

# Experimental and Modeled Results Describing the Adsorption of Acetone and Benzene onto Activated Carbon Fibers

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*Activated carbon fibers (ACF) were used to adsorb ppmv concentrations of volatile organic compounds (VOCs) from laboratory generated gas streams. VOCs considered were benzene and acetone because the VOC are commonly found in indoor air and have potential to increase health risks to humans. ACF were used as the adsorbent because they typically exhibit higher adsorption capacities and faster adsorption kinetics than commercially available granular activated carbons (GAC) and show potential as an adsorbent to effectively remove VOCs from indoor air.*

*Adsorption models by Dubinin and coworkers (Dubinin, 1975), based on the theory of volume filling of micropores, and an empirical model by Freundlich were used to fit the measured adsorption isotherms. Agreement between the modeled and experimental results for acetone and benzene using the Dubinin-Radushkevich equation generally improved with increasing BET surface area and produced reasonable fits of the adsorption isotherms for both acetone and benzene. The Freundlich equation produced values for correlation coefficients (R) between modeled and experimental data from 0.980 to 0.997, indicating the validity of using the Freundlich equation to model the adsorption isotherms over the concentration range of interest.*

*These results indicate that ACF show potential as an adsorbent for removing low concentrations of VOCs from indoor air.*

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## INTRODUCTION

In this study, we have experimentally and numerically characterized the equilibrium adsorption capacities of activated carbon fibers (ACF) for gas streams containing acetone or benzene in air. For many adsorption applications, ACF provide greater ease of use than granular activated carbon (GAC) because ACF are not granules but can be manufactured in the form of a cloth. Moreover, ACF typically exhibit higher adsorption capacities and faster adsorption kinetics than GAC [1]. ACF have additional advantages: the surfaces of ACF can be regenerated in-situ with electrical resistance heating, their surfaces can be chemically tailored to allow preferential adsorption of certain compounds, and the pore sizes of ACF typically lie over a narrow range in the micropore region (pore width < 2 nm) [1]. The narrow pore size allows use of ACF as a molecular sieve in some applications.

Adsorption isotherms were measured and modeled for ACF with three different BET surface areas using two individual adsorbates: acetone and benzene at concentrations between 10 ppmv and 1000 ppmv in air. Adsorption isotherms are important to describe how adsorbates will interact with ACF and so are critical in optimizing the use of ACF as an adsorbent. Acetone and benzene were selected as the adsorbates because they commonly exist in indoor air and have potential to cause health risks for humans [2]. Additionally, benzene is commonly used as a reference or test adsorbate for microporous carbon adsorbates.

An adsorption isotherm is a standard method for characterizing the adsorption capacity of adsorbents and is constructed for equilibrium adsorption of individual compounds over a range of concentrations. Specifically, adsorption iso-

therms describe the adsorbate mass adsorbed at equilibrium per unit mass of adsorbent as a function of adsorbate concentration in the bulk gas phase.

The objective of this study was to evaluate ACF as an adsorbent for removal of VOCs commonly found in indoor air environments. Specifically, the adsorption isotherms for ACF were measured with individual adsorbates (either benzene or acetone) at concentrations ranging from 10 ppmv to 1000 ppmv. The isotherms were then fitted to existing adsorption isotherm models. This investigation is an important step in developing a better understanding of ACF as an air quality control technology to remove volatile organic compounds (VOCs) from indoor air. Removing the low concentrations of VOCs that exist in indoor air is of interest because of the carcinogenic or mutagenic nature of many of these gases and the long exposure times that humans have to indoor air [2].

## EXPERIMENTAL

### Activated Carbon Fibers

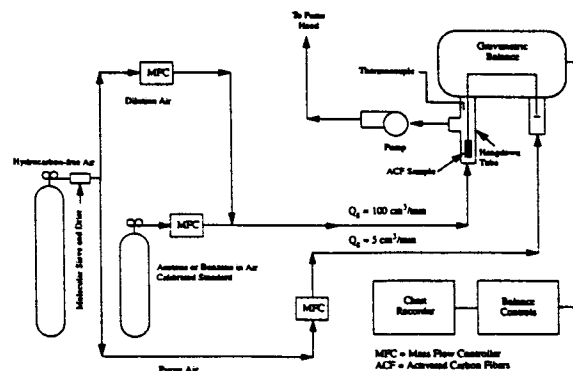
The ACF evaluated in this research were obtained from American Kynol, Inc. (New York, New York) and are produced from a phenolic based synthetic fiber, Kynol. Cloth is woven from the Kynol fibers, and the resulting fabric is carbonized and activated. Depending on the activation time, select Brunauer, Emmett, and Teller (BET) surface areas can be produced [3, 4]. BET surface areas and pore volumes of the ACF samples used in this study were measured previously [5] and are summarized in Table 1. BET surface areas were measured with nitrogen at liquid nitrogen temperature ( $\approx 77$  K). Total pore volumes were determined by measuring the mass of acetone and benzene that adsorbed onto the ACF at  $25^\circ\text{C} \pm 1^\circ\text{C}$  and a total pressure of 1 atm for saturated gas phase concentrations of the adsorbates. The masses adsorbed were then converted to a liquid volume to obtain the total pore volumes.

**Table 1 Measured Properties of ACF Samples [5]**

Adsorbent	BET Surface Area [m <sup>2</sup> /g]	Pore Volume Using Acetone [cm <sup>3</sup> /g]	Pore Volume Using Benzene [cm <sup>3</sup> /g]
ACF-15	900	0.326	0.345
ACF-20	1610	0.613	0.653
ACF-25	2420	0.859	0.849

### Experimental Apparatus to Measure Adsorption Isotherms

The experimental procedure has been discussed previously [5, 6], but a brief summary will be provided here for clarity. The experimental apparatus (Figure 1) used to measure adsorption isotherms for VOC concentrations in the ppmv range consists of a gas generation system and a gravimetric balance (Cahn Model C-2000). The gravimetric balance is used to detect the mass of an ACF sample that is exposed to a gas stream containing a known concentration of a select organic compound in a carrier gas of hydrocarbon-free air (Matheson Gas). The gravimetric balance is able to sense changes in mass as small as 1  $\mu\text{g}$ . The compressed hydrocarbon-free air has a certified maximum hydrocarbon concentration of less than 0.1 ppmv and a water vapor concentration of less than 3 ppmv. The oxygen content is between 19.5 and 23.5 percent by volume. Additionally, the hydrocarbon free air is passed through a gas purifier and drier (Drierite Model No. L68GP) which uses silica gel to remove water vapor to a terminal dryness of 0.005 mg/L or a dew point temperature of  $-37.7^\circ\text{C}$ . A 5 Å



**FIGURE 1. Apparatus for adsorption measurements of VOCs in the 10 to 1000 ppmv range.**

molecular sieve is also part of the purifier to remove dilute concentrations of hydrocarbons. The adsorption isotherms were measured at room temperature ( $25^\circ\text{C} \pm 1^\circ\text{C}$ ) and a total pressure of 1 atm.

Manufacturer certified compressed gas cylinders (Matheson Gas) were used to generate gas streams containing the organic adsorbates in hydrocarbon free air. Mass flow controllers (Ty-lan Model FC-280) regulated the amount of VOC and dilution air entering the system. Once the gas stream was generated, it was passed through the gravimetric balance containing the ACF sample. The ACF sample adsorbed VOCs and thus gained mass until equilibrium was achieved. Adsorption equilibrium was assumed to occur when the change in mass of the sample approached zero with respect to time (no noticeable change in mass over approximately a 4 hour period). The gain in sample mass was recorded, and the mass ratio of adsorbed material to ACF was determined. For contaminant concentrations in the 10 to 50 ppmv range, the time required to reach equilibrium was typically between two to six days for ACF masses of 10 to 30 mg and total gas flows of  $100\text{ cm}^3/\text{min}$ . The experimental system also provides for thermal regeneration of the ACF prior to the adsorption measurement to desorb any volatile materials that may have adsorbed onto the ACF sample during its manufacture, storage, and handling.

## EQUILIBRIUM ADSORPTION MODELING

The Freundlich [7] and Dubinin-Radushkevich (DR) [8] equations were used to model the experimental acetone and benzene adsorption data. The Freundlich equation is an empirical expression often used to describe adsorption isotherm data. The DR equation is a theoretically based equation which assumes that the adsorbent is composed of energetically homogeneous adsorption sites.

### The Freundlich Equation

The Freundlich equation [7] is an empirical expression used to describe adsorption isotherms where there is a linear response for adsorption capacity as a function of adsorbate concentration when adsorption data are plotted on a log-log scale. The valid concentration range for the Freundlich equation varies according to the adsorbate-adsorbent combination and the range of experimental data points. The Freundlich equation is represented as:

$$\frac{x}{m} = kC^{1/n} \quad (1)$$

where  $x$  is the mass of adsorbate adsorbed;  $m$  is the mass of adsorbent;  $k$  and  $n$  are empirical constants; and  $C$  is the concentration of the adsorbate in the bulk gas phase. The constants

$k$  and  $n$  in equation (1) are determined by measuring  $x/m$  as a function of  $C$ , and plotting  $\log(C)$  on the abscissa and  $\log(x/m)$  on the ordinate, and finding the slope (equal to  $1/n$ ) and ordinate intercept (equal to  $\log k$ ) of the best fit line through the experimental points. The Freundlich equation is especially useful where the actual identity of the adsorbate is not known. The disadvantages of using the Freundlich plot is that it is only useful for limited adsorbate concentration ranges and it has limited predictive ability with regard to adsorption isotherms for similar adsorbates. Ideally, a new Freundlich plot is produced for each adsorbent-adsorbate combination.

### The Dubinin-Radushkevich Equation

Dubinin and coworkers [8, 9] have developed several equations that describe equilibrium adsorption of gaseous adsorbates onto different types of microporous carbon adsorbents with energetically homogeneous adsorption sites. These equations are based on the concept of volume filling of the micropores, which describes adsorption as a pore filling effect, rather than a layer by layer adsorption effect. One of these equations is the DR equation, which has successfully described the adsorption of many individual compounds onto carbon adsorbents [8]. The equation generally works well with single component vapors and with gas mixtures of one strongly adsorbed component and other weakly adsorbed components. The DR equation is presented below:

$$W = W_0 \exp(-m x_0^2 A^2) \quad (2)$$

$W$  = volume adsorbate per unit mass of adsorbent [ $\text{cm}^3/\text{g}$ ]  
 $W_0$  = limiting pore volume of adsorption (volume of micropores) per unit mass of adsorbent [ $\text{cm}^3/\text{g}$ ]  
 $A = RT \ln(p_s/p)$ , differential molar work [ $\text{kJ}/\text{mol}$ ]  
 $R$  = ideal gas constant,  $8.314 \text{ kJ}/\text{mol}\cdot\text{K}$   
 $T$  = absolute temperature [ $\text{K}$ ]  
 $p$  = partial pressure of adsorbate [ $\text{torr}$ ]  
 $p_s$  = saturated partial pressure of adsorbate [ $\text{torr}$ ]  
 $m = (1/\beta k)^2 [\text{mol}^2/\text{kJ}^2\cdot\text{nm}^2]$   
 $\beta$  = affinity coefficient of the adsorbate  
 $k = 12.0 \pm 1.4 \text{ kJ}\cdot\text{nm}/\text{mol}$ , a structure factor  
 $x_0$  = slit-pore half-width [ $\text{nm}$ ]

$W_0$  and  $x_0$  can be determined by plotting the experimental adsorption isotherm data in the form of the characteristic adsorption equation:

$$\ln W = \ln W_0 - \left( \frac{1}{\beta \frac{k}{x_0}} \right)^2 A^2 \quad (3)$$

By plotting  $\ln(W)$  on the ordinate and  $A^2$  on the abscissa, and applying a linear regression to the experimental data,  $W_0$  and  $x_0$  can be determined from the intercept of the ordinate and the slope of the linear regression line, respectively.

The attraction forces of the adsorbent to the adsorbate differ for different adsorbates. These differences can be accounted for using the affinity coefficient,  $\beta$ , which is the ratio of the adsorption potentials of the adsorbate of interest to a reference adsorbate. Therefore, if the adsorbate of interest is different from the reference adsorbate, the difference is accounted for in (equation 2) by setting  $\beta$  to a value other than unity. A common method to approximate  $\beta$  is with the ratio of the parachor of the compound of interest to the parachor of the reference substance [8]. A more rigorous approach, which is derived from the theory of dispersion interaction, is to approximate  $\beta$  using the polarizability of compounds [10]. An appropriate reference vapor must be chosen for the DR equation to give good results [11]. Benzene was used as the reference

vapor in this study, so  $\beta=1$  for benzene. Benzene was also used as the reference vapor for acetone, giving a  $\beta$  value of 0.78 for acetone adsorption onto ACF [12].

Once the DR equation has been used to describe the adsorption isotherm of a reference adsorbate, the equation can be used in a predictive capacity. Knowing the important parameters of an adsorbent (micropore volume and slit-pore half-width) and those of the adsorbate (actual vapor pressure, saturation vapor pressure and affinity coefficient), the DR equation can predict adsorption isotherms for adsorption systems similar to the reference system. This method of using the DR equation in a predictive capacity can be useful when adsorption isotherms do not exist for adsorbates of interest, but do exist for some reference compound, such as benzene.

## RESULTS AND DISCUSSION

The experimental adsorption isotherm data for acetone and benzene were fitted with the Freundlich and DR equations. Duplicate measurements were taken for each adsorbate concentration and ACF sample. Agreement between the duplicate measurements, was generally within 10 percent (Figures 2 and 3).

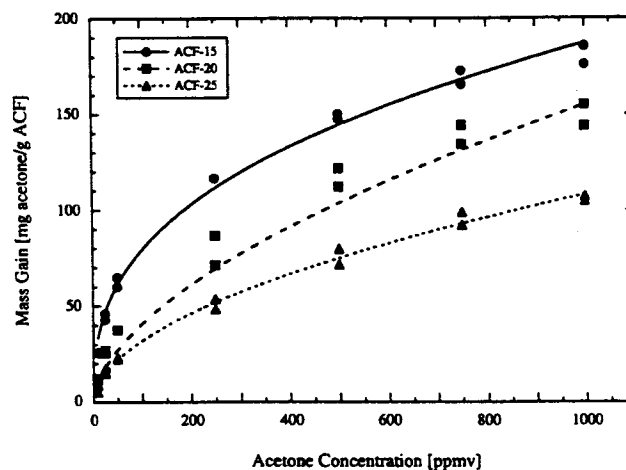


FIGURE 2. Experimental isotherms for acetone adsorption onto ACF. Lines through the data points represent fits with the Freundlich equation.

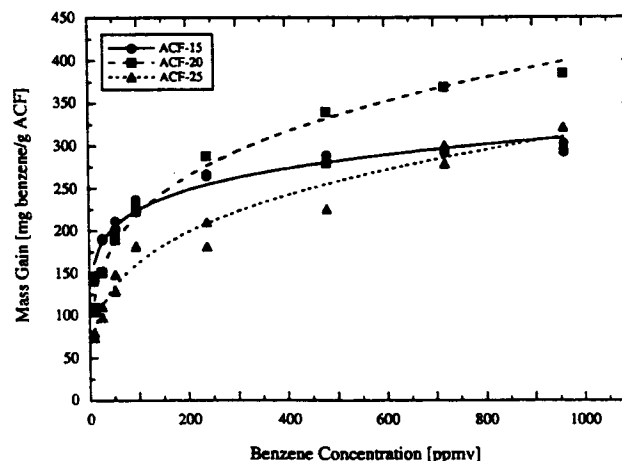


FIGURE 3. Experimental isotherms for benzene adsorption onto ACF. Lines through the data points represent fits with the Freundlich equation.

## Experimental Adsorption Isotherms

In the case of acetone (Figure 2), there was a trend of the lower BET surface area ACF having the higher adsorption capacity at a specific adsorbate concentration for concentrations between 10 and 1000 ppmv. For example, at 1000 ppmv acetone, ACF-15 adsorbed 180 mg/g compared to 150 mg/g for ACF-20 and 105 mg/g for ACF-25.

The experimental results indicate that the three ACF samples had a higher adsorption capacity for benzene than acetone (Figure 3). For example, at 1000 ppmv, ACF-15 adsorbed 67 percent by mass more benzene than acetone. ACF-15 had a higher adsorption capacity for benzene than ACF-20 at concentrations between 10 ppmv to about 200 ppmv, but at higher concentrations ACF-20 exhibited higher adsorption capacity than ACF-15. ACF-25 had a lower adsorption capacity than ACF-20 and ACF-15 for benzene in the 10 to 1000 ppmv range. Adsorption capacity for ACF-25 increased to the adsorption capacity for ACF-15 at 1000 ppmv of benzene.

For both adsorbates, as the concentration of the adsorbate in the gas stream increases, ACF-25 will eventually have a greater adsorption capacity than ACF-20, and ACF-20 will have a greater adsorption capacity than ACF-15. This fact is evident from the pore volume data, previously measured [5] and summarized in Table 1.

## Freundlich Equation

Freundlich fits to the experimental adsorption data for acetone and benzene in the 10 to 1000 ppmv range onto ACF are presented in Figures 2 and 3, respectively. The lines through the data points in Figures 2 and 3 are results from fitting the Freundlich equation with constants presented in Tables 2 and 3. The correlation coefficients (*R*) between the experimental data and the results from the Freundlich equation range from 0.980 to 0.997.

The accuracy of using the Freundlich equation varies for different adsorbate-adsorbent systems and concentration ranges, but it can be seen in Figures 2 and 3 that the Freundlich equation provides an adequate fit to the adsorption data over the 10 to 1000 ppmv concentration range for acetone and benzene.

**Table 2 Freundlich Parameters for Acetone Adsorption onto ACF**

Adsorbent	<i>k</i>	1/ <i>n</i>	<i>R</i>
ACF-15	14.1	0.374	0.996
ACF-20	2.82	0.580	0.983
ACF-25	2.81	0.528	0.997

## Dubinin-Radushkevich Equation

The DR parameters in equation (2) were calculated for benzene, and then used in combination with a value for  $\beta$  of 0.78 to predict acetone adsorption onto ACF. The parameters  $W_0$  and  $x_0$  were determined for benzene using equation (3). The DR parameters for acetone and benzene data are presented in Tables 4 and 5. Results for the fit of the DR equation to

**Table 3 Freundlich Parameters for Benzene Adsorption onto ACF**

Adsorbent	<i>k</i>	1/ <i>n</i>	<i>R</i>
ACF-15	117	0.142	0.980
ACF-20	65.1	0.264	0.997
ACF-25	43.2	0.287	0.980

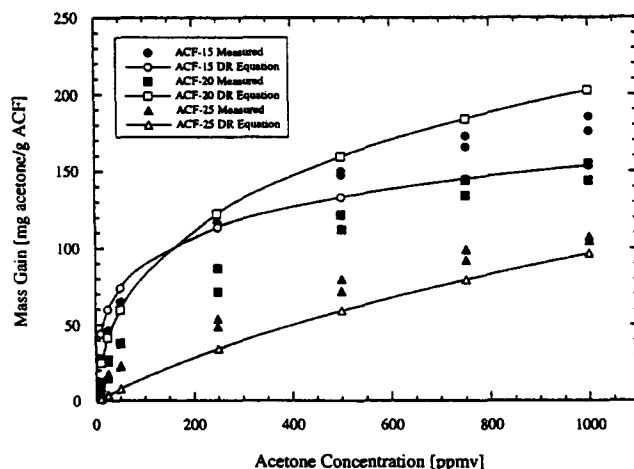
**Table 4 DR Parameters for Acetone Modeling**

Adsorbent	$W_0$ [cm <sup>3</sup> /g]	$x_0$ [nm]	$\beta$
ACF-15	0.338	0.492	0.78
ACF-20	0.648	0.637	0.78
ACF-25	0.827	0.915	0.78

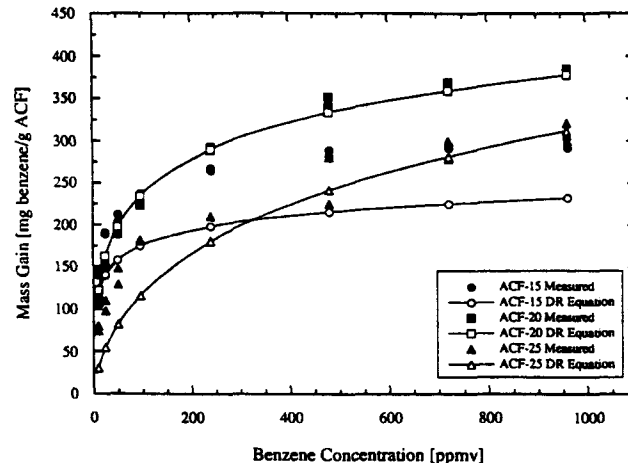
experimental data for acetone and benzene are presented in Figures 4 and 5. For benzene, agreement between experimental points and the DR equation improved for the higher BET surface area ACF. Using the DR parameters calculated for benzene to predict the adsorption isotherms of acetone onto ACF, provided a reasonable approximation of the experimental data. Better predictions were obtained for acetone adsorption onto ACF-15 and ACF-25 than onto ACF-20. The use of a reference compound more chemically similar to acetone than benzene may improve the quality of the DR fits to the experimental data. Benzene, however, is a common reference vapor, and was therefore used as reference for acetone in this study.

**Table 5 DR Parameters for Benzene Modeling**

Adsorbent	$W_0$ [cc/g]	$x_0$ [nm]	$\beta$
ACF-15	0.338	0.492	1.00
ACF-20	0.648	0.637	1.00
ACF-25	0.827	0.915	1.00



**FIGURE 4. Measured and modeled results for acetone and ACF using the DR equation.**



**FIGURE 5. Measured and modeled results for benzene and ACF using the DR equation.**

The results from fitting the DR equation to the experimental data indicate that ACF with higher BET surface areas have larger  $x_0$  values (Tables 4 and 5). It is believed that as the ACF are activated for longer time periods the pores widen [13]. Longer activation times produce ACF with greater BET surface areas and concomitantly produce larger mean pore sizes. The adsorption potential between an adsorbate and an adsorbent is greater for smaller pore sizes, due to the overlapping of energy potentials between the adjacent pore walls [14]. This effect is important in maximizing adsorption capacity at low adsorbate concentrations. Available pore volume does become a limiting factor for adsorption capacity at higher adsorbate concentrations. This relationship between activation time, pore size, pore volume, and BET surface area may explain why an increase in surface area of the ACF is accompanied by a decrease in the equilibrium mass of organic compound adsorbed at low concentrations ( $\leq 1000$  ppmv depending on the adsorbate), as observed in Figures 4 and 5.

The pore size and the total pore volume are also important considerations in the adsorption process, especially for ACF [14]. Additionally, the technical literature indicates that the ratio of the adsorbate molecule diameter to pore size of microporous carbons appear to be an important factor for the adsorption of organic gases [14]. Large molecules may not fit into the small pores of the adsorbent, which would decrease the adsorption capacity of ACF for that compound. These observations should be considered when evaluating an adsorbate-adsorbent combination for removal of VOCs from indoor air.

## CONCLUSIONS

Adsorption isotherms were developed for the adsorption of acetone and benzene onto activated carbon fibers (ACF). The Freundlich equation produced correlation coefficients (R) between the modeled and experimental data of 0.980 to 0.997, indicating the validity of using the Freundlich equation to model the adsorption isotherms over the concentration range of interest. The DR equation produced adequate fits of both the benzene and the acetone adsorption isotherm data and the three ACF samples. Using benzene as a reference compound for the prediction of acetone adsorption provided satisfactory results for ACF-15 and ACF-25, with poorer results for ACF-20. The DR equation may give a better prediction of acetone adsorption if another reference vapor with chemical properties more similar to acetone is used.

As the surface area of the ACF increases, so does the mean pore size (slit-pore half-width), determined from the DR equation. It is hypothesized that ACF with smaller slit-pore half-widths (related to lower BET surface areas) are more effective adsorbents at low adsorbate concentrations than are ACF with larger mean pore sizes (higher BET surface areas) due to the overlap of adsorption potentials in the smaller pores. These observations indicate that mean pore size, BET surface area, and pore volume of the ACF are important when characterizing adsorption capacities. Such observations need to be considered when selecting microporous adsorbents to remove volatile organic compounds from indoor air. These results also indicate that ACF have the potential as an adsorbate to effectively remove volatile organic compounds from indoor gas streams.

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