

Adsorption of Organic Contaminants from Water Using Tailored ACFs

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Six activated carbon fibers (ACFs) with different chemical and physical properties were prepared by first curing a phenolic resin-coated glass fiber, followed by activation and post-treatment. Their adsorption properties were investigated to evaluate the removal of benzene, toluene, ethylbenzene, and *p*-xylene (BTEX) and the chemical warfare simulants disopropylmethyl phosphonate (DIMP) and half mustard (HM) from water. The adsorption isotherms showed that ACF SL-2 (activated with CO₂/H₂O at 800 °C) has a higher adsorption capacity for BTEX, DIMP, and HM than other ACFs. This suggests that the high adsorption affinity of SL-2 is related to its higher surface area, larger average micropore size of 11.6 Å (especially effective for the adsorption of DIMP), and lower oxygen content of the surface. The adsorption isotherms are well represented by the Freundlich equation. For BTEX, the adsorption parameters based on carbon coating showed that, in all cases, ACFs have a higher *K* value than the best available data obtained on granulated activated carbon (GAC). The adsorption isotherms of DIMP and HM on ACFs are also presented.

Introduction

Toxic organic chemicals can be introduced into ground and surface water from the waste effluents of chemical and petrochemical industries. This represents one of the most severe environmental problems facing the United States, with costs for site assessment, long-term monitoring, and remediation exceeding billions of dollars annually. The military often must depend on access to water supplies within a hostile war zone. They are specifically concerned with hazardous organic compounds, such as benzene, toluene, ethylbenzene, and xylene (BTEX) from gasoline spills, as well as the potential for contamination by chemical warfare agents (CWAs). Thus, the removal of organic contaminants from water has a great benefit to the military as well as industry and the general public.

Traditionally, granular activated carbon has been widely used to remove organic contaminants from water.^{1–3} Unfortunately, such activated carbons suffer from a number of drawbacks including slow adsorption kinetics, poor selectivity, the need for expensive containment systems, and less than 100% working capacity. Another problem is the lack of design flexibility when using granulated carbons.

To address some of these disadvantages, Economy⁴ reported on the development of phenolic-based activated

carbon fibers (ACFs), which displayed significantly improved adsorption capacities over those of granulated activated carbons (GACs). The fibers offered a number of advantages over the GACs, including greatly improved contact efficiency with the media, leading to greater rates of adsorption, much higher surface areas (up to 2500 m²/g), and the potential for greatly simplified in situ regeneration through electrical resistance heating. Unfortunately, the ACFs are very expensive (~\$100/lb)⁵ and are not very durable during handling.

To address the limitations of current ACFs, Economy et al. has recently devised a new low-cost preparation which consists of coating glass fiber textiles with a phenolic resin and then activating the coating to produce a microporous structure.⁶ Such fibers appear to be cost competitive to the GACs (\$1–2/lb). The wear resistance of these new fibers is much better than that of the commercially available ACFs.⁷ The excellent wear characteristics are a direct result of the carbon coating protecting the glass fiber surface. The results of gas adsorption studies showed that, by tailoring the pore surface chemistry, these new fibers displayed far superior performance over that of existing activated carbons.⁸

The present study was undertaken to evaluate the coated-glass ACFs for removing trace amounts of benzene, toluene, ethylbenzene, and *p*-xylene and the chemical warfare simulants disopropylmethyl phos-

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Table 1. Preparation Chart for Glass-Coated ACFs

ACF designation	activation conditions			
	<i>T</i> (°C)	<i>t</i> (min)	gases	post-treatment
SL-1	600	300	CO ₂ /H ₂ O	
SL-2	800	300	CO ₂ /H ₂ O	
SL-3	600	240	NH ₃	
SL-4	600	60	N ₂	
SL-5	600	240	CO ₂ /H ₂ O	nitric acid oxidation for 1 h
SL-6	600	240	CO ₂ /H ₂ O	nitric acid oxidation for 1 h, then heat in N ₂ flow at 600 °C for 30 min

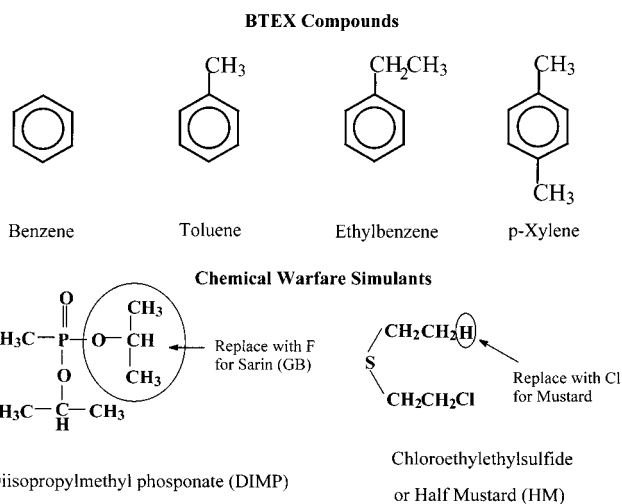
ponate (DIMP) and half mustard (HM) from water. Six different ACFs were prepared, and their chemical and physical properties were characterized. Variables that were examined included pore size, pore surface chemistry, and the related question of controlling the hydrophobicity of the surface. One- or two-point isotherms were examined in order to compare their maximum adsorption capacities. After this initial screening adsorption, full isotherms were recorded to develop a fundamental understanding of the adsorption mechanism of BTEX, DIMP, and HM onto the glass-coated ACFs.

Materials and Methods

Materials. The coated-glass ACF materials were prepared by first curing a phenolic resin-coated glass fiber, followed by activation and post-treatment. The phenolic precursor was impregnated on a fiberglass mat consisting of 13 μm diameter fibers with 10% submicron fiber dispersed throughout. This was specially prepared by Johns Manville and had 55 wt % phenolic resin content. The precursor was stabilized at 170 °C in an oven for 3 h. The stabilized material was cooled in air, transferred to a separate tube furnace, and purged with flowing N₂. The sample was carbonized in flowing N₂ by heating at ~30 °C/min to a given temperature and then switching to a selected activation gas and holding for various times. The activation gas CO₂/H₂O was generated by bubbling 2 L/min of CO₂ through liquid water. After activation, the ACF was cooled in flowing N₂. The post-treatment was carried out by immersing the ACF in fuming nitric acid for 1 h and then thoroughly washing with deionized water. In addition, the nitric acid-treated ACF can be decarboxylated by heating the sample in a N₂ flow at 600 °C for 30 min. The various activation conditions used to produce samples are delineated in Table 1. The surface chemistry and pore size of the prepared fibers can be modified by using different activating agents/conditions and chemical post-treatments.^{8,9} All the samples were washed with deionized water and dried under vacuum at 150 °C before use.

The six organic materials were obtained from Aldrich, including BTEX, diisopropylmethyl phosphonate (DIMP), and chloroethylethyl sulfide (half mustard (HM)). The two CWA simulants DIMP and HM were used to avoid worker exposure to hazardous materials. The chemical structures for BTEX and the differences between the two CWA simulants and actual agents are shown in Figure 1.

Methods. Adsorption isotherms were conducted in 40 mL vials sealed with a septum cap. Several difficulties were encountered in working with the sparingly soluble solvents and the ACFs. Direct injection of the solvent through the septum cap resulted in a small globule of the solvent in the vial. Premixing the solvents in open reactors resulted in large losses of the solvent. In addition, the entrained air in ACFs resulted in air bubbles in the vials. All of these could lead to

**Figure 1.** Chemical structures of compounds tested.

erroneous results. Thus, a process was developed whereby a small amount of water (10 mL) was added to a vial containing a known mass of ACF. The vial was then subjected to a vacuum to remove the air entrained in the ACFs. After the entrained air was removed, the vial was filled with water containing the target compound, and the volume of water was determined by weighing the vial. The water solution containing the target compound was prepared by mixing the solvent and water in a 10 L glass reservoir. The water with dissolved solvent to be used in the isotherm experiment was drawn off the bottom of the reservoir. If 30 vials were required for the experiment, only 1 L of contaminated water would be used, resulting in a relatively constant concentration for such a specimen. After the vials were fully prepared, they were placed in a Millipore rotary agitator and tumbled for 5 days. Control blanks containing no ACF were used to ensure that there were negligible losses during the contact period. All experiments were carried out at ~20 °C.

One- or two-point screening isotherms were run in order to quickly test for the most likely candidate with maximum adsorption capacity. Identical weights of six different kinds of ACFs were used to ensure that the adsorption capacities were comparable.

Adsorption isotherms were carried out using 10 to 15 ACF samples with different weights from 0 to 500 mg. Two samples were applied for each point. That is, 20 to 30 vials were utilized with different ACF masses, followed by adding 10 mL of water, driving out the air in the ACFs under vacuum, and then carefully adding ~30 mL of prepared stock solution to completely fill the vial, capping the vial, and tumbling for 5 days at 20 °C. The vials were weighed at each step to calculate the exact volume of water.

After adsorption of the BTEX, the water was first analyzed by liquid chromatography (LC). When the concentration of BTEX was below the limit of detection for HPLC, the purge and trap (P & T) method with gas chromatographic/mass spectrometric (GCMS) equipment was employed to detect very low concentrations. For DIMP and HM contaminant measurement, they were first extracted from water with CH₂Cl₂ for 6 h, and then the extracted solution was injected into the GCMS system to detect the concentration level.

HPLC was carried out using a Waters LC Module 1 with Millennium 32 version 3.105 software (Waters Corp.). The analytical column was a Supelco ABZ+ (Supelco), 15 cm × 4.6 mm × 5 μm, with UV/vis absorption detection (Waters). The GCMS equipment was a Hewlett-Packard (HP) 5890 GC/5970 MS controlled by HP ChemStation version B.02.04 (HP). This system was also used in the purge and trap (P & T) experiments with a Tekmar ALS 2016 sampler and LSC 2000 controller (Tekmar). The analytical column was a DB-5 capillary column (J & W Scientific), with a 5% phenylmethylsiloxane stationary phase and a 30 m × 0.25 mm × 0.25 μm film thickness.

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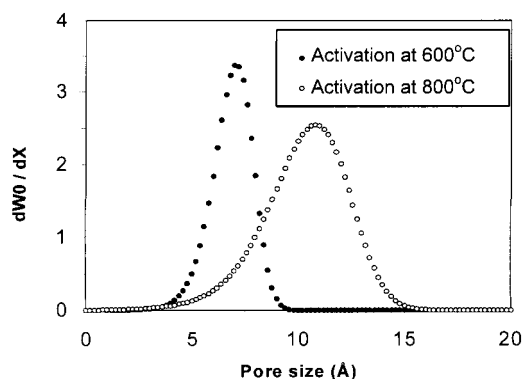


Figure 2. Representative ACF pore size distributions.

Carbon content on glass was measured using a Hi-Res TA Instruments 2950 thermogravimetric analyzer (TGA) by burning off the coating in air at 700 °C. A Model CE440 elemental analyzer (EA) was used to determine the C, H, and N weight percentages. O weight percent was calculated by mass difference, combining the results of TGA and assuming only C, H, N, O, and inert glass were present. Analysis of surface area, pore size distributions (PSDs), and micropore volumes was carried out with an Autosorb-1 controlled by Autosorb-1 for windows 1.19 software (Quantachrome Corp.). The nitrogen surface area and micropore volume of the samples were determined using the BET and Dubinin–Radushkevich (DR) equations, respectively.

Results and Discussion

1. Glass-Coated ACF Characterization. Six different ACFs, obtained by different activation conditions (Table 1) were tested to span a range of surface chemistries (Table 2) and two distinct pore size regimes (Figure 2). ACFs with much larger pore sizes were not investigated, since the overlap in potential between the pore walls decreases rapidly with pore size. The results of PSDs show that ACFs activated at 600 °C have a similar pore size distribution and their micropore sizes are smaller than that in SL-2 activated at 800 °C. In general, the more aggressive the activation treatment, the lower the yield, and the higher the surface area. In most cases, these two parameters are inversely proportional, the one exception being SL-5. In this case, the surface area was lower than expected due to the additional weight of oxygen-containing functional groups resulting from the nitric acid treatment. The atmosphere of activation and post-treatments can greatly alter the surface chemistry.^{8,9} Thus, activation with steam/water at high temperature displayed a slightly acidic pore surface due to the presence of carboxylic acids and phenolic hydroxyls. These groups can be

decomposed with increasing temperature (above 350 °C) and prolonged treatment time. The number of these groups can be greatly increased upon treatment with strong acid, making the surface much more acidic and very polar. Conversely, activation with ammonia gas will result in a basic pore surface chemistry due to nitrogen-containing functional groups resembling aniline and pyridine. Finally, one can produce an unsaturated surface through oxidation followed by outgassing at high temperatures.

The elemental analysis results as shown in Table 2 provide insight into the extent to which the pore surface modification has altered the chemical nature. To obtain accurate values, the carbon weight percent was measured using thermogravimetric analysis (TGA) by burning off the coating in air. The numbers are displayed for both the ACF (glass + carbon) and normalized to the carbon coating to allow for easier comparison. For ACFs SL-1 and SL-2 one notes a very high carbon content with only a small amount of oxygen. The ammonia treatment produced a high nitrogen content of 6.52 wt %, indicating a reasonably basic surface. The nitric acid treatment resulted in a greatly increased amount of oxygen-containing functional groups (from 0.39 up to 12.79 wt %).

2. One- or Two-Point Isotherms. The first set of experiments examined one- or two-point isotherms for the six contaminants in order to screen for the most likely candidate with maximum adsorption capacity. In most cases, it appeared that SL-2 was the most effective adsorbent, as shown in Figures 3 and 4. This is not unexpected, since the higher initial concentration of the contaminants would be more readily removed using an ACF with an increased micropore volume. The benefits of chemical modification are not as apparent, especially for BTEX, since they are relatively neutral molecules. In all cases, the worst sample was SL-5. Although the highly oxidized surface has been shown to be advantageous for adsorption of molecules from air,^{8,9} in aqueous solution this is not the case, due to the high polarity of water. For BTEX, the second highest capacity ACF was SL-6, which contains unsaturated sites that interact favorably with the delocalized π -bonds of the aromatic ring (especially apparent for *p*-xylene).

Comparison of the percent removal of BTEX in Figure 3 to the surface area in Table 2 suggested that adsorption of BTEX is related to the surface area of ACFs. In general, the percent removal of BTEX from water increased with increasing surface area of ACFs. Thus, the adsorption affinity of BTEX onto six ACFs could be

Table 2. Chemical and Physical Properties of Glass-Coated ACFs

ACF	carbon yield ^a (%)	carbon coating content ^b (wt %)	BET surface area			EA based on ACF (wt %)				EA based on carbon (wt %)			
			m ² /g of ACF	m ² /g of carbon	micropore volume (cc/g)	C ^c	H ^c	N ^c	O ^d	C ^c	H ^c	N ^c	O ^d
SL-1	49	43.40	289	666	0.1165	42.31	0.37	0.55	0.16	97.49	0.85	1.27	0.39
SL-2	38.7	34.85	483	1386	0.1766	35.23	0.06	0.03	0	99.74	0.17	0.09	0
SL-3	47.9	39.73	335	843	0.1228	36.15	0.31	2.59	0.68	90.99	0.79	6.52	1.7
SL-4	54.4	45.55	252	553	0.1159	43.13	0.61	0.06	1.74	94.69	1.34	0.14	3.83
SL-5	53	45.72	171	374	0.0891	38.46	0.41	1.00	5.85	84.14	0.89	2.19	12.79
SL-6	50	42.4	339	800	0.1443	40.28	0.23	0.58	1.31	95.00	0.55	1.37	3.08

^a Data calculated from the changes in weight between precursor and resulting ACF and assuming that the glass weight remained unchanged after activation. ^b Data from an average of four samples tested by TGA. ^c Each result of elemental analysis is an average of three samples. ^d Data calculated from the results of elemental analysis (EA) and TGA. The elemental analyses of C, H, and N have associated errors of $\pm 0.40\%$; thus, the %O results determined by difference are subject to a cumulative error.

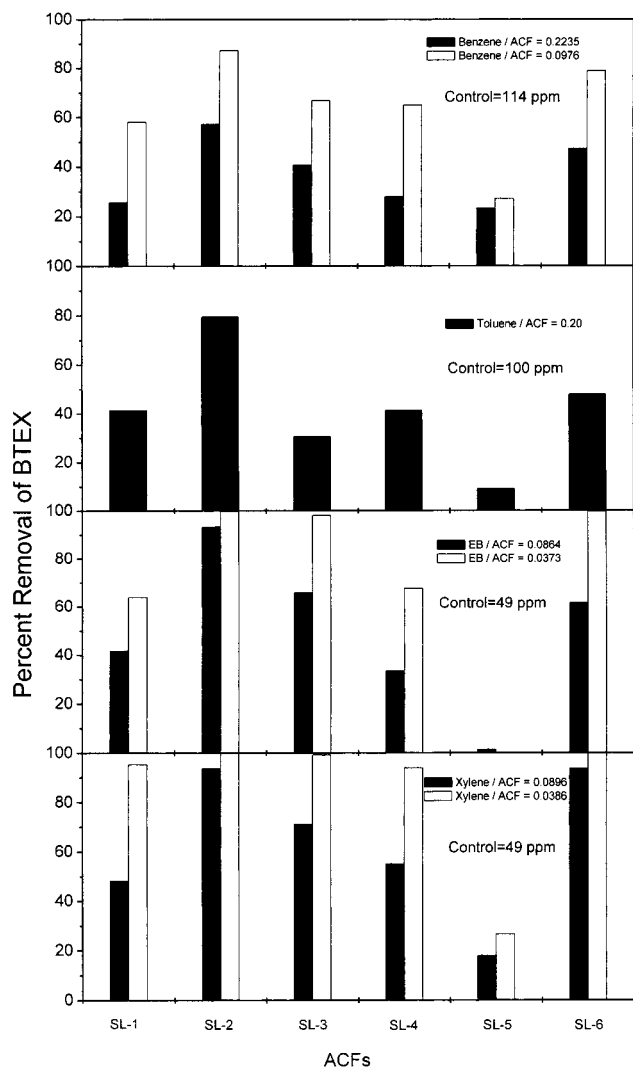


Figure 3. One- or two-point isotherms of BTEX on ACFs.

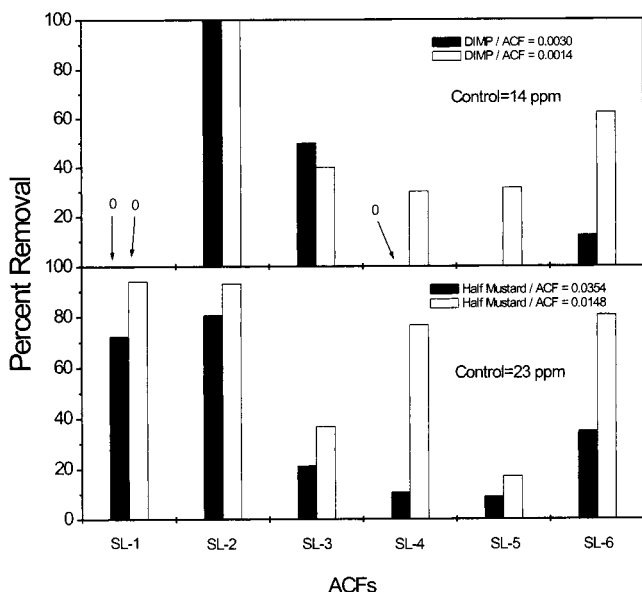


Figure 4. Two-point isotherms of DIMP and half mustard on ACFs.

ranked in decreasing order as follows: SL-2, SL-6, SL-3, SL-1, SL-4, and SL-5.

For adsorption of DIMP (Figure 4), several materials had little or no capacity. This can be explained as due

to a molecular sieving effect whereby the DIMP molecule is too large to enter the microporous structure. However, the larger pore (11.6 Å) SL-2 (see Figure 2) results in the higher percent removal of DIMP. The second highest capacity ACF was SL-3, which has basic surface chemistry due to activation with ammonia gas. This adsorption affinity undoubtedly results from an acid/base interaction, since the DIMP molecule has some acidic character.

For HM adsorption (Figure 4), the effective ACFs are SL-2 and SL-1, which were activated with CO₂/H₂O without any post-treatment. It is suggested that the adsorption affinity of half mustard should be related to the pore surface chemistry of ACFs.

Micropore surface chemistry of ACFs, such as a hydrophobic surface, is undoubtedly one of main factors influencing the adsorption affinity of six compounds onto ACFs in water.

Karichoff et al.¹⁰ showed that hydrophobic chemicals are readily adsorbed by organic carbon. The literature^{11,12} shows the log octanol-water partition coefficient ($\log(k_{ow})$) for BTEX to be as follows: benzene, 2.13; toluene, 2.69; ethylbenzene, 3.15; *p*-xylene, 3.10. These values indicate that BTEX are moderately hydrophobic. Also, DIMP and HM are hydrophobic chemicals, which is found from both molecular structures and experiments where they were difficult to dissolve into water (usually takes several days) and easy to extract from water with CH₂Cl₂.

SL-2 should have a more hydrophobic micropore surface chemistry than other ACFs due to the high activation temperature up to 800 °C (Table 1) and high carbon content (Table 2). Obviously, this hydrophobic micropore surface chemistry can be used as another explanation for the higher adsorption affinity of BTEX, DIMP, and HM onto SL-2.

3. Adsorption Isotherms. The Freundlich isotherm is a very common expression employed to describe the adsorption of BTEX onto activated carbon.¹³ The univariate expression, modeling adsorption of one contaminant from water, has the form of a power model:

$$Q = KC_e^{1/n} \quad (1)$$

where Q = mass of the target compound adsorbed per unit mass of adsorbent (mg/g); C_e = equilibrium concentration of the adsorbable compound in the liquid (mg/L); K = adsorption equilibrium constant (mg/g)-(mg/L)^{-1/n}; and n = constant indicative of adsorption intensity.

On the basis of this equation, adsorption isotherms of BTEX and two CWA simulants on ACFs were obtained by plotting the data on a log 10 graph. The scattered data are shown in Figures 5 and 6 along with the best-fit line. The solid line is based on actual experimental data, the dashed line is based on normalized data using only the carbon coating content on the

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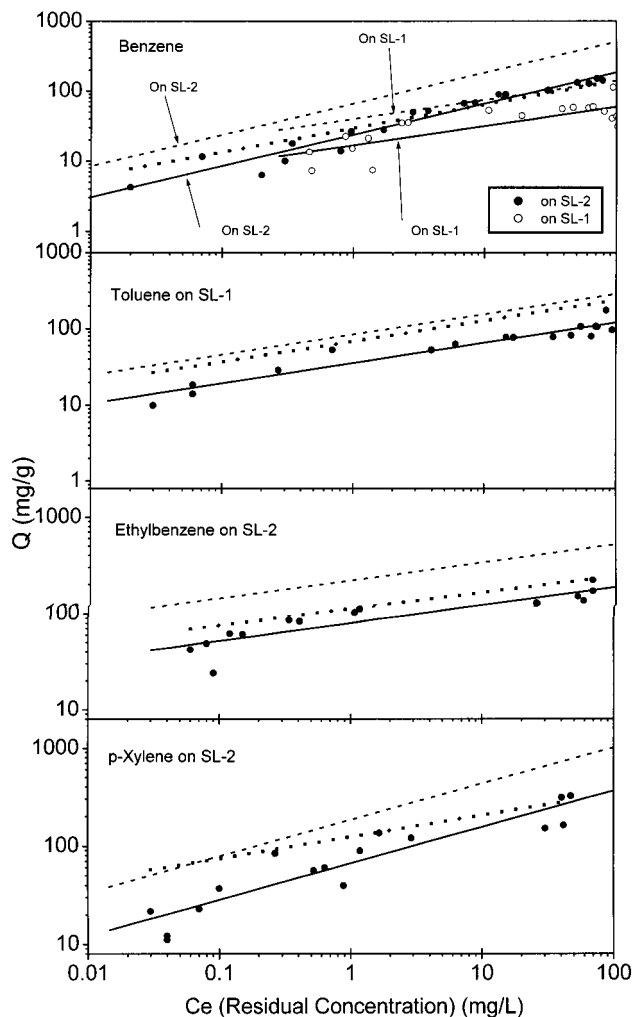


Figure 5. BTEX adsorption isotherms (—, based on total material; ---, based only on carbon coating; ···, calculated from GAC data²).

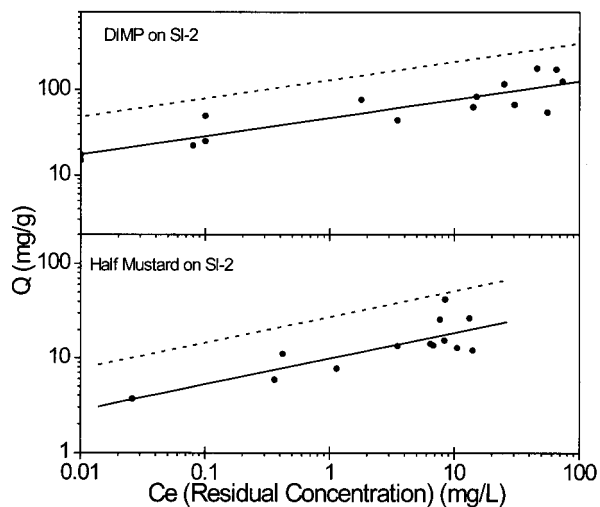


Figure 6. DIMP and half mustard adsorption isotherms (—, based on total material; ---, based only on carbon coating).

glass, and the dotted line is calculated from GAC data.² The correlation coefficient values (r), calculated adsorption parameters K , and $1/n$ values from normalized data are given in Table 3, along with the best available data obtained on granulated activated carbon (GAC).² According to the correlation coefficient values (r) in Table

Table 3. Summary of Adsorption Parameters for ACFs

contaminant	SL-1			SL-2			GAC ²	
	K	$1/n$	r	K	$1/n$	r	K	$1/n$
benzene	40	0.27	0.80	66	0.45	0.97	29.5	0.34
toluene	85	0.27	0.96				69.1	0.27
ethylbenzene				237	0.16	0.94	112	0.17
<i>p</i> -xylene				185	0.37	0.93	124	0.22
DIMP				129	0.21	0.89		
half mustard				28	0.27	0.84		

3, adsorption isotherms are well represented by the Freundlich isotherm, specifically for the adsorption of BTEX.

For an effective adsorption system, high adsorption capacity (Q) and low equilibrium concentration of target compound (C_e) after adsorption are needed. Thus, the larger the K value and the smaller the $1/n$ value, the more effective the ACF is for adsorption.

Adsorption parameters based on the Freundlich equation (Table 3) show that, in most cases, ACFs (SL-2 and SL-1) have higher adsorption capacities based on the carbon coating as compared with the best available data obtained on granulated activated carbon (GAC). Therefore, the micropores of ACFs have a higher affinity for BTEX than GAC. However, GAC is still better than SL-2 and SL-1 due to a moderately low carbon content of ACFs used when the adsorption isotherms are compared on the basis of the total material. This could easily be remedied by using higher phenolic impregnations during processing.

For benzene, the adsorption isotherms were carried out on both SL-2 and SL-1 to assess the effect of two distinct micropore sizes, shown in Figure 5. The results indicate that SL-2 is more effective at higher concentrations as compared to SL-1, but a comparison of the slope values (i.e. a measure of the adsorption strength—Table 3) shows SL-2 at 0.45 and SL-1 at 0.27. Thus, at much lower concentrations, the smaller pore size of SL-1 will dominate due to the higher overlap in potential between the pore walls. On the basis of data extrapolation, these two fibers will cross over at ~ 0.05 mg/L, so pore size dominates below that concentration and pore volume above.

For toluene, adsorption isotherms were carried out only on SL-1, but it appeared that SL-1 was a more effective adsorbent than GAC due to a high K value in SL-1. However, adsorption capacities were found to be twice as high on SL-2 (Figure 3).

The results for ethylbenzene and *p*-xylene show similar trends to those described above, although the capacities tend to be higher. This effect arises from their lower solubility in water, so that the molecules would prefer to come out of solution and adsorb on the carbon surface.

Finally, for DIMP and HM, the adsorption isotherms and adsorption parameters based on the Freundlich equation are shown in Figure 6 and Table 3. Unfortunately, no data for GAC were available on these two molecules.

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