

Trichloroethylene Adsorption by Fibrous and Granular Activated Carbons: Aqueous Phase, Gas Phase, and Water Vapor Adsorption Studies[†]

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The important adsorption components involved in the removal of trichloroethylene (TCE) by fibrous and granular activated carbons from aqueous solutions were systematically examined. Namely, adsorption of TCE itself (i.e., TCE vapor isotherms), water molecules (i.e., water vapor isotherms), and TCE in water (i.e., TCE aqueous phase isotherms) were studied, side-by-side, using 20 well-characterized surface-modified activated carbons. The results showed that TCE molecular size and geometry, activated carbon surface hydrophilicity, pore volume, and pore size distribution in micropores control adsorption of TCE at relatively dilute aqueous solutions. TCE adsorption increased as the carbon surface hydrophilicity decreased and the pore volume in micropores of less than 10 Å, especially in the 5–8 Å range, increased. TCE molecules appeared to access deep regions of carbon micropores due to their flat geometry. The results indicated that characteristics of both adsorbate (i.e., the molecular structure, size, and geometry) and activated carbon (surface hydrophilicity, pore volume, and pore size distribution of micropores) control adsorption of synthetic organic compounds from water and wastewaters. The important micropore size region for a target compound adsorption depends on its size and geometry.

Introduction

Trichloroethylene (TCE) is one of the most frequently detected groundwater contaminants at hazardous waste sites in the United States (1). It has been designated as a priority pollutant by the United States Environmental Protection Agency and is regulated by the Safe Drinking Water Act Amendment of 1987 (2). Activated carbon adsorption has been widely used to remove various synthetic organic contaminants (SOCs), including TCE, from potable water supplies and industrial wastewaters (3). The main objective of this paper is to systematically investigate adsorption of TCE by modified fibrous and granular activated carbons. The important adsorption components involved in the TCE removal were examined in the context of carbon surface chemistry and porosity. Namely, adsorption of TCE itself

(i.e., TCE vapor isotherms), water molecules (i.e., water vapor isotherms), and TCE in water (i.e., TCE aqueous phase isotherms) were studied, side-by-side, using various well-characterized granular and fibrous activated carbons with a wide range of physicochemical characteristics. Although different researchers have studied TCE adsorption by activated carbons (e.g., refs 4–13), to the best of our knowledge, this is the first time that all of these adsorption components have been vigorously investigated in a single study using a broad range of activated carbons.

Background

Three types of interactions control adsorption of a SOC by activated carbon from water (i.e., single-solute adsorption): (i) SOC–activated carbon, (ii) SOC–water, and (iii) activated carbon–water. SOC–activated carbon interaction can be a function of three factors: molecular structure of the SOC, surface chemistry of the activated carbon, and solution chemistry. Adsorption of a SOC by an activated carbon may involve various combinations of chemical, electrostatic, and physical (i.e. nonspecific dispersion forces) interactions (14). For example, in addition to adsorption by nonspecific dispersion forces, SOC may specifically interact with carbon surface, including basal plane electrons, unpaired electrons located at the edges of terminated basal planes, and surface functional groups. Chemical and electrostatic interactions may also be influenced by the background water chemistry (i.e., pH and ionic strength). In the case of relatively nonpolar TCE, nonspecific dispersion interactions are thought to play the major role in the adsorption. Furthermore, the microporous nature of activated carbons has a positive impact on the adsorption of small molecular weight SOC. With all other factors being equal, sorption energy is greater in micropores. As pore width approaches adsorbate dimensions, multiple contact points on the adsorbent surface become possible and surface forces overlap. Therefore, higher pore volume in pore sizes close to the dimensions of the target SOC is expected to increase the uptake of activated carbons.

SOC–water interactions relate primarily to the chemical compatibility between SOC and water. With increasing hydrophobicity of SOC, an increasing driving force develops for SOC molecules to escape to interfaces. This is known as solvent-motivated adsorption. It is an important factor in the adsorption of relatively hydrophobic TCE by activated carbon.

Activated carbon–water interactions depend on the surface polarity of carbon surfaces. Surface polarity results from hydrophilic surface sites that may include both acidic (e.g., oxygen-containing) and basic (e.g., nitrogen-containing) functionalities and inorganic (e.g., metal) species that may exist on the carbon surface. These polar sites act as the growing centers of water clusters (15), which hinder removal of hydrophobic SOC by preventing their access to the micropores where the majority of the activated carbon surface area for adsorption is located. Water cluster formation is particularly important for adsorption of SOC at low concentrations, as typically encountered in environmental treatment systems. It has been shown that TCE uptake from water can be significantly enhanced through thermal degradation of acidic surface functionalities on activated carbons or carbon fibers (11, 12).

Experimental Section

Sorbents. Two wood-based (Macro and Meso, Westvaco Inc.) and one coal-based (F400, Calgon Inc.) granular activated

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carbons (GACs) and two activated carbon fibers (ACF10 and ACF20H, American Kynol Inc.) were used in this study. Meso and Macro are phosphoric acid-activated and mesoporous carbons, whereas F400 is a steam-activated microporous carbon. ACF10 and ACF20H are phenol formaldehyde-based and highly microporous carbon fibers.

All carbons, except ACF20H, were modified using a combination of various gas and/or liquid treatment pathways. The objective of these treatments was to produce carbons with different surface chemistries (including different levels of surface basicity and acidity and various levels of surface polarity). The code used after the name of each sorbent describes the surface treatment pathway(s) employed. For example, modified ACF10 carbons are labeled as follows: (i) ACF10,He, heat-treated under helium at 900 °C for 2 h; (ii) ACF10,H, heat-treated under hydrogen at 900 °C for 2 h; (iii) ACF10,He,16NO, heat-treated under helium at 900 °C for 2 h and oxidized using boiling concentrated (15.7 N) nitric acid for 1 h; (iv) ACF10,He,16NO,8N1H, heat-treated under helium at 900 °C for 2 h, oxidized by nitric acid, and treated with ammonia at 800 °C for 1 h; and (v) ACF10,He,16NO,4N1H, heat-treated under helium at 900 °C for 2 h, oxidized by nitric acid, and treated with ammonia at 400 °C for 1 h. The details of the surface treatment procedures were described elsewhere (16). Overall, 20 modified sorbents were produced for the study. All sorbents were stored in sealed containers.

Characterization of Sorbents. Surface chemistry of carbons was characterized by: (i) elemental analysis using X-ray photoelectron spectroscopy (XPS); (ii) NaOH and HCl uptakes; and (iii) pH of point of zero charge (pH_{PZC}) experiments. N_2 isotherms at 77 K were used to determine (i) surface area from the BET equation, (ii) total pore volume from the uptake at the relative pressure of 0.98, and (iii) pore volume distribution from the Density Functional Theory (DFT) using the Micromeritics software (Micromeritics Instrument Corporation, Norcross, GA). Detailed information about the characterization methods and procedures was previously described (16).

TCE and Water Vapor Isotherms. TCE and water vapor adsorption isotherms of sorbents were volumetrically obtained at 273.15 K, using a Micromeritics ASAP 2010 instrument. Approximately 50–100 mg of activated carbon sample was degassed for 1 h at 90 °C and overnight at 200 °C for the removal of moisture and other adsorbed vapors/gases. The degassed samples were loaded on the analysis port, and adsorption data points were obtained from the low relative pressures (10^{-2} for water vapor and 10^{-4} for TCE vapor) up to relative pressures close to one.

Aqueous TCE Isotherms. Constant-dose aqueous phase isotherm experiments for a wide range of initial TCE concentration were performed using both virgin and modified carbons. GAC particles between the U.S. standard sieve sizes of 30 and 40 (i.e., 600 and 425 μm) were used in all experiments. Ten milligrams of carbons was equilibrated with various TCE concentrations in 250-mL amber glass bottles (headspace free) on a rotary tumbler for 2 weeks, a time that was sufficient to reach equilibrium as demonstrated by preliminary studies in this and previous work (17). No carbon-wetting problem was encountered while preparing the isotherm bottles. After the equilibration period, reactors were sampled and analyzed, after hexane extraction, by gas chromatography using an electron-capture detector calibrated with external standards. All isotherms were conducted in the presence of a phosphate buffer at the pH of 7 and room temperature (21 ± 3 °C). Moisture contents of sorbents were measured and corrections were made for the isotherm calculations.

Results and Discussion

Carbon Characterization. The objective of carbon surface modification was to prepare activated carbons with different surface chemistries. Since various carbon precursors with different pore size distributions were employed for surface modification, it was possible to simultaneously examine the effects of carbon surface chemistry and porosity on TCE adsorption. The physical and chemical characteristics of virgin and modified granular activated carbons and carbon fibers are provided in Tables 1 and 2, respectively.

One way of increasing carbon hydrophobicity is to remove hydrophilic surface functionalities, particularly various acidic groups, by heat treatment of carbon in an inert atmosphere (e.g., He) or under the hydrogen flow. The major impact of heat treatment at 900 °C for 2 h was to remove a considerable portion of oxygen surface functionalities and to decrease the surface acidity of carbons (Table 2). This is consistent with the previous reports that decomposition temperature of majority of oxygen functionalities on carbon surface is below 900 °C (18, 19). The results also indicated that hydrogen treatment was more effective than helium for permanent removal of oxygen groups (20, 21). This was attributed to the fact that H_2 can more effectively stabilize the carbon surface by deactivation of surface active sites by formation of stable C–H bonds as well as gasification of unstable and reactive carbon atoms (20). In addition to changes in surface chemistry, some considerable structural changes (i.e., decreases in surface area and pore volume) were also observed for the wood-based Macro and Meso carbons, whereas there was relatively minimal impact on F400 and ACF10.

Nitric acid oxidation of heat-treated carbons significantly increased their surface acidities and oxygen contents. Furthermore, surface areas and total pore volumes of all oxidized carbons were lower than their heat-treated precursors. The impact was more noticeable on Macro, Meso, and ACF10 than F400. This decrease was due to (i) alteration of carbon pores and (ii) addition of oxygen-containing groups to the surface that increase the carbon weight, therefore decreasing weight-normalized parameters (e.g., surface area and pore volume).

The objective of ammonia treatment was to increase basicity of activated carbons by introducing basic nitrogen-containing functionalities to the surface. One approach to prepare carbons with high nitrogen contents is to first introduce oxygen-containing functionalities to the surface. These functionalities decompose during the subsequent ammonia treatment and serve as reaction or anchor sites for ammonia molecules or nitrogen-containing radicals (22). Furthermore, oxidized carbons were exposed to ammonia at two different temperatures (400 and 800 °C) to produce carbons with different amounts and types of nitrogen-containing functionalities on the surface. Ammonia treatment after the surface oxidation reduced surface acidity while increasing surface basicity and nitrogen content. Overall, high-temperature ammonia treatment produced more basic surfaces (i.e., higher HCl uptakes and pH_{PZC}) as compared to low-temperature ammonia treatment.

The pore size distribution results for carbon fibers were also compared with those reported by other researchers for similar fibers (12, 23). In general, the results were in agreement; however, some differences were observed in the micropore size distributions. The ACF10 and ACF20 fibers used in this study were also analyzed by Micromeritics Instrument Corporation Laboratory, the manufacturer of the gas adsorption analyzer employed for this research. The results were in perfect agreement with those independently obtained in this study and reported in this paper (Figure SI-1, Supporting Information). Therefore, the differences in the pore size distribution of similar carbon fibers obtained

TABLE 1. Physical Characterization of Virgin and Modified Carbons from Nitrogen, TCE, and Water Vapor Isotherms^a

carbon	nitrogen						TCE		water			
	S _{ABET} (m ² /g)	V _{tot,N2} (cm ³ /g)	DFT pore volume distribution (cm ³ /g)					V _{tot,TCE} (cm ³ /g)	V _{tot,TCE} / V _{tot,N2}	V _{P/P₀=0.4} (cm ³ /g)	V _{tot,H2O} (cm ³ /g)	V _{tot,H2O} / V _{tot,N2}
			<7 Å	7–10 Å	<10 Å	<20 Å	<1000 Å					
ACF20H	1983	0.860	0.198	0.135	0.333	0.691	0.717	0.732	0.851	0.005	0.760	0.884
ACF10	963	0.374	0.240	0.046	0.286	0.314	0.314	0.310	0.828	0.094	0.310	0.829
ACF10,He	1005	0.459	0.198	0.065	0.263	0.305	0.370	0.320	0.786	0.026	0.328	0.806
ACF10,H	1085	0.456	0.211	0.071	0.282	0.338	0.362	0.354	0.777	0.028	0.356	0.781
ACF10,He,16NO	768	0.305	0.113	0.052	0.165	0.231	0.231	0.308	1.009	0.272	0.320	1.049
ACF10,He,16NO,4N1H	1053	0.503	0.129	0.058	0.187	0.344	0.411	0.384	0.764	0.152	0.400	0.795
ACF10,He,16NO,8N1H	1272	0.606	0.131	0.083	0.214	0.407	0.486	0.465	0.767	0.137	0.488	0.805
F400	1035	0.553	0.122	0.083	0.205	0.326	0.447	0.459	0.831	0.047	0.414	0.749
F400,He	1058	0.545	0.106	0.095	0.201	0.332	0.416	0.459	0.843	0.018	0.466	0.855
F400,H	1084	0.598	0.087	0.110	0.197	0.332	0.481	0.476	0.796	0.009	0.466	0.779
F400,He,16NO	970	0.531	0.059	0.105	0.164	0.294	0.425	0.473	0.891	0.195	0.392	0.738
F400,He,16NO,4N1H	1005	0.582	0.064	0.086	0.150	0.295	0.467	0.476	0.818	0.113	0.500	0.859
F400,He,16NO,8N2H	970	0.611	0.063	0.043	0.106	0.260	0.476	0.487	0.798	0.071	0.510	0.835
Macro	1569	1.282	0.104	0.014	0.118	0.376	1.130	1.136	0.886	0.108	1.010	0.788
Macro,He	1261	0.992	0.107	0.038	0.145	0.317	0.870	0.847	0.854	0.060	0.910	0.917
Macro,H	1358	1.110	0.082	0.043	0.125	0.313	0.990	0.950	0.856	0.043	1.020	0.919
Macro,He,16NO	1084	0.878	0.089	0.036	0.125	0.262	0.788	0.771	0.878	0.180	0.732	0.834
Macro,He,16NO,4N1H	996	0.741	0.070	0.036	0.106	0.239	0.643	0.691	0.933	0.130	0.702	0.947
Macro,He,16NO,8N2H	1767	1.443	0.110	0.037	0.147	0.374	1.289	1.156	0.801	0.095	1.240	0.859
Meso	1710	1.110	0.075	0.039	0.114	0.403	0.953	0.982	0.885	0.126	0.920	0.829
Meso,He	1310	0.833	0.106	0.044	0.150	0.355	0.721	0.698	0.838	0.079	0.788	0.946
Meso,H	1324	0.875	0.078	0.055	0.133	0.319	0.764	0.741	0.847	0.027	0.828	0.946
Meso,He,16NO	1153	0.734	0.101	0.054	0.155	0.309	0.631	0.623	0.849	0.194	0.674	0.918
Meso,He,16NO,4N1H	1275	0.898	0.066	0.068	0.134	0.308	0.785	0.778	0.867	0.116	0.856	0.953
Meso,He,16NO,8N2H	1504	0.954	0.109	0.052	0.161	0.370	0.799	0.865	0.907	0.091	0.820	0.860

^a V_{tot,TCE} and V_{tot,H2O} were obtained at P/P₀ = 0.95 and 0.98, respectively.

TABLE 2. Chemical Characteristics of Virgin and Modified Carbons

carbon	pH _{PZC}	NaOH uptake (mequiv/g)	HCl uptake (mequiv/g)	O (atom %)	N (atom %)	C (atom %)
ACF20H	9.6	0.091	0.451	3.3	0.4	96.1
ACF10	8.6	0.156	0.294	4.1	0.8	94.6
ACF10,He	10.0	0.086	0.381	3.6	0.4	94.9
ACF10,H	10.8	0.006	0.404	2.6	0.8	96.3
ACF10,He,16NO	1.9	3.046	0.000	13.3	2.5	83.4
ACF10,He,16NO,4N1H	7.8	0.790	0.348	7.6	4.1	87.1
ACF10,He,16NO,8N1H	9.7	0.291	0.488	3.8	2.7	91.7
F400	8.5	0.238	0.411	5.9	0.5	92.3
F400,He	9.8	0.098	0.498	4.6	0.4	93.8
F400,H	10.5	0.001	0.471	4.8	0.8	93.5
F400,He,16NO	1.9	1.864	0.097	11.3	1.2	86.1
F400,He,16NO,4N1H	7.1	0.544	0.251	7.5	2.6	88.6
F400,He,16NO,8N2H	8.5	0.201	0.476	5.7	3.9	89.0
Macro	1.9	1.232	0.000	7.5	0.7	90.6
Macro,He	2.8	0.637	0.000	5.8	0.8	92.5
Macro,H	4.5	0.649	0.000	5.3	0.5	93.3
Macro,He,16NO	1.9	3.570	0.000	14.0	2.4	82.8
Macro,He,16NO,4N1H	5.7	1.112	0.061	8.6	4.1	86.7
Macro,He,16NO,8N2H	6.9	0.424	0.508	4.1	4.5	90.7
Meso	6.2	0.623	0.405	7.6	0.6	90.7
Meso,He	7.1	0.243	0.263	5.7	0.4	92.3
Meso,H	7.8	0.197	0.352	5.3	0.3	93.3
Meso,He,16NO	1.9	3.518	0.000	13.3	0.5	85.6
Meso,He,16NO,4N1H	6.1	0.992	0.165	7.4	3.7	88.5
Meso,He,16NO,8N2H	8.8	0.356	0.523	3.9	3.9	91.9

in various studies may have resulted from the different batches used and/or variability in the pore size distribution analyses among different laboratories.

Water Vapor Adsorption. Water vapor adsorption experiments were conducted to obtain direct information about the surface hydrophilicity of activated carbons produced for this study. The results are shown in the Supporting Information Figure SI-2. The water vapor uptakes at the low relative pressure (P/P₀) range (e.g., 0.0 to 0.4) have been related to the extent of water cluster formation on the hydrophilic sites

(15, 24). In this study, the water vapor uptake at the relative pressure of 0.4 was selected to semiquantitatively compare the hydrophilicity of activated carbons (Table 1). In terms of the impact of different treatment pathways on the affinity of each carbon for water, the following observations were made. The heat-treated carbons, because of the degradation of surface functionalities, were less hydrophilic than their precursors (Figure SI-2 in the Supporting Information and Table 1). Hydrogen treatment (except for ACF10 that both helium- and hydrogen-treated carbons behaved similarly)

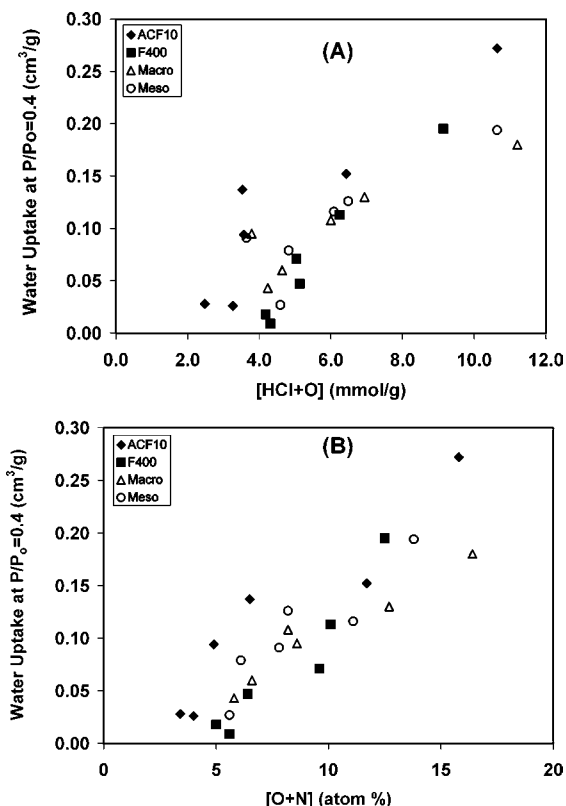


FIGURE 1. Water vapor uptake at $P/P_0 = 0.4$ as a function of (A) $[\text{HCl} + \text{O}]$ and (B) oxygen and nitrogen contents of activated carbons.

produced surfaces with less affinity for water in comparison to helium treatment. On the other hand, both oxidized and ammonia-treated carbons demonstrated higher affinities for water. The surface polarity of oxidized carbons is predominantly from the contribution of acidic groups, while the surface polarity of ammonia-treated basic carbons results from newly created basic nitrogen functionalities as well as some remaining acidic groups. Nitric acid oxidation produced carbons with the highest water affinity. While ammonia treatment of ACF10 and F400 produced more hydrophilic carbons as compared to their virgin precursors, it did not considerably change the hydrophilicity of the virgin Macro and Meso (Figure SI-2 in the Supporting Information).

In literature, the sum of oxygen and nitrogen contents (12) or oxygen content and HCl uptake (25) has been used as an indirect measure of carbon surface hydrophilicity. When the water vapor uptakes of carbons at $P/P_0 = 0.4$ were plotted against these parameters, an increasing trend in the water uptake was observed (Figure 1). This supports the fact that surface functionalities play an important role in water adsorption. However, a considerable amount of scatter was also apparent in the observed trends. These findings indicate that direct measurement of water adsorption is the most realistic and accurate method to properly evaluate hydrophilic nature of carbon surfaces. Indirect measures, such as the sum of HCl uptake and oxygen content or oxygen and nitrogen contents, may be useful to qualitatively compare carbons with large differences in surface polarities. However, they are not sensitive to distinguish small differences.

Surface polarity of activated carbons plays an important role in the adsorption of hydrophobic compounds, such as TCE. The polar and hydrophilic functionalities that exist on the carbon surface, including those located at the entrances to the carbon micropores, attract water molecules. The water clusters that are thought to grow on the hydrophilic sites have much lower mobility as compared to those existing in the bulk solution due to enhanced overlapping adsorption

forces existing in narrow micropores. Kaneko et al. (26) from their X-ray diffraction studies of water adsorbed by an activated carbon fiber reported that the state of adsorbed water (at room temperature) was similar to “a solid-like structure”. Therefore, water clusters may effectively hinder TCE accessing and utilizing the micropore region of activated carbons for adsorption.

Water vapor uptakes at high P/P_0 values (e.g., close to the saturation condition, at $P/P_0 = 0.98$) were well-correlated with the total pore volumes (determined from nitrogen gas adsorption experiments) but not with the surface chemistry of activated carbons. The average values of $V_{\text{tot,H}_2\text{O}}/V_{\text{tot,N}_2}$ ratios for all carbons, listed in Table 1, was 0.860 with a standard deviation of 0.075.

TCE Vapor Adsorption. TCE vapor adsorption experiments were conducted to examine interactions between TCE molecules and carbon surfaces in the absence of water molecules. The isotherms are provided in Supporting Information Figure SI-3. Analysis of pore size distribution results obtained from nitrogen adsorption with the TCE vapor isotherms provided information about the accessible carbon pore regions for TCE molecules. TCE has a planar shape with approximate dimensions of $6.6 \text{ \AA} \times 6.2 \text{ \AA} \times 3.6 \text{ \AA}$ (Figure 2). The total pore volumes obtained from TCE and N_2 (a relatively spherical molecule with dimensions of $4.5 \text{ \AA} \times 3.0 \text{ \AA} \times 3.0 \text{ \AA}$, Figure 2) isotherms are provided in Table 1. The ratio of total pore volumes determined from TCE to those obtained from N_2 isotherms was calculated (i.e., $V_{\text{tot,TCE}}/V_{\text{tot,N}_2}$). The average ratio for all of the fibrous and granular activated carbons with various pore size distributions was 0.846 with a standard deviation of 0.055. This indicated that 85% of pore volume accessed by nitrogen molecules was also accessible for TCE. On the other hand, pore size distribution of the activated carbons from nitrogen adsorption indicated that a significant portion of pore volumes was in the micropores and especially in the pores less than $7 \text{ \AA}$, which is about the second and third largest dimensions of TCE. Specifically, the pore volumes of ACF10 and F400 in the pores less than $7 \text{ \AA}$ were 64% and 22% of the total pore volumes, respectively. Therefore, for the observed 83% ratios of total pore volumes between nitrogen and TCE for ACF10 and F400 (Table 1), a substantial portion of TCE must have adsorbed in pores less than $7 \text{ \AA}$. Considering the slit-shaped geometry of activated carbon pores (27) or elliptical geometry suggested for carbon fibers (28), these findings indicated that planar TCE molecules diffused in a *flat* form into the deep portions of carbon micropores.

TCE Aqueous Phase Adsorption. TCE aqueous adsorption isotherms for virgin and modified carbons are shown in Figure 3. An overall evaluation of these isotherms with the water and TCE vapor isotherms leads to the general conclusion that the TCE uptake from aqueous solutions is controlled by both carbon microporosity and surface hydrophobicity (or inversely correlated to the surface polarity).

To evaluate microporosity effect, the TCE isotherm of ACF20H was compared with those of ACF10,He and ACF10,H. These three sorbents were selected for comparison because they were produced from the same precursor material and had similar surface chemistries, as indicated by their similar pH_{PZC} , NaOH, and HCl uptakes, elemental composition, and water vapor uptakes at P/P_0 of 0.4 (Tables 1 and 2). The main difference among them was in their surface areas and pore size distributions. The isotherm results indicated that TCE uptakes of ACF10,He and ACF10,H were higher than that of ACF20H (Figure 4A). It is evident that surface area was not the factor controlling TCE adsorption. The maximum TCE uptake by these three fibers was about 100 mg of TCE/g within the concentration range of conducted isotherms. Given the density of TCE at 25°C as 1.46 g/mL (29), the volume of the adsorbed TCE molecules in fiber pores is

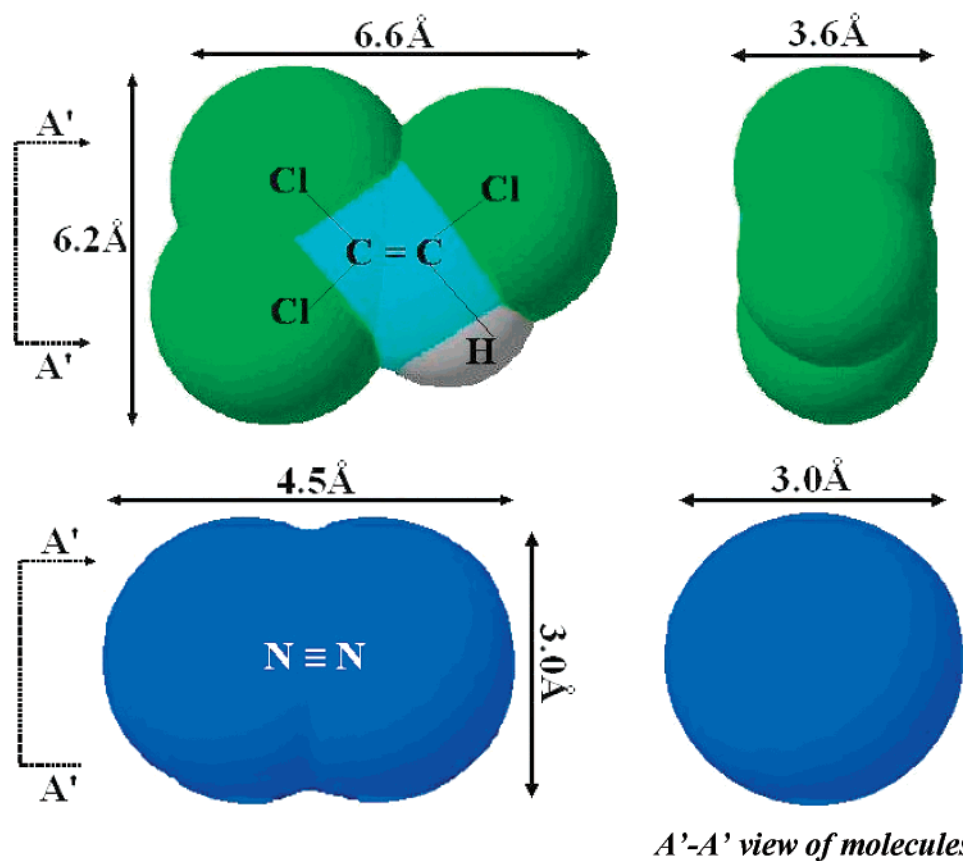


FIGURE 2. Molecular dimensions of TCE and N_2 calculated using molecular mechanics force field method in PCMODEL Version 9 (Serena Software).

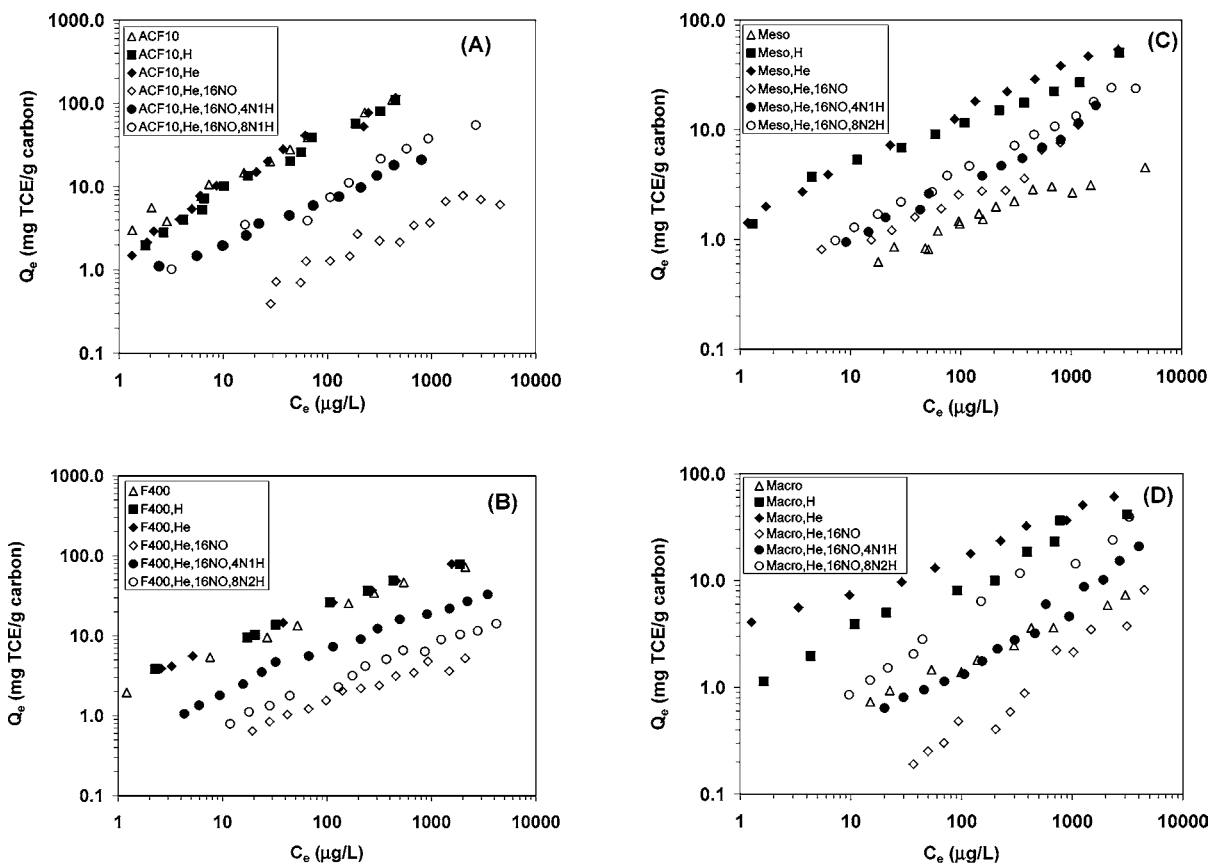


FIGURE 3. Aqueous phase adsorption of TCE by (A) ACF10, (B) F400, (C) Meso, and (D) Macro carbons.

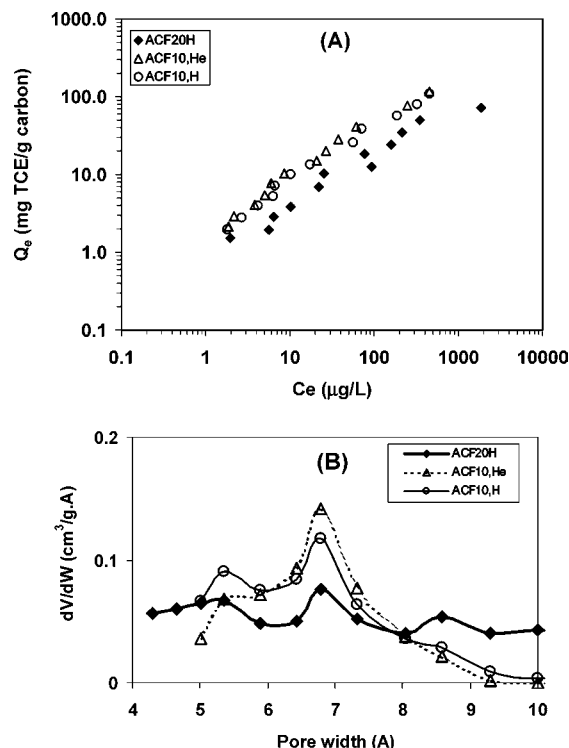


FIGURE 4. (A) Aqueous phase adsorption of TCE by ACF20H, ACF10,He, and ACF10,H. (B) Pore size distributions of ACF20H, ACF10,He, and ACF10,H within the pores less than 10 Å.

approximately $0.07 \text{ cm}^3/\text{g}$. The micropore volumes within pores less than 10 Å for all three fibers were 3–4 times higher than the pore volume required to accommodate the adsorbed TCE molecules. The higher uptakes exhibited by ACF10 fibers than ACF20H was attributed to the difference in their pore size distributions within the pores less than 10 Å (Figure 4B). The pore volume of ACF10 fibers in this region was mainly distributed in pores with widths of 5–8 Å (about the dimensions of a TCE molecule). On the other hand, ACF20H had a uniform distribution without showing an apparent dominant pore size. This analysis indicates that both *pore volume* and *size distribution* in pores less than 10 Å are important for TCE adsorption. It has been reported that the available pore volume in the pores 7–10 Å primarily controls aqueous phase TCE adsorption by carbons with similar surface chemistries (12). The findings obtained in this study do not support this observation. The volume required by the adsorbed TCE molecules was about the volume available between the pores of 7–10 Å of ACF10,H and ACF10,He. In contrast, ACF20H had sufficient pore volume in the same pore region but showed lower TCE uptake than ACF10 fibers (Table 1 and Figure 4A).

The effect of carbon surface hydrophobicity on the TCE adsorption can be seen by comparing adsorption isotherms of Macro and Meso, two acidic carbons, before and after heat treatment. The uptake of Macro and Meso for TCE increased significantly after the heat treatment (Figure 3). As expected, water vapor isotherms showed a considerable decrease in the affinity of these carbons for water as a result of heat treatment. The pore size distribution data indicated that the impact of heat treatment on the pore volume and pore size distribution in the pores less than 10 Å was relatively small (Figure 5). Therefore, the observed significant increase in the TCE uptake was primarily a result of increase in surface hydrophobicity. Comparison of the results obtained from the oxidized F400 and ACF10 and their virgin precursors, two basic and hydrophobic carbons, were also consistent with this explanation.

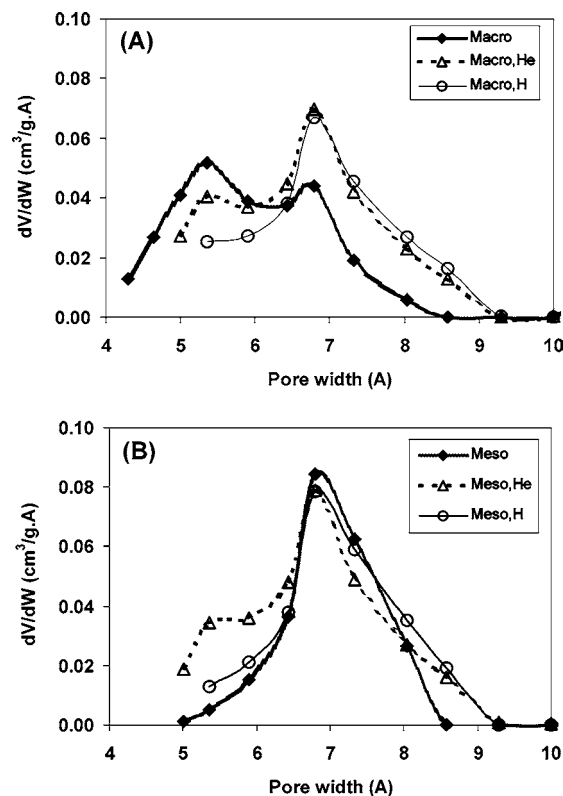


FIGURE 5. Pore size distributions of Macro and Meso within the pores less than 10 Å before and after heat treatment.

In general, the impact of various treatment pathways on carbon microporosity and/or surface chemistry was reflected on the TCE uptake. Heat treatment significantly increased the capacity of Macro and Meso, while the impact was minimal on ACF10 and F400 (Figure 3). As discussed above, the enhanced TCE removal by heat-treated Macro and Meso was due to the increase in their surface hydrophobicity, while fairly preserving the pore volume and size distribution in pores less than 10 Å (Figures 3 and 5 and Table 1). On the other hand, since virgin ACF10 and F400 had relatively hydrophobic surfaces and heat treatment did not have a major impact on their pore size distributions, no considerable impact was observed on their TCE uptakes. Oxidation of activated carbons with nitric acid significantly reduced the TCE adsorption (Figure 3). This was mainly due to a substantial increase in the carbon surface polarity. For ACF10 and F400, a noticeable reduction was also observed in the volume of pores less than 10 Å after oxidation (Table 1). In most cases, ammonia-treated carbons showed TCE uptakes between heat-treated and oxidized carbons (Figure 3). This was consistent with their affinities toward water and pore volumes and size distributions in pores less than 10 Å as compared to those of heat-treated and oxidized carbons.

Overall, the results obtained in this study indicated that characteristics of both adsorbate (i.e., the molecular size and geometry) and activated carbon (surface hydrophilicity, pore volume, and pore size distribution in micropores) control adsorption of SOCs from water and wastewater at relatively low concentrations. In terms of the effect of carbon surface chemistry, TCE adsorption increased as the carbon surface hydrophilicity decreased. To examine the role of carbon pore size distribution, adsorption of TCE by all heat-treated carbons was compared (Figure 6). Since all carbons were heat-treated, the impact of carbon surface polarity on the TCE removal was less important than the impact of carbon porosity. The results indicated that at low equilibrium concentrations (e.g., $<10 \mu\text{g/L}$), TCE uptake of all carbons

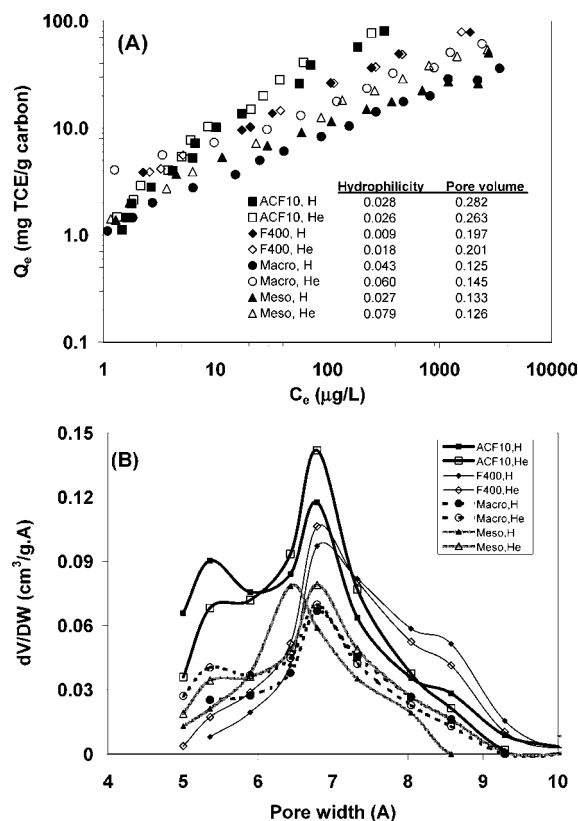


FIGURE 6. (A) TCE aqueous isotherms and (B) pore size distributions of all heat-treated carbons within the pores less than 10 Å. The hydrophilicity is the water vapor uptake value (cm^3/g) at $P/P_0 = 0.4$ from Table 1. The listed pore volume <10 Å values (cm^3/g) are also from Table 1.

were fairly comparable. However, with increasing equilibrium concentration, TCE adsorption became primarily correlated with the pore volume and size distribution in the pores less than 10 Å. At equilibrium concentrations of 100 $\mu\text{g}/\text{L}$ or higher, TCE uptake was in the order of $\text{ACF10, He} \approx \text{ACF10, H} > \text{F400, He} \approx \text{F400, H} > \text{Macro, He} \approx \text{Meso, He} > \text{Macro, H} \approx \text{Meso, H}$. All these carbons had enough pore volume in pores <10 Å for the highest TCE uptakes (~100 mg/g) observed. When the correlations between the TCE uptake and the pore volumes in different regions of carbon micropores (e.g., 5–8, 7–10, and <10 Å) were examined, the best correlation was obtained for 5–8 Å (Figure 7). This was also in agreement with the observations from the gas-phase adsorption experiments that TCE molecules were able to access pores smaller than 7 Å due to their flat geometry. Previously, it has been reported that the available pore volume in pores 7–10 Å primarily controls adsorption of TCE (12). The different optimum pore size range found in this study compared to this previous work may result from the variability in pore size distributions between different laboratories. The results clearly indicate both the molecular size and the geometry of the adsorbate are important factors controlling the SOC adsorption and will determine the important pore size region of an activated carbon for adsorption. In the case of TCE tested in this study, carbons that had hydrophobic surfaces and higher pore volumes in the 5–8 Å region showed higher TCE uptakes.

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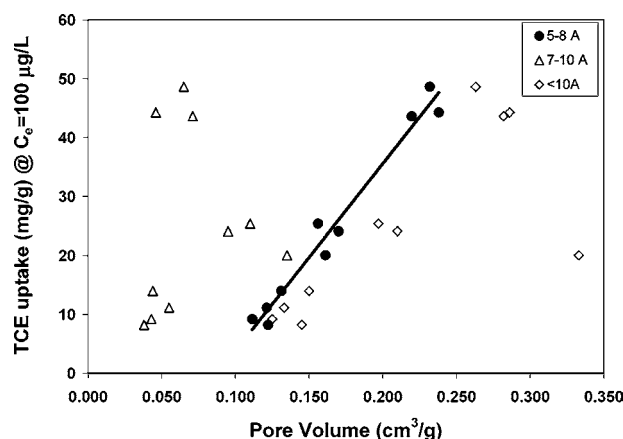


FIGURE 7. TCE uptake at equilibrium concentration of 100 $\mu\text{g}/\text{L}$ vs pore volumes in different pore size ranges for all heat-treated carbons shown in Figure 6 as well as virgin ACF10 and ACF20H. The line is to show the trend for the 5–8 Å data.

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Supporting Information Available

Comparison of pore size distributions of ACF10 and ACF20 fibers, independently measured at Clemson University (Environmental Engineering and Science) and Micromeritics Instrument Corporation Laboratories, and water and TCE vapor isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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