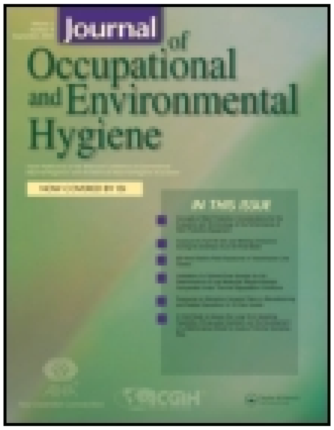

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Adsorption Characteristics of Activated Carbon Fibers (ACFs) for Toluene: Application in Respiratory Protection

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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 in poor compliance in their 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 three different surface areas per form were tested. Each ACF type was challenged with six concentrations of toluene (50, 100, 200, 300, 400, 500 ppm) at constant air temperature (23°C), relative humidity (50%), and airflow (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 measured surface area of 1614 ± 5 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). Based on these studied adsorption characteristics, it is concluded that ACF has great potential for application in respiratory protection against toluene, particularly the ACFC2000, which is the best candidate for developing thinner and efficient respirators.

Keywords activated carbon fiber, toluene, critical bed depth, adsorption capacity, respirator

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INTRODUCTION

Granular activated carbon (GAC) is the most common adsorbent used in respiratory protection against gas phase contaminants, such as volatile organic compounds (VOCs). However, GAC has some drawbacks, which include the need for containment, attrition of the granular material, and particle entrainment.(1) Because it is granular, GAC needs to be contained in a cartridge or canister, which adds to the weight and bulkiness of the respirator, contributing to user discomfort. Many studies have shown that respirator use is associated with overall discomfort.(2–7) Moreover, a series of surveys of safety professionals revealed a high rate of noncompliance in wearing personal protective equipment (PPE) when necessary, with discomfort as the main cause.(8)

Activated carbon fibers (ACFs) have been considered as an alternative adsorbent—for controlling VOCs—that overcomes some of the drawbacks of GAC. ACFs are obtained from the carbonization and activation of polymeric fibers that can be prepared from novoloid, polyacrylonitrile (PAN), pitch, and rayon precursors, with diameters ranging from 10–20 um.(9) This small diameter allows homogeneous activation of the fibers, thus yielding a material with a narrow pore size distribution in the micropore range.(1) Compared to GAC, ACFs have larger adsorption capacities and rates, higher surface area, a higher number of micropores, and faster heat and mass transfer properties.(9–12) A comparison of the toluene adsorption between GAC and ACF types showed that ACFs with BET surface areas of 1,500 m^2/g have higher adsorption capacities than GAC with a higher BET surface area of 1,800 m^2/g.(13) Moreover, activated carbon fiber is easier to handle than GAC since it can be manufactured in various forms, such as woven cloth and unwoven felt.(14) These advantages makes ACF a good adsorbent candidate for the development of thin, lightweight, and efficient respirators that may be used as short-term protection by first responders and the public in the case of a catastrophic event.(13)

TABLE I. Denotation of ACF Types Based on Form and Surface Area

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

To utilize ACF for respiratory protection, certain characteristics, of different types of commercially available ACFs for specific chemicals must be understood. These include *critical bed depth and adsorption capacity*. These characteristics will determine in advance how thin a respirator can be made and the predicted service life of the adsorbent, respectively. The purpose of this study was to determine and compare the critical bed depths and adsorption capacities of different types of commercially available ACFs for toluene. The main goal of such comparison is to determine the type of ACF that is most suitable for respirator application.

METHODS

Materials

Two forms of ACF, which are the woven cloth and unwoven felt, were used as adsorbents. The thickness of the ACF cloth (ACFC) is 0.0625 cm and 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 different manufacture-specified surface areas (1000, 1500, and 1800 (felt) or 2000 (cloth) m^2/g) were tested. Thus, six types of ACF were analyzed in this study. Table I shows the denotation of each ACF based on its surface area and form.

ACFC1000, ACFC1500, ACFF1500, and ACFC2000 are manufactured from phenol aldehyde-based, or novoloid fiber precursors by American Kynol, Inc. (Pleasantville, N.Y.), while ACFF1000 and ACFF1800 are made from viscose rayon fibers by Beijing Evergrow Resources Co. (Beijing, China). The ACFs were cut into 4-cm discs and thermally degassed in an oven (Thermo Electron Corporation, Waltham, Mass) at 200°C overnight prior to testing to eliminate moisture and volatile impurities.

The adsorbate used was toluene (laboratory grade) as the representative VOC since it is one of the most common VOCs in the workplace and is one of the major indoor organic vapors.[15,16] Toluene exposures measured in various industries ranged from 1–80 ppm.[17,18] Several studies that tested ACF materials have considered toluene as a representative for the VOC group.[19–24] Its adverse effects on humans, due to exposure to concentrations from 200–1,100 ppm, range from eye, skin, and mucous membrane irritation, to drowsiness, nausea, and memory loss, to a damaged liver and kidneys, and unconsciousness or even death.[25] Toluene was purchased from Fisher Scientific (Waltham, Mass.) and used in the experiments without further purification.

Determination of Surface Characteristics

The surface and micropore area 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, Ga.). High-purity nitrogen (99.99%) (Airgas, Inc., Radnor, Pa.) was used in the measurements. Three analyses ($n = 3$) were performed for each ACF type, with a total of 18 physisorption analyses. The actual BET surface area was measured to verify the surface area specified by the ACF manufacturer (nominal surface area).

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 Institute of Applied Physics, National Council of Scientific and Technical Research, National University of San Luis, San Luis, Argentina, for pore size distribution analyses. The Density Functional Theory (DFT) method was used to calculate the micropore size distribution of the samples, based on a molecular model of adsorption of nitrogen in porous solids.[26]

Scanning electron microscopy (SEM) images of the different ACF samples were obtained for the purpose of visualizing the organization, structure, and texture of the fibers. SEM images at 40.8x magnification were obtained from the Department of Material Science and Engineering, School of Engineering, University of Alabama at Birmingham.

Breakthrough Determination

The materials were challenged with toluene in a stainless steel sample chamber at a constant airflow (16 LPM), temperature (23°C), and relative humidity (50%) and at 5 different bed depths and mass for a certain concentration. The sample chamber has an internal diameter of 4 cm and was immersed in water for temperature control at 23°C. The mass of the adsorbents was determined before the chemical challenge by using a Denver Model APX-100 analytical balance (Denver Instrument, Denver, Co.). The adsorbent bed depths were measured using a caliper. Breakthrough curves were obtained for each ACF type at six different toluene concentrations: 50, 100, 200, 500, 400, and 500 ppm. Duplicates were conducted for 20% of the breakthrough runs.

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 settings used in previous studies on ACF testing, as well as by National Institute of Occupational Safety and Health (NIOSH) in testing respirators for organic vapors.[19,21,27] The airflow of 16 LPM was used to obtain the air velocity that is comparable to that used in NIOSH respirator testing, in which actual respirator cartridges with higher surface areas were used. Such experimental airflow was determined by considering the constant airflow used by NIOSH for the testing of the service life of respirator chemical cartridges (32–64 LPM), possible respirator cartridge diameters (6.9 and 7.2 cm), and the sample chamber diameter of 4 cm.

Toluene vapor was generated by injecting continuously a pre-calculated constant flow of liquid toluene using an Aladdin-1000 automated syringe pump (World Precision Instruments, Sarasota, Fla.) into a preconditioned 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, Ohio). The temperature, relative humidity, and flow of the air were controlled prior to mixing with toluene using a Miller-Nelson Model HCS-401 instrument (Assay Technology, Inc., Livermore, Calif.). Breakthrough of the ACF samples for toluene was determined by gas chromatography using an Agilent Model 6850 gas chromatograph (Agilent Techonologies, Alpharetta, Ga.) fitted with a flame ionization detector (FID) for quantification. The analytical column used was an HP-1 (100% methyl siloxane) capillary column, 30.0 m × 0.32 mm (I.D.) × 0.25 μm. The oven temperature 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 setup for breakthrough determination is shown in Figure 1 and is similar to that used in a previous study.[13]

Determination of Critical Bed Depth

Critical bed depth is the minimum adsorbent thickness required to obtain an acceptable chemical concentration at time zero and, thus, determines how thin a respirator can be made. In this study, critical bed depth was 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 (min) obtained were plotted against the adsorbent bed depth (cm) to obtain a regression line. The bed depth at which the regression line intersects the x-axis was determined to be the critical bed depth, which was determined for each ACF type and challenge concentration of toluene.[28] Thus, six critical bed depths were obtained for each ACF type.

Statistical analysis of the data was performed using the SPSS version 20 software (SPSS Institute, Chicago, Ill.). The standard error of the critical bed depth was calculated based on the standard error of the estimate (SE_y). The upper confidence

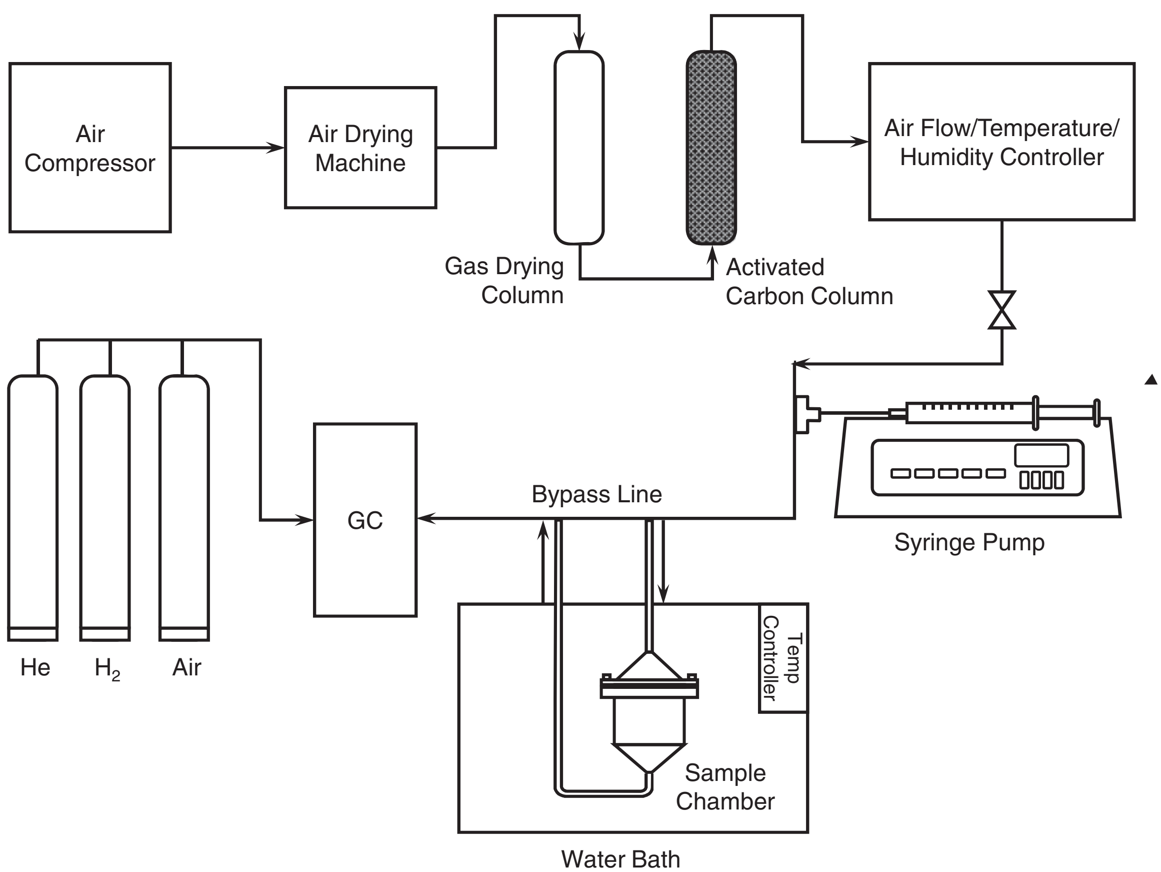

FIGURE 1. Experimental setup for breakthrough determination

TABLE II. ACF Type Pairs Analyzed for Adsorption Characteristics Using Paired t-Test

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

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 projected 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.[29]

Determination of Adsorption Capacity

Adsorption capacity is the amount of chemical adsorbed per mass of material and is used to determine the service life of the adsorbent. The time (min) 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 (min) 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, as shown below[30,31]:

$$t_b = \frac{W_e}{C_0 Q}\left[W - \frac{\rho_B Q}{k_v}\text{In}(C_0/C_x)\right] \qquad \textbf{(1)}$$

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/cm^3)
k_v = first order rate constant of adsorption (min^{-1})
W_e = kinetic adsorption capacity (g/g)

Data at 50% breakthrough were chosen to determine the adsorption capacity to be more consistent throughout the experiment, since the lower (e.g., 10%) and the upper (100%) parts of the breakthrough curves have more variability in the breakthrough concentration data. The equation for calculating the adsorption capacity, $W_e = aC_0Q$, was derived, wherein a is the slope of the regression line. The equation was used to determine concentration of toluene for each challenge. Thus, six 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 version 20 software (SPSS Institute). The standard error of the adsorption capacity was calculated based on the standard error of the slope.

Comparison of Adsorption Characteristics among ACF Types

The critical bed depths and adsorption capacities of all the ACF types were compared according to ACF form and surface area using the analysis of covariance (ANCOVA). ANCOVA was performed to determine whether the critical bed depth (CBD) or the adsorption capacity is significantly different among six 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 same analysis was done for the comparison of adsorption capacity (AC) among the ACF types.

Pairwise comparison of adsorption characteristics was also conducted between ACF types using independent (or one-way ANOVA) t-test. The comparison was done in three 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 3) between ACFC and ACFF in general.

For the comparison of specific ACFs, the critical bed depths or adsorption capacities at different concentrations were pooled for each ACF type. A total of 15 pairs were analyzed per adsorption characteristic but only 9 pairs, as shown in Table II, were of interest in this study. The α is calculated by 0.05 divided by the number of ACF types compared pairwise, which is $0.05/6 = 0.008$. 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, with $\alpha = 0.05$.

RESULTS

Characterization by ACF Form, Surface Area, and Porosity

Table III summarizes the surface characteristics of each ACF type, including the average surface area and micropore area (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

TABLE III. Average Surface Area and Micropore Area by ACF Type (n = 3)

ACF Type	Parameters			
	Nominal surface area (m^2/g)	BET surface area (m^2/g)	Micropore area[A] (m^2/g)	% Micropore by area
ACFC1000	1000	891.8 ± 7.8	840.2 ± 7.5	94.2 ± 0.6
ACFC1500	1500	1470.8 ± 8.9	1336.9 ± 2.4	90.9 ± 0.5
ACFC2000	2000	2052.8 ± 6.2	1726.7 ± 18.9	84.1 ± 0.7
ACFF1000	1000	979.9 ± 19.0	876.8 ± 27.3	89.5 ± 1.3
ACFF1500	1500	1407.3 ± 14.8	1277.9 ± 11.3	90.8 ± 0.2
ACFF1800	1800	1861.1 ± 7.4	1041.8 ± 54.3	56.0 ± 3.1

[A] *By t-plot method.*

ACFF1800 but may still be comparable. Thus, ACFC2000 and ACFF1800 were considered counterparts.

For the ACFC types, as the surface area increases, the micropore area also increases, but the percentage of micropore by area decreases. 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 but very different micropore area, 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.

The adsorption and desorption isotherms of nitrogen for each ACF type at a temperature of 77 K were obtained and illustrated elsewhere.[12] The shape of the nitrogen isotherms for all ACF types shows they are of type 1 form, indicating that the materials are essentially microporous.

Pore Size Distribution of ACF Materials

The pore size distribution of an adsorbent affects its adsorption capacity for molecules of various shapes and sizes, and is one of the criteria by which carbon adsorbents are selected for a specific application. As shown in Figure 2, which was also published elsewhere,[12], the pore size of all the ACFs is less than 2.5 nm. For ACFC1000, the majority of the micropores have 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. As the ACFF surface area increases (ACFF1500 and ACFF 1800), the volume of micropores increases but the pore size range also widens.

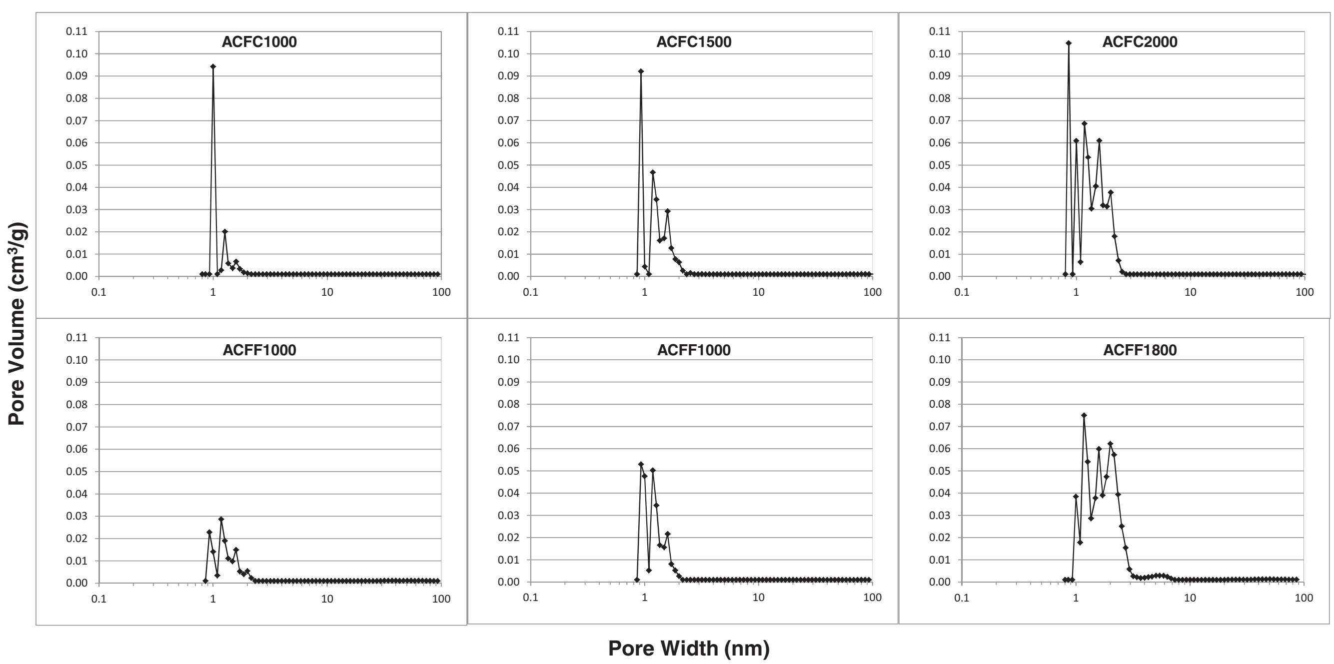

FIGURE 2. Pore size distribution of ACF types

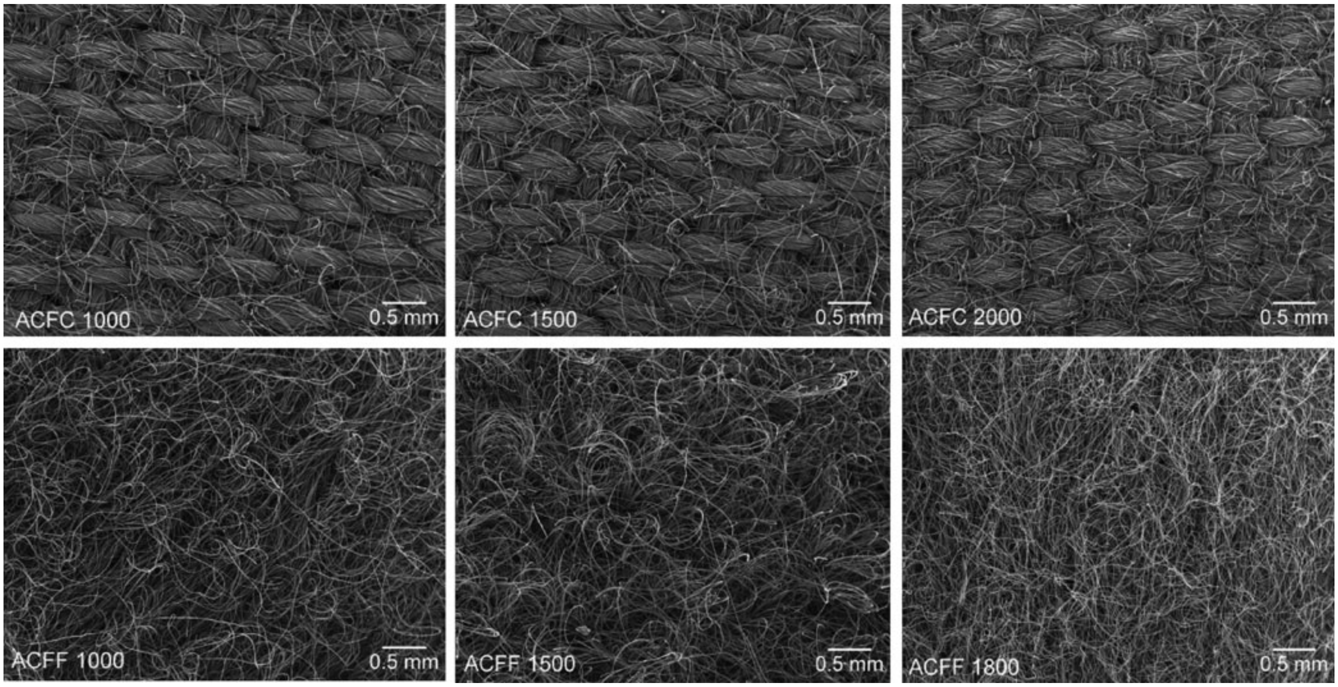

FIGURE 3. SEM images of activated carbon fibers at 40.8x magnification

Comparing by ACF form, the ACFC types have greater volume of micropores with smaller diameters.

Scanning Electron Microscopy (SEM) Images

The images obtained from SEM analysis basically illustrated the fiber organization of the ACF materials. At 40.8x SEM magnification as shown in Figure 3 (also published elsewhere[12]), 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 3, 1–3). With the ACFF, the higher the surface area, the more fibers per area of the material (see Figure 3, 4–6).

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. Figure 4 shows the critical bed depths of the three ACFC and three

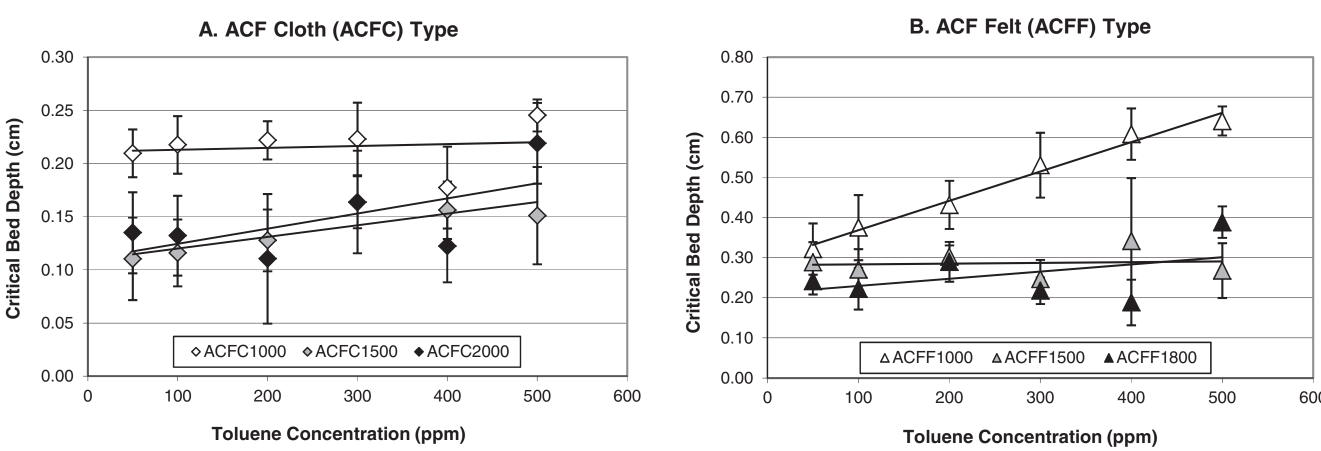

FIGURE 4. Critical bed depth by ACF type at different toluene concentrations

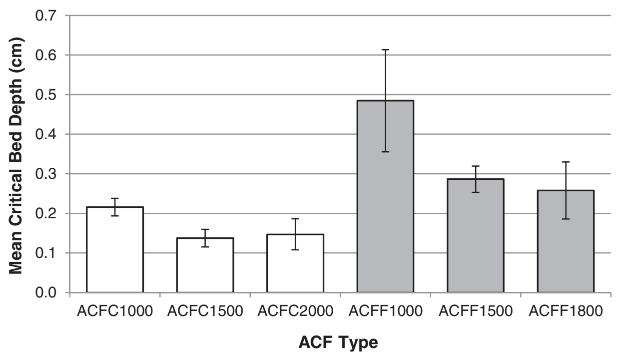

FIGURE 5. Mean critical bed depth by ACF type

TABLE V. P-values for Differences in Adsorption Characteristics per ACF Pair with Same Forms and Different Surface Areas

	p-value	
ACF Pairs	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

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. Among the ACF types, ACFC 1500 and 2000 (two highest surface areas) have the lowest critical bed depths (0.110–0.164 cm and 0.111–0.219 cm, respectively) for each toluene concentration, making them good candidates for thinner respirators.

The mean critical bed depths of all the ACF types tested are demonstrated in Figure 5 and were compared according to fiber form and surface area. The cloth and felt with similar surface areas were compared using a t-test to determine if the form of the ACF influences the critical bed depth, Table IV shows that there are significant differences in critical bed depth ($p < 0.008$; $p = 0.000$–0.004) between the cloth and felt forms with similar surface area. The difference between the overall mean critical bed depth of ACFC (0.167 ± 0.045 cm) and that of ACFF (0.343 ± 0.132 cm) is statistically significant ($p = 0.000$, $\alpha = 0.05$).

The cloth or felt forms with different surface areas were compared against each other using a paired t-test to determine the influence of ACF surface area to the critical bed depth. Table V shows 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.

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

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

Adsorption Capacity

Figure 6 shows the adsorption capacities of the three ACFC and three ACFF types for different toluene challenge concentrations. The adsorption capacity has an increasing trend as the surface area increases for both ACFC and ACFF types. The ACFC generally has higher adsorption capacities (range: 345–878 mg/g) compared to the ACFF (range: 221–616 mg/g). Among the ACF types, ACFC 2000 (highest surface area) has the highest adsorption capacity (range: 595–878 mg/g) for each toluene concentration. The adsorption capacities of all the ACF types tested were compared according to fiber form and surface area, as shown in Figure 7, demonstrating an increasing trend as the ACF surface area increases.

To determine the influence of ACF form on the adsorption capacity, the cloth and felt with similar surface areas were compared using a t-test. Table IV shows that there are significant differences in adsorption capacity between the cloth and felt forms with similar surface area ($p < 0.008$, $p = 0.000$–0.001). The difference between the overall mean adsorption capacity of ACFC (522.7 ± 158.7) and that of ACFF (377.7 ± 90.9) is statistically significant ($p = 0.000$, $\alpha = 0.05$).

To determine if the surface area of the ACF influences the adsorption capacity, the cloth or felt forms with different surface areas were compared using a paired t-test. Table V shows 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 ACFF1500 and ACFF1800 (highest surface areas) is insignificant ($p > 0.008$).

DISCUSSION

Influence of ACF Surface Area and Form on Critical Bed Depth

Critical bed depth (CBD) is defined in this study as the minimum bed depth of the adsorbent required to reduce the

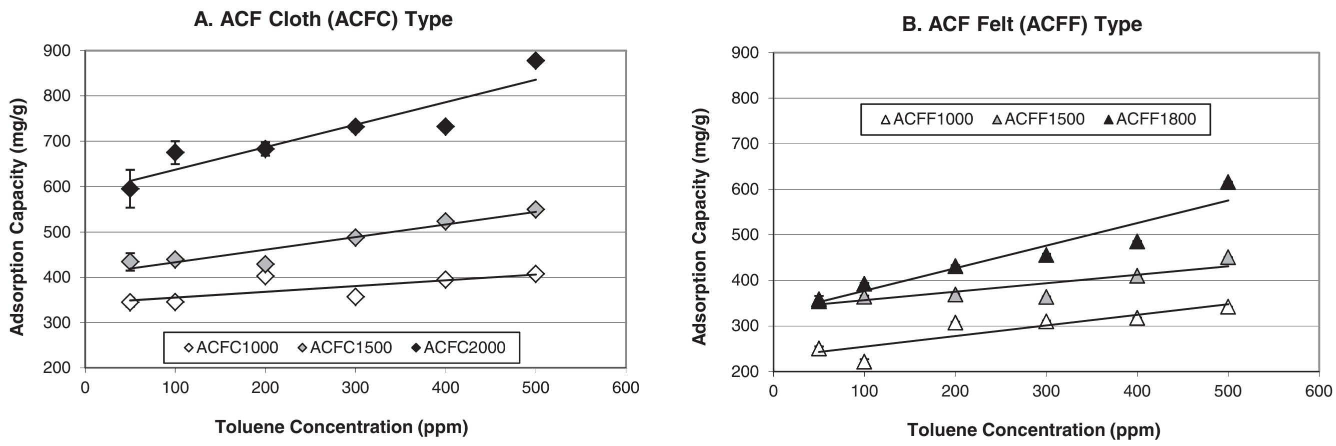

FIGURE 6. Adsorption capacity by ACF type at different toluene concentrations

concentration of toluene by 90%. The lower the critical bed depth, the better the adsorbent because it takes a smaller depth of the material to prevent the penetration of 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 may 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 materials to adsorb a particular amount of toluene. For each ACF form, the two ACFs with the highest surface areas (ACFC1500 vs. ACFC2000; ACFF1500 vs. ACFF1800) do not have significantly different mean critical bed depths. Apparently, the critical bed depth is dependent on the surface area only to a certain extent because further increase in surface area does not seem to significantly decrease the critical bed depth further. 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.

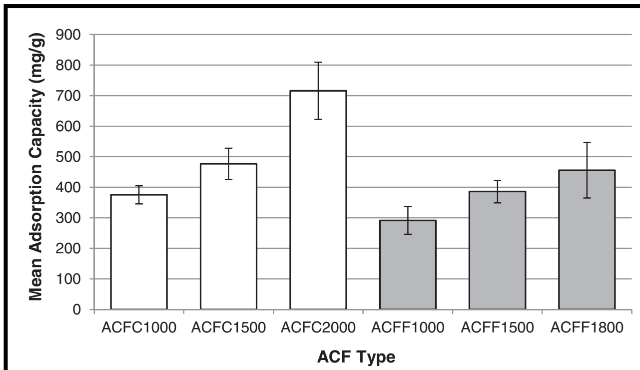

FIGURE 7. Mean adsorption capacity by ACF type

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 an ACFC type is significantly lower ($p < 0.008$) than that of its ACFF counterpart. Overall, ACFC still has a significantly lower CBD compared to ACFF because 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, 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 Surface Area and Form 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 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 for toluene molecules at a given ACF mass, which is expectedly greater in high-surface area ACFs. Previous studies have

TABLE VI. Comparison between ACF Cloth and Felt in This and Previous Study

	Cloth		Felt	
	Balanay	Lorimier et al.[21]	Balanay	Lorimier et al.[21]
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 ppm toluene	434–549	200–270	354–616	250–430

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.[32,33] A study by Tanada investigated the adsorption of nonafluorobutyl methyl ether (NFE) onto ACF and demonstrated that the increasing specific surface area increased the adsorption capacity to NFE.[32]

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 than ACFF1500, but has a lower micropore area and percentage of micropores. 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 has an influence. With ACFF1800 having more wider pores (i.e., mesopores) compared to ACFF1500, the amount of adsorption is effectively lowered due to less overlap of attractive forces in opposite pore walls in mesopores, as compared to the adsorption in micropores. The difference in microporosity 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.[26] If the amounts 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 can also be influential.

The ACFC generally has significantly higher mean adsorption capacities ($p < 0.05$) compared to the ACFF. Specifically, an ACFC type 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 in 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.[34] 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 in pore widening and a 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).[21] However, such comparison is flawed because the surface area of the ACF felt forms are higher than the cloth. Table VI 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 show that this study obtained higher adsorption capacities for both cloth and felt forms. This may be attributed to differences in precursor fibers for cloth, and probably differences in the activation methods used for the manufacture of the ACFs for both cloth and felt forms.

Adsorption capacity is demonstrated to be dependent on both the surface area and physical form of the ACF. The ACF with the highest surface area has 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 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 more 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 of the requirements tested by NIOSH for respirator use approval. This can be a concern for ACFC types because they are much denser than the ACFF due to their tightly woven fibers that may restrict airflow. Thus, to further investigate the possible application of ACFs in respiratory protection, the pressure drop across ACFs in actual respirator cartridges and filters must be studied further to determine the optimum dimensions (i.e., thickness) and density of ACF materials that will result in acceptably breathable respirators.

CONCLUSION

The ACF materials were demonstrated to be mainly composed of micropores based on their type I nitrogen adsorption isotherms, micropore area, and pore size distribution, making the ACF suitable for adsorbing toluene at low concentrations.

The ACF with the lowest surface area, regardless of form, has the highest critical bed depth (CBD) due to the least amount of available adsorption sites per ACF bed depth. The ACFC has a significantly lower CBD than the ACFF with similar surface area because of its denser and thinner form. The critical bed depth is not fully dependent on the surface area of the ACF and is dependent on the physical form of the ACF.

The adsorption capacity increases as the surface area increases for both forms of ACF due to the increasing amount of available adsorption sites per ACF mass. The ACFC has a significantly higher adsorption capacity than the ACFF with similar surface area due to their difference in micropore size distribution, with ACFC having micropores of smaller diameter. The adsorption capacity of the ACF for toluene is dependent on its surface area and physical form.

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 VOCs. 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. However, pressure drop across ACFC may be a concern due to its dense characteristic and, thus, must be further investigated in actual respirators to continue to assess the use of ACF for respiratory protection.

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