Adsorption of Gas Phase Contaminants

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Grant number: NIOSH/CDC - ROH008080
Start date: April, 2006
End date: July 31, 2010

LIST OF ABBREVIATIONS

ACF	Activated Carbon Fiber
ACFC	Activated Carbon Fiber Cloth
ACFF	Activated Carbon Fiber Felt
ANCOVA	Analysis of Covariance
BET	Brunauer, Emmett and Teller
CBD	Critical Bed Depth
CO_2	Carbon Dioxide
DFT	Density Functional Theory
D-R	Dubinin-Radushkevich
FID	Flame Ionization Detector
GAC	Granular Activated Carbon
IUPAC	International Union of Pure and Applied Chemistry
LPM	Liter per minute
MEK	Methyl Ethyl Ketone
NFE	Nonafluorobutyl Methyl Ether
NIOSH	National Institute of Occupational Safety and Health
PAN	Polyacrylonitrile
PPE	Personal Protective Equipment
SEM	Scanning Electron Microscopy
SE_x	Standard Error of X
SE_y	Standard Error of the Estimate
TVFM	Theory of Volume Filling of Micropores

UL_x	Upper Confidence Limit of X
UL_y	Upper Confidence Limit of Y
VOC	Volatile Organic Compounds

Abstract

Granular activated carbon (GAC) is currently the standard adsorbent in respirators against several gases and vapors because of its efficiency, low cost and available technology. However, a drawback of GAC due to its granular form is its need for containment, adding weight and bulkiness to respirators. This makes respirators uncomfortable to wear, resulting to poor compliance in its use. Activated carbon fibers (ACF) are considered viable alternative adsorbent materials for developing thinner, light-weight and efficient respirators because of their larger surface area, lighter weight and fabric form. This study aims to determine the critical bed depth and adsorption capacity of different types of commercially available ACFs for toluene to understand how thin a respirator can be and the service life of the adsorbents, respectively. ACF in cloth (ACFC) and felt (ACFF) forms with 3 different surface areas per form were tested. Each ACF type was challenged with 6 concentrations of toluene (50, 100, 200, 300, 400, 500 ppm) at constant air temperature (23°C), relative humidity (50%) and air flow (16 LPM) at different adsorbent weights and bed depths. Breakthrough data were obtained for each adsorbent using gas chromatography with flame ionization detector. The ACFs' surface areas were measured by an automatic physisorption analyzer. The results showed that ACFC has a lower critical bed depth and higher adsorption capacity compared to ACFF with similar surface area for each toluene concentration. Among the ACF types, ACFC2000 (cloth with the highest average BET surface area of 2053 ± 6 m^2/g) has one of the lowest critical bed depths (ranging from 0.11 – 0.22 cm) and has the highest adsorption capacity (ranging from 595 – 878 mg/g). It is concluded that ACF has great potential for application in respiratory protection, particularly the ACFC2000, which are the best candidates for developing thinner and efficient respirators. The Dubinin-Radushkevich (D-R) equation may successfully predict the adsorption capacities of the ACF types at lower concentrations depending on the toluene concentrations used and their corresponding experimental adsorption capacities. Using the highest two toluene challenge concentrations to predict the lower concentrations resulted to the underestimation of adsorption capacities

which is attributed to the microporosity of the ACF materials, while using lower toluene challenge concentrations improved such prediction for some of the ACF types.

Highlights/Significant Findings

Based on the breakthrough characteristics of toluene, particularly the breakthrough and saturation times, ACF may provide longer protection against toluene at lower ambient concentrations. Comparing the ACF forms, ACFC provides longer protection against toluene than ACFF based on its longer breakthrough time. This may be attributed to the denser woven form of ACFC compared to the non-woven form of the ACFF. Moreover, at a certain toluene concentration, the 10% breakthrough time generally increases as the ACF surface area increases. This may be explained by the increasing density of each ACF form as the surface area increases. Considering all these breakthrough data, this implies that ACFC 2000 may provide the longest respiratory protection against toluene, particularly at low ambient concentrations.

The ACF materials were demonstrated to be mainly composed of micropores based on their type I nitrogen adsorption isotherms, micropore area, micropore volume, average pore size and pore size distribution, making the ACF suitable for adsorbing toluene at low concentrations. The surface area of the ACF materials were increased through increasing the bulk density and degree of activation of the adsorbents. Particularly for ACFC, the increase in surface area also increases the total pore volume, micropore volume, micropore area and pore width, but decreases the percentage of micropores by area and volume.

The ACF with the lowest surface area, regardless of form, has the highest critical bed depth due to the least amount of available adsorption sites per ACF bed depth. Critical bed depth is not dependent on the surface area of ACF alone but also on the amount of micropores and micropore width of the adsorbent. As the toluene challenge concentration increases, the critical bed depth also increases because more material is needed to adsorb more toluene molecules. The ACFC has a significantly lower critical bed depth than the ACFF with similar surface area because of its denser and thinner form. Based on the critical bed depth alone, the ACFC1500 and ACFC2000 are the best adsorbents because they have the lowest critical bed depths.

Translation of Findings

Given its advantages over the GAC, the ACF shows promise in the development of disposable respirators for short-term protection against toluene, and probably other VOC with similar molecular weight. Based on both the critical bed depth and the adsorption capacity, the ACFC2000 is the best adsorbent candidate for the development of thinner, lighter and more efficient respirators that may be more comfortable to wear and thus, improving compliance in its use among workers. However, pressure drop across the respirator is one important factor considered before a respirator is approved. Since the ACFF was shown to have a lower pressure drop than the ACFC due to its lower bulk density, the ACFF may be a better adsorbent candidate for respirators in the long run. It is therefore important to balance the bulk density and permeability of the ACF material for practical application in respiratory protection.

Outcomes/Relevance/Impact

A large number of workers in the United States are required to use and rely daily on respirators for their protection against airborne pollutants. However, workers have poor compliance in using respirators because of the difficulties they encounter in performing certain tasks while wearing them. Such difficulties include the heaviness and bulkiness of respirators, resulting in discomfort of the wearer. Surveys of safety professionals, conducted 3 years in a row from 2006-2008, revealed a high rate of noncompliance in wearing personal protective equipment (PPE) when necessary, with discomfort as the main cause of noncompliance. The development of lightweight respirators that are efficient in protecting against airborne pollutants may improve worker compliance on respirator use. Moreover, light respirator masks made of ACF, when readily available for immediate use, may be worn for short term protection by workers and the public at large in the case of accidental or intentional release of a toxic gas or vapor that could harm a significant number of people.

Scientific Report

Background

Granular activated carbon (GAC) is currently the standard adsorbent in chemical cartridges of respirators against several gases and vapors because of its efficiency, low cost and available technology. However, a drawback of GAC due to its granular form is the need for its containment, adding weight and bulkiness to respirators. This makes some respirators uncomfortable to wear, resulting in poor compliance in their use.

Activated carbon fiber (ACF) is considered as good alternative adsorbents for developing thinner, light-weight and efficient respirators because of their larger surface area, larger adsorption capacities, lighter weight and fabric form. To achieve such application, adsorption characteristics of different types of commercially available ACFs for specific chemicals must be understood in advance. To determine how thin a respirator can be and its service life, the critical bed depth (minimum adsorbent thickness required) and adsorption capacity (mass of chemical adsorbed per mass of material) of sorbents need to be determined.

Furthermore, obtaining the adsorption capacity for different combinations of adsorbent/adsorbate systems through experiments can be time consuming and costly. The Dubinin-Radushkevich (D-R) equation has been widely used to predict the adsorption capacity of a particular GAC for a number of volatile organic compounds (VOC) at high concentrations. However, the D-R equation overestimates the adsorption capacity of GAC at relatively low VOC concentrations and, thus, needs to be modified by combining it with other models for successful prediction. ACF is mainly composed of micropores which are primarily responsible for adsorption at low VOC concentrations in ambient air, while GAC contains a combination of macropores, mesopores and micropores. This difference may yield a higher adsorption capacity of ACF for low VOC concentrations and may not result in overestimation by the D-R equation. Investigating if the unmodified D-R equation will efficiently predict the adsorption capacity of ACF for toluene will make such prediction more straightforward.

Hypotheses

Hypothesis 1:

The critical bed depth is dependent on the surface area and physical form of the activated carbon fiber. The ACF with the highest surface area is expected to have the smallest critical bed.

Hypothesis 2:

The adsorption capacity is dependent on the surface area and physical form of the activated carbon fiber. The surface area of an adsorbent is considered the general predictor of adsorption capacity and, thus, it is expected that the ACF with the highest surface area will have the highest adsorption capacity.

Hypothesis 3:

The unmodified D-R equation can successfully predict the adsorption capacity of ACF at a lower range of toluene concentrations. Successful prediction of adsorption capacity means that the absolute difference between the predicted and experimental adsorption capacities is within 10% of the experimental adsorption capacity. This hypothesis considers the difference in the pore size distribution between GAC and ACF.

Specific Aims

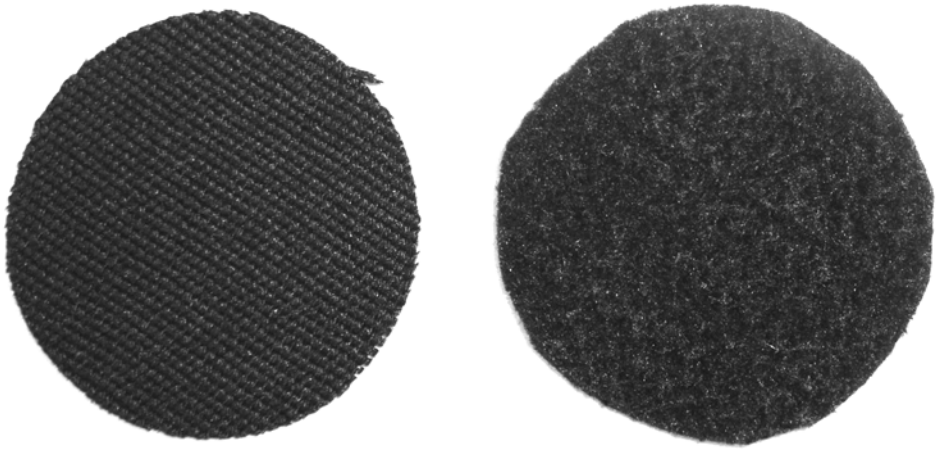
1. To characterize commercially available ACFs by form, surface area and porosity. These physical characteristics will be associated with the adsorption characteristics obtained for each type of ACF tested for toluene.
2. To determine the adsorption characteristics of commercially available ACF for toluene. Breakthrough curves, which are a function of the effluent concentration and the elapsed time, will be obtained using gas chromatography with flame ionization detector. The time at which 10% and 50% of effluent concentration is detected will be obtained to determine for each adsorbent the (i) critical bed depth and (ii) adsorption capacity, respectively, which will be compared across the adsorbents to determine the ACF type that has the best potential for application in respiratory protection against toluene.

3. Assess the capability of the D-R adsorption equation in predicting the adsorption capacity of ACF for toluene. Predicted adsorption capacities of ACF for toluene at tested concentrations using the D-R equation will be compared to the experimental data to evaluate the predictive capability of this equation. Using the experimental adsorption capacities for two different challenge concentrations of toluene, two constant parameters (maximum adsorption space available for condensed adsorbate, W_o, and structural constant of the adsorbent, K) will be determined for each ACF type to predict the adsorption capacity of the ACF at different toluene concentrations.

Research Design and methods

Adsorbents and Adsorbate

Two forms of ACF were used as adsorbents: the woven cloth and the unwoven felt (see figure 5). The thickness of the ACF cloth (ACFC) is 0.0625 cm and that of the ACF felt (ACFF) is from 0.2 to 0.3 cm, which is 3 – 5 times greater than that of the ACFC. For each form, three (3) different manufacture-specified surface areas (1000, 1500 and 1800 or 2000 m^2/g) were tested. Thus, six (6) types of ACF were analyzed in this study.



ACF Cloth (ACFC) ACF Felt (ACFF)

Forms of Activated Carbon Fiber (ACF)

The Table below shows the denotation of each ACF based on its form and surface area. ACFC1000, ACFC1500, ACFF1500 and ACFC2000 are manufactured from phenol aldehyde-based, or novoloid, fiber precursors by American Kynol, Inc. (Pleasantville, NY). The novoloid fibers contain approximately 76% carbon, 18% oxygen, and 6% hydrogen. ACFF1000 and ACFF1800 are manufactured from viscose rayon fibers by Beijing Evergrow Resources Co. (Beijing, China). The ACFs were cut into 4-cm disks and treated in an oven (Thermo Electron Corporation, Waltham, MA) at 200 °C overnight prior to testing to desorb any volatile impurities on the adsorbent materials.

Denotations of ACF Types Based on ACF Characteristics

Form	Surface Area, m^2/g			
	1000	1500	1800	2000
Cloth	ACFC1000	ACFC1500	---	ACFC2000
Felt	ACFF1000	ACFF1500	ACFF1800	---

The adsorbate used was toluene (laboratory grade) which was selected as representative volatile organic compound. Toluene was purchased from Fisher Scientific and was used in the experiments without further purification. The properties of toluene are summarized in the above table.

Physical and Chemical Properties of Toluene

Property	
Formula	$C_6H_5CH_3$
Molecular weight	92.14 g/mol
Density	0.865 g/mL @ 25 °C
Boiling point	110.5 °C @ 760 mmHg
Melting point	-95 °C
Vapor pressure	22 mmHg @ 20 °C
Vapor density	3.1 (air = 1.0)
Viscosity	0.6 mPa·s @ 20 °C
Molecular diameter	0.568 nm
Polarity index	2.4

Characterization of ACF by Form, Surface Area and Porosity

The surface area and pore size distribution of the ACF samples were measured by nitrogen adsorption at 77 K in the range of relative pressure (P/P_0) from 0.02 to 1 using a Micromeritics ASAP 2020 automatic physisorption analyzer (Micromeritics Corp., Norcross, Georgia). High purity nitrogen (99.99%) was used in the measurement. All samples underwent both the degassing and analysis processes in the instrument. The degassing process pretreats the adsorbent sample by applying some combination of heat, vacuum and/or flowing gas to remove adsorbed contaminants acquired from atmospheric exposure, and will be performed at 300 °C for 1 hour prior to the analysis. The analysis process involves the incremental dosing of nitrogen to the adsorbent samples. The quantity of nitrogen required to form a monolayer over the external surface of the adsorbent and its pores was determined at particular pressures. With the area covered by each adsorbed nitrogen gas molecule known, the surface area was calculated.

Three analyses (n = 3) were performed for each ACF types, with a total of 18 physisorption analyses. The actual surface area was specifically measured

to verify the surface area specified by the manufacturer of the ACF. The pore volume and size were measured to determine how they may be related to the adsorption characteristics of the ACF.

The Brunauer, Emmett and Teller (BET) surface area measurements were used as the actual surface area of each ACF type. The BET theory involves the concept of multimolecular layer adsorption. Its fundamental assumption is that the forces active in the condensation of gases are also responsible for the binding energy in multimolecular adsorption. Since the adsorption of toluene involves its condensation in micropores, the BET surface area is more appropriate for the ACF materials.

The pore size distribution of each ACF material was obtained to determine the percentages of micropores, mesopores and macropores in the adsorbent. The ACF materials were sent to the Instituto de Física Aplicada, Consejo Nacional de Investigaciones Científicas y Técnicas – Universidad Nacional de San Luis **(**Institute of Applied Physics, National Council of Scientific and Technical Research – National University of San Luis) in Argentina for pore size distribution analyses. The Density Functional Theory (DFT) method was used to calculate particularly the micropore size distribution of the samples, and is based on a molecular model of adsorption of nitrogen in porous solids.

Scanning electron microscopy (SEM) images of the different ACF samples were obtained for the purpose of visualizing the structure of the fibers and pores of the ACF. SEM images obtained from the Department of Material Science and Engineering, School of Engineering, University of Alabama at Birmingham were taken at 4 magnifications: 40.8x, 203x, 1010x and 5450x. SEM images obtained from the Department of Metallurgical and Materials Engineering, College of Engineering, University of Alabama in Tuscaloosa were taken at 6000x and 100,000x magnification.

Determination of Adsorption Characteristics for Toluene

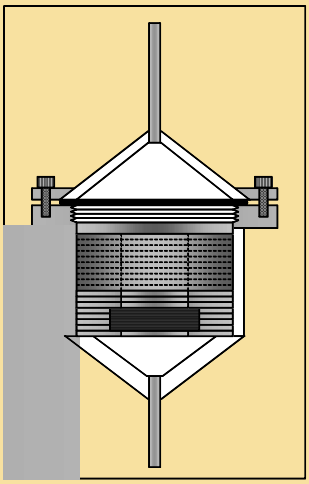
Critical bed depth and adsorption capacity are the two adsorption characteristics that were obtained and compared among the ACF types tested.

Critical bed depth is the minimum adsorbent thickness required to obtain an acceptable chemical concentration (i.e. 10% of challenge concentration) at time zero and, thus, determines how thin a respirator can be. Adsorption capacity is the amount of chemical adsorbed per mass of material and is used to determine the service life of the adsorbent. The main purpose of such comparison is to determine the type of ACF that is most suitable for respirator application.

Breakthrough Determination

The materials were challenged with toluene in a stainless steel sample chamber (see figure 6) at a constant airflow (16 LPM), temperature (23 ± 1.5 °C) and relative humidity (50 ± 5 %) and at 5 different bed depths and mass for a certain concentration. The sample chamber has an internal diameter of 4 cm and will be immersed in water for temperature control at 23 ± 0.5 °C. The mass of the adsorbents was determined before the chemical challenge by using a Denver Model APX-100 analytical balance (Denver Instrument, Denver, Colorado). The adsorbent bed depths were measured using a caliper. Breakthrough curves were obtained for each ACF type at 6 different toluene concentrations: 50, 100, 200, 500, 400 and 500 ppm. Duplicates were conducted for 20% of the breakthrough runs and were performed at every 6^{th} analysis. Based on this, a total of 216 breakthrough runs [(6 ACF types x 6 challenge concentrations x 5 bed depths) + 36 duplicates] were performed.

The challenge concentrations chosen for toluene are realistic ambient concentrations found in workplace settings. The air temperature and relative humidity were set at 23 °C and 50%, respectively, as these are the standard experimental conditions in laboratory setting in previous studies. The airflow of 16 LPM was determined by considering the constant airflow used by the NIOSH for the testing of service life of respirators for chemical cartridges, such that the air velocity used in the NIOSH respirator testing must be similar to that in the sample chamber used in this study. Based on the constant airflow used for respirator testing ranging from 32 – 64 LPM and cartridge diameters of 6.9 and 7.2 cm, the air velocity through the chamber must be between 7.9 and 17.0

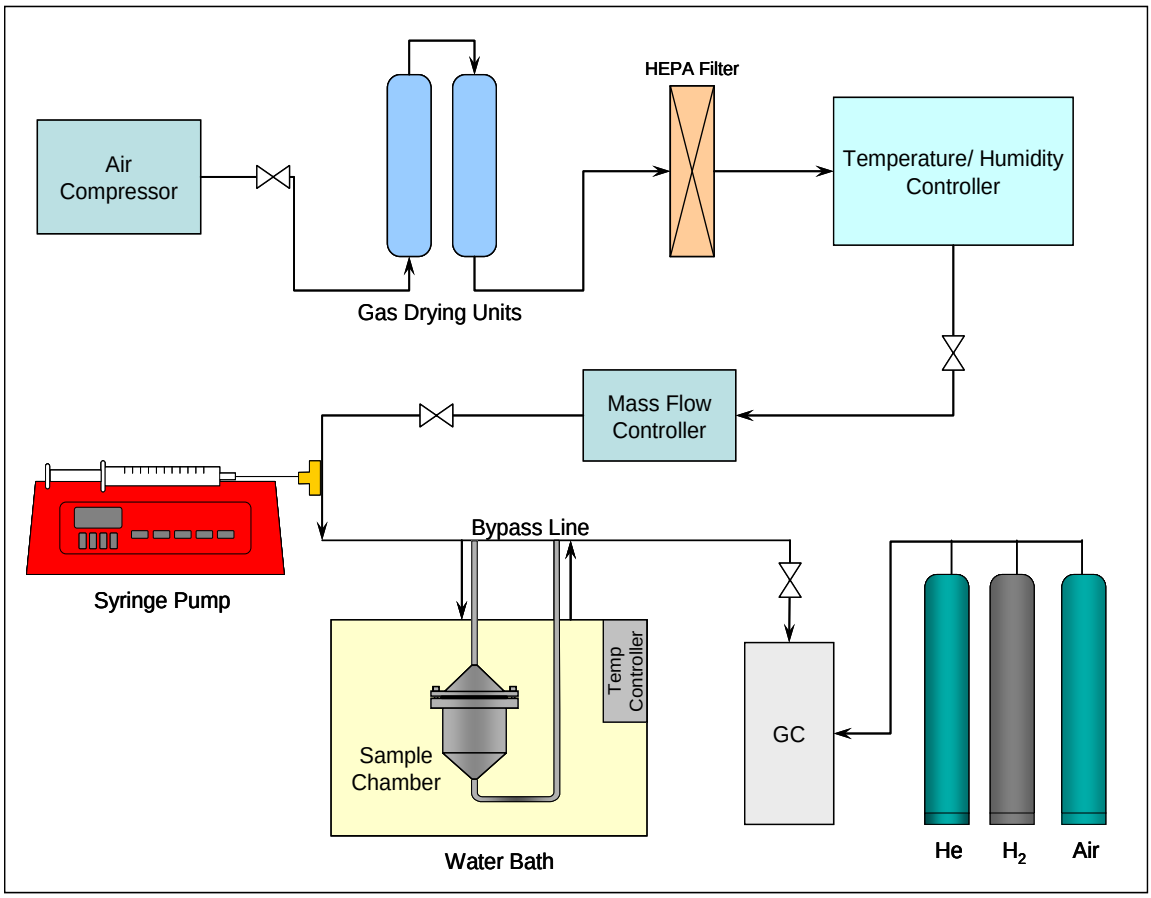


Sample Chamber for Breakthrough Determination (This figure is proprietary information)

Experimental Setup

The toluene vapor was generated by injecting a constant flow of liquid toluene using a automated syringe pump into a pre-conditioned stream of air of constant flow. The air was dried by passing through an air drying machine (Hankison, Canonsburg, PA) and a Drierite gas drying unit (W.A. Hammond Drierite Co. Ltd., Xenia, OH). The temperature and relative humidity of the air were controlled prior to mixing with toluene using a Miller-Nelson Model HCS-401 instrument. The pressure resistance across the ACF samples in the chamber was monitored during the entire challenge experiments with toluene using a Magnehelic analog manometer (Dwyer Instruments Inc., Michigan City, IN). Breakthrough of the ACF samples for toluene was determined by gas chromatography using an Agilent Model 6850 gas chromatograph (Agilent Techonologies, Alpharette, GA) fitted with a flame ionization detector (FID) for quantification. The analytical column used was a HP-1 (100% methyl siloxane) capillary column, 30.0 m x 0.32 mm (I.D.) x 0.25 μm. The oven temperature program was 115 °C for 2 minutes. The FID temperature was 230 °C. The

carrier gas was helium. A 5-point calibration curve was established using the external method. The schematic diagram of the experimental set-up for breakthrough determination is shown bellow.



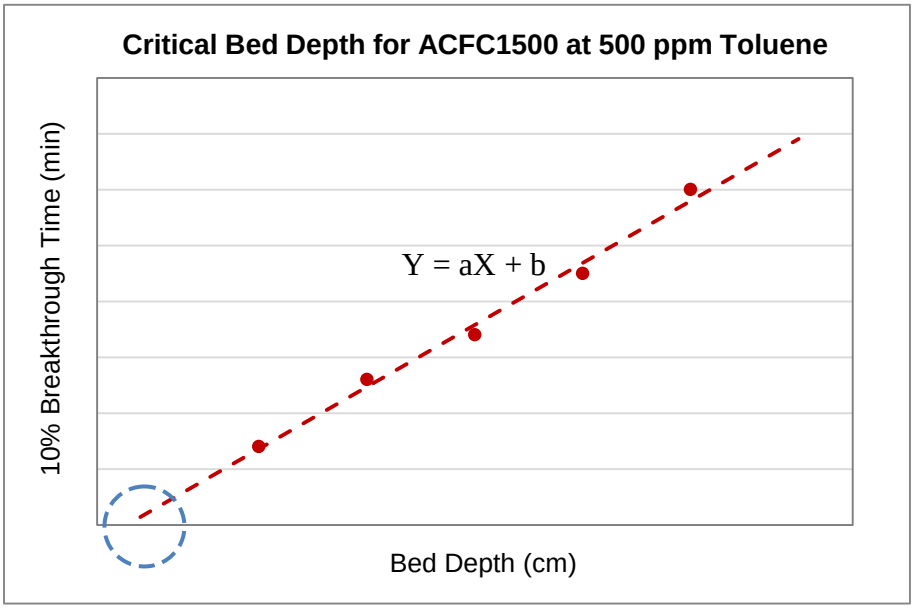
Experimental Setup for Breakthrough Determination. (This figure is proprietary information)

Determination of Critical Bed Depth

Critical bed depth is the minimum adsorbent thickness required to obtain an acceptable chemical concentration at time zero. In this study, critical bed depth is specifically defined as the minimum bed depth of the adsorbent that is required to reduce the challenge concentration of toluene by 90% or at C_x/C_0 = 0.1, wherein C_x is the effluent concentration and C_0 is the initial challenge concentration. The time in minutes when C_x/C_0 = 0.1 is referred to as the 10% breakthrough time, which was determined for each breakthrough curve at

different adsorbent bed depths. The average time for duplicate breakthrough curves was calculated.

Per ACF type and challenge concentration, the 10% breakthrough times (minutes) obtained were plotted against the adsorbent bed depth (cm), to obtain a regression line. Figure 8 shows a sample graph for determining the critical bed depth. The bed depth at which 10% breakthrough time is 0 (or the x-intercept) is the critical bed depth, which was determined for each challenge concentration of toluene. Thus, a total of 6 critical bed depths were obtained for each ACF type.

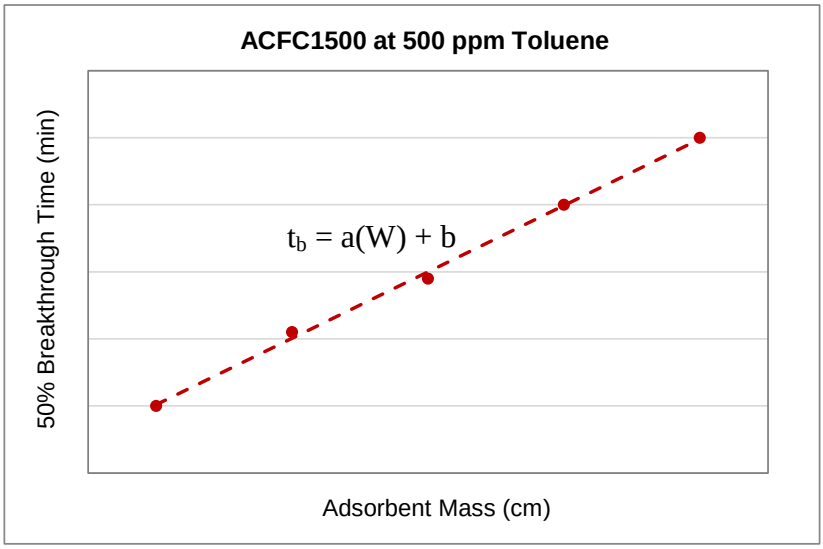


Sample Graph for Critical Bed Depth Determination

Statistical analysis of the data was performed using the SPSS software. The standard error of the critical bed depth was calculated based on the standard error of the estimate (SE_y). The upper confidence limit of Y (UL_y) at 95% confidence level was calculated using the equation $UL_y = Y + t_3 (SE_y)$, where Y = 0 and $t_3 = 3.182$. The upper confidence limit of X (UL_x) was then obtained using the equation $UL_x = (UL_y – b)/a$ where a is the slope of the line and b is the y-intercept. Finally, the standard error of X, and thus the critical bed depth, was calculated using the equation $SE_x = (UL_x – CBD)/t_3$ where CBD is the critical bed depth.

Determination of Adsorption Capacity

Adsorption capacity is the amount of chemical adsorbed per mass of material. The time in minutes when $C_x/C_0 = 0.5$ is referred to as the 50% breakthrough time, which was determined for each breakthrough curve at different adsorbent mass. The average time for duplicate breakthrough curves was calculated. Per ACF type and challenge concentration, the 50% breakthrough times (minutes) obtained were plotted against the adsorbent mass (g) to obtain a regression line, as shown in the next figure for the calculation of the adsorption capacity (W_e) of each adsorbent at a certain concentration using the modified Wheeler equation.



Sample Graph of 50% Breakthrough Time vs Adsorbent Mass

The modified Wheeler equation is shown below, wherein t_b – breakthrough time (min); C_x – exit concentration (g/cm^3); C_0 – inlet concentration (g/cm^3); Q – volumetric flow rate (cm^3/min); W – weight of adsorbent (g); ρ_B – bulk density of packed bed (g/cm3); k_v – kinetic adsorption rate constant (min-1); and W_e – kinetic adsorption capacity (g/g).

$$t_b = \frac{W_e}{C_0 Q}\left[W - \frac{\rho_B Q}{k_v}\ln\left(C_0 / C_x\right)\right]$$

The equation was transformed to the following:

$t_b = \frac{W_e W}{C_0 Q} - \frac{W_e \rho_B}{k_v C_0} \ln(C_0 / C_x)$. The slope of the regression line, $a = \frac{W_e}{C_0 Q}$, was transformed to obtain an equation for calculating the adsorption capacity, $W_e = aC_0 Q$, which was determined for each challenge concentration of toluene. Thus, a total of 6 adsorption capacities were obtained for each ACF type. The adsorption capacity (mg/g) was plotted against the challenge concentration to obtain the adsorption isotherms of each adsorbent for toluene. Statistical analysis of the data was performed using the SPSS software. The standard error of the adsorption capacity was calculated based on the standard error of the slope.

The kinetic adsorption rate constant, k_v, for each ACF type may be calculated if the bulk density of the adsorbents are known. However, determining the k_v is not within the scope of this study.

Comparison of Adsorption Characteristics among ACF Types

All the ACF types tested in this study were compared according to fiber form, surface area and porosity, critical bed depth and adsorption capacity.

The critical bed depth and adsorption capacity among the ACF types were statistically compared using the analysis of covariance (ANCOVA). ANCOVA was performed to determine whether the critical bed depth or the adsorption capacity is significantly different among 6 ACF types, when adjusted for toluene concentration. The critical bed depths in all challenge concentrations were pooled together for each ACF type to calculate the adjusted mean scores of the critical bed depth, which were compared among the ACF types. The adjusted mean scores of critical bed depth (CBD) for the 6 ACF types were determined using the following general regression model:

$$CBD = \beta_0 + \beta_1 Z_1 + \beta_2 Z_2 + \beta_3 Z_3 + \beta_4 Z_4 + \beta_5 Z_5 + \beta_6 CONC + \beta_7 CONCZ_1 + \beta_8 CONCZ_2 + \beta_9 CONCZ_3 + \beta_{10} CONCZ_4 + \beta_{11} CONCZ_5$$

The adjusted CBD mean scores for the 6 ACF types were determined by substituting the values of the overall mean $\overline{CONC}$ into the fitted equations for the 6 ACF types.

ACF 1 (Z_1 = 1, other Z_j = 0): $\overline{CBD}_1(adj) = (\hat{\beta}_0 + \hat{\beta}_1) + \hat{\beta}_6 \overline{CONC}$

ACF 2 (Z_2 = 1, other Z_j = 0): $\overline{CBD}_2(adj) = (\hat{\beta}_0 + \hat{\beta}_2) + \hat{\beta}_6 \overline{CONC}$

ACF 3 (Z_3 = 1, other Z_j = 0): $\overline{CBD}_3(adj) = (\hat{\beta}_0 + \hat{\beta}_3) + \hat{\beta}_6 \overline{CONC}$

ACF 4 (Z_4 = 1, other Z_j = 0): $\overline{CBD}_4(adj) = (\hat{\beta}_0 + \hat{\beta}_4) + \hat{\beta}_6 \overline{CONC}$

ACF 5 (Z_5 = 1, other Z_j = 0): $\overline{CBD}_5(adj) = (\hat{\beta}_0 + \hat{\beta}_5) + \hat{\beta}_6 \overline{CONC}$

ACF 6 (all Z_j = 0): $\overline{CBD}_6(adj) = \hat{\beta}_0 + \hat{\beta}_6 \overline{CONC}$

Wherein:

	ACF 1 = ACFC1000	ACF 4 = ACFF1000
	ACF 2 = ACFC1500	ACF 5 = ACFF1500
	ACF 3 = ACFC2000	ACF 6 = ACFF1800

To determine whether these adjusted means are significantly different from one another, the null hypothesis H_0: $\beta_1 = \beta_2 = \beta_3 = \beta_4 = \beta_5 = 0$, was tested using a multiple-partial F-test with 5 (k – 1 = 6 – 1; k – number of groups) and 29 (*n*–p–k = 36–1–6; n = ACF x conc; p – number of covariates (conc)) degrees of freedom. If the H_0 is rejected, it is concluded that there are significant differences among the adjusted means. The same analysis was done for the comparison of adsorption capacity among the ACF types.

Pairwise comparison of adsorption characteristics was also conducted between ACF types using paired t-test to determine if there are significant differences in critical bed depth or adsorption capacity between the 2 ACF forms: cloth and felt. This determines if the form of the ACF influences the adsorption characteristics. The comparison was done in 3 approaches: 1) between specific ACF types with different forms but similar surface areas, 2) between specific ACF types with same forms but different surface areas and 2) between ACFC and ACFF in general.

For the comparison of specific ACF, the critical bed depths or adsorption capacities at different concentrations were pooled for each ACF type. A total of fifteen (15) pairs were analyzed per adsorption characteristic but only the following nine (9) pairs will be of interest in this study:

Different form/Same surface area	Same form/ Different surface area	
ACFC1000/ACFF1000	ACFC1000/ACFC1500	ACFF1000/ACFF1500
ACFC1500/ACFF1500	ACFC1000/ACFC2000	ACFF1000/ACFF1800
ACFC2000/ACFF1800	ACFC1500/ACFC2000	ACFF1500/ACFF1800

The α is calculated by 0.05 divided by the number of ACF types compared pairwise. Thus, α is equal to 0.05/6 = 0.008.

For the comparison of ACFC and ACFF in general, the critical bed depths or adsorption capacities at different concentrations were pooled for each ACF form. The α is equal to 0.05.

It is important to note that the pooling of the critical bed depths or the adsorption capacities for all toluene concentrations to obtain the average of these adsorption characteristics per ACF type was done for the main purpose of statistical comparison. The mean critical bed depth or adsorption capacity, however, cannot be practically applied for the assessment of ACF for use in respiratory protection.

Prediction of Adsorption Capacity for Toluene

The adsorption capacities obtained in the previous section for each of the ACF types were compared to the predicted adsorption capacities calculated using the D-R equation as shown:

$$\ln W_v = \ln W_0 - K\left[RT \ln\left(p^0 / p\right)\right]^2 / \beta^2$$ where in:

W_v – adsorption space occupied by the condensed adsorbate (cm^3/g)

W_0 – maximum adsorption space available for condensed adsorbate (cm^3/g)

K – constant related to the structure of the sorbent (M^2/cal^2)

R – gas constant (1.987 cal / M °K)

T – absolute temperature (°K)

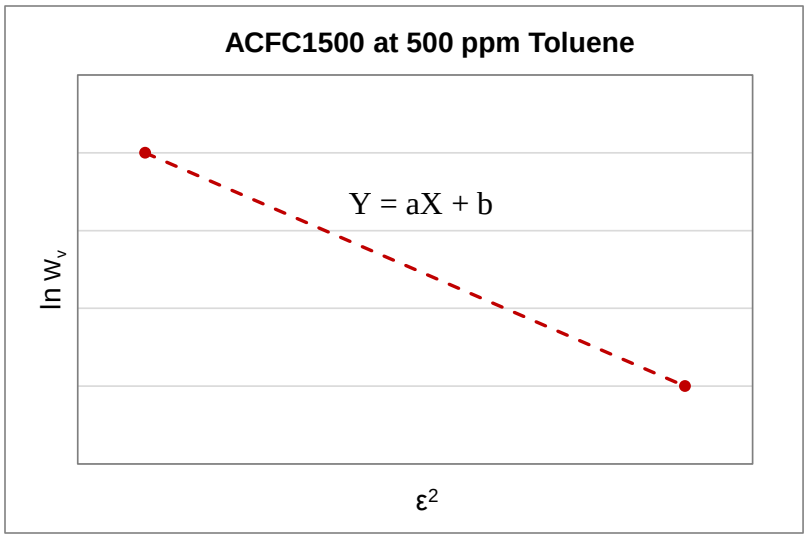
p – equilibrium pressure of the adsorbate vapor at T °K

p^0 – saturated vapor pressure of liquid adsorbate at T °K

β – dimensionless affinity coefficient that compares the strength of the adsorptive interaction of the adsorbate under consideration to a reference adsorbate

To perform such prediction, 2 constant parameters were determined for each ACF type to predict the adsorption capacity of the ACF at other toluene concentrations: the maximum adsorption space available for condensed adsorbate (W_o) and the structural constant of the adsorbent (K).

First, using the adsorption capacities, W_e, obtained from the highest two (2) challenge concentrations of toluene (400 and 500 ppm), the adsorption space, W_v in cm^3/g was calculated using the equation $W_v = W_e/d_l$, wherein d_l is the density of the condensed toluene vapor (0.8669 g/mL). The adsorption potential of the surface, ϵ in cal/mole was then calculated using the equation $\varepsilon = RT \ln\left(p^0 / p\right)$. The ln W_v was plotted against the ε^2 to obtain a regression line, as shown in figure 10. The slope of the line is equal to –K since this is the reference and $\beta^2 = 1$ by definition. The y-intercept is equal to ln W_0. The parameters K and W_0 determined were used to predict the adsorption capacity of each ACF for different toluene concentrations by substituting these values into the D-R equation.

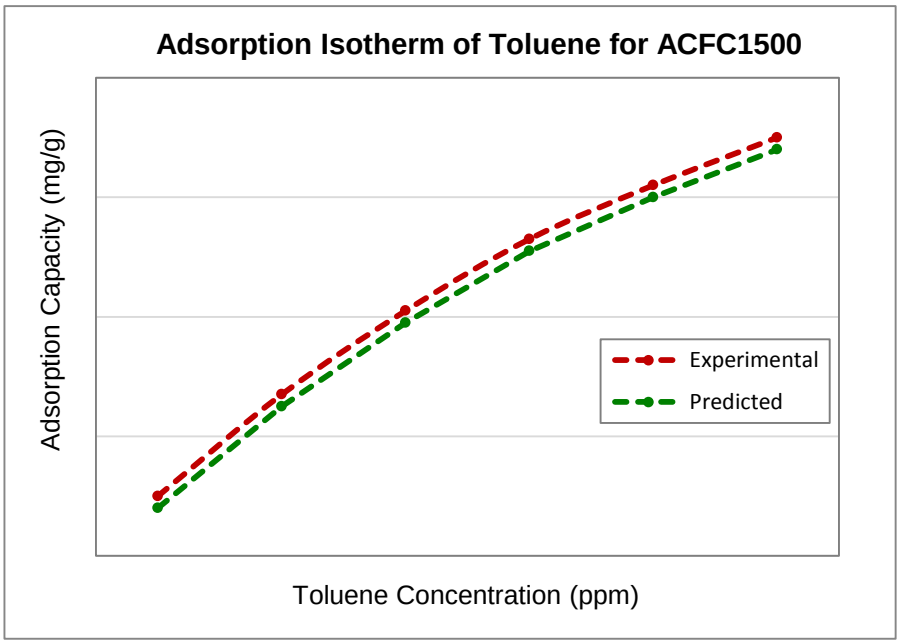


Sample Graph of ln W_v vs ε^2 for D-R Parameter Determination

The characteristic energy of adsorption (E_0) in kJ/mol provides information about the interaction energies between the molecule and adsorbent. Since $K = 1/(\beta E_0)^2$ and $\beta = 1$, E_0 was deduced from the D-R model for each ACF type by obtaining the square root of 1/K and then multiplied with 0.004184 to convert calorie to kilojoule (kJ).

The experimental and predicted adsorption capacities for all challenge concentrations per ACF type were plotted together for comparison, as shown in the next figure The differences in percentage between the experimental and predicted adsorption capacities were also calculated as follows:

$$\% \text{ Difference} = \left| \frac{\text{Experimental} - \text{Predicted}}{\text{Experimental}} \times 100 \right|$$



Sample Graph on the Comparison of Experimental and Predicted Adsorption Capacities

Results (All the results, tables and figures presented in this chapter are considered proprietary)

Characterization by Form, Surface Area and Porosity

The next table summarizes the surface characteristics of each ACF type, including the average surface area, pore volume and pore size (n = 3). The results demonstrate that the measured surface area of the ACFC is similar to its ACFF counterpart (e.g. ACFC1000 vs. ACFF1000). Moreover, the ACFC2000 has a measured surface area that is slightly higher than that of the ACFF1800 but may still be comparable. Thus, the ACFC2000 and ACFF1800 can be considered as counterparts and may be compared against each other. See Appendix A for individual parameter values of surface area, pore volume and pore sizes per ACF sample.

For both cloth and felt forms, the total pore volume increases as the surface area increases. The average pore sizes across all the ACF types are very similar, ranging from 1.67 – 1.84 nm. For the ACFC types, as the surface

area increases, the micropore area and volume also increase, but the percentage of micropore by area and volume decrease. This trend is not observed in ACFF types, which may imply that factors other than surface area affect the porosity of the materials. Furthermore, ACFC2000 and ACFF1800 have relatively close surface area and pore size but very different micropore area and volume, which is much lower for ACFF1800. This may be due to the fact that different precursors were used in manufacturing of these ACFs, thus resulting to different pore structures.

Average Surface Area, Pore Volume and Pore Size by ACF Type (n = 3)

Parameters	ACF Type					
	ACFC1000	ACFC1500	ACFC2000	ACFF1000	ACFF1500	ACFF1800
Surface Area						
Nominal surface area (m^2/g)	1000	1500	2000	1000	1500	1800
BET surface area (m^2/g)	891.8 ± 7.8	1470.8 ± 8.9	2052.8 ± 6.2	979.9 ± 19.0	1407.3 ± 14.8	1861.1 ± 7.4
Micropore area[a] (m^2/g)	840.2 ± 7.5	1336.9 ± 2.4	1726.7 ± 18.9	876.8 ± 27.3	1277.9 ± 11.3	1041.8 ± 54.3
% Micropore by area	94.2 ± 0.6	90.9 ± 0.5	84.1 ± 0.7	89.5 ± 1.3	90.8 ± 0.2	56.0 ± 3.1
Pore volume[b] (cm^3/g)	0.39 ± 0.00	0.62 ± 0.00	0.86 ± 0.01	0.43 ± 0.01	0.59 ± 0.01	0.86 ± 0.01
Micropore volume[a] (cm^3/g)	0.36 ± 0.01	0.54 ± 0.00	0.69 ± 0.01	0.36 ± 0.01	0.51 ± 0.01	0.42 ± 0.02
% Micropore by volume	92.0 ± 0.8	87.5 ± 0.7	78.2 ± 1.5	83.9 ± 3.3	87.4 ± 0.3	49.2 ± 3.1
Pore size[c] (nm)	1.74 ± 0.01	1.69 ± 0.01	1.71 ± 0.01	1.74 ± 0.08	1.67 ± 0.01	1.84 ± 0.02

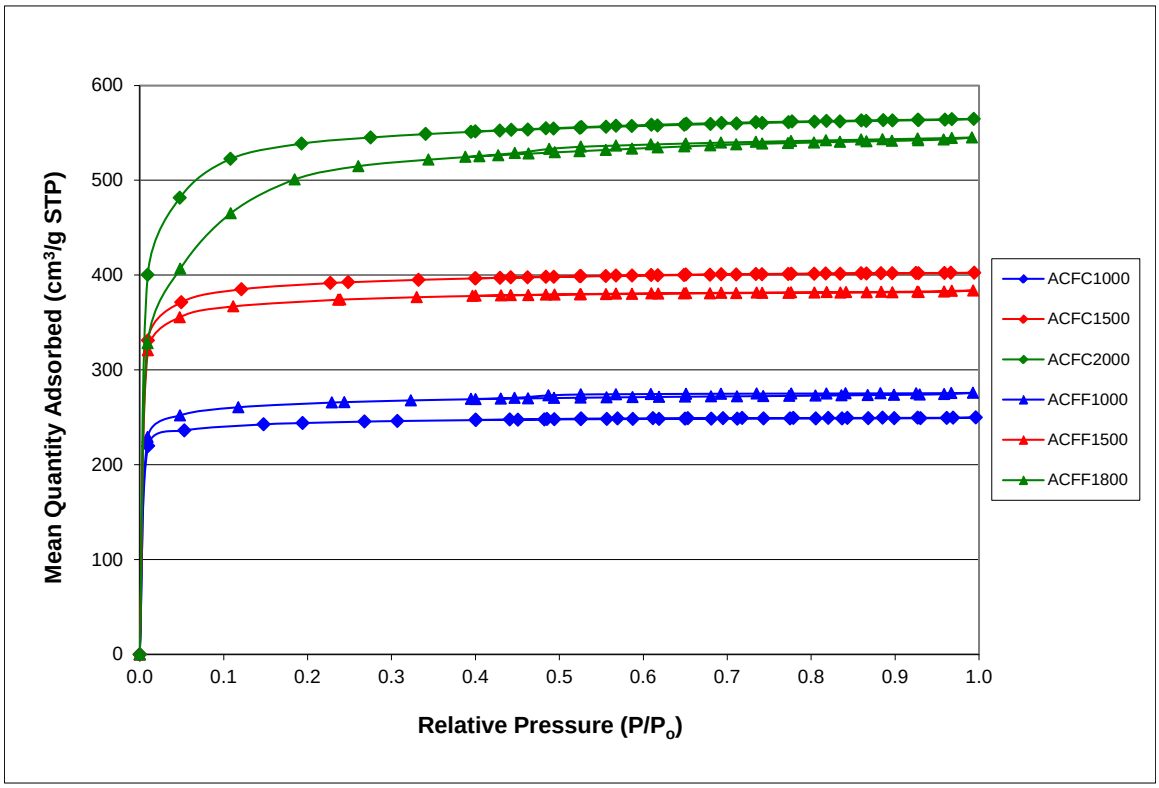
[a] *By t-plot method*
[b] *Single point adsorption total pore volume estimated at relative pressure* ≥ 0.95
[c] *Adsorption average pore width (4V/A by BET)*

v

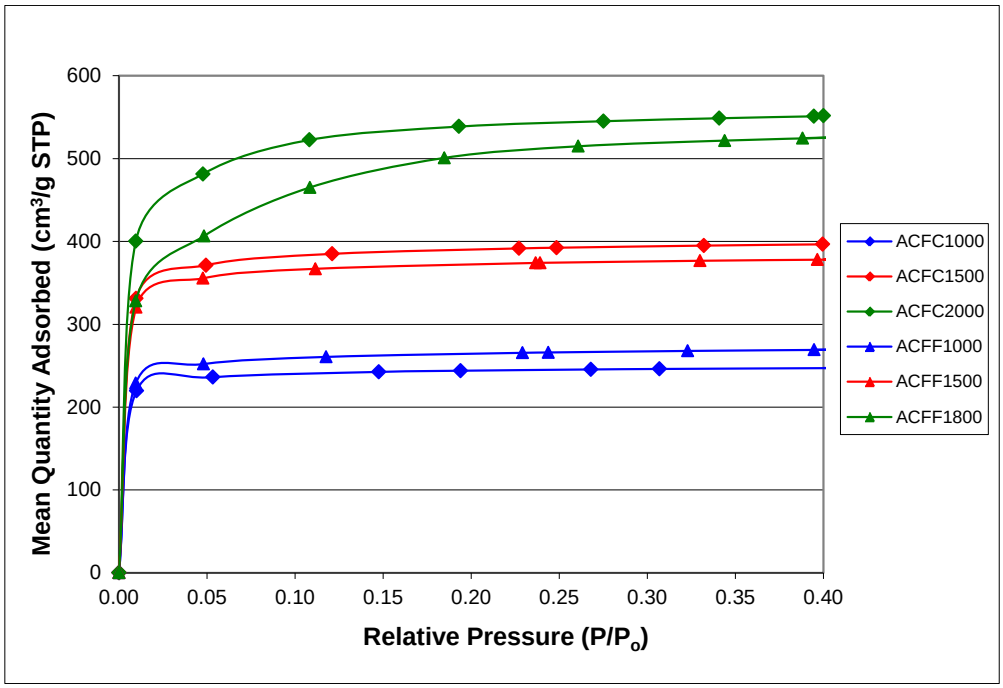
Nitrogen Adsorption by ACF Types

Figure 14 shows the adsorption and desorption isotherms of nitrogen for each ACF type at a temperature of 77 K. The shape of adsorption isotherms for all ACF types indicates that they are of Type I or the Langmuir-type form. Such isotherm type indicates that the materials are microporous. It is apparent that most of the pore volumes of the ACFs, except of ACFF1800, are filled below $P/P_0 \approx 0.1$, showing that these materials are highly microporous. For the ACFF1800, most the pore volumes are filled below $P/P_0 \approx 0.3$, as shown in the next figure. After a sharp increase to 0.1, the isotherms gradually bends, indicating smaller increments in further adsorption. As relative pressure increases, the adsorption

of all the ACF types becomes almost horizontal, which cuts the $P/P_0 = 1$ axis sharply, demonstrating that saturation has already been reached. For each ACF form, the greater the surface area of the adsorbent, the higher the quantity of nitrogen absorbed.



Nitrogen Adsorption/ Desorption Isotherms at 77 K for Different ACF Types

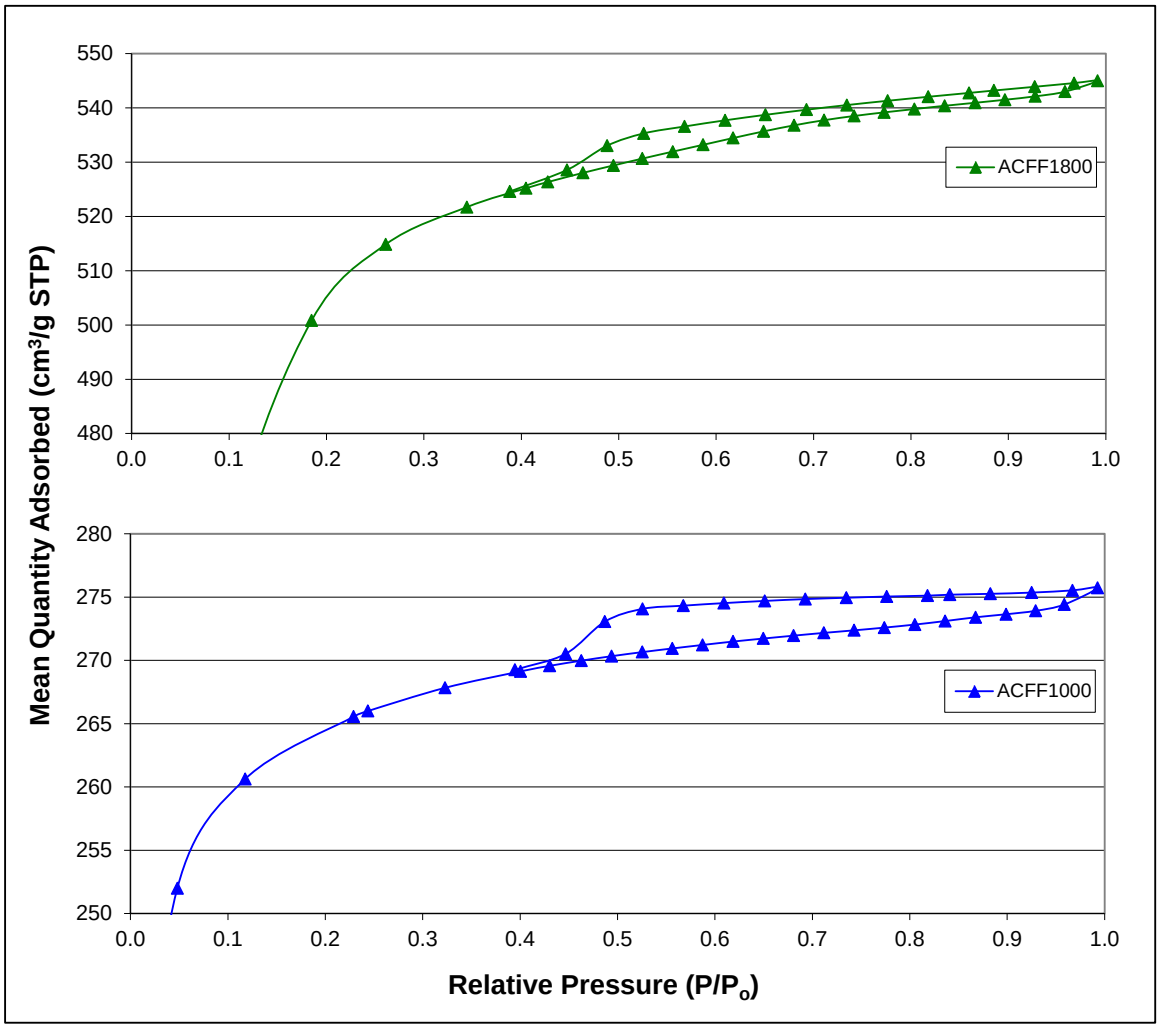


Nitrogen Adsorption Isotherms at 77 K for Different ACF Types from 0.0 – 0.4 Relative Pressure

Generally, the ACFC has a slightly higher nitrogen adsorption than the ACFF with similar surface area, except for the ACFC1000 and ACFF1000 wherein the felt has a higher nitrogen adsorption than the cloth.

Generally, an adsorption isotherm rises as the relative pressure is increased and reversing the procedure, known as desorption, by reducing the relative pressure leads to a retracing of the adsorption curve. However, the adsorption curve of certain adsorbents is not retraced by the desorption curve, resulting to a loop on the isotherm. This phenomenon is known as hysteresis, which is typical of mesoporous and macroporous materials with pores that are likely to have a wide range of sizes and shapes. Hysteresis loops were observed for the isotherms of ACFF1000 and ACFF1800, which are both manufactured by Beijing Resources (see figure). These hysteresis loops are closed in the pressure region near saturation, which shows that these ACF types contain mesopores with an upper size restriction.[44] This unique characteristic may be attributed to the fiber precursor and the activation process used, which are

different from those of the rest of the ACF types, resulting to a different pore structure.

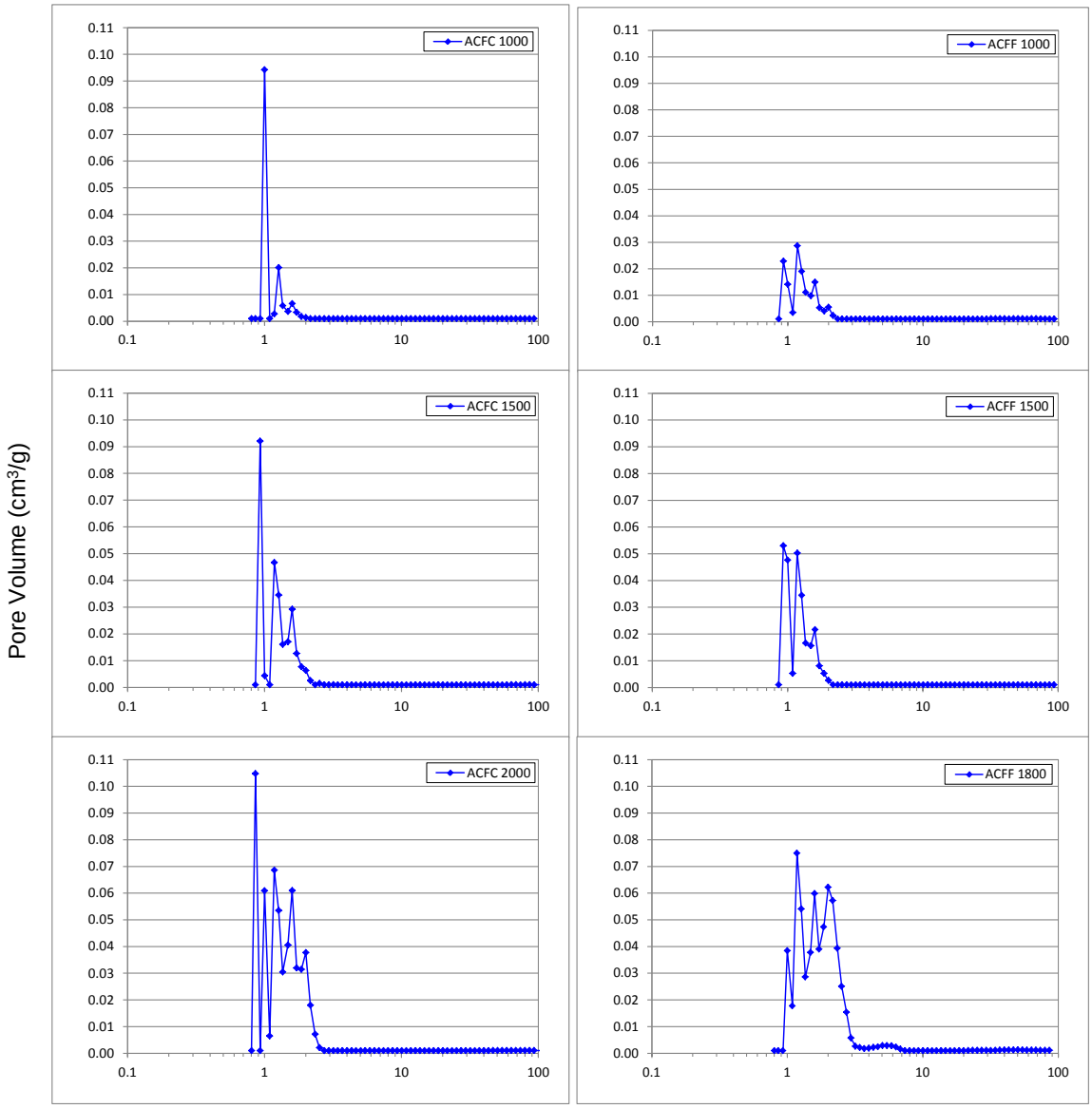


Hysteresis Loops in Nitrogen Adsorption/Desorption Isotherms at 77 K for ACFF1000 and ACFF1800

Pore Size Distribution of ACF Materials

Analyzing the entire pore size distribution of adsorbent is important because the difference in the pore size affects the adsorption capacity for molecules of various shapes and sizes. The pore size distribution is also one of the criteria by which carbon adsorbents are selected for a specific application.

Using the DFT method, the pore size distributions of the ACF samples were determined. As shown in figure, the pore size of all the ACFs is less than 2.5 nm. For ACFC1000, majority of the micropores has a diameter at around 1 nm. ACFC1500 has most of its micropores at around 0.9 nm but also has a secondary peak at around 1.2 nm. In addition to 0.9 nm-micropores, ACFC2000 has smaller peaks from 1 – 2 nm. Thus, for the ACFC types, there is an increasing volume of larger micropores as the surface area increases. ACFF1000 has mainly micropores distributed from 0.9 – 2 nm, and has a lower volume of micropores with 1 nm diameter. ACFF1500 has a higher volume of micropores than ACFF1000 but size range remains the same. ACFF1800 has the highest volume of micropores and mesopores among the ACFF types, and pore size range increased from 0.9 – 3 nm. Comparing by ACF form, the ACFC types have greater volume of micropores with smaller diameters.



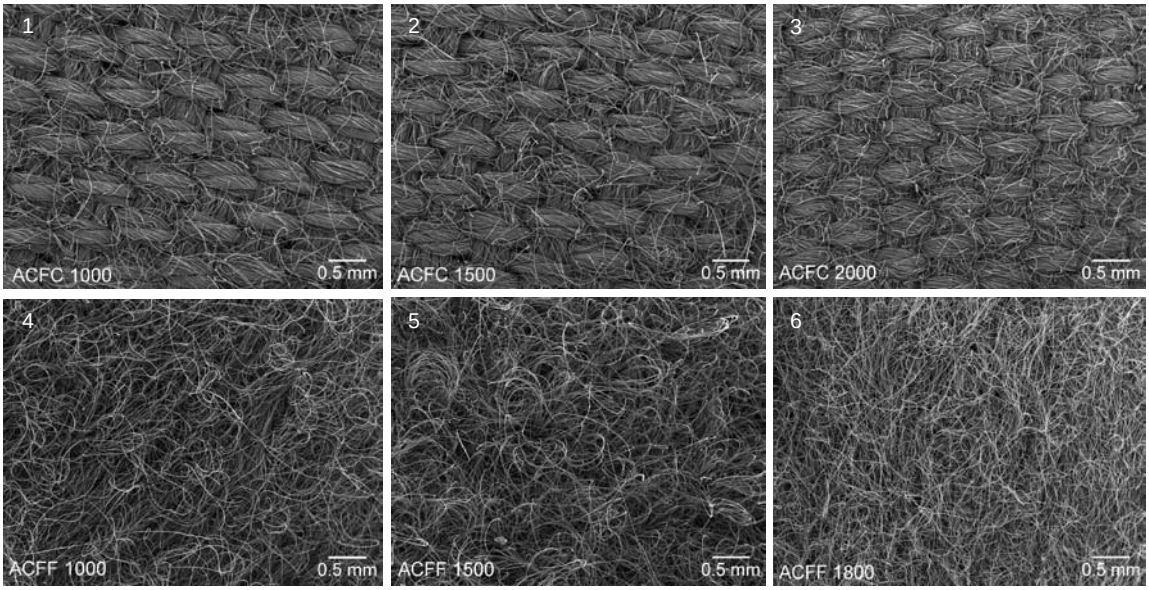
Pore Size Distributions of Different ACF Types

Scanning Electron Microscopy (SEM) Images

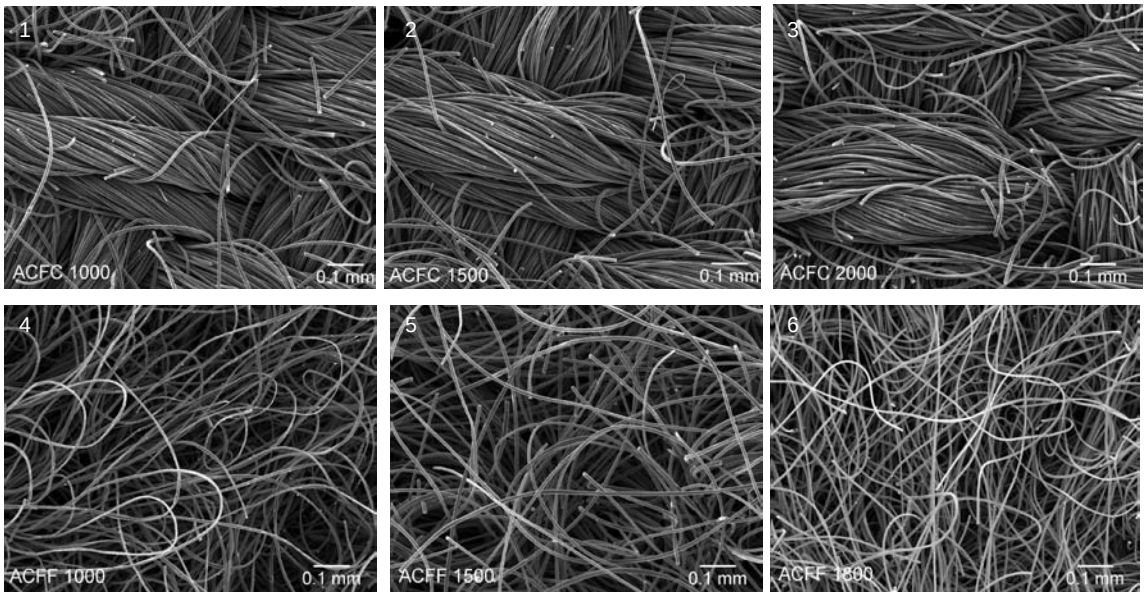
The images obtained from SEM analysis basically illustrated the fibers of the ACF materials at lower magnifications, and the porosity of the materials are higher magnifications. At the lowest SEM magnification (40.8x), it is demonstrated that the inter-fiber structures of the cloth and felt forms are very different. The ACFC is composed of woven yarns of twisted fibers, while the ACFF is composed of non-woven, randomly distributed fibers. Thus, this characteristic gives the ACFC cloth a much denser form compared to the ACFF. With the ACFC, the higher the surface area, the tighter the weaving of the fibers (see figure). With the ACFF, the higher the surface area, the more fibers per area of the material (see figure).

At 5450x magnification, individual fibers are clearly shown but are not zoomed enough to visualize the pores. In this magnification, it is shown that the fibers are 8 – 10 μm in diameter, cylindrical and apparently have smooth surfaces, except for ACFF1000 and ACFF1800, which have ridged surfaces and thinner fibers (5 – 8 μm). It is interesting to note that these 2 ACF types were from the same manufacturer (Beijing) and the other 4 ACF types were from another company (American Kynol).

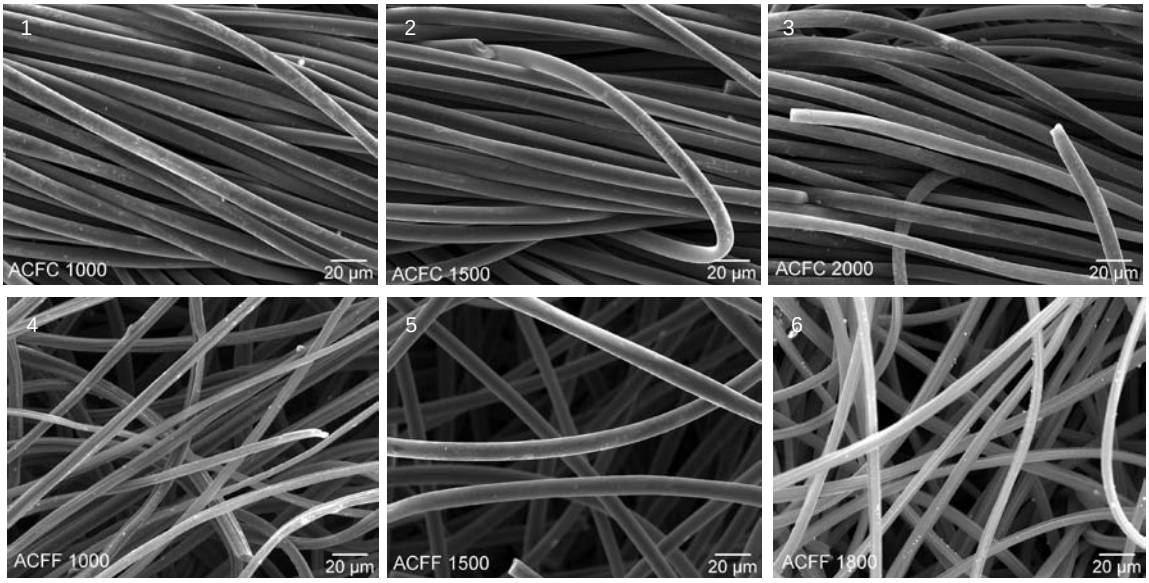
The fiber end of each ACF type was magnified 6000x, as shown in figure. The ACFF1000 and ACFF1800 were also shown to have ridged fibers, with smooth surfaces. The rest of the ACFs with cylindrical fibers have more prominent pores on the fiber surfaces. This is also demonstrated at 100,000x magnification in figure 18F, wherein ACFF1000 and ACFF1800 have smoother surfaces compared to the other ACF types that have obviously more porous surfaces. The surface area of ACFF1000 and ACFF1800 may be attributed to the ridges on the fiber and not on the pores since the fibers are smoother (not very porous) compared to the other ACFs. At these higher magnifications, white spots are observed on some of the fiber surface which may be particle impurities.



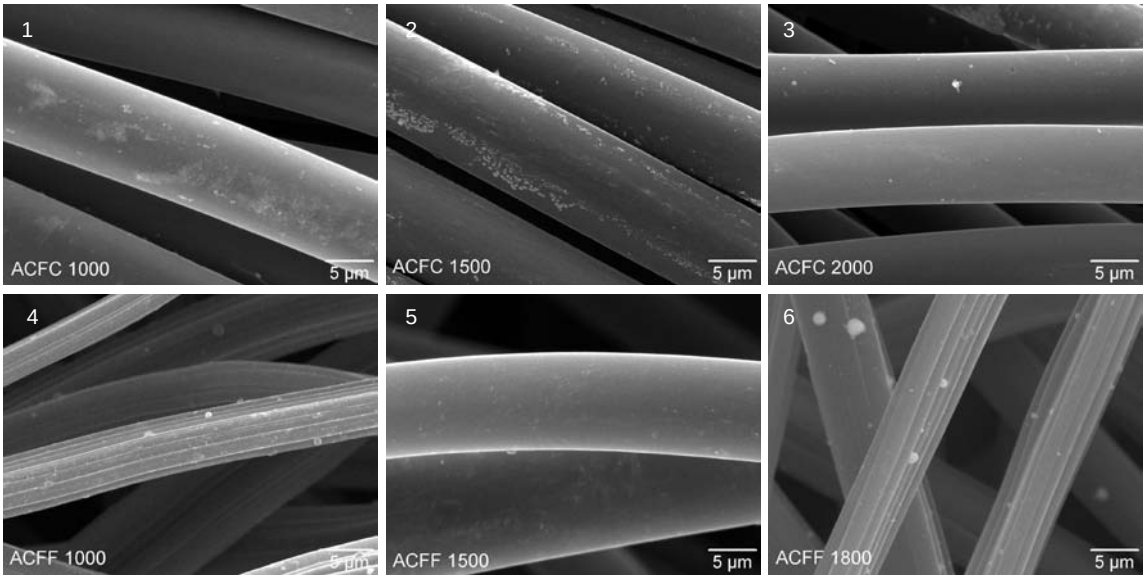
SEM Images of Activated Carbon Fibers at 40.8x Magnification



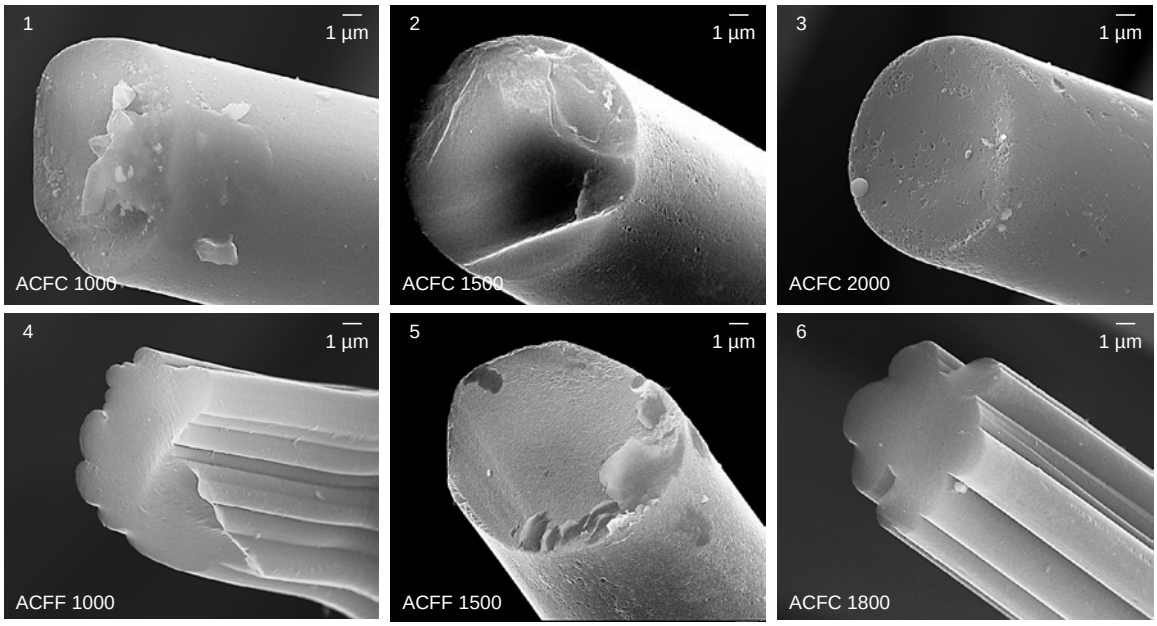
SEM Images of Activated Carbon Fibers at 203x magnification



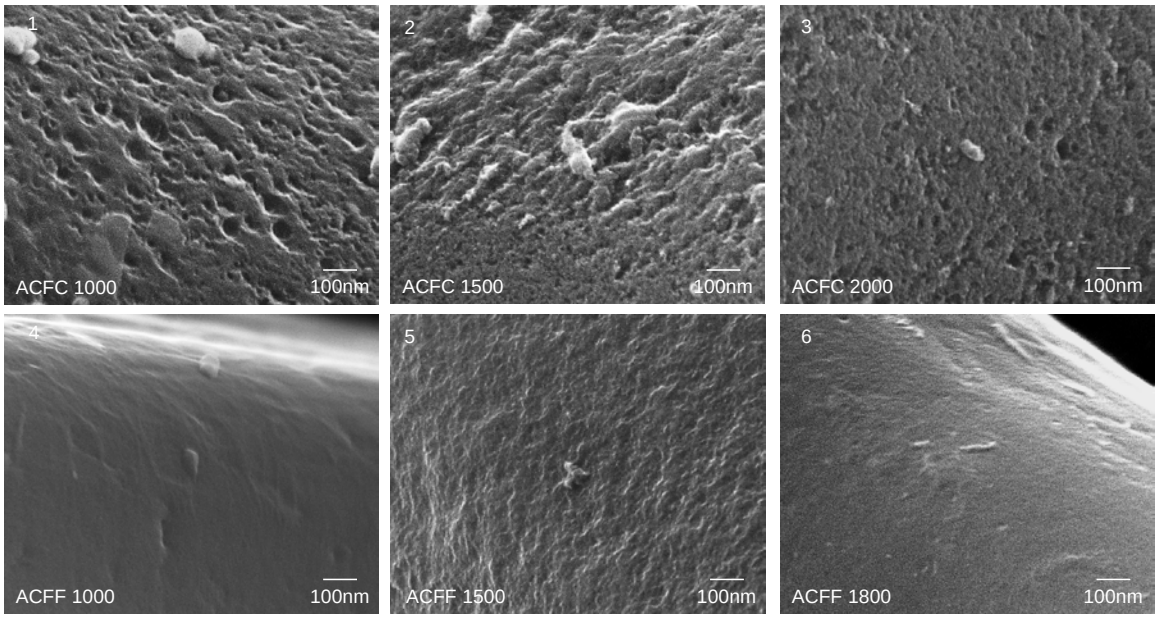
SEM Images of Activated Carbon Fibers at 1010x magnification



SEM Images of Activated Carbon Fibers at 5450x Magnification



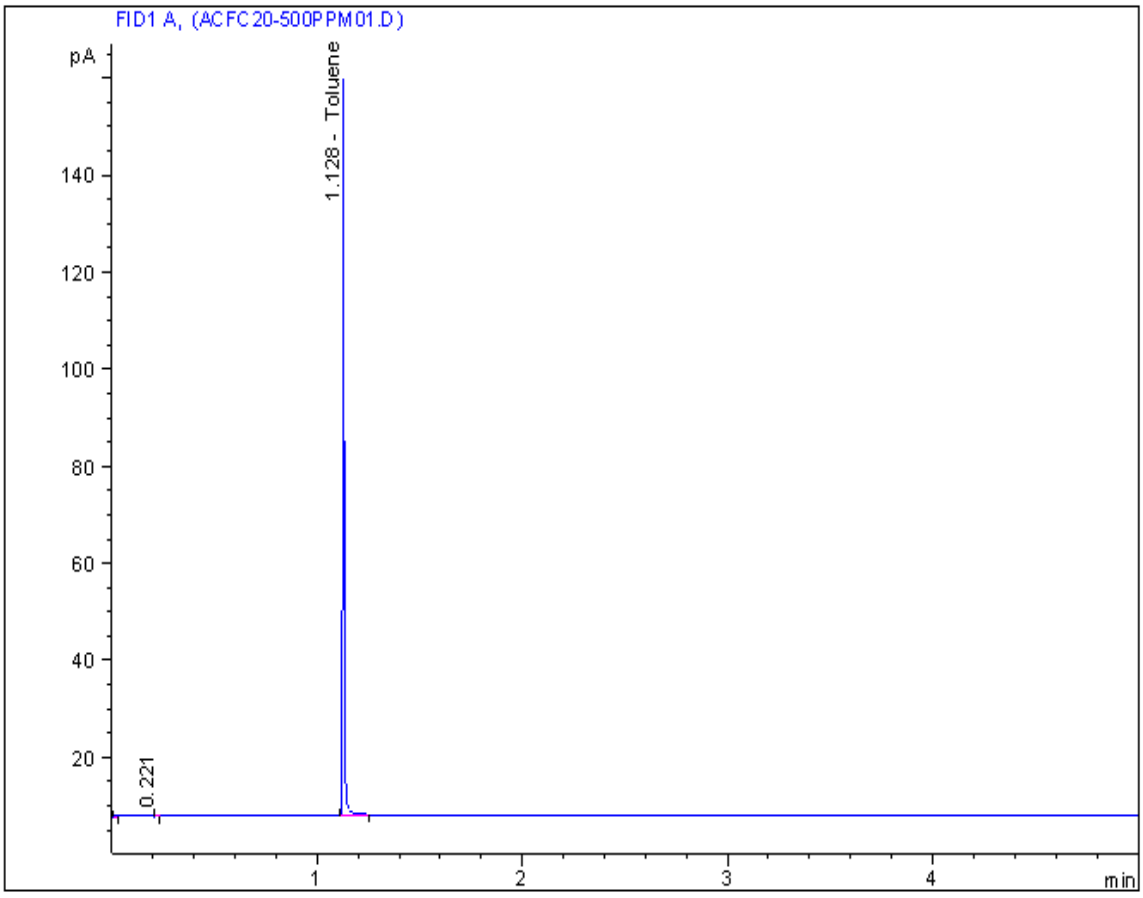
SEM Images of Activated Carbon Fibers at 6000x Magnification



SEM Images of Activated Carbon Fibers at 100,000x Magnification

Breakthrough Determination

Gas chromatograph was utilized to determine the concentration of toluene in the effluent. These toluene concentrations comprise the breakthrough curves needed to determine the adsorption characteristics of interest. Next figure shows a sample chromatogram demonstrating a toluene peak corresponding to 500 ppm. Additionally, the pressure resistance across the ACF samples remained constant from the start of the toluene challenge until breakthrough occurred.



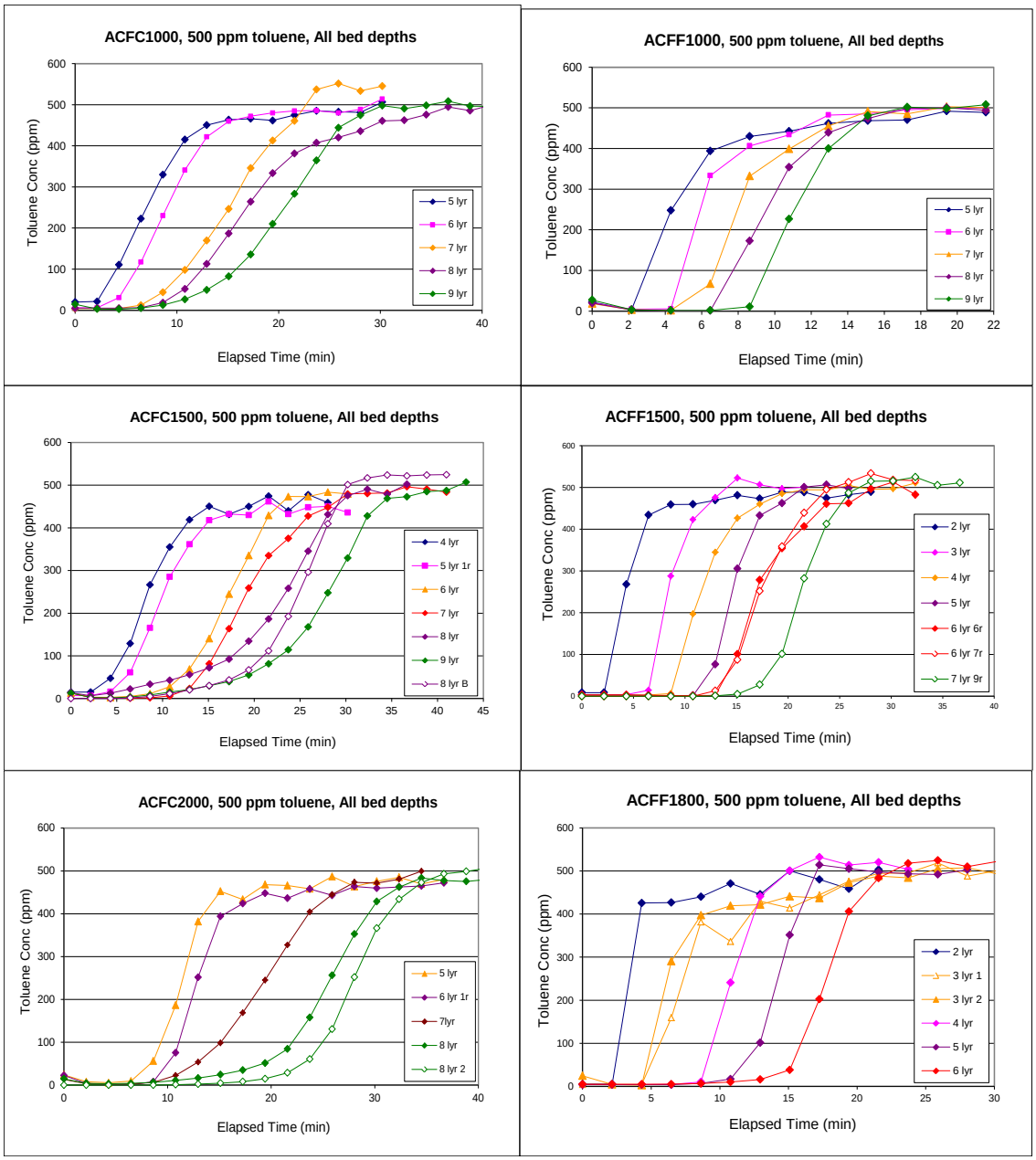
Sample Chromatogram for 500 ppm Toluene

Breakthrough Characteristics by ACF Form

Breakthrough curves of toluene at 6 different concentrations were obtained for the 6 different ACF types at different adsorbent bed depths. Next figure shows sample breakthrough curves of 500 ppm toluene for each ACF type. It is demonstrated that the latest occurrence of breakpoint occurs at the highest adsorbent bed depth for all ACF types at all toluene concentrations. See appendix C for all the breakthrough curves of all ACF types at 6 toluene concentrations.

The breakthrough curves show unique shapes for each ACF form. With ACFC, the increase in toluene concentration occurs slowly at the breakpoint. Such gradual increase is more prominent as the number of adsorbent layers increase. With ACFF, the increase in toluene concentration occurs abruptly from the time the breakpoint starts. However, the increase in concentration slows down as 100% breakthrough is being approached. This trend becomes more prominent as the challenge concentration decreases.

Comparing the cloth and felt with similar surface area, it is shown that it takes a shorter time for toluene to approach near saturation from the start of the breakpoint (C/C_o= +0) with the ACFF compared to the ACFC, showing steeper breakthrough curves for ACFF. This indicates that the ACFC may have a longer service life and, thus, provide longer respiratory protection against toluene, particularly with the greater number of layers (e.g. 7 layers).

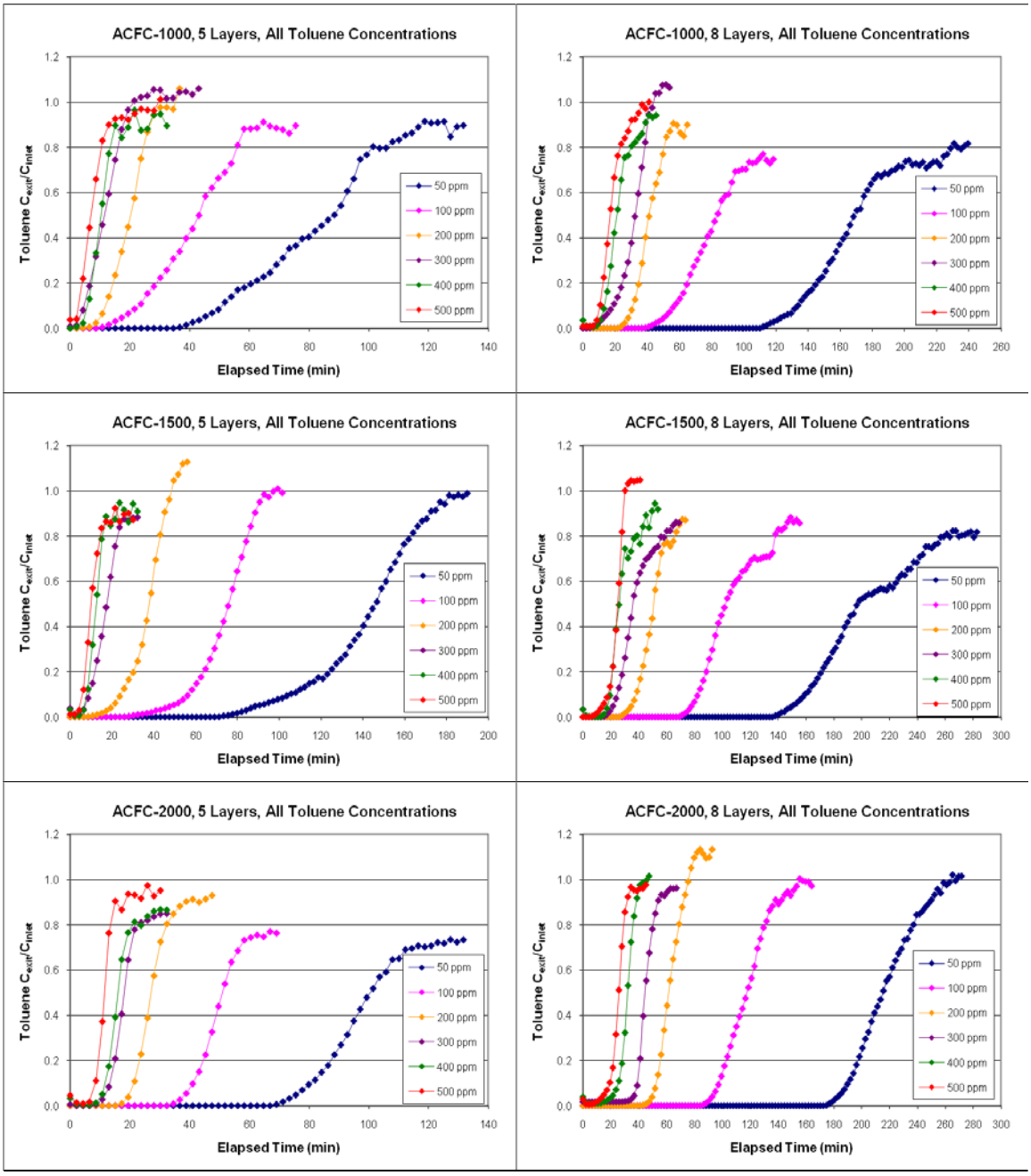


Breakthrough Curves of 500 ppm Toluene for 6 ACF Types

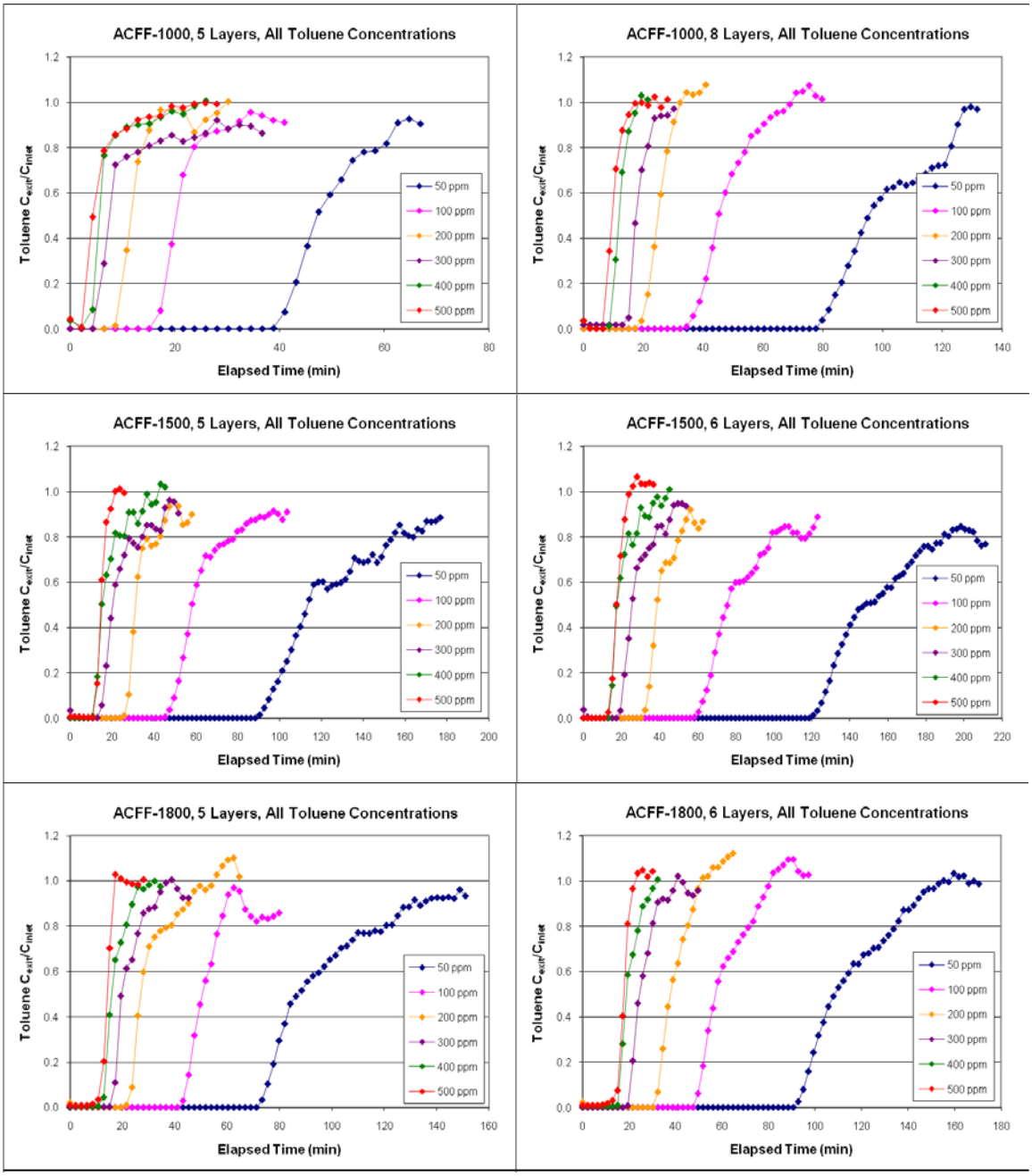
Effect of Toluene Concentration on Breakthrough Characteristics

The effects of the concentration of toluene on the breakthrough characteristics curves were determined at a certain number of ACF layers. Next figures show the experimentally obtained breakthrough curves for different toluene concentrations which are expressed as the ratio of the concentration at the gas exit to the concentration at the gas inlet (C_{exit}/C_{inlet}) for the ACFC and ACFF types, respectively, at 2 different number of layers (bed depth).

As observed for all ACF types, the breakthrough time (e.g. 10% breakthrough) of toluene through a certain adsorbent bed depth increases as the toluene concentration decreases. Such increase in breakthrough time is not linear with the concentration, such that the time increase from 50 to 100 ppm is larger compared to the time increase from 400 to 500 ppm. Moreover, the steepness of the breakthrough curves changes as the toluene concentration increases. The time it takes to reach near saturation from the start of breakthrough (referred to as saturation time in this study) is shorter as the concentration increases. For example, at 5 layers of ACFC 1000, it takes 22 minutes to reach near saturation from breakpoint at 500 ppm toluene, while it takes 80 minutes at 50 ppm toluene. The increase in both the breakthrough and saturation times with the decrease in toluene challenge concentration may be explained in terms of the decreasing amount of toluene molecules entering the pores of the ACF. The saturation of the ACF is therefore delayed and occurs after a longer time period.



Concentration Effects on Breakthrough of Toluene for ACFC Types at 2 Different Adsorbent Bed Depths (Number of Layers)

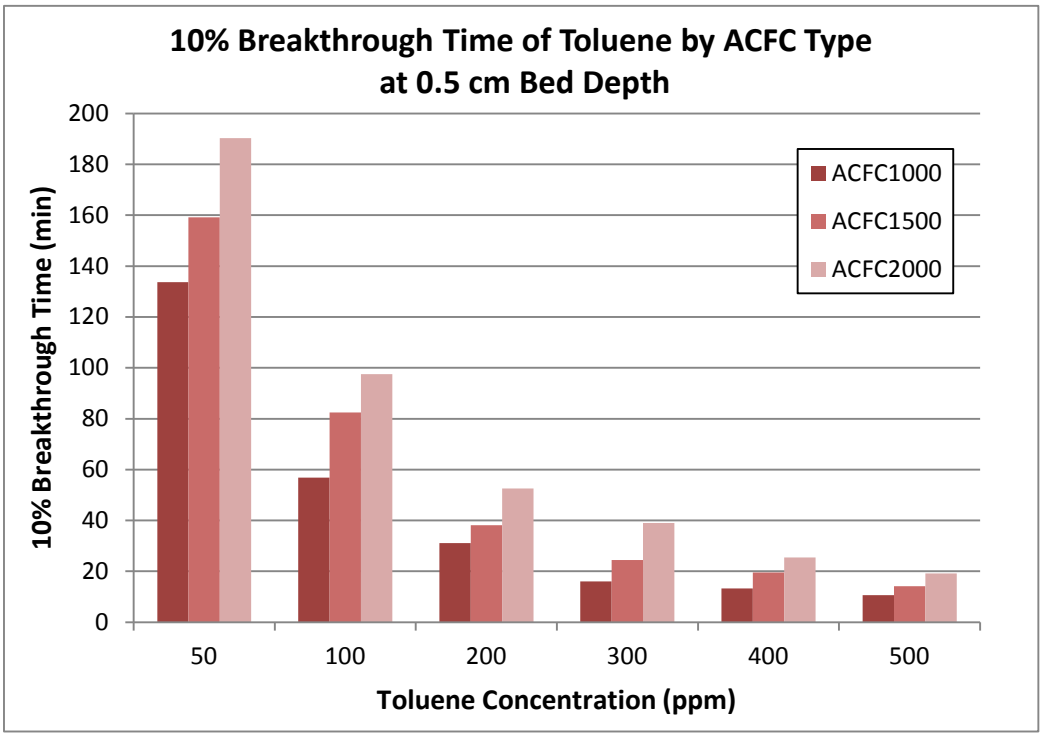


Concentration Effects on Breakthrough of Toluene for ACFF Types at 2 Different Adsorbent Bed Depths (Number of Layers)

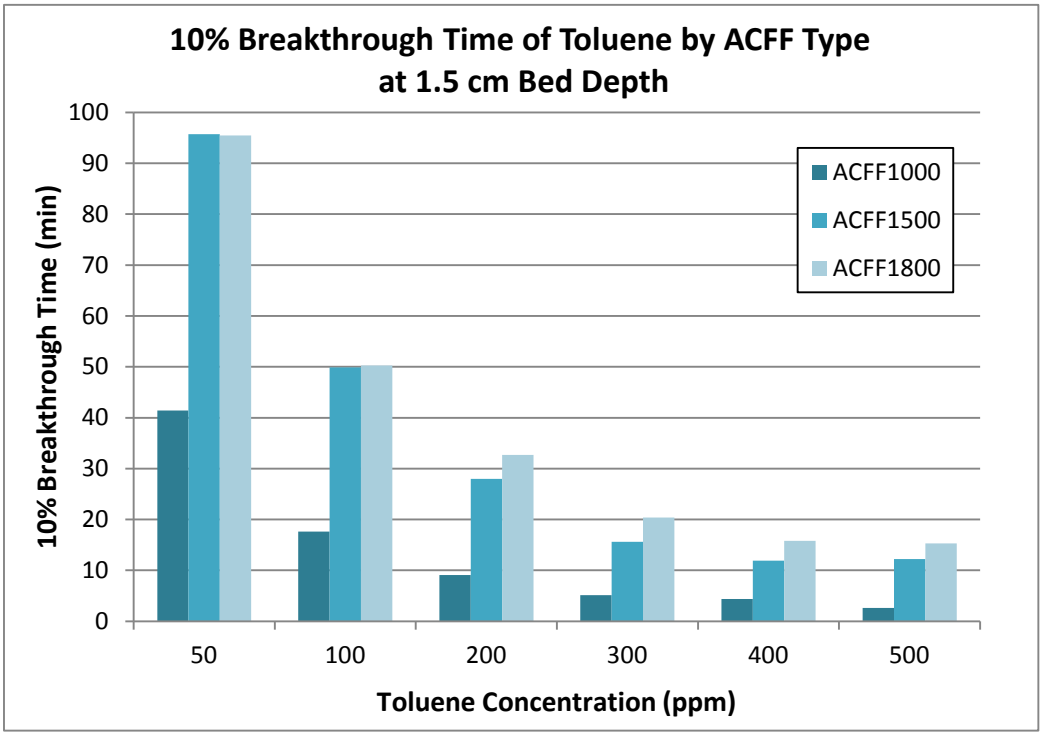
10% Breakthrough Time

The time, in minutes, when 10% of the challenge concentration is breaking through the adsorbent is referred to as 10% breakthrough time. This is the time chosen in this study to determine the critical bed depth for each ACF type.

At the same bed depth, the 10% breakthrough time of certain ACF types were compared amongst each other. The purpose of this is to determine which among the compared ACF would give a longer protection against airborne toluene at the same bed depth and at different toluene concentrations. As shown in figure A, at an adsorbent thickness of 0.5 cm, the ACFCs in a respirator may give protection to the wearer from 10.6 – 19.2 min before 10% breakthrough of 500 ppm toluene occurs, and from 133.7 – 190.3 min for 50 ppm toluene. Moreover, at an adsorbent thickness of 1.5 cm, as shown in figure B, the ACFFs may give protection from 2.6 – 15.3 min before 10% breakthrough of 500 ppm toluene occurs, and from 41.4 – 95.7 min for 50 ppm toluene. For each concentration, the 10% breakthrough time generally increases as the ACF surface area increases. For each ACF type, the 10% breakthrough time decreases as the challenge toluene concentration increases.



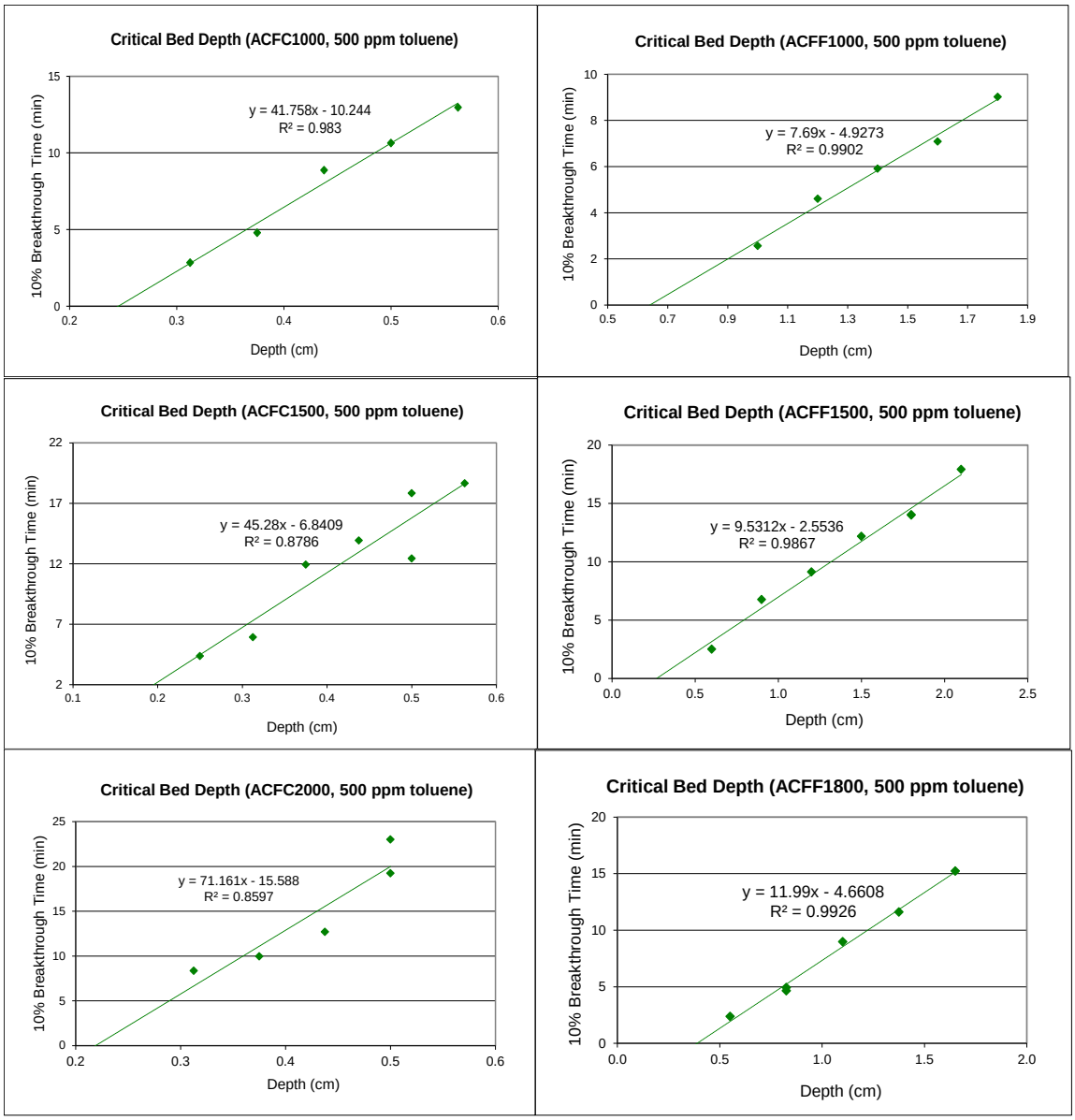
A. ACFC Types at 0.5 cm Bed Depth



B. ACFF Types at 1.5 cm Bed Depth

Critical Bed Depth

Per ACF type and challenge concentration, the 10% breakthrough times (minutes) obtained were plotted against the adsorbent bed depth (cm) to obtain a regression line. Next figure shows sample graphs of the 6 ACF types for determining the critical bed depth at 500 ppm toluene. See Appendix D for the graphs at 6 different toluene concentrations.



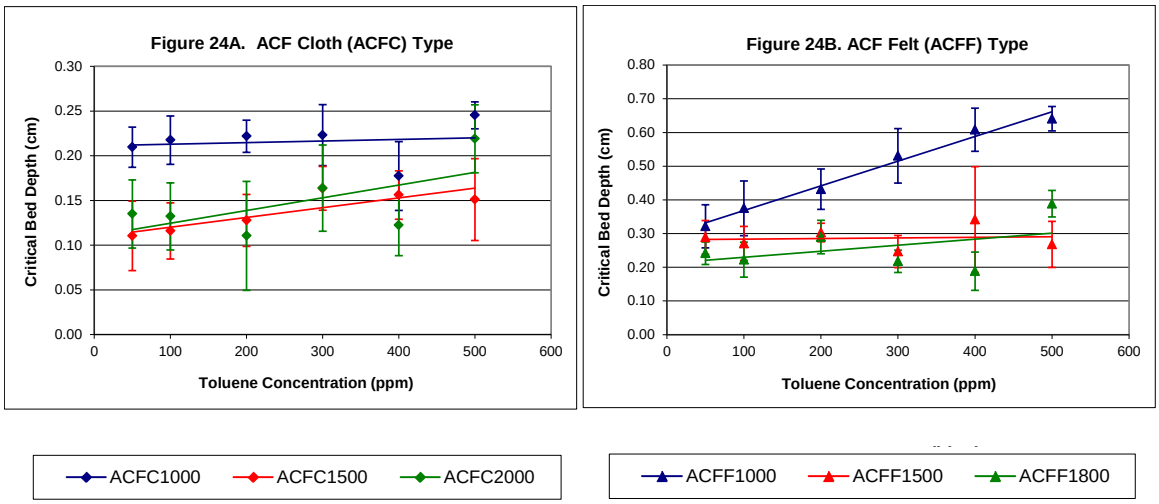
Plots for Determining Critical Bed Depth at 500 ppm Toluene for 6 ACF Types

Next Table shows the critical bed depth of each ACF type for 6 toluene challenge concentrations. Using the SPSS software, the standard error of the critical bed depth, SE_x, was calculated based on the standard error of the estimate, SE_y.

Critical Bed Depth (cm) of ACF Materials by Toluene Concentration (ppm)

ACF Type	Toluene Concentration					
	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
ACFC 1000	0.210 ±0.022	0.218 ±0.027	0.222 ± 0.018	0.223 ± 0.034	0.177 ±0.038	0.245 ±0.015
ACFC 1500	0.110 ±0.039	0.116 ±0.032	0.128 ± 0.029	0.164 ± 0.024	0.156 ±0.027	0.151 ±0.046
ACFC 2000	0.135 ±0.038	0.132 ±0.038	0.111 ± 0.061	0.164 ± 0.048	0.122 ±0.034	0.219 ±0.038
ACFF 1000	0.322 ±0.064	0.375 ±0.081	0.432 ± 0.060	0.531 ± 0.081	0.608 ±0.064	0.641 ±0.036
ACFF 1500	0.288 ±0.050	0.271 ±0.051	0.303 ± 0.027	0.247 ± 0.048	0.342 ±0.157	0.268 ±0.069
ACFF 1800	0.242 ±0.033	0.223 ±0.052	0.290 ± 0.050	0.218 ± 0.033	0.189 ±0.057	0.389 ±0.039

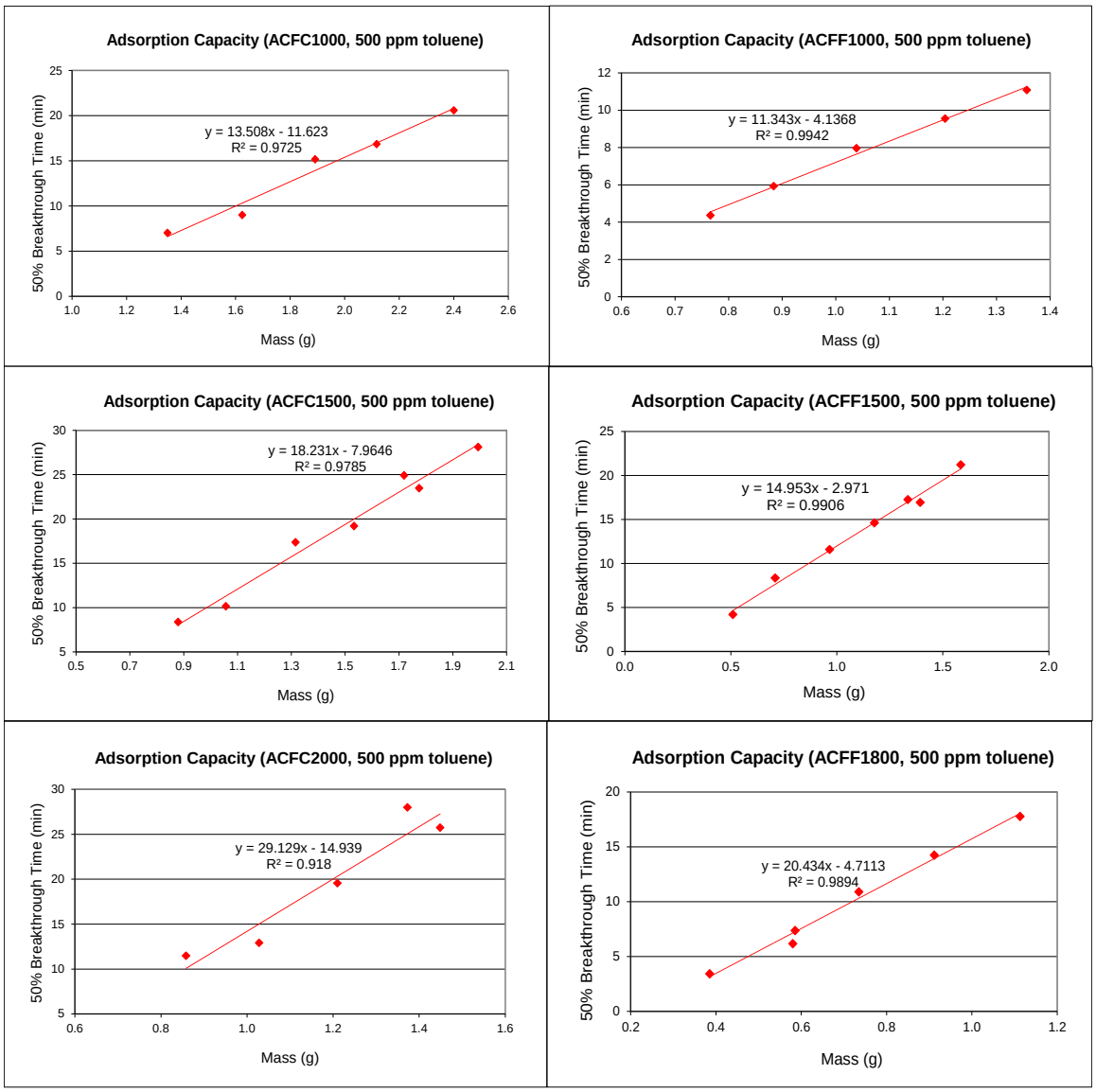
Next Figures show the critical bed depth of the 3 ACFC and 3 ACFF types, respectively, for different toluene challenge concentrations. These graphs show that the ACF with the lowest surface area has the highest critical bed depth, ranging from 0.18 – 0.25 cm for ACFC and 0.32 – 0.64 cm for ACFF. There is also an increasing trend in critical bed depth as the challenge toluene concentration increases, particularly for ACFF1000. Among the ACF types, ACFC 1500 and 2000 (2 highest surface areas) have the lowest critical bed depths for each toluene concentrations, making them good candidates for thinner respirators.



Critical Bed Depth by ACF Type at Different Toluene Concentrations

Adsorption Capacity

Per ACF type and challenge concentration, the 50% breakthrough times (minutes) obtained were plotted against the adsorbent mass (g) to obtain a regression line for the calculation of the adsorption capacity (W_e) of each adsorbent at a certain concentration using the modified Wheeler equation. Next Figure shows sample graphs of the 6 ACF types demonstrating the obtained regression lines at 500 ppm toluene. See Appendix E for the graphs of all ACF types for all toluene challenge concentrations.



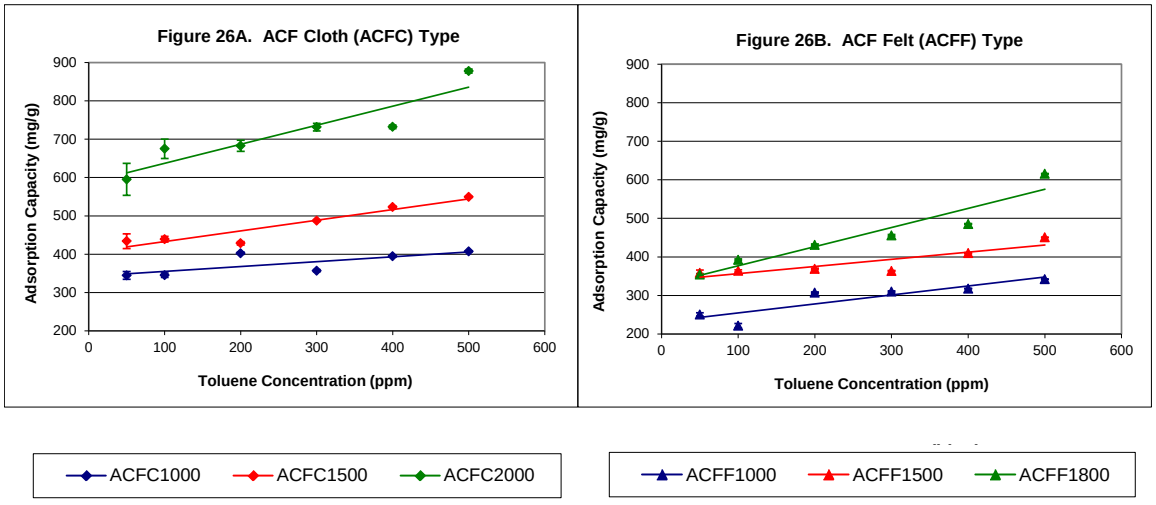
Graph of 50% Breakthrough Time vs ACF Mass at 500 ppm Toluene for 6 ACF Types

Next Table shows the adsorption capacities of each ACF type for 6 toluene challenge concentrations. Using the SPSS software, the standard error of the adsorption capacity, SE_a, (see Appendix F) was determined using the slope of the regression line.

Adsorption Capacity (mg/g) of ACF Materials by Toluene Concentration (ppm)

ACF Type	Toluene Concentration					
	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
ACFC 1000	344.7 ±10.0	345.2 ±5.9	402.6 ±2.7	356.8 ±2.7	394.8 ±2.4	407.1 ±1.3
ACFC 1500	433.9 ±19.3	439.0 ±7.3	428.6 ±4.4	487.6 ±2.2	523.0 ±2.8	549.4 ±1.2
ACFC 2000	595.2 ±41.6	675.0 ±25.4	683.0 ±14.7	731.5 ±10.0	732.2 ±4.7	877.8 ±5.0
ACFF 1000	250.5 ±4.3	221.3 ±5.7	307.1 ±1.9	309.8 ±1.8	317.8 ±0.6	341.8 ±0.5
ACFF 1500	358.3 ±7.7	363.9 ±2.8	368.7 ±2.0	363.7 ±1.2	409.6 ±1.8	450.6 ±0.7
ACFF 1800	354.1 ±2.6	392.5 ±2.1	431.4 ±2.0	455.9 ±2.0	485.4 ±1.0	615.8 ±1.1

Next Figures show the adsorption capacity of the 3 ACFC and 3 ACFF types, respectively, for different toluene challenge concentrations. These graphs show that the adsorption capacity increases as the toluene challenge concentration increases for all of the ACF types. The adsorption capacity also has an increasing trend as the surface area increases for both ACFC and ACFF types. This applies to all toluene concentrations, except for the ACFF types tested at 50 ppm toluene. Comparing the ACFC with the ACFF types, the ACFC generally has higher adsorption capacities compared to the ACFF. Among the ACF types, ACFC 2000 (highest surface area) has the highest adsorption capacity for each toluene concentration.



Adsorption Capacity by ACF Type at Different Toluene Concentrations

Comparison of Adsorption Characteristics

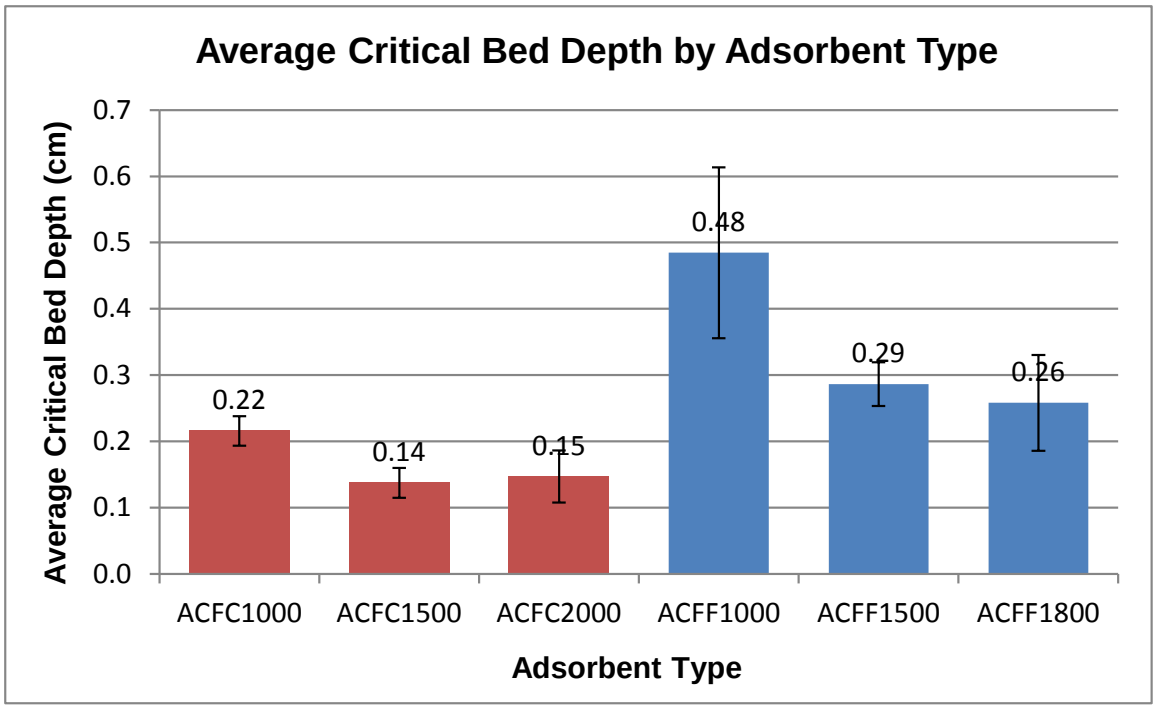
All the ACF types tested in this study were compared according to fiber form, surface area and porosity, critical bed depth and adsorption capacity. Such comparisons were performed using ANCOVA and paired t-test.

Critical Bed Depth

The mean critical bed depth of each ACF typed is calculated by pooling the critical bed depths for all toluene concentrations (n = 6). The results are shown next. The Table shows the mean critical bed depth (pooled for all 6 toluene concentrations) for each ACF type. Next Figure shows that the critical bed depth seems to have a decreasing trend as the ACF surface area increases.

Mean Critical Bed Depth (cm) by ACF Type

ACF Type	Mean	Standard Deviation	N
ACFC1000	.216	.022	6
ACFC1500	.137	.022	6
ACFC2000	.147	.039	6
ACFF1000	.485	.129	6
ACFF1500	.286	.033	6
ACFF1800	.258	.072	6
Total	.255	.132	36



Mean Critical Bed Depth by ACF Type

Under the tests of between-subjects effects, the results showed that the critical bed depths among the 6 ACF types are significantly different ($p = 0.000$, $\alpha = 0.05$). See Appendix G for SPSS output on ANCOVA.

To determine if the form of the ACF influences the critical bed depth, the cloth and felt with similar surface areas were compared against each other using paired t-test. Results showed that there are significant differences in critical bed depth ($p < 0.008$) between the cloth and felt forms with similar surface area (see table).

P-values for Differences in Adsorption Characteristics per ACF Pair with Different Forms and Similar Surface Areas

ACF Pairs	p-value	
	Critical Bed Depth	Adsorption Capacity
ACFC1000/ ACFF1000	0.004	0.001
ACFC1500/ ACFF1500	0.000	0.000
ACFC2000/ ACFF1800	0.004	0.000

To determine if the surface area of the ACF influences the critical bed depth, the cloth or felt forms with different surface areas were compared against

each other using paired t-test. Results showed that the critical bed depth of ACFC1000 (lowest surface area) is significantly different ($p < 0.008$) from ACFC1500 and ACFC2000. However, the critical bed depths of ACFC1500 and ACFC2000 are not significantly different ($p > 0.008$). For ACFF types, only the critical bed depths of ACFF1000 and ACFF1800 are significantly different (see table).

P-values for Differences in Adsorption Characteristics per ACF pair with Same Forms and Different Surface Areas

ACF Pairs	p-value	
	Critical Bed Depth	Adsorption Capacity
ACFC1000/ ACFC1500	0.002	0.002
ACFC1000/ ACFC2000	0.002	0.000
ACFC1500/ ACFC2000	0.536	0.000
ACFF1000/ ACFF1500	0.013	0.001
ACFF1000/ ACFF1800	0.007	0.001
ACFF1500/ ACFF1800	0.467	0.032

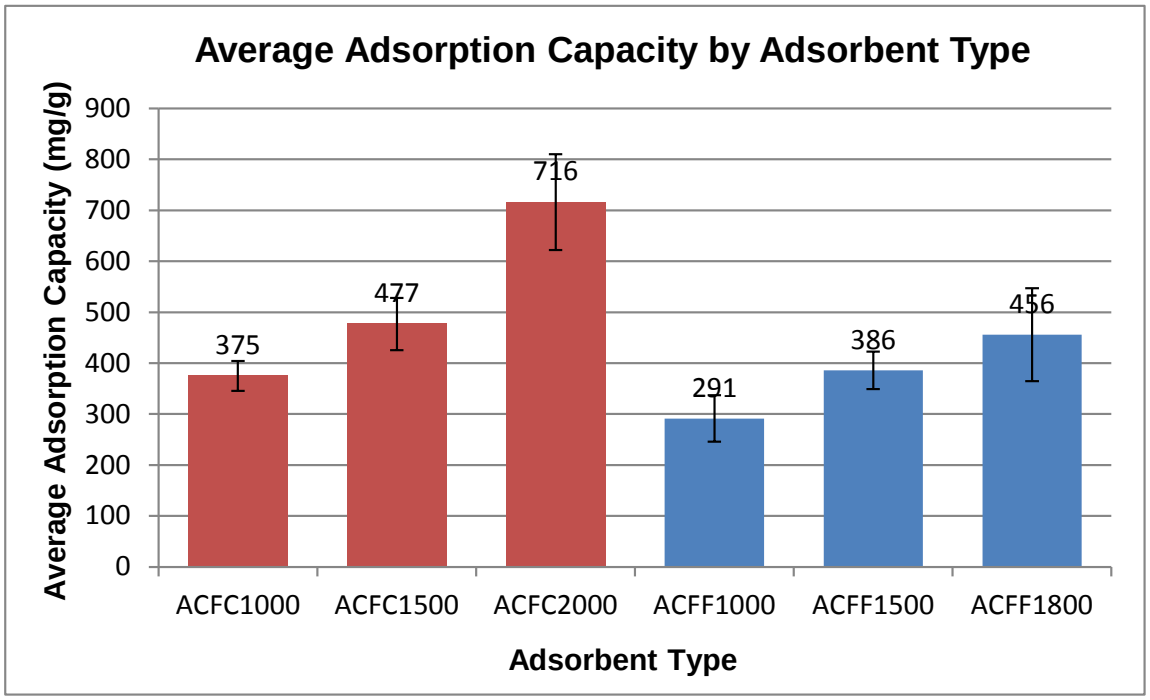
The mean critical bed depth of ACFC in general is 0.167 ± 0.045 and that of ACFF is 0.343 ± 0.132. The difference between the mean critical bed depth of ACFC and ACFF is significant ($p = 0.000$, $\alpha = 0.05$).

Adsorption Capacity

The mean adsorption capacity of each ACF typed is calculated by pooling the adsorption capacities for all toluene concentrations ($n = 6$). The results are shown in the next table and figure. Next Table shows the mean adsorption capacity (pooled for all 6 toluene concentrations) for each ACF type. The Figure shows that the adsorption capacity seems to have an increasing trend as the ACF surface area increases.

Mean Adsorption Capacity (mg/g) by ACF Type

ACF Type	Mean	Std. Deviation	N
ACFC1000	375.2	29.4	6
ACFC1500	476.9	51.2	6
ACFC2000	715.8	93.9	6
ACFF1000	291.4	45.6	6
ACFF1500	385.8	36.8	6
ACFF1800	455.9	91.0	6
Total	450.2	147.1	36



Mean Adsorption Capacity by ACF Type

Under the tests of between-subjects effects, the results showed that the adsorption capacities among the 6 ACF types are significantly different ($p = 0.000$, $\alpha = 0.05$). See Appendix G for SPSS output on ANCOVA.

To determine if the form of the ACF influences the adsorption capacity, the cloth and felt with similar surface areas were compared against each other using paired t-test. The Table shows that there are significant differences in adsorption capacity between the cloth and felt forms with similar surface area ($p < 0.008$).

To determine if the surface area of the ACF influences the adsorption capacity, the cloth or felt forms with different surface areas were compared against each other using paired t-test. Results in the table showed that there are significant differences ($p < 0.008$) in adsorption capacity between all ACFC pairs with different surface areas. For ACFF pairs, only the difference in adsorption capacities between ACFF 1500 and ACFF 1800 (highest surface areas) is

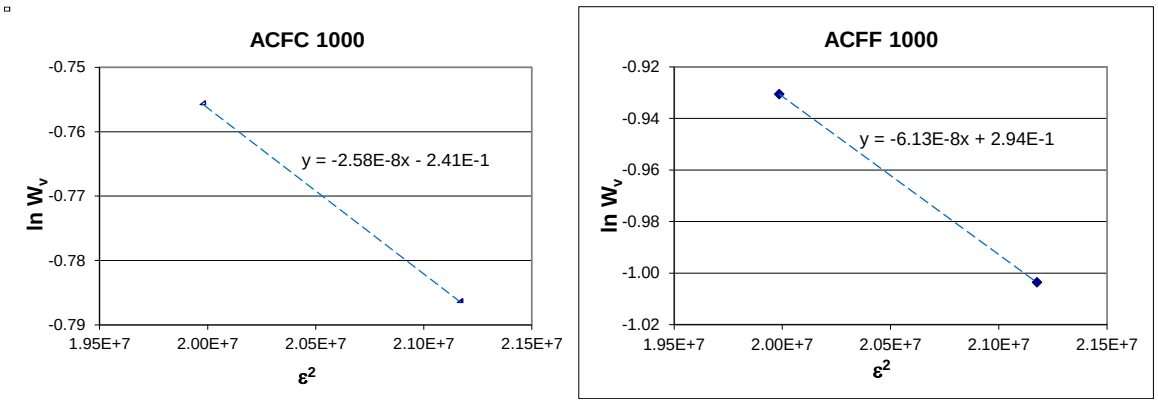
insignificant ($p > 0.008$). See Appendix H for the SPSS data outputs on paired t-test.

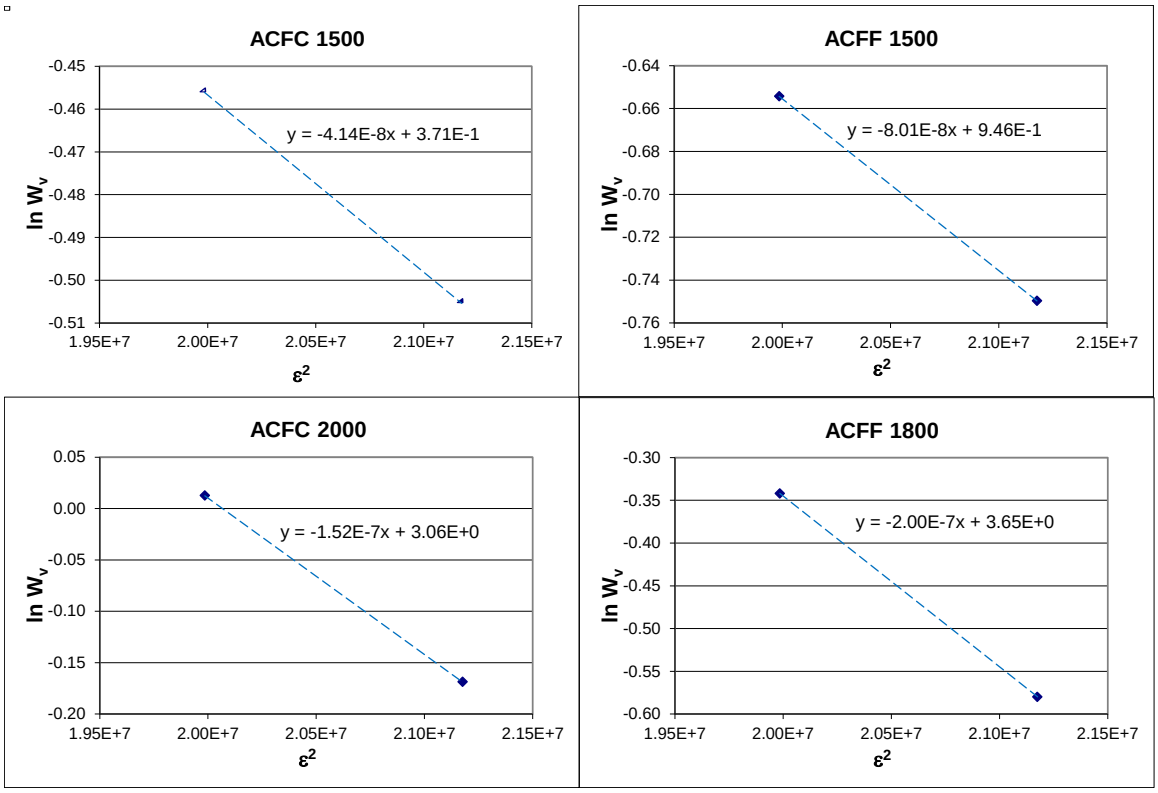
The mean adsorption capacity of ACFC in general is 522.7 ± 158.7 and that of ACFF is 377.7 ± 90.9. There is a significant difference between the mean adsorption capacity of ACFC and ACFF ($p = 0.000$, $\alpha = 0.05$).

Prediction of Adsorption Capacity for Toluene

Using the experimental adsorption capacities of each ACF type for the highest 2 challenge concentrations of toluene (400 and 500 ppm), the adsorption space, W_v, was calculated for each ACF type.

Next Figure shows the graphs of ln W_v plotted against ε^2 and the obtained regression line, from which the maximum adsorption space available, W_o, and the structural constant of the adsorbent, K, were calculated for each ACF type. These parameters are shown in the next table. The values for these constant parameters were used in the D-R equation to predict the adsorption capacity of each ACF type at lower challenge concentrations. For each ACF form, W_o increases as the surface area of the adsorbent increases.





Graphs of ln W_v plotted against ε^2 for Different ACF Types

Constant Parameters for the D-R Equation by ACF Type

ACF Type	Adsorbent Structural Constant, K (M^2/cal^2)	Maximum Adsorption Space, W_o (cm^3/g)
ACFC1000	2.58 E-08	0.786
ACFC1500	4.14 E-08	1.449
ACFC2000	1.52 E-07	21.243
ACFF1000	6.13 E-08	1.342
ACFF1500	8.01 E-08	2.577
ACFF1800	2.00 E-07	38.492

The other parameters used in the D-R equation are as follows:

R – gas constant = 1.987 cal / M °K

T – absolute temperature = 296 °K

p^0 / p – saturated vapor pressure of liquid adsorbate at T °K divided by the equilibrium pressure of the adsorbate vapor at T °K

β – dimensionless affinity coefficient = 1

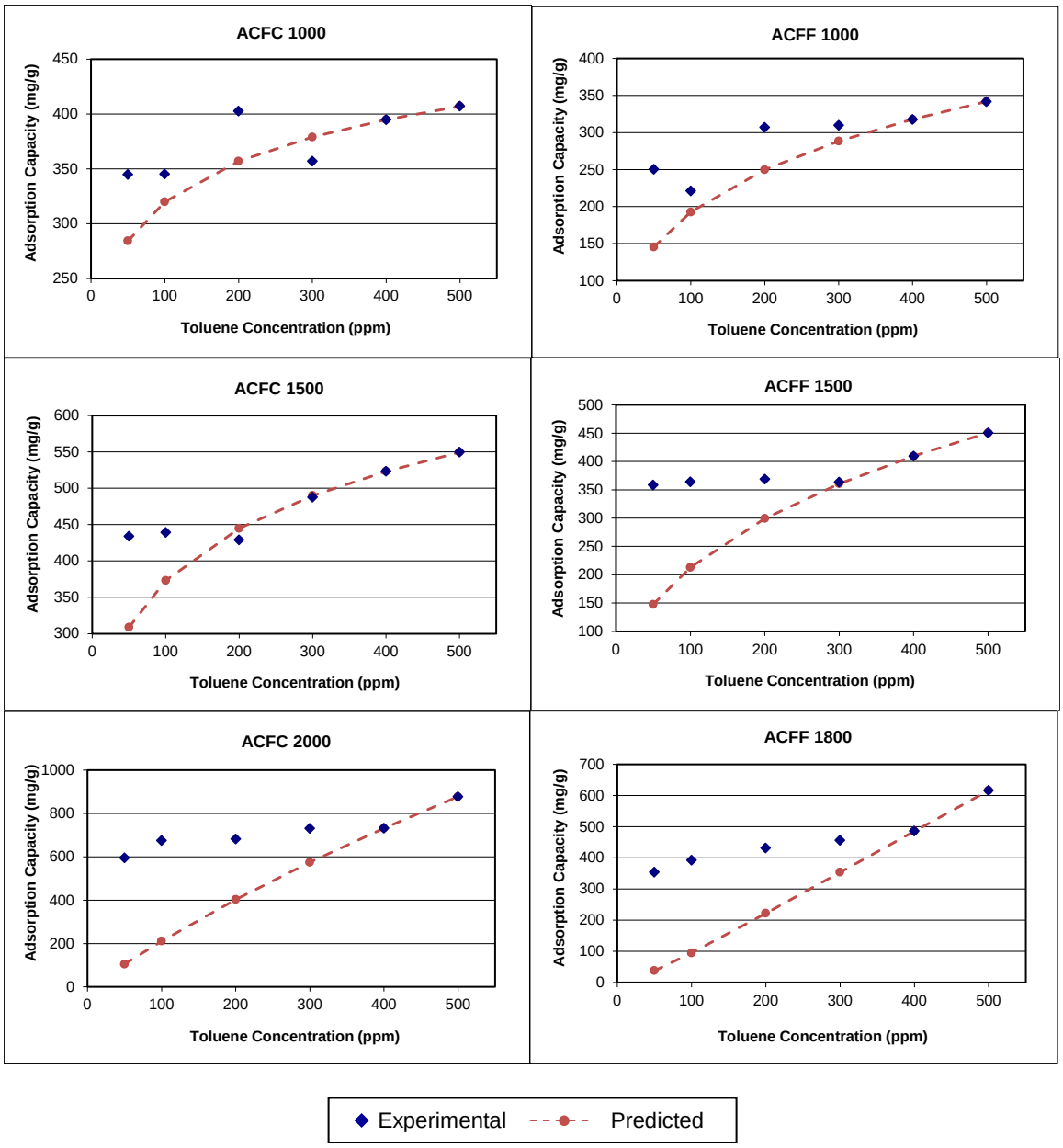
In addition, the characteristic energy of adsorption (E_0) in kJ/mol may provide information about the interaction energies between the molecule and adsorbent. Next Table shows the molecule-adsorbent interaction energies for each ACF type. The ACFC types gave generally higher interaction energies, ranging from 10.72 – 26.06 kJ/mol, than the ACFF types, ranging from 9.36 – 16.90 kJ/mol. A study by Fournel[27] demonstrated similar results. The interaction energy for toluene was 15.3 kJ/mol for the felt and 26.5 kJ/mol for the cloth. It was concluded in this study that the interaction energies were relatively low compared to energies found by differential calorimetry analysis, which may indicate that VOC-fiber interactions are physical, reversible, and may allow a successful regeneration of the adsorbents.

Molecule-Adsorbent Interaction Energies (E_0) Between Toluene and ACF Types

ACF Type	E_0 (kJ/mol)
ACFC1000	26.06
ACFC1500	20.57
ACFC2000	10.72
ACFF1000	16.90
ACFF1500	14.78
ACFF1800	9.36

Comparison between Experimental and Predicted Adsorption Capacities

For the assessment of the capability of the Dubinin-Radushkevitch (D-R) adsorption equation in predicting the adsorption capacity of ACF for toluene, the experimental and predicted adsorption capacities for all challenge concentrations per ACF type were plotted together for comparison (shown in the Figure). Based on this, there seems to be an underestimation of adsorption capacities, which increases as the challenge concentration decreases. Moreover, such underestimation is greater in ACF types with the highest surface areas (e.g. ACFC2000 and ACFF1800).



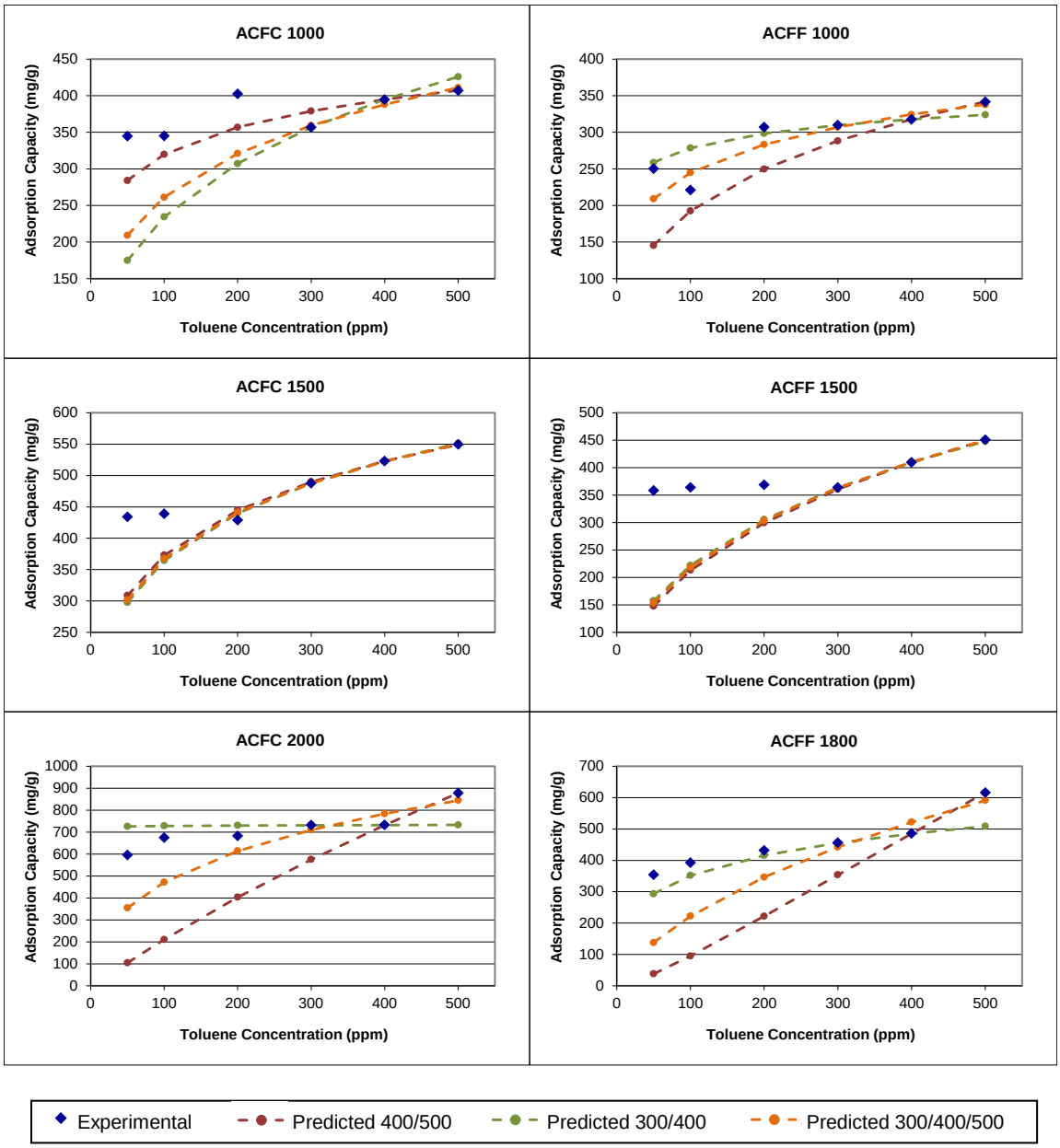
Comparison of Experimental and Predicted Adsorption Capacities by ACF Type (Using 400 and 500 ppm Data for Adsorption Capacity Prediction)

The data points from toluene challenge concentrations used for the prediction of lower concentrations were changed to determine any effect in the degree of underestimation of the adsorption capacities. Changing the data points used for predictions was done in two ways: 1) using two lower toluene concentrations, and 2) increasing the number of toluene concentrations used as data points. The second set of predicted adsorption capacities was calculated

using 300 and 400 ppm toluene concentration data points to determine if using two lower toluene concentrations will improve the prediction of adsorption capacities at lower concentrations. The third set of predicted adsorption capacities was calculated using 300, 400 and 500 ppm toluene concentration data points to determine if increasing the number of data points will improve such prediction. The experimental data, the first set (400 and 500 ppm), the 2nd set (300 and 400 ppm) and the third set (300, 400 and 500 ppm) of predicted adsorption capacities per ACF type were plotted together for comparison as shown in the next Figure.

The graphs show the different effects of lowering the challenge concentration data points used for prediction. For ACFC2000, ACFF1000 and ACFF1800, the change in concentration points used improved the prediction of the adsorption capacities for lower toluene concentrations. Moreover, lowering the concentration points used has no effect on the adsorption capacity prediction for ACFC1500 and ACFF1500, while it increased the underestimation of the adsorption capacities for lower toluene concentrations.

Moreover, the graphs also show the effects of increasing the number of data points used for prediction. Compared to using only 400 and 500 ppm as data points, using three data points improved the prediction of adsorption capacities at lower toluene concentrations for ACFF1000, ACFC2000 and ACFF1800. However, increasing the number of data points used has no effect on the adsorption capacity prediction for ACFC1500 and ACFF1500, while has increased the underestimation of the adsorption capacities for lower toluene concentrations. The types of changes in the prediction (i.e. no change, increase or decrease in estimation) for specific ACF types were the same as compared to those when the concentration data points used for prediction were lowered. However, the use of lower concentration data points resulted to better predictions when compared to the use of more concentration data points.



Comparison of Experimental and 3 Sets of Predicted Adsorption Capacities by ACF Type

The differences in percentage between the experimental and the two sets of predicted adsorption capacities were calculated and summarized in the next table. For the 1st set of predicted adsorption capacities using 400 and 500 ppm data points, the % differences in adsorption capacity for ACFC1000, ACFF1000 and ACFC1500 (generally the ACF with the lowest surface) are relatively small, reaching up to 18, 42 and 29%, respectively. Moreover, the % differences in adsorption capacity for ACFF1500, ACFC2000 and ACFF1800 (some of the ACF with the highest surface area) are quite high, reaching up to 59, 82 and 89%, respectively. For the 2nd set of predicted adsorption capacities, the % differences in adsorption capacity for ACFC2000, ACFF1000 and ACFF1800 decreased down to 22%, 3% and 17% from 82%, 42% and 89% based on the 1st set of predicted adsorption capacities, respectively. For the 3rd set of predicted adsorption capacities, the % differences in adsorption capacity for ACFC2000, ACFF1000 and ACFF1800 decreased down to 40%, 17% and 61% based on the 1st set of predicted adsorption capacities, respectively. The % differences for ACFC1500 and ACFF1500 between the 3 sets of predicted adsorption capacities are similar. For ACFC1500, the % differences are 29% and 31% and 31% for the 1st, 2nd and 3rd respectively. For ACFF1500, the % differences are 59%, 56% and 57% for the 1st, 2nd and 3rd respectively.

Experimental and 3 Sets of Predicted Adsorption Capacities of Different ACF Types for Toluene

Challenge Conc (ppm)	Experimental	400 and 500 ppm		300 and 400 ppm		300, 400 and 500 ppm	
		Predicted	%Difference	Predicted	%Difference	Predicted	%Difference
			ACFC1000				
50	344.7	284.2	17.54	174.9	49.25	209.4	39.25
100	345.2	319.8	7.34	234.4	32.1	261.4	24.28
200	402.6	356.9	11.35	307.4	23.63	321	20.25
300	356.8	379	6.22	356.8	0	359.4	0.74
400	394.8	394.8	0	394.8	0	388.1	1.7
500	407.1	407.1	0	425.9	4.64	411.1	0.98
			ACFC1500				
50	433.9	308.6	28.88	297.5	31.43	301.6	30.5
100	439	373	15.03	364.4	17	367.4	16.31
200	428.6	444.7	3.75	439.8	2.6	441.2	2.93
300	487.6	489.8	0.45	487.6	0	487.8	0.06
400	523	523	0	523	0	522.3	0.13
500	549.4	549.4	0	551.3	0.34	549.8	0.07
			ACFC2000				
50	595.2	105	82.35	726	21.97	354.7	40.4
100	675	211	68.73	728.2	7.88	471.7	30.12
200	683	403.2	40.96	730.3	6.93	614.4	10.03
300	731.5	575.1	21.37	731.5	0	710.4	2.89
400	732.2	732.2	0	732.2	0	784	7.07
500	877.8	877.8	0	732.8	16.52	844.2	3.82
			ACFF1000				
50	250.5	145.5	41.94	258.8	3.32	209.1	16.54
100	221.3	192.6	12.96	278.6	25.91	244.8	10.62
200	307.1	249.9	18.62	298.4	2.85	283.4	7.73
300	309.8	288.3	6.92	309.8	0	307.1	0.87
400	317.8	317.8	0	317.8	0	324.3	2.06
500	341.8	341.8	0	323.9	5.24	337.9	1.16
			ACFF1500				
50	358.3	147.5	58.84	157.4	56.08	153.6	57.12
100	363.9	212.9	41.48	222	39	218.7	39.88
200	368.7	299.3	18.84	305.3	17.2	303.5	17.68
300	363.7	360.7	0.8	363.7	0	363.3	0.1
400	409.6	409.6	0	409.6	0	410.6	0.23
500	450.6	450.6	0	447.9	0.6	450	0.13
			ACFF1800				
50	354.1	38	89.27	293.3	17.17	137.6	61.15
100	392.5	94.9	75.82	351.5	10.45	222.1	43.41
200	431.4	221.9	48.56	415.8	3.61	346.4	19.7
300	455.9	353.6	22.44	455.9	0	442.1	3.05
400	485.4	485.4	0	485.4	0	521.8	7.48
500	615.8	615.8	0	508.8	17.37	590.9	4.04

Discussion

Respiratory Protection by ACF Types Based on Breakthrough Characteristics

The extent of respiratory protection that the different ACF types may provide against can be described based on the characteristics of their breakthrough curves. The increase in both the breakthrough and saturation times with the decrease in toluene challenge concentration suggests a longer service life for ACF at lower toluene concentrations. At 50 ppm, respiratory protection against toluene may be provided by 5 layers of ACFC for 40 – 70 min, and 5 layers of ACFF for 40 – 90 min until breakthrough starts. At this number of layers or less, the ACF may be used for short-term protection in performing quick tasks. Protection against toluene at high concentrations may last only for a few minutes. At 300 – 500 ppm toluene, 5 layers of ACFC may provide protection for 2 – 8 min and 5 layers of ACFF for 2 – 14 min. Thus, some of these ACF types may be used for emergency purposes, such as escaping from an area with high-volume spills resulting to high ambient concentration of toluene. Similar results on the effect of influent concentration on the breakthrough characteristics of toluene for ACF were found by Das et al in 2004. At a certain adsorbent mass, bed temperature and flow rate, the breakthrough curve becomes steeper as the toluene challenge concentration increases from 2,000 to 10,000 ppm, which is demonstrated by the decrease in total adsorption time from 80 to 40 min for 2 ACF types. Therefore, in a safety standpoint, the ACF is indicated to be more suitable for respiratory protection against toluene at lower ambient concentrations.

Comparing the cloth and felt with similar surface area, it is shown that it takes a shorter time for toluene to approach near saturation from the start of the breakpoint (C/C_o= +0) with the ACFF compared to the ACFC, as demonstrated by the steeper slope of the breakthrough curves for ACFF. However, at near saturation (i.e. 80% breakthrough), the toluene concentration increases gradually to 100% breakthrough after such an abrupt rise from breakpoint. This

characteristic may be due to the difference in density of the ACF forms. As shown in the SEM images of the ACF at lower magnifications (40.8x to 1010x), the ACFC has tightly-woven fibers and are denser than the ACFF, which has loosely packed fibers that are distributed randomly. Because of the ACFF's less dense form, toluene molecules easily pass through the entire thickness of the ACFF bed, as shown in the abrupt rise of effluent concentration at the breakpoint. However, the first ACF layers are not yet saturated and it takes times for the toluene molecules to look for the rest of the available adsorption sites, as demonstrated by the slow increase of concentration near saturation. On the other hand, the effluent concentration increases gradually with time in the case of the ACFC types at all toluene challenge concentrations, implying a larger mass transfer resistance. This trend may be due to the ACFC's denser form, making toluene molecules more difficult to pass through the entire thickness of the ACFC bed. Based on its longer breakthrough times and delayed adsorbent saturation, the ACFC may have a longer service life and, thus, provide better respiratory protection against toluene.

Surface Characterization of ACF

All the ACF types were demonstrated to be generally composed on micropores based on the nitrogen adsorption isotherm type (Type I), the percentage of micropores by area (ranging from 56.0 – 94.2%) and by volume (ranging from 49.2 – 92.0%), the average pore size (ranging from 1.67 – 1.84 nm) and the pore size distribution (most pores have width less than 2 nm). However, ACFF1800 was also shown to have some mesopores ranging from 2 – 3 nm based on the pore size distribution and the presence of hysteresis on the nitrogen isotherm. The microporosity of the ACF was thought to be responsible for the adsorption of adsorbates at low concentrations and, thus, making the ACF suitable for capturing toluene at realistic ambient concentrations.

Based on the pore size distribution and SEM images, the surface area of the ACF materials may have been increased by two ways: 1) increasing the density of the material, and 2) increasing the degree of activation. First, the SEM images showed the density of the ACF, and the morphology and organization of

the fibers. Per ACF form, the surface area was apparently increased by increasing the density of the ACF, which is the fiber mass per volume. This was done by making the weaving of fibers tighter for the ACFC and making the fiber more packed for the ACFF. Secondly, increasing the degree of activation may have also resulted to increased surface area, as well as pore volume. The increased activation duration may be evidenced by the widening of the micropores as shown in the pore size distribution, particularly of the ACFC types. The size range of the micropores increased while the volume of the bigger micropores also increased. This phenomenon has also been shown in several studies, wherein as the degree of activation is increased, the surface area increases. Specifically, a study by Tanada et al has shown that the ACF that has received the strongest activation has the highest specific surface area and the largest pore volume, but the lesser the pore volume of micropores. In addition, a study by Foster that the duration of activation acts to enlarge the micropores shifting the distribution of pores to higher pore sizes.

Increasing the surface area of the ACFC types apparently increases the total pore volume, micropore volume and micropore area, but decreases the percentage of micropores by area and volume. This decrease in micropore percentage may be attributed to the widening of pores resulting to the formation of some mesopores due to increased degree of activation. This trend was observed in ACFC forms because several factors are controlled for these ACF forms, including fiber precursor, carbonization and activation process, since they came from a common manufacturer. On the other hand, this trend is not observed in ACFF because they came from 2 manufacturing sources and, thus, many factors are not controlled among these ACF forms.

Influence of ACF Form and Surface Area on Critical Bed Depth

Critical bed depth is defined in this study as the minimum bed depth of the adsorbent required to reduce the concentration of toluene by 90%. This bed depth is required to prevent immediate breakthrough of toluene at the start of the challenge. The lower the critical bed depth, the better the adsorbent because it

takes a smaller depth of the material to adsorb a certain amount of chemical, and thus may make a thinner respirator.

Regardless of form, the ACF with the lowest surface area has the highest critical bed depth, which is significantly different from those of ACF with the highest surface area. This can be explained by the amount of available adsorption sites at a given ACF thickness, which is evidently less in low-surface area ACFs. Thus, ACFC1000 and ACFF1000 need more material to adsorb a particular amount of toluene. Per form, the two (2) ACFs with the highest surface areas (ACFC1500 vs ACFC2000 and ACFF1500 vs ACFF1800) do not have significantly different mean critical bed depths. It is apparent that the critical bed depth is dependent on the surface area only to a certain extent. A low-surface area ACF has a higher critical bed depth compared to a high-surface area ACF. However, at relatively high surface areas, there seems to be a level wherein the surface area is not very significant in decreasing the critical bed depth. Therefore, at this point, surface area alone may not predict the trend on critical bed depth but other factors may have come into play, such as the percentage of micropores and micropore width in the adsorbent. On the other hand, the critical bed depth was shown to increase as the challenge toluene concentration increases, which is more pronounced with ACFF1000. This trend may be explained by the amount of material required to adsorb a certain amount of toluene. At higher concentration, more ACF material is needed to adsorb more toluene molecules present in the atmosphere.

The ACFC has a lower critical bed depth compared to that of the ACFF with similar surface area per toluene concentration. When pooled at all concentrations, the mean critical bed depth of ACFC is significantly lower ($p < 0.008$) than that of the ACFF counterpart. In general, ACFC still has a significantly lower CBD compared to ACFF. This may be attributed to the fact that an ACFC layer is thinner and denser than an ACFF layer, which is more spongy in nature. As ACFF is thicker than its ACFC counterpart at similar surface area and weight, its density is lower than that of the ACFC. Thus, ACFC has more mass per bed depth, which entails more fibers and more surface area

for adsorption. The critical bed depth, therefore, depends on the physical form of the ACF and is mainly affected by the density and thickness of the material.

Based on the critical bed depth, the ACFC1500 and ACFC2000 are the best adsorbents because they have the smallest critical bed depths for each toluene concentration, making them good candidates for the development of thinner respirators.

Influence of ACF Form and Surface Area on Adsorption Capacity

Adsorption capacity is the maximum amount of substance adsorbed by a material per unit mass. The higher the adsorption capacity, the better the adsorbent is because it captures more chemicals at a certain amount of material.

Adsorption capacity increases as the toluene challenge concentration increases for all of the ACF types. This trend is common in adsorbent materials and is typically demonstrated in an adsorption isotherm. The greater the adsorbate concentration, the greater the relative pressure, and the more molecules are pressed onto the adsorbent surface.

The adsorption capacity has an increasing trend as the surface area increases for both ACFC and ACFF types. This can be explained by the amount of available adsorption sites at a given ACF mass, which is obviously less in low-surface area ACFs. The higher the surface area, the more the adsorption sites that will capture more toluene molecules. Previous studies have demonstrated similar results for other VOCs, wherein a linear relationship was found between the adsorption capacities of organic compounds and the surface areas of adsorbents, independent of the type of adsorbent. A study by Tanada investigated on the adsorption of nonafluorobutyl methyl ether (NFE) onto ACF and demonstrated that the increasing specific surface area and pore volume of ACF increased the adsorption capacity to NFE.

ACF of the same forms but different surface areas have significantly different mean adsorption capacity ($p < 0.008$), except for ACFF1500 (386 mg/g) when compared to ACFF1800 (456 mg/g). ACFF1800 has a higher BET surface area and total pore volume than ACFF1500, but has a lower micropore area,

micropore volume and percentage of micropores, and more mesopores. With the adsorption capacity of ACFF1800 being higher than that of ACFF1500 but not significantly different, it is implied that surface area may affect the adsorption capacity of the ACF but the microporosity of the material also plays an important role. ACFF1800 has a higher volume of mesopores compared to ACFF1500. Within these wider pores, attractive forces of opposite pore walls overlap less and, thus, the amount of adsorption is effectively lowered as compared to the adsorption in micropores. The difference in porosity between the ACFF1500 and ACFF1800 may be influenced by the type of precursor fiber used and the manufacturing processes (i.e. duration and type of activation) performed on these adsorbents since these factors have strong influences on the porous structure and adsorption properties of the resulting adsorbents.[14] If the amount of micropores in these two ACFFs were similar, the adsorption capacity of ACFF1800 could have been higher than the ACFF1500. Therefore, the surface area may be considered a determinant of adsorption capacity for toluene but the microporosity of the ACF, particularly the micropore size, area and volume, can also be influential.

The ACFC generally has significantly higher mean adsorption capacities ($p < 0.05$) compared to the ACFF. Specifically, ACFC also has a significantly higher mean adsorption capacity ($p < 0.008$) when compared to the ACFF with similar surface area. This may be explained by the difference in their micropore size distribution. The ACFC has micropores of smaller diameter, resulting to greater adsorption energies within these micropores. This shows the importance of the development of narrow microporosity of adsorbents in order to optimize toluene adsorption at low concentration, as shown in previous studies. One study found that the amount adsorbed at low adsorbate concentrations depends on the pore size distribution of the sample, particularly its microporosity. In turn, the difference in micropore size distribution may be attributed to the density of the ACF and the accessibility of the fiber surface to the activating gas during the activation process. Since the ACFC has tightly woven fibers compared to the ACFF, some of its fiber surfaces are less accessible to the activating gas that

etches away the pores, resulting to pore widening and decrease in the volume of smaller micropores. Therefore, the adsorption capacity depends on the physical form of the ACF.

A previous study by Lorimier compared the adsorption capacity of different forms of ACF for toluene, and concluded that the felt has a higher adsorption capacity (250 – 430 mg/g) than the cloth form (200 – 270 mg/g). However, such comparison is flawed because the surface area of the ACF felt forms are higher than the cloth. Next Table compares the results of this study and Lorimier's on the adsorption capacities of ACF felt and cloth with comparable BET surface area. The data shows that this study obtained higher adsorption capacities for both cloth and felt forms.

Comparison between ACF Cloth and Felt in This and Previous Study

	Cloth		Felt	
	Balanay	Lorimier et al[23]	Balanay	Lorimier et al[23]
Designated name	ACFC1500	WWP3	ACFF18	FC1501
Fiber precursor	phenol aldehyde	Rayon	Rayon	Rayon
BET Surface Area (m^2/g)	1173	1026	1559	1498
Pore volume (cm^3/g)	0.62	0.496	0.84	0.748
Adsorption Capacity at 50 – 500 ppm toluene (mg/g)	434 – 549	200 – 270	354 – 616	250 – 430

To address the second hypothesis, the adsorption capacity is dependent on both the surface area and physical form of the ACF. The ACF with the highest surface area have the highest adsorption capacity per ACF form. The ACFC has a higher adsorption capacity than the ACFF at all toluene concentrations.

Based on the adsorption capacity, ACFC 2000 is the best adsorbent because it has the highest adsorption capacity across all toluene concentrations.

Application of ACF Form and Surface Area on Respirator Development

The assessment of the potential of the ACF for use in respiratory protection in this study is exclusively based on the critical bed depth and adsorption capacity alone. Based on these two characteristics, the ACFC 2000 is the best adsorbent candidate for the development of thinner and efficient respirators against toluene because it has both the lowest critical bed and the highest adsorption capacity. However, pressure drop across the respirator is another important factor to consider and is one requirement tested by NIOSH before a respirator can be approved for use. The ACFF was demonstrated to have less pressure drop compared to ACFC. This may be explained by the fact that ACFC is much denser than the ACFF due to its tightly woven fibers that the permeability of air is being constricted.

The equivalent number of layers corresponding to the critical bed depth for each ACF type is shown in the next table. These are the minimum number of layers needed to reduce the toluene concentration to 10% at the start of the challenge. The highlighted numbers of layers are those that have pressure drop equal to 1.5 inches of water or less, which is a NIOSH requirement for the approval on respirator use. The critical bed depths of all the ACFF types passed this pressure drop requirement for all the tested concentrations. For the ACFC types, only the ACFC1500 passed this requirement for all concentrations, while the rest passed for the first three concentrations only.

Number of ACF Layers Equivalent to Critical Bed Depth by ACF Type

ACF Type	Layer Thickness (cm)	Toluene Concentration (ppm)					
		50	100	200	300	400	500
ACFC1000	0.0625	3	3	4	4	3	4
ACFC1500	0.0625	2	2	2	3	2	2
ACFC2000	0.0625	2	2	2	3	2	4
ACFF1000	0.2	2	2	2	3	3	3
ACFF1500	0.3	1	1	1	1	1	1
ACFF1800	0.275	1	1	1	1	1	1

Apparently, the greater density of ACFC which attributes to its greater adsorption capacity for may also cause the disadvantage of having a greater pressure drop across the adsorbent, which is an important factor in the approval of respirators for worker use. Therefore, despite the higher adsorption capacity and lower critical bed depth of ACFC, it is possible that ACFF may still be better as an adsorbent in respirators if additional factors, such as pressure drop, will be considered.

Adsorption uptake of the ACF is determined by its bulk density, while the pressure drop across the ACF is determined by its permeability. The permeability of the adsorbent can be controlled by changing its bulk density. In this consideration, a compromise between the bulk density and permeability must be reached.

Prediction of Adsorption Capacity

The adsorption capacity of the ACF at the highest two toluene concentrations, 400 and 500 ppm, do not accurately predict the adsorption capacity at the lower toluene concentrations using the D-R equation, with the difference between the experimental and predicted adsorption capacities reaching up to 89%. The adsorption capacities at these lower concentrations

were underestimated, with such underestimation increasing as the challenge concentration decreases.

The third hypothesis of this study states that the D-R equation will estimate the adsorption capacities within 10% of the experimental data, with the expectation that the D-R equation will not overestimate the adsorption capacities of ACF at lower concentrations. However, the use of the D-R equation did not only result to the absence of overestimation but even to the underestimation of the adsorption capacity, which may be translated to a higher amount of toluene adsorbed at lower concentrations on the ACF than expected. This may be attributed to the fact that the ACF materials tested are composed mainly of micropores. The micropores have very small widths that the potential fields from neighboring walls overlap and the interaction energy of the adsorbent with the toluene molecule is enhanced correspondingly. Substantial evidence exists showing that the interaction may be strong enough to cause a complete filling of the pores at low relative pressures or concentrations. The degree of packing of adsorbates in the pores of activated carbon fibers was found to be greater than that in the pores of the GAC. Moreover, the micropores of the ACF are also assumed to be more readily accessible to toluene molecules because of their location on the ACF surface instead of passing first through macropores or mesopores, thus being filled more easily.

The greatest underestimation of the adsorption capacities is observed in ACFC2000 and ACFF1800. This observation may be explained by both their highest surface areas among the ACF types. The more surface area, which is mainly micropore, the greater the overall adsorption potential resulting to a much larger amount of toluene molecules adsorbed on the ACF than expected.

Moreover, using the adsorption capacities at lower toluene concentrations, 300 and 400 ppm, lead to varied results in terms of predicting the adsorption capacities but has resulted to improved prediction using the D-R equation in some ACF types, particularly those with the highest surface areas, ACFC2000 and ACFF1800. As shown in figure 31, the adsorption isotherms have a portion at the lower end that demonstrates a “leveling off” at lower concentrations,

meaning that the decrease in adsorption capacity slows down as the toluene concentration decreases. For both ACFC2000 and ACFF1800, the this “leveling off” ends at 400 ppm, and using the last 2 toluene concentrations (300 and 400 ppm) resulted to a better prediction of the adsorption capacities at lower concentrations. Based on this, toluene concentrations as high as 500 ppm do not accurately predicting the adsorption capacities of these ACFs at lower concentrations. However, there is a particular low toluene concentration level for each ACF type that is appropriate enough to be used to predict at even lower concentration, which is based on where the “leveling off” ends on the isotherm. Therefore, the D-R equation may decently estimate the adsorption capacities at lower concentrations within 10% of the experimental data using the experimental data from appropriate toluene concentrations.

However, the underestimation of the adsorption capacities of the tested ACF types at lower toluene concentrations using the D-R equation is not a great concern when applied to respiratory protection. These predicted adsorption capacities may be considered as the minimum for the actual adsorption capacities of the ACF materials with a significant margin of safety, and is therefore useful in a safety standpoint. Thus, for such purpose, the D-R equation may still be used to safely predict the adsorption capacities of ACF as a respirator adsorbent, even when data from higher toluene concentrations are used, with the confidence that the ACF actually has a higher adsorption capacity and a longer service life.

The D-R equation may be improved as a tool for accurately predicting adsorption capacity at lower concentrations in two ways. First, experimental adsorption capacities from lower challenge concentrations may be used (i.e. 300 and 400 ppm) to predict the adsorption capacities at even lower concentrations, such as 10 ppm. However, such certain low concentrations to use are those located on the adsorption isotherm where the “leveling off” starts, which is best determined by experimentation. Secondly, increasing the number of data points (i.e. 3 experimental adsorption capacities) used from lower challenge concentrations may improve the prediction of adsorption capacities using the D-R

equation. However, using more than 3 data points would defeat the purpose of saving time and resources from not having to conduct experiments to determine an adsorbent's adsorption capacity.

Publications

Claudiu T. Lungu and Jo Anne G. Balanay: *Toluene Adsorption on Various Types of Activated Carbon Fibers*, Carbon, in review.

Abstracts

J.G. Balanay, S. Crawford and C. Lungu: *Comparison of Adsorption Characteristics between Granular Activated Carbon (GAC) and Activated Carbon Fibers (ACF) for Toluene.* American Industrial Hygiene Conference and Exposition, Minneapolis, MN, June 2008.

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Jo Anne Balanay and Claudiu T. Lungu: *Adsorption Characteristics of Activated Carbon Fibers for Toluene: Application on Respiratory Protection*" accepted for podium presentation for the American Industrial Hygiene Conference and Exposition, Portland, OR, May 2011.

Dissertation

Balanay, Jo Anne: [2010] Adsorption Characteristics of Activated Carbon Fibers (ACFs) for Toluene, Ph.D. Dissertation, University of Alabama at Birmingham.