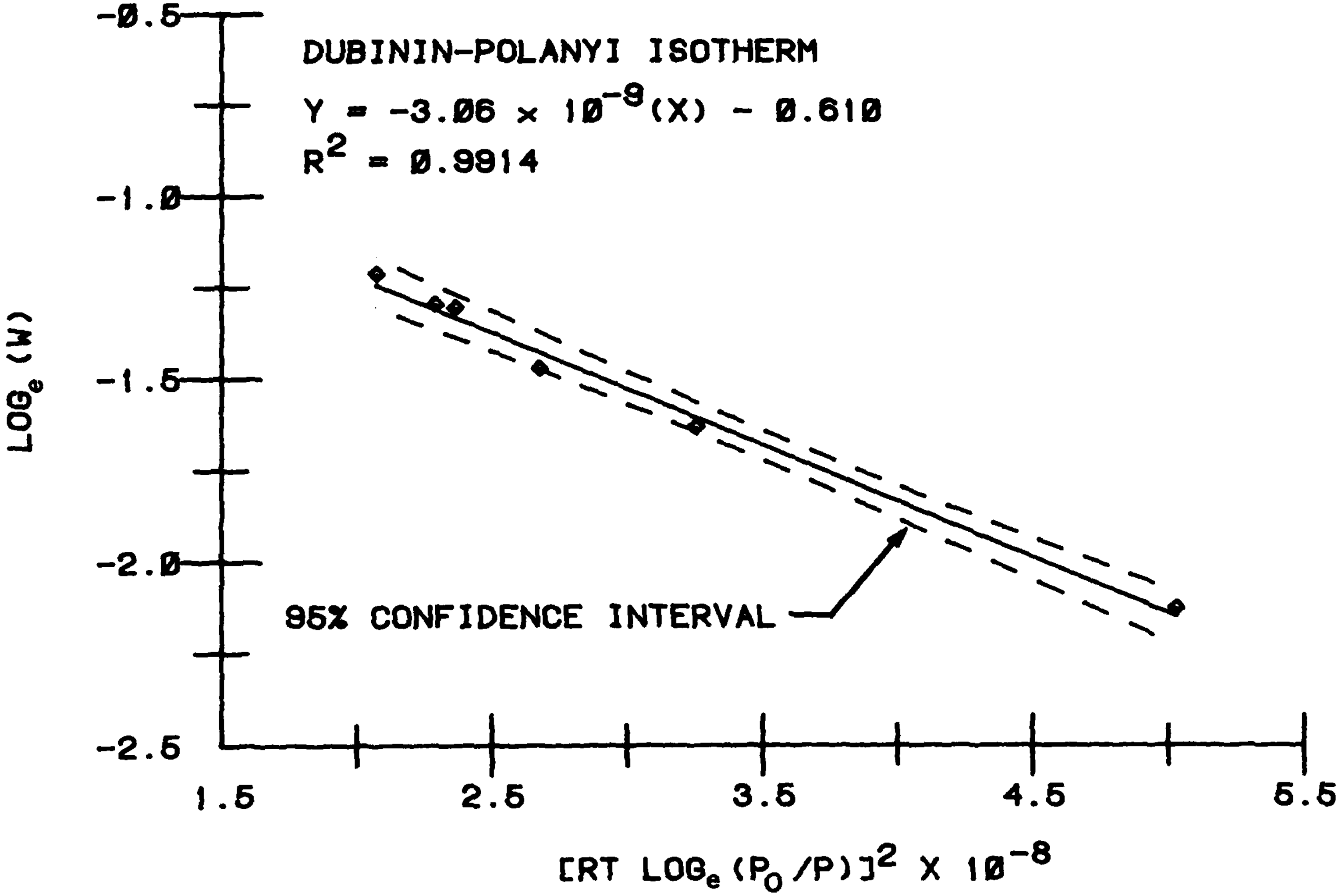


Figure 4. Experimental TCE Adsorption Data Fit to the Dubinin-Polanyi Isotherm Equation.

A comparison between actual results for trichloroethylene adsorption on activated carbon and theoretical predictions is presented in Figure 5. The parameter values used for the prediction were: $\beta = 1.14$; $K_r = 2.8 \times 10^{-9}$ mol^2 J^{-2}; and $W_o = 0.505$ mL/g. Values for β and K_r are those suggested by Urano et al. (Reference 5). The value for $V_{3.2nm}$ was not available for the carbon used in this experiment, so the value (0.45 mL/g) for a closely related carbon, CECA GAC 410, was used. The largest deviation between predicted and actual values was 25 percent. The predicted values represent maximum adsorption which would be measured under static conditions, while experimental results are from dynamic adsorption conditions. It is expected that they would be lower than maximum adsorption values.

B. THEORY OF STATISTICAL MOMENTS

Grubner and coworkers (References 4,6,7) suggest a system of equations based on the theory of statistical moments to help understand dynamic gas adsorption. The equations are useful for describing adsorption breakthrough curves and can be used to predict the times for various levels of contaminant breakthrough during the operation of carbon adsorption processes. Unlike static adsorption, for which the adsorption capacity of the carbon is singularly important, kinetic effects resulting from the carrier gas (e.g. air) and adsorbate being forced through a porous bed of adsorbate at some velocity are important additional considerations for dynamic adsorption.

The basis of the dynamic gas adsorption model (References 4, 6) is the idea that the velocity of an individual adsorbate molecule through an adsorbent bed is affected not only by adsorption and desorption (as with static adsorption), but also by other phenomona of a random nature. The latter phenomena result largely from variable flow profiles occuring in the adsorption bed due to variable sizes and shapes of adsorbent particles. Since the distribution of velocities among adsorbate molecules through a carbon bed arises from random phenomena which fluctuate about some mean value, a reasonable expectation is that the change in concentration of adsorbate molecules exiting the carbon adsorption bed should follow the pattern of a cumulative normal probablility curve (Reference 6).

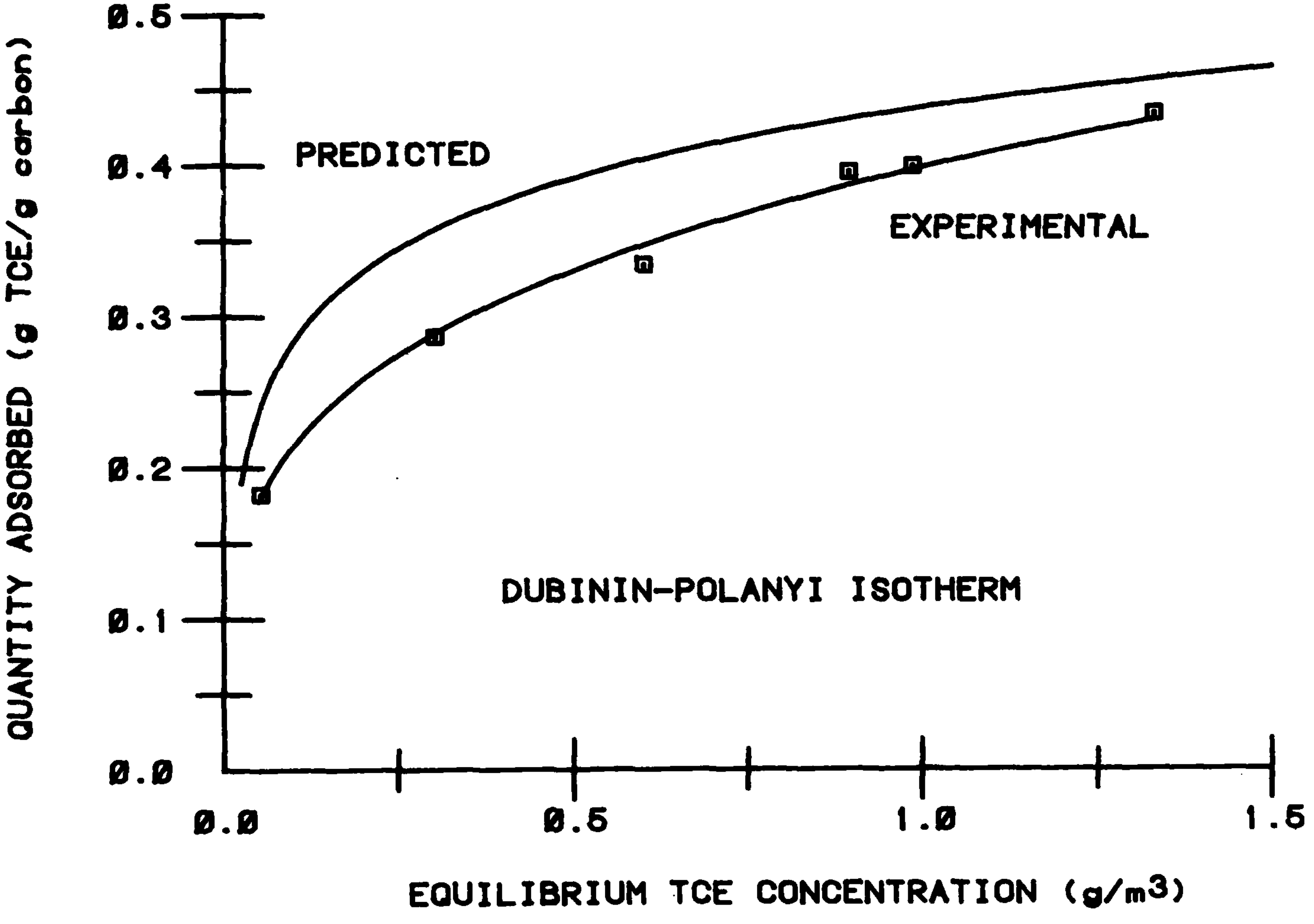


Figure 5. Experimental Dynamic Adsorption Capacity of Activated Carbon Compared to Predicted Capacity (Based on the Dubinin-Polanyi Isotherm).

Assuming that the breakthrough curve follows the normal probability pattern, the variance of adsorbate molecules' velocities through an adsorbent column could be predicted by as few as two effluent concentrations analysed during adsorbate breakthrough. After the variance, or distribution, of adsorbate molecule velocities is estimated, the entire breakthrough curve can be constructed. Thus, the adsorbent's capacity can be calculated without experimentally determining the entire breakthrough curve.

Entire breakthrough curves for TCE adsorption were experimentally determined. Breakthrough curves under the same conditions were also estimated based on time to breakthrough of 10 percent and 50 percent of the influent TCE concentration and the Theory of Statistical Moments applied to dynamic adsorption. Comparisons of the carbon's adsorption capacity estimated by the two means are presented in Table 1 for four TCE concentrations at the lowest relative humidity (< 5 percent). Deviations between the estimates ranged from -3.50 to + 3.68 percent. Deviations from predictions for the higher humidity levels were not calculated, but plots drawn for each indicated the magnitude of deviation was similar to that at the lowest humidity. Plots of the shape of the actual breakthrough and estimated curves are presented in Figures 6 and 7 to help visualize the degree of deviation. The comparison demonstrates that the actual breakthrough curve for TCE adsorption on the activated carbon closely followed the pattern of a normal probability curve as predicted (References 4,6).

TABLE 1. COMPARISONS OF MEASURED CARBON CAPACITY FOR TCE AND PREDICTED CAPACITY FROM THEORY OF STATISTICAL MOMENTS (TSM)[a]

INFLUENT TCE CONCENTRATION (mg/m^3)	MEASURED ADSORPTION CAPACITY (mg TCE/g carbon)	ESTIMATED ADSORPTION CAPACITY BY TSM (mg TCE/g carbon)	PERCENT DEVIATION
303	276	286	+3.68
602	329	334	+1.62
987	398	399	+0.14
1331	450	434	-3.50

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[a] Relative humidity < 5 percent

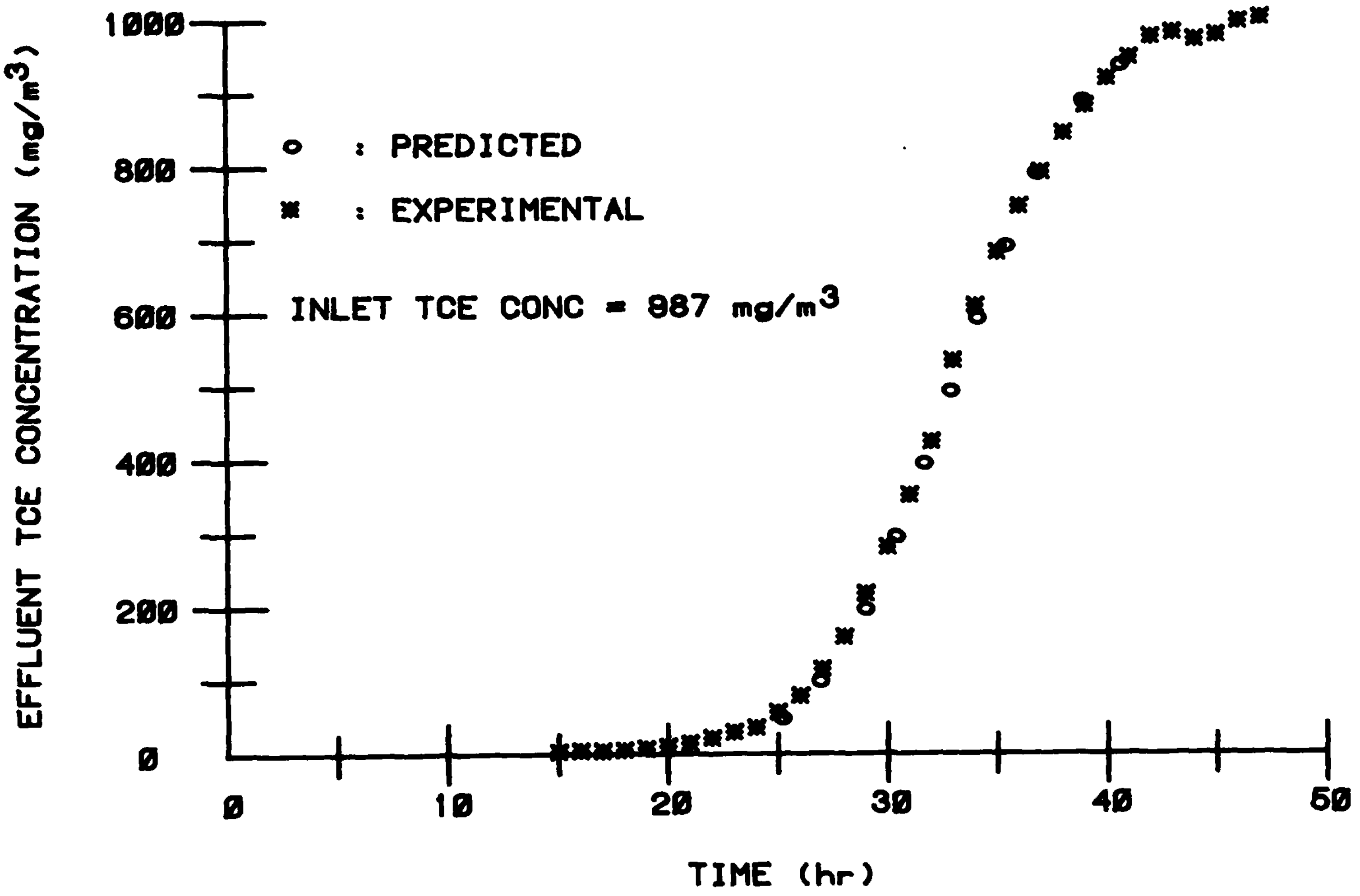

Figure 6. Experimental TCE Breakthrough Curve Compared to Breakthrough Predicted by the Theory of Statistical Moments (Inlet TCE Concentration of 987 mg/m^3).

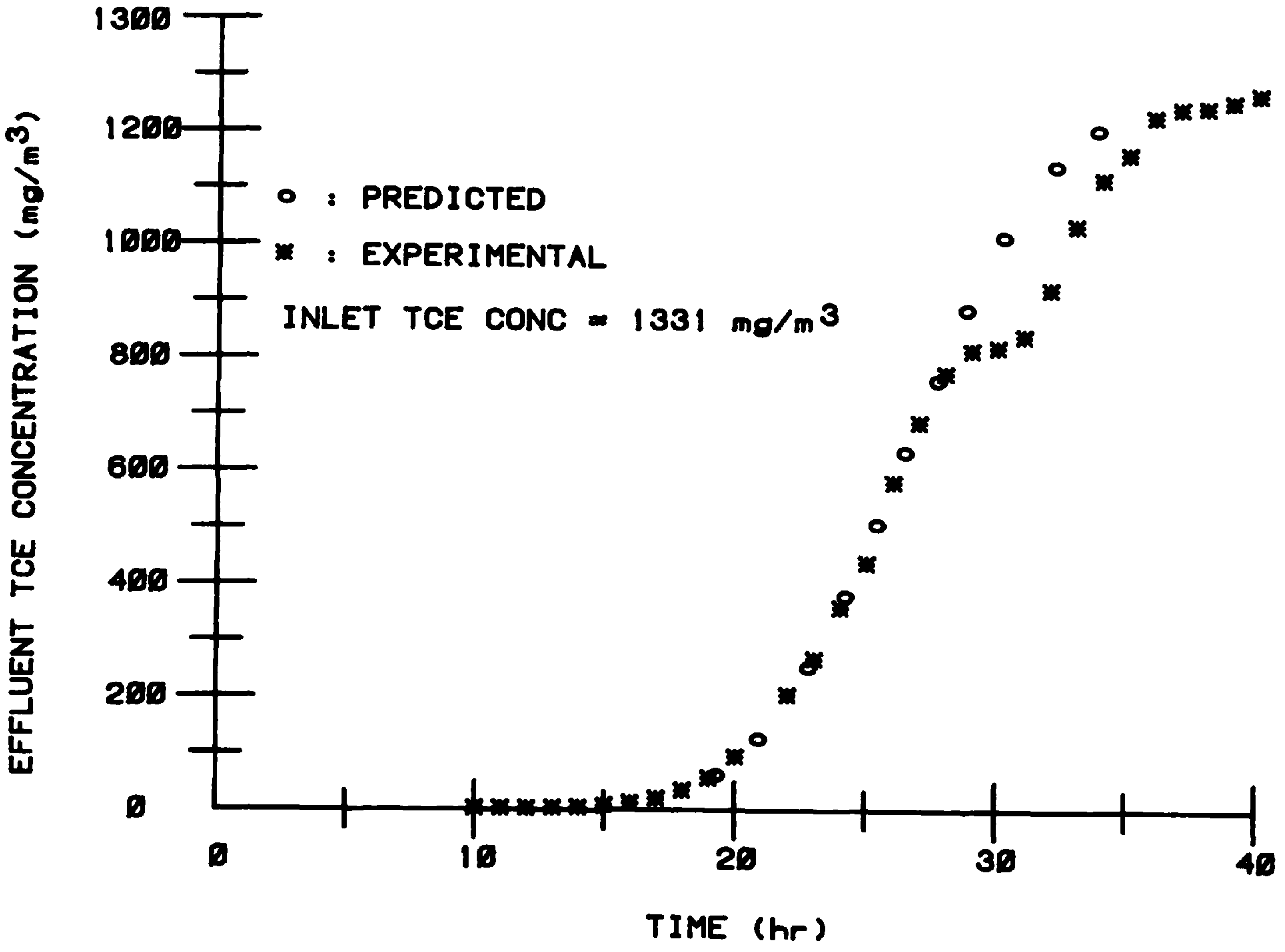

Figure 7. Experimental TCE Breakthrough Curve Compared to Breakthrough Predicted by the Theory of Statistical Moments (Inlet TCE Concentration of 1331 mg/m^3).

Grubner and Burgess (References 6,7) argue that the relative degree of dispersion of a breakthrough curve (resulting from the normal distribution of velocities of adsorbate molecules through an adsorption bed) should be independent of the adsorbate concentration. The authors define the degree of dispersion, or standard deviation, of the curve as the following:

$$\sigma = T_{50} - T_{16} \tag{18}$$

where σ is the standard deviation of the curve, T_{50} is time to 50=percent influent breakthrough, and T_{16} is time to 16-percent influent breakthrough. The value of σ can be estimated from the time to any two levels of contaminant breakthrough (not only T_{50} and T_{16}), although the calculation is more complicated. Basically, the calculation requires obtaining the change in the normal probablity distribution (from statistical tables) which corresponds to the differences in the two times selected, then dividing that time difference by the tabular statistical value. An example will help illustrate:

$$1.28\sigma = T_{50} - T_{10} \tag{19}$$

Since a change from 0.5 to 0.1 corresponds to a change in σ of 1.28 (based on the normal probability distribution), it is necessary to divide the time difference (T_{50}-T_{10}) by 1.28. (See Grubner and Burgess, Reference 6, for more detail.) Now, the relative degree of dispersion (or relative standard deviation) is defined as

$$\sigma_r = \sigma/T_{50} \tag{20}$$

As stated, σ_r is expected to be independent of adsorbate concentration under constant adsorption conditions (Reference 11). The values of σ_r for adsorption at low humidity are given in Table 2. The range of σr values is from 0.100 to 0.232 with a coefficient of variation of 35 percent. The coefficient of variation is significantly reduced if the trial for the lowest TCE concentration is not included (Table 2). Experimental error may have invalidated that trial since a number of analyses with this data reveal that it is a consistant anomaly. In addition, extrapolation of the concepts being analyzed to such a low adsorbate concentration may not be reliable. Additional research at the lower range of influent adsorbate concentrations is

TABLE 2. MEASURES OF DISPERSION OF TCE BREAKTHROUGH CURVES AT AIR RELATIVE HUMIDITY < 5 PERCENT

CONCENTRATION (mg/m^3)	σ	T_{50}	σ_r
53	65.1	281.0	0.232
303	8.6	76.5	0.112
602	4.5	45.1	0.100
895	3.8	35.9	0.107
987	4.7	32.8	0.143
1331	4.4	26.4	0.167

	with 53 mg/m^3 TCE conc.	without 53 mg/m^3 TCE conc.
Ave σ_r	0.1435	0.126
Standard Deviation	0.0502	0.0283
Coeff. of Variation	35%	22%

needed to further test the theory. Based on the present data set, it is apparent that some variations in σ_r ocurred but that the values are within a fairly small range. Figure 8 graphically demonstrates the difference between predictive breakthrough curves when an actual value for σ_r is used and when the mean value is used. The case chosen for this comparison represents the greatest deviation between the mean and actual value of σ_r. The degree of agreement indicates the potential usefulness and validity of assuming that σ_r is independent of adsorbate concentration. If the assumption is valid, the potential exists for predicting an entire breakthrough curve by knowing only a single point on the curve and the value of σ_r obtained at another adsorbate concentration. Additionally, if the capacity of the adsorbent can be calculated for a given influent adsorbate concentration (e.g., by Equation 16), then the breakthrough curve can be estimated with no laboratory data by assuming a value for σ_r. Potentially, the time to a critical level of contaminant breakthrough can be estimated with few, if any, effluent samples by combining the theories reviewed up to this point and determing the value for σ_r.

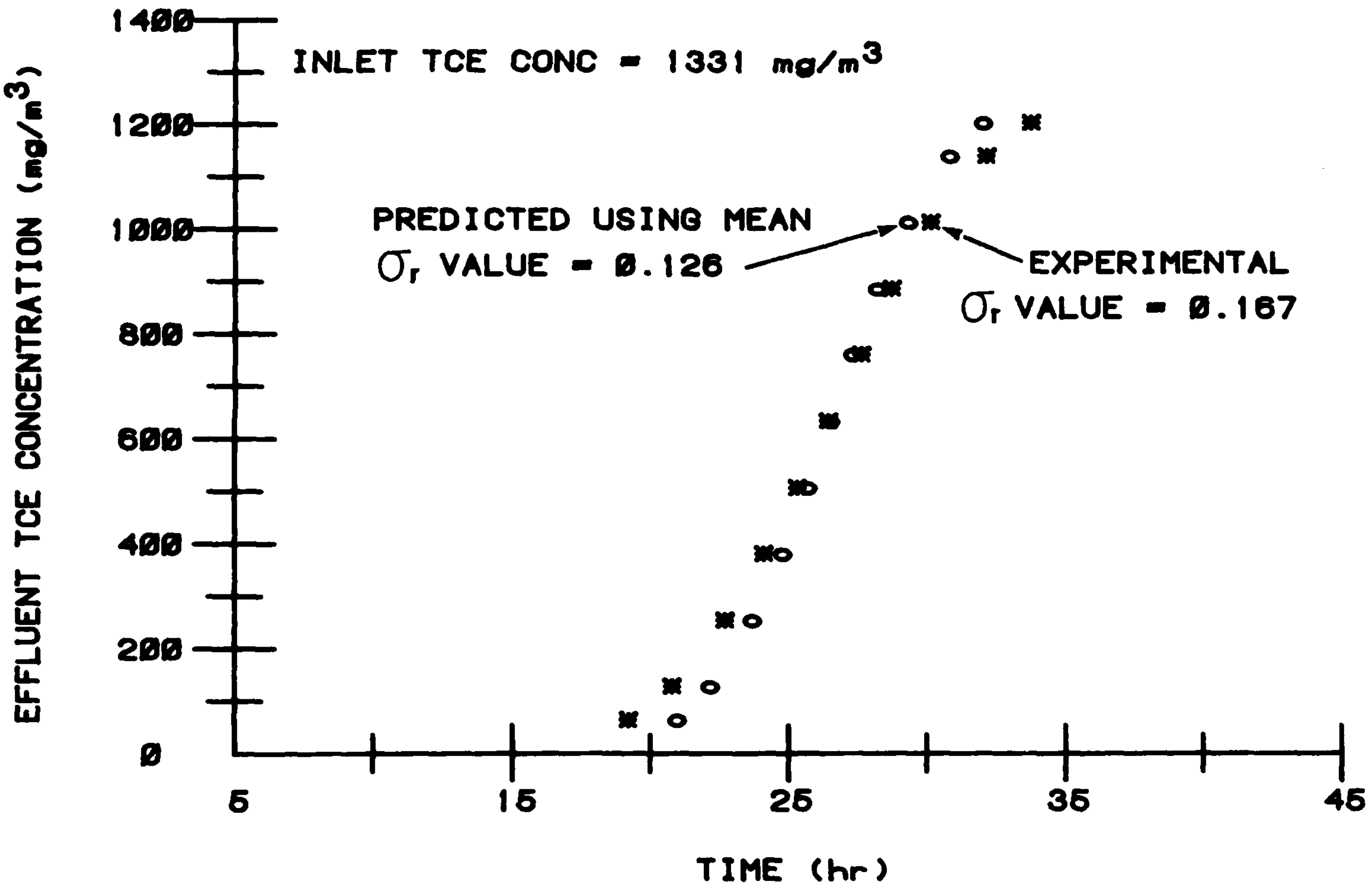

Figure 8. Comparison of TCE Breakthrough Curves Based on Experimental and Predicted Values of σ_r.

C. PREDICTIONS UNDER VARIABLE CONDITIONS OF ADSORPTION

The theory that a contaminant breakthrough curve follows the pattern of the cumulative normal probablility curve and that a standardized measure of dispersion is independent of adsorbate concentration has been reviewed (and illustrated with TCE adsorption data) in previous sections. However, for predictive purposes, this is of limited practical use since it applies only to situations for which certain important factors (such as adsorbent particle size, gas flow velocity, adsorbate diffusivity, etc.) are constant. Ideally, the time to a critical level of contaminant breakthrough should be predictable for different adsorbates and adsorbents under any of the conditions that would be encountered in an actual process operation. Grubner and Burgess (Reference 7) present a series of equations developed to make that prediction. Basically, their predictive model is based on a combination of the theory of statistical moments and a generalized Lewis Isotherm Equation. Full development of the equations is beyond the scope of this report, although the equations and a definition of terms are presented in Appendix A. For additional information the reader is referred to the original work. In short, the model considers physical factors affecting adsorbate movement within the adsorbent column (such as dimensions of the column, dimensions of an average adsorbent particle, adsorbent porosity, adsorbate diffusivity, carrier gas velocity, etc.), in addition to critical aspects of static adsorption including physico-chemical qualities of the adsorbent and adsorbate. Predicted and actual times to 50 percent and 10 percent TCE breakthrough are listed in Table 3 (predicted values were calculated as outlined in Appendix A). The predicted values for T_{50} are within 7 percent of the actual values for TCE concentrations between 300 and 1350 mg/m^3. The deviation between the actual and predicted value for the 53 mg/m^3 trial was 49 percent. The reason for the large discrepancy may be due to either of two factors: the generalized Lewis Isotherm did not extend to this low an influent concentration so the isotherm was extrapolated beyond available data or the reliability of trial is questionable, as discussed previously. Overall, the agreement of the T_{50} prediction to the TCE adsorption data suggest the Grubner and Burgess model may be quite accurate and useful for actual carbon adsorption operations.

TABLE 3. ACTUAL AND PREDICTED TIMES TO 10 AND 50 PERCENT INFLUENT TCE BREAKTHROUGH (BASED ON EQUATIONS OF GRUBNER AND BURGESS (REFERENCE 8))

INFLUENT TCE CONCENTRATION (mg/m^3)	TIME TO 50% BREAKTHROUGH (T_{50})			TIME TO 10% BREAKTHROUGH (T_{10})		
	Actual	Predicted	% Deviation	Actual	Predicted	% Deviation
53	281.0	143.4	-49.0	197.7	99.7	-49.6
303	76.5	71.2	-6.9	65.5	49.5	-24.4
602	45.1	45.6	+1.1	39.3	31.7	-19.3
895	35.9	34.6	-3.6	31.0	24.1	-22.3
987	32.8	32.2	-1.8	26.8	22.4	-16.4
1331	26.4	25.9	-1.9	20.8	18.0	-13.5

Agreement between predicted and actual results was not as close for T_{10} as they were for T_{50}. The dispersion of the actual breakthrough curve was greater than predicted by the model in every case (as shown by the greater actual time values compared to those predicted). The consistent underestimation of dispersion may have resulted from wall effects caused by the small adsorption column used in these experiments (2.54 cm diameter). Additional research using larger diameter columns would be necessary to confirm the above explanation.

SECTION IV

EFFECT OF WATER VAPOR ON ADSORPTION OF TCE

The quantity of TCE adsorbed per gram of activated carbon at each influent TCE concentration and level of relative humidity tested is presented in Figure 9. (Actual values obtained during the study are listed in Appendix B.) Excluding the trials with 25 percent relative humidity at 1000 and 1300 mg/m^3 influent TCE concentrations, increasing concentrations of water vapor had increasing deleterious effects on the carbon's capacity to adsorb TCE. Although numerical differences in adsorption capacity between high and low humidities are generally less at low TCE influent concentrations than for higher concentrations, the relative differences are greater for the former. The example presented in Table 4 will help to illustrate this. The decrease in adsorption capacity due to humidity was 0.259 and 0.313 grams TCE/gram carbon at the lowest and highest TCE influent concentrations, respectively; however, 28 percent of the original adsorption capacity was retained at the highest influent concentration, while only 9 percent remained at the lowest concentration.

TABLE 4. COMPARISON OF CARBON CAPACITY FOR TCE AT TWO HUMIDITY LEVELS

TCE INFLUENT CONC. (mg/m^3)	RELATIVE HUMIDITY (Percent) <5 AMT ADSORBED (g TCE/g carbon)	RELATIVE HUMIDITY (Percent) 85 AMT ADSORBED (g TCE/g carbon)	DECREASE DUE TO EFFECT OF HUMIDITY (g TCE/g carbon)	ADSORPTION CAPACITY RETAINED (Percent)
300	0.286	0.027	0.259	9
1300	0.434	0.121	0.313	28

Loss of the carbon's adsorptive capacity due to the presence of water vapor was calculated for each humidity trial within an influent TCE concentration. The amount adsorbed relative to the low humidity level appears in Table 5. In all cases, relative adsorptive capacities decreased faster with increasing relative humidity at low TCE concentrations than at higher TCE concentrations. Thus, the interaction between relative humidity and TCE concentration must be considered when designing a gaseous-phase carbon adsorption process. This can be exemplified by an air stripping/gaseous-phase carbon adsorption process. In some cases it might be beneficial to reduce the air-to-water ratio of the stripping operation (although that would reduce

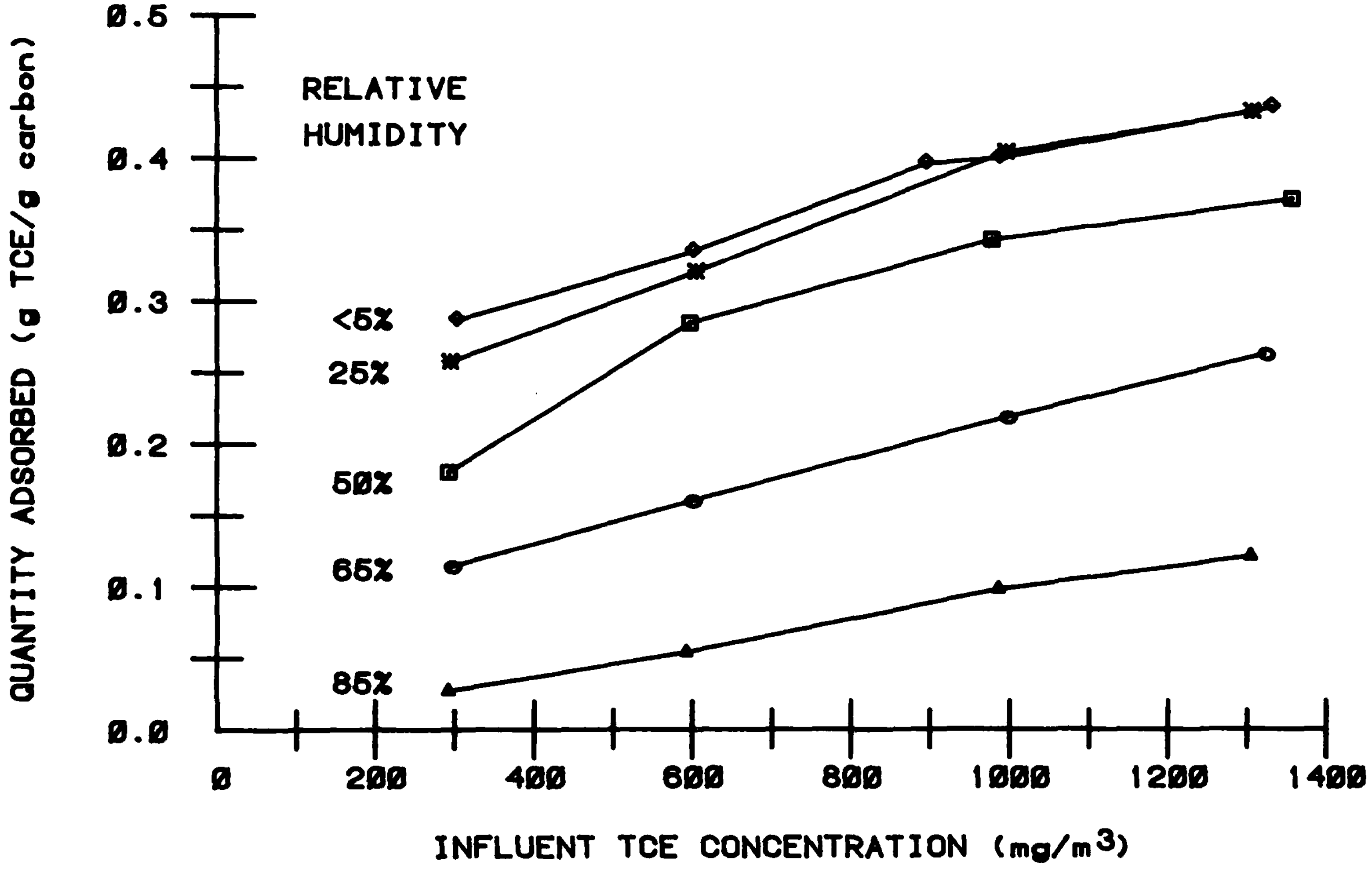

Figure 9. Measured Adsorption Capacities of Carbon at Various Influent TCE Concentrations and Levels of Relative Humidity.

TABLE 5. TCE ADSORBED AT SEVERAL HUMIDITY LEVELS STANDARDIZED TO THAT ADSORBED AT RELATIVE HUMIDITY <5 PERCENT

TCE INFLUENT CONC (mg/m^3)	RELATIVE HUMIDITY (%) <5	25	50	65	85
	RELATIVE AMOUNT OF TCE 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

stripping efficiency) to obtain a higher VOC concentration in the air, and obtain a higher VOC concentration in the air, and thereby reduce the negative impact of water vapor during the gaseous-phase adsorption portion of the operation. Similarly, the effect of humidity and the interaction between humidity level and adsorbate concentration should be accounted for during the design and operation of any gaseous phase adsorption process.

The shape of a contaminant breakthrough curve, in addition to the overall carbon adsorption capacity, is a factor which can influence the length of time a batch of activated carbon can be utilized. As discussed previously in this report, dispersion associated with a breakthrough curve can be described by the relative standard deviation (σ_r) of the curve. Greater dispersion of a breakthrough curve results in quicker breakthrough of a critical level of contaminant, if the critical level is less than 50 percent of the influent concentration of contaminant. The mean relative standard deviations for the low humidity trials was 0.126 with a range of 0.100 to 0.167. The mean of that same value for all trials above the minimum humidity was 0.210 with a range of 0.156 to 0.298. (Appendix C contains the values of σ_r for individual trials). Thus, water vapor not only reduced the adsorption capacity of the carbon in these experiments but also caused the breakthrough curve to be more dispersed. Table 6 shows the time to breakthrough for 10 percent of the influent TCE concentration standardized to the breakthrough time for the lowest humidity level (i.e., the humidity level at which water vapor is assumed to have no effect). If water vapor had no effect on the dispersion of the breakthrough curve, the values in Tables 5 and 6 would be identical. The lower values in Table 6 reflect increased dispersion due to humidity that could decrease effective carbon life in a process if a single carbon column was used. However, if two or more columns were employed in series, the entire adsorption capacity of the first column could be exhausted before being taken out of service; then the degree of dispersion of the breakthrough curve would be of no practical significance.

TABLE 6. TIME TO BREAKTHROUGH FOR 10 PERCENT OF THE INFLUENT TCE CONCENTRATION FOR SEVERAL HUMIDITIES STANDARDIZED TO THAT VALUE AT RELATIVE HUMIDITY <5 PERCENT

	RELATIVE HUMIDITY (%)				
	<5	25	50	65	85
TCE INFLUENT Conc (mg/m^3)	RELATIVE AMOUNT OF TCE 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

Data from each humidity level were fit to the Dubinin-Polanyi Isotherm equation. As shown in Figure 10, results at all humidity levels fit the model equally well (the correlation coefficient was greater than 0.92 for all cases). The changing slopes from one humidity level to another clearly

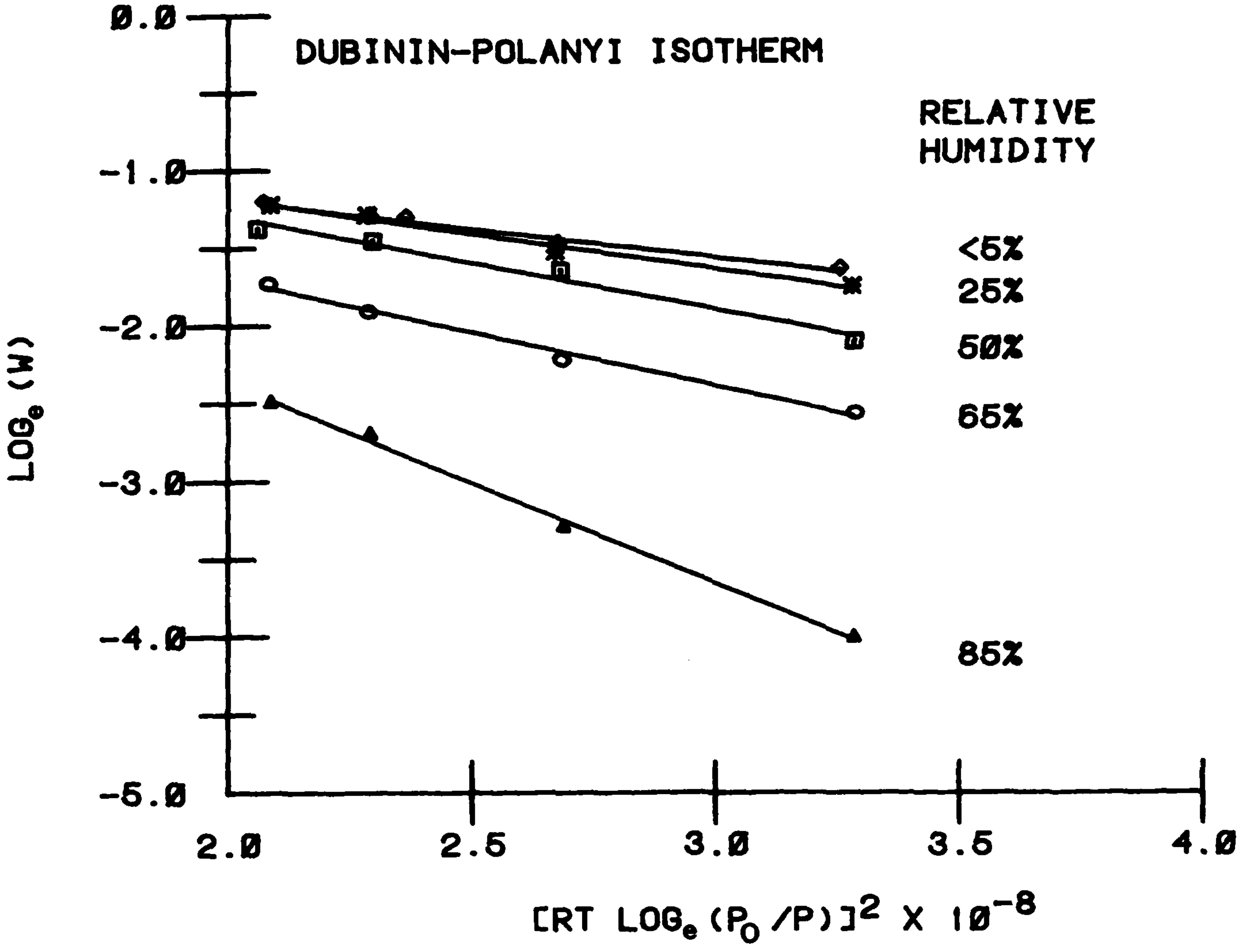

Figure 10. TCE Adsorption Results at Five Levels of Relative Humidity Fit to the Dubinin-Polanyi Isotherm Equation.

demonstrates the interaction between humidity level and adsorbate concentration. As shown previously, humidity exerted a greater effect at low TCE concentrations than at high concentrations.

Since the Dubinin-Polanyi isotherm equation is followed so closely at all humidities it can be assumed that water vapor is exerting a predictable effect on the carbon's capacity to adsorb TCE. Such predictability suggests that the effect of water vapor on gaseous-phase adsorption on a porous adsorbent may be accurately modeled. A predictive model to treat the effect of humidity on adsorption would be an important contribution since humidity at some level will be present for any application of gaseous-phase adsorption and the effect of humidity on the process can be very significant, as illustrated in this study.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

1. Models exist which predicted results of trichloroethylene (TCE) adsorption on activated carbon from air at low levels of relative humidity with fair accuracy. The important models were based on the Dubinin-Polanyi Isotherm equation and the Theory of Statistical Moments. Because the body of theory is based on theoretically sound assumptions, the models should be useful for adsorption of other adsorbates under varying conditions. The following important factors were predicted during this research effort:

   a. Adsorption capacity of activated carbon.
   b. Shape of the contaminant breakthrough curve.
   c. Time to breakthrough of a given contaminant concentration.

2. Water vapor exerted a deleterious effect on activated carbon's adsorptive capacity. Increasing levels of relative humidity had increasing deleterious impacts. The effect of humidity was greater at low TCE concentrations than at high TCE concentrations. In general, water vapor also caused a greater degree of dispersion in the contaminant breakthrough curve which reduces the efficiency of the carbon more than that suggested by the reduction caused to the carbon's adsorptive capacity alone.

3. The Dubinin-Polanyi equation fit the data obtained at all levels of relative humidity equally well, indicating the effect of water vapor on TCE adsorption, and possibly other organic contaminants, could be accurately modeled.

B. RECOMMENDATIONS

This research demonstrated the accuracy of several models for predicting important aspects of gaseous phase carbon adsorption at low relative humidity and the predictable effect water vapor has on the effectiveness of the adsorption process. Both of these were demonstrated for a single adsorbate, TCE, under constant experimental conditions. It is recommended that these findings be applied to the design and operation of full-scale adsorption processes. To extend the usefulness of the results, three areas of additional research are recommended. First, adsorption models need to be tested on a variety of adsorbates in different classes of organic compounds under varying conditions of adsorption (e.g., different carbons, different air flow rates and different temperatures). The object of the testing would be to determine how robust existing models are. Existing adsorption studies which have been published could be used for this analysis. Second, a model should be developed to predict the effect of humidity on gaseous-phase carbon adsorption for different adsorbates under various levels of relative humidity. Results of this research indicate the effect of water vapor on adsorption should be amenable to accurate modeling. Third, the interaction between adsorbates in a multiadsorbate system (i.e., competitive adsorption) needs to be investigated. The approach to this problem could be similar to that taken for the second research recommendation.

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APPENDIX A

GRUBNER AND BURGESS EQUATIONS FOR CALCULATING TIME TO THE CRITICAL LEVEL OF CONTAMINANT BREAKTHROUGH

APPENDIX A

GRUBNER AND BURGESS EQUATIONS FOR CALCULATING TIME TO THE CRITICAL LEVEL OF CONTAMINANT BREAKTHROUGH (REFERENCE 7)[a]

$$t_c = (24.1 \times 10^9)(G \rho_L B' y) / (60 M C_i w)$$

where

t_c = time to a critical level of contaminant breakthrough

G = weight of adsorbent (37.5 grams)

ρ_L = adsorbate's liquid density (1.466 grams/mL)

M = molecular weight of adsorbate (139.39 grams/mole)

C_i = influent adsorbate concentration in ppm

C_o = adsorbate concentration leaving the adsorbent bed at breakthrough in ppm

w = carrier gas flow rate (128.3 mL/s)

$B' = 1 + 0.365 X_c (R/2)(W/V\varepsilon_e D_i)^{0.5}$

where

X_c = argument of normal probability distribution curve for the ratio C_o/C_i ($0 = T_{50}$; $-1.28 = T_{10}$)

R = average radius of adsorbent particle (0.19 cm)

V = Volume of adsorbent bed (68.4 cm^3)

ε_e = external porosity of adsorbent (0.5)

D_i = diffusion coefficient of adsorbate (0.0796 cm^2/s)

$y = 0.749 - 8.307x + 14.826 x^2$ (polynomial equation representing a general Lewis Isotherm) where $X = \rho_L M \log_e(P_s/P)$ and

P_s = adsorbate's saturated vapor pressure (60 mm Hg)

P = adsorbate's equilibrium vapor pressure in mm Hg

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[a] Values used to calculate times given in Table 3 are in parentheses

APPENDIX B

TCE ADSORBED AT VARIOUS INFLUENT CONCENTRATIONS AND LEVELS OF RELATIVE HUMIDITY.

APPENDIX B

TCE ADSORBED AT VARIOUS INFLUENT CONCENTRATIONS AND LEVELS OF RELATIVE HUMIDITY

RELATIVE HUMIDITY PERCENT	TCE INFLUENT CONC (mg/m^3)	TCE ADSORBED (g TCE/g CARBON)
<5	303	0.286
25	295	0.257
50	293	0.180
65	295	0.114
85	293	0.027
<5	602	0.334
25	605	0.320
50	597	0.284
65	599	0.160
85	593	0.054
<5	895	0.395
<5	987	0.399
25	995	0.403
50	978	0.342
65	996	0.218
85	986	0.098
<5	1331	0.434
25	1306	0.431
50	1356	0.370
65	1322	0.262
85	1304	0.121

APPENDIX C

RELATIVE STANDARD DEVIATION (σ_r) VALUES FOR TCE BREAKTHROUGH CURVES (ALL EXPERIMENTAL TRIALS)

RELATIVE HUMIDITY (PERCENT)	TCE INFLUENT CONC (mg/m^3)	RELATIVE STANDARD DEVIATION (σ_r)
5	303	0.1123
	602	0.1000
	895	0.1070
	987	0.1430
	1331	0.1667
25	295	0.2984
	605	0.1958
	995	0.1924
	1306	0.2546
50	293	0.1847
	597	0.1978
	978	0.1937
	1356	0.1697
65	295	0.2580
	599	0.2396
	996	0.2135
	1322	0.2720
85	293	0.1797
	593	0.1560
	986	0.1642
	1340	0.1933

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