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# Compositions and Sorptive Properties of Crop Residue-Derived Chars

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Chars originating from the burning or pyrolysis of vegetation may significantly sorb neutral organic contaminants (NOCs). To evaluate the relationship between the char composition and NOC sorption, a series of char samples were generated by pyrolyzing a wheat residue (*Triticum aestivum* L.) for 6 h at temperatures between 300 °C and 700 °C and analyzed for their elemental compositions, surface areas, and surface functional groups. The samples were then studied for their abilities to sorb benzene and nitrobenzene from water. A commercial activated carbon was used as a reference carbonaceous sample. The char samples produced at high pyrolytic temperatures (500–700 °C) were well carbonized and exhibited a relatively high surface area (>300 m<sup>2</sup>/g), little organic matter (<3%), and low oxygen content (≤10%). By contrast, the chars formed at low temperatures (300–400 °C) were only partially carbonized, showing significantly different properties (<200 m<sup>2</sup>/g surface area, 40–50% organic carbon, and >20% oxygen). The char samples exhibited a significant range of surface acidity/basicity because of their different surface polar-group contents, as characterized by the Boehm titration data and the NMR and FTIR spectra. The NOC sorption by high-temperature chars occurred almost exclusively by surface adsorption on carbonized surfaces, whereas the sorption by low-temperature chars resulted from the surface adsorption and the concurrent smaller partition into the residual organic-matter phase. The chars appeared to have a higher surface affinity for a polar solute (nitrobenzene) than for a nonpolar solute (benzene), the difference being related to the surface acidity/basicity of the char samples.

## Introduction

The recent interest in the role of black carbon in soils and sediments has to do with their potential to contribute to the uptake of neutral organic contaminants (NOCs) by adsorption

over the well-known contaminant partition with the soil/sediment organic matter (SOM) (1–4). Since the black carbon level in soils or sediments is usually low relative to the SOM content, the potential for black carbon to significantly adsorb NOCs occurs mainly at the low NOC relative concentrations (5–11), that is, the region where the NOC single-solute isotherms are nonlinear with a concave-downward shape (5–9). The isotherms are usually practically linear over the intermediate-to-high relative concentration range because of the dominant partition effect. As such, the NOC sorption at low concentrations has been modeled as the sum of the surface adsorption on black carbon and the solute partition with SOM (10–13). Various attempts have now been made to identify, isolate, and quantify black carbon in different environmental matrixes (10, 11, 14–17).

Chars, a form of black carbon, are a ubiquitous form of carbon comprising a range of materials from polyaromatic to elemental or graphitic carbon, in comparison with organic carbon which forms covalent bonds with other elements such as H and O. Chars in the environment are believed to originate largely from the thermal alteration of various organic precursors (e.g., the burning of coal and vegetation) (9, 18). Chars may thus resemble activated carbon in some respects as surface adsorbents for NOCs. While the activated carbon is usually manufactured at high temperatures (>400 °C) under well-controlled activation conditions, chars are formed under natural conditions through partial or complete carbonization of organic precursors depending on charring temperature. They may thus possess a wide range of compositions and surface properties (18, 19). Heteroatoms such as oxygen, hydrogen, and nitrogen, which are found as minor contents in activated carbon (18, 20), are also anticipated to be present in the molecular network of chars. In particular, the oxygen atoms, the most active minor element in chars and activated carbon, are present in various forms of surface functional groups (21). Titration and spectroscopic analyses have revealed both acidic and basic oxygen-containing groups, the former including carboxyl, lactonic, carbonyl, and phenolic species, and the latter including ketone, pyrone, as well as chromene species (e.g., refs 18, 20, and 22–24). The charring temperature and other system conditions may cause a significant change in the char composition and surface-group content (25, 26). Polar functional groups on the activated carbon surfaces preferentially adsorb water molecules and polar adsorbates (27, 28) to form water clusters on the surfaces (29, 30) and to hinder nonpolar molecules from occupying the most energetic sites in the pores (20, 31, 32).

An improved understanding of the char contribution to the soil sorption of NOCs requires isolation and subsequent characterization of the char samples produced under various conditions to account for variations in their compositions and surface properties. The importance of such char characterization while preserving intact surface properties has not been well recognized in the past, and there have been few studies to relate the composition and surface properties of chars to their sorptive affinities. With this in mind, a characterization of laboratory-generated char samples under various well-controlled conditions and a subsequent analysis of their surface groups and sorptive behaviors would seem warranted. In agricultural soils, the field burning of vegetation and crop residues is expected to be the primary source of chars. In earlier studies, we showed that the char resulting from the burning of wheat residue, one of the most frequently burned crop residues worldwide, exhibited a high uptake power (33, 34). In this study, a range of char samples were

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obtained by pyrolyzing wheat residue at various temperatures. The samples were then extensively characterized via elemental analysis, surface area measurement, Boehm titration, nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and the NOC sorption characteristics. The objective of this study was to evaluate the effect of charring temperature on the crop residue-derived char composition and surface acidity, which affects the char's performance in agricultural soils to sorb NOCs from water solution.

## Experimental Section

**Char Samples.** An activated carbon, Darco G-60 (high-purity 100-mesh powder manufactured by American Norit Co.), was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as a reference char. Wheat (*Triticum aestivum* L.) residue was collected from the Arkansas Agricultural Research and Extension Center in Fayetteville, AR. The crop residue was washed with water four times, air-dried in a greenhouse for 2 d, and subsequently oven-dried overnight at 80 °C. The crop residue (20 g) was placed in a ceramic pot, covered with a fitting lid, and pyrolyzed under the oxygen-limited conditions for 6 h at 300, 400, 500, 600, and 700 °C. The resulting charred residues, known to contain high contents of Si and metal salts, were weighed and pulverized for subsequent demineralization with acids. The samples were treated in 200 mL of 1 M HCl solution for 4 h and centrifuged to remove the supernatants. The treatment was repeated four times. Next, the same procedure was employed except that 1 M:1 M HCl–HF solution was instead used. Finally, the samples were thoroughly washed with distilled water four times to remove residual acids, Si, and soluble salts. The char samples were oven-dried overnight at 80 °C and weighed. Such purification has proven effective in removal of Si and mineral salts and in enrichment of chars while maintaining the char surfaces largely unaltered (33). The activated carbon and char samples are hereafter referred to as AC, WC-300, WC-400, WC-500, WC-600, and WC-700, respectively, where the suffix X00 ( $X = 3-7$ ) to WC represents the pyrolysis temperature.

**Surface Areas.** The surface areas of char samples were measured with N<sub>2</sub> adsorption at liquid nitrogen temperature determined by a Gemini 2360 Micromeritics surface area analyzer. A char sample (~0.2 g) was outgassed overnight (~15 h) at 105 °C under a helium gas flow at 20 mL/min before N<sub>2</sub> adsorption. The molecular surface area of 16.2 Å<sup>2</sup> for N<sub>2</sub> and the BET (Brunauer–Emmett–Teller) equation were used to calculate the surface area of the char sample.

**Elemental Analysis.** The contents (%) of carbon, oxygen, and hydrogen of the char samples (AC, WC-300, WC-500, and WC-700) were measured in a commercial analytical laboratory (Huffman Laboratories, Inc., Golden, CO).

**Boehm Titration.** The oxygenated acidic and basic surface groups of char samples were determined using the Boehm's titration method (22, 23). Prior to measurement, the char sample was equilibrated with dilute HCl solution at pH 2 for 3 d, followed by a thorough washing with deionized water until it is free of Cl<sup>−</sup> as detected by AgNO<sub>3</sub>. A dried char sample (0.1–0.5 g) was mixed with 25 mL of the 0.05 N solution of NaHCO<sub>3</sub>, NaOH, or HCl. The sample suspensions were shaken for 24 h. The excess of base and acid in 5 mL of the filtrate was titrated with 0.01 N HCl and NaOH, respectively. Surface acidity and basicity were calculated on the basis of the assumption that NaHCO<sub>3</sub> neutralizes carboxyl groups only, NaOH neutralizes all acidic groups including carboxyl, lactonic, and phenolic groups, and HCl neutralizes all basic groups including ketonic, pyronic, and chromenic groups.

**<sup>13</sup>C NMR.** The <sup>13</sup>C NMR spectra of WC-300, WC-500, WC-700, and AC were obtained on a Bruker DSX 300 MHz

spectrometer. For the first two samples, the spectra were run by using the CPMAS-TOSS technique (cross-polarization magic-angle spinning with total sideband suppression). For the latter two samples, the ramp CPMAS technique was used because of the lack of signal using CPMAS-TOSS as well as a very low signal-to-noise ratio using DPMAS (direct-polarization MAS). For CPMAS-TOSS, the sample (~0.7 g) was packed in a 7-mm-diameter zirconia rotor with a Kel-F cap and run at 75 MHz (<sup>13</sup>C). The spinning speed was 4.5 kHz. A <sup>1</sup>H 90° pulse was followed by a contact time ( $t_{cp}$ ) of 2 ms, and then a TOSS sequence was used to remove sidebands (35–37). Line broadening of 50 Hz was used. The 90° pulse length was 3.4 μs and the 180° pulse was 6.4 μs. The recycle delay was 1 s with the number of scans ~8000. There was no signal observed for the rotor and Kel-F cap (35), thus no background correction was made. For ramp CPMAS (36, 38), the sample was packed in a 4-mm-diameter zirconia rotor with a Kel-F cap. Contact time was 2.5 ms with line broadening of ~50 Hz and the number of scans was 8000. The spin rate was 8 kHz.

**Diffuse-Reflectance FTIR.** Char samples in KBr wafers (2.0%) were prepared for FTIR measurements. The diffuse-reflectance IR spectra were obtained using a Nicolet Impact 410 FTIR spectrometer (Nicolet Instrument Corporation) with 4 cm<sup>−1</sup> resolution and 64 scans between wavenumbers of 700 and 2000 cm<sup>−1</sup>. The instrument was run with the AC sample as background, and the spectra for all other samples were obtained by subtracting the background.

**NOC Uptake.** Benzene and nitrobenzene were selected as model nonpolar and polar NOCs, respectively. NOC uptake by char samples was measured by the batch equilibration method, as described elsewhere (e.g., refs 6 and 39). The char sample (~0.006–0.025 g) was first mixed with 4 mL of deionized water in 5-mL glass vials for 24 h to allow the surface of the char to hydrate. Between 0.8 and 5.6 μL of neat benzene or nitrobenzene was then delivered into the vials using a Hamilton microsyringe. The vials were immediately closed with Teflon-lined screw caps and rotated end-over-end at 40 rpm at room temperature (~24 °C) for 48 h. Previous studies showed that the uptake of NOCs by chars reaches apparent equilibrium within 48 h (24, 33, 34). After equilibrium, the char and aqueous phases were separated by centrifugation at 6000 rpm (RCF = 5210 g) for 20–30 min. A volume of 2 mL of supernatant was extracted with 4 mL of hexane in a glass tube by agitating for 60 min on a reciprocating shaker. A portion of the hexane phase containing the extracted benzene or nitrobenzene was then analyzed using gas chromatography. Blank samples not containing char samples were also prepared and analyzed using the same procedure. The measured recoveries were ~97% for both NOCs. Concentrations were adjusted for the recovery. The amount of benzene or nitrobenzene sorbed was calculated from the difference between the amount added and that remaining in the final solution. All measurements were in duplicate, with the difference being generally <5%, and the average data were reported.

Concentrations of benzene and nitrobenzene in hexane extracts were measured by gas chromatography using a Shimadzu GC-14A gas chromatograph fitted with a flame ionization detector and a packed column with 10% AT-1000 on 80/100 Chromosorb W-AW (Alltech Co.). Helium was used as the carrier gas. A Shimadzu AOC-20i autoinjector was used to automate runs. No dilution of extracts was necessary because the concentrations of benzene and nitrobenzene were within the analytical linear range. Peak areas were recorded with a Nelson 900 series interface and compared to external standards to determine the concentrations.

TABLE 1. Surface Areas, Elemental Compositions, and Water Uptake of Char Samples

sample	pyrolysis temp (°C)	surface area (m <sup>2</sup> /g)	elemental composition (w%)				molar H/C	molar O/C	water uptake <sup>a</sup> (mL/m <sup>2</sup> ) × 10 <sup>-4</sup>
			C	O	H	C+O+H			
WC-300	300	116	69.2	26.6	3.2	99.0	0.55	0.29	13.0
WC-400	400	189							
WC-500	500	309	83.4	10.1	2.5	96.0	0.36	0.09	4.10
WC-600	600	438							
WC-700	700	363	88.0	6.0	1.1	95.1	0.15	0.05	4.10
AC		776	87.6	7.0	0.9	95.5	0.12	0.06	3.47

<sup>a</sup> Measured when equilibrated with the water vapor of saturated NH<sub>4</sub>Cl solution at room temperature,  $p/p_0 = 0.79$  (45).

## Results and Discussion

**Surface Areas.** Table 1 presents the measured surface areas of the char samples generated at various pyrolytic temperatures. As a commercial activated carbon, AC has a large surface area, which reflects the sample's fine-pore structure created through a well-controlled activation process. Considering that WC samples were produced without an activation process, it is not surprising that their surface areas and thus porosities are significantly lower, ranging from 15% to 56% of that of the AC. However, these values are much higher than those of all the fractions of various lithocomponents of natural solids reported by Kleinedam et al. (14), rendering these char samples potential sorbents in agricultural soils for NOCs. The low surface areas of the lithocomponents of natural solids were due probably to the presence of organic matter in these components. In general, the char surface area increases with increasing charring temperature, consistent with the making of activated carbon. The high surface areas of WC-500, WC-600, and WC-700 (309–438 m<sup>2</sup>/g) suggest that the char samples possess some fine-pore structures. That the surface area of WC-700 (363 m<sup>2</sup>/g) is lower than that of WC-600 (438 m<sup>2</sup>/g) suggests that some fine-pore structures may have been destroyed at 700 °C. The surface areas for chars produced at low temperatures, that is, WC-300 (116 m<sup>2</sup>/g) and WC-400 (189 m<sup>2</sup>/g), are significantly lower. As shown later, these low-surface-area samples contain a significant amount of the residual plant organic matter. As the surface area is a key indicator of the char uptake ability, temperature is clearly an important factor on the char surface area during the char formation.

**Elemental Compositions.** According to Kuhlbusch (40), when the remains of vegetation from a field fire was heated at 340 °C for 2 h in an atmosphere of pure oxygen, the organic matter in the sample was effectively destroyed, while the black carbon remained intact (41). A recent study showed that the thermal treatment of Kuhlbusch (40) was reliable for determination of soot carbon (42). When subjected to the same thermal treatment, WC-300 and WC-400 previously oven-dried at 105 °C lost 52% and 40% of their original dry weights, respectively, illustrating a significant amount of the organic residue in these chars. Furthermore, wheat residue completely lost its carbon under the same thermal conditions. By contrast, the AC lost 0.5% and other chars (WC-500, WC-600, and WC-700) lost <3% with the same thermal treatment. Thus, an almost complete carbonization of wheat residue apparently occurred at pyrolysis temperatures ≥ 500 °C. Table 1 shows that the total elemental content of C, H, and O accounted for >95% for WC-300, WC-500, WC-700, and AC, further indicating the effectiveness of acid demineralization in the removal of most Si and metal salts (33). With increasing pyrolytic temperature, the C content increased while the O and H contents decreased, indicating an increasing degree of carbonization of the chars. This is consistent with the thermal treatment results described above. The degree of carbonization may also be described by the molar H/C ratio,

TABLE 2. Boehm Titration Results and Surface Density of Functional Groups

sample	Boehm titration (mmol/g)				density of groups (group/nm <sup>2</sup> )
	carboxyl	acidic	basic	all	
WC-300	0.74	2.83	0.04	2.87	14.9
WC-400	0.35	1.13	0.11	1.24	3.95
WC-500	0.20	0.42	0.19	0.61	1.19
WC-600	0.16	0.35	0.26	0.61	0.84
WC-700	0.17	0.30	0.29	0.59	0.98
AC	0.10	0.27	0.34	0.61	0.47

because H is primarily associated with plant organic matter (40). By reference to AC with a H/C ratio of 0.12 (Table 1), the observed H/C ratio of 0.15 for WC-700 indicates that the char sample is highly carbonized. On the other hand, the much higher H/C ratio for WC-300 (H/C = 0.55) suggests that the char contains a good amount of plant organic residues. The high organic-residue content of WC-300 is related apparently to the low pyrolytic temperature, which preserves certain original organic structures (mostly, carbohydrates such as cellulose of wheat residue), as further revealed by a molar H/O ratio of ~2 for WC-300.

The polar groups on the activated carbon surfaces act as water adsorption centers and facilitate the formation of water clusters on the carbon surfaces (27–30, 43, 44). A similar effect is expected for char samples. Thus, the molar O/C ratio of a char should partially indicate its surface hydrophilicity. The O/C ratios of WC-500 (0.09) and WC-700 (0.05) are comparable with that of AC (0.06), indicating that the compositions of these two chars are similar to that of the AC, and thus their surfaces should have a low affinity for water. By contrast, WC-300 should be far more hydrophilic, as it has a much higher O/C ratio of 0.29. This indicates that the WC-300 has a much higher polar-group content, derived most likely from the carbohydrates or the like from the wheat residue. To substantiate the effect with chars, we measured the water uptake by equilibrating selected char samples with water vapor (at  $p/p_0 = 0.79$ ) from the saturated NH<sub>4</sub>Cl solution inside a desiccator for one week (45). The water uptake capacities of WC-500 and WC-700, when normalized to their surface areas, are practically the same as that of AC (Table 1), which is consistent with their comparable elemental compositions and O/C ratios. The much higher water uptake for WC-300 is reflective of both its higher surface affinity for water and the additional water partition into the sample's organic matter.

**Surface Acidity/Basicity.** The oxygen-containing functional groups on the surfaces of activated carbon result in an apparent surface acidity/basicity of the material (46–48). Similar properties are expected for the char samples. Table 2 presents the total acidity and basicity from the Boehm titration (22, 23). Although the carboxylic acid is included along with other weaker acids (i.e., lactic and phenolic acids) into the total acidity, it is also separately measured.



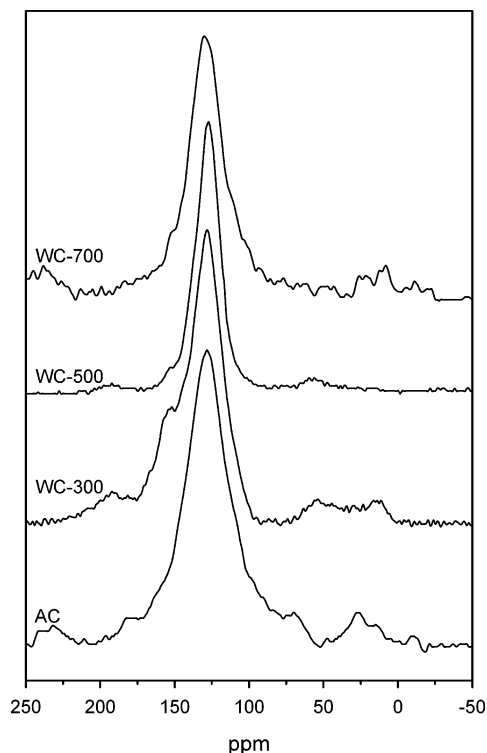


FIGURE 1. Solid-state  $^{13}\text{C}$  NMR spectra of selected char samples.

For a better correlation with the NOC uptake data in the later discussion, the total acidity/basicity is normalized to the surface area of corresponding char to obtain the surface density of oxygen-containing groups (Table 2). The data indicate that the total acidity decreased and the basicity increased with increasing pyrolysis temperature. The carboxyl acidity decreased in a similar trend. The surface density of functional groups also decreased with an increase in pyrolysis temperature. All the high-temperature char samples (viz. WC-500, WC-600, and WC-700) showed a total acidity/basicity value similar to that for AC, although the surface functional-group density of these chars is higher than that of the AC and thus their surfaces are more hydrophilic (Table 1). Apparently because of the partial carbonization, the low-temperature char samples (WC-300 and WC-400) exhibited much higher total acidity/basicity and the surface functional-group densities, showing the more polar nature of the chars in keeping with their water uptake data (Table 1). The ratio of the total acidity to the carboxyl acidity decreased with increasing pyrolysis temperature, further illustrating that the low-temperature chars are more organic in nature.

**$^{13}\text{C}$  NMR.** A dominant peak at 130 ppm was observed for all chars (Figure 1), indicating that these carbons are primarily aromatic in nature. Because WC-300 and WC-500 were analyzed by CPMAS-TOSS, all bands in the spectra were real structural carbon peaks. Spectra of WC-700 and AC exhibited symmetric sidebands at 235 and 25 ppm, because they were measured by ramp CPMAS. The spectrum of WC-300 had obvious peaks at 155 ppm and 160–190 ppm for phenolic and carboxyl groups (24), respectively, and other peaks at 0–50 ppm and 50–100 ppm for aliphatic carbons and carbohydrates, respectively. The spectrum of WC-500 showed much smaller peaks at 50–100 ppm (carbohydrates), 155 ppm (phenolic), and 160–190 ppm (carboxyl). Considering the effect of sidebands and lower signal-to-noise ratio, the spectra of WC-700 and AC had only 130 ppm peak. These NMR results are in agreement with the elemental analysis and the Boehm titration data.

**FTIR.** The char surface properties as affected by the pyrolysis temperature are further illustrated by the FTIR data

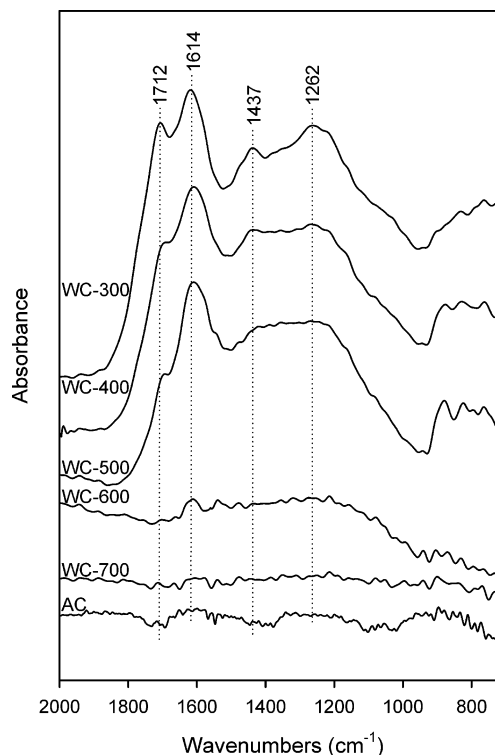


FIGURE 2. Diffuse-reflectance FTIR spectra of char samples.

in Figure 2. Few distinguishable bands for AC were observed between wavenumbers of 2000–700  $\text{cm}^{-1}$ , because of a high degree of carbon matrix. The spectra of WC samples are characterized by four principal bands at wavenumbers of 1712, 1614, 1437, and 1262  $\text{cm}^{-1}$ . Specifically, the band at 1262  $\text{cm}^{-1}$  is assigned to the aromatic CO– and phenolic –OH stretching (25, 26), at 1437  $\text{cm}^{-1}$  to the COOH and CHO stretching (49), and at 1712  $\text{cm}^{-1}$  to the aromatic carboxyl/carbonyl (C=O) stretching (25, 26). All these bands appeared with high intensities for WC-300, but the band intensities gradually decreased for WC-400 and WC-500 with increasing pyrolysis temperature from 300 to 500  $^{\circ}\text{C}$  and disappeared at higher temperatures for WC-600 and WC-700. This indicates a decrease in acidic groups with increasing temperature and a near complete absence of acidic groups at high temperatures. The band at 1614  $\text{cm}^{-1}$  for the aromatic C=O ring stretching seems to be reflective of both acidic and basic groups (49), the intensity of which remained largely unchanged between 300 and 500  $^{\circ}\text{C}$ , diminished at 600  $^{\circ}\text{C}$ , and disappeared at 700  $^{\circ}\text{C}$ . This may have resulted from an increase in basicity with pyrolysis temperature, but is generally consistent with the decrease in the total groups. Overall, the FTIR-derived characteristics of the chars are in keeping with the data from all other characterization techniques.

**NOC Uptake.** The uptake of benzene and nitrobenzene by the char samples is shown in Figure 3, in which the volume sorbed ( $\text{mL/g}$ ) is plotted against the relative concentration ( $C_e/C_s$ ). Curves representing sorption isotherms were not fit to a mathematical model but were drawn to assist visualization of data. Use of the Polanyi-based plot (i.e., adsorbed volume vs  $C_e/C_s$ ) for solute condensation onto a porous space allows us to directly compare the uptake of benzene and nitrobenzene. Adsorbed volumes of benzene and nitrobenzene were obtained from their adsorbed masses assuming that the condensed solutes (liquids, in this case) have densities identical to those of normal liquids. At low solute concentrations for both sorbates, sorption increases in the order of WC-300 < WC-400 < WC-500 < WC-700 < WC-600, in agreement with the surface area measurements. All the

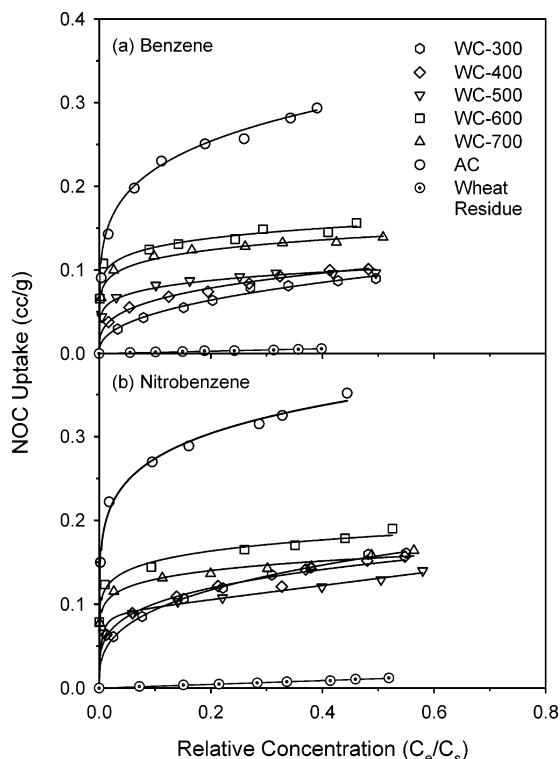


FIGURE 3. Isotherms of (a) benzene and (b) nitrobenzene uptake by char samples from water.

TABLE 3. Uptake of Benzene and Nitrobenzene (NB) by Char Samples at Two Relative Concentrations Normalized to Corresponding Char Surface Areas

sample	volume sorbed on unit surface area ( $\text{mL}/\text{m}^2$ ) $\times 10^{-4}$			
	$C_e/C_s = 0.1$		$C_e/C_s = 0.3$	
	benzene	NB	benzene	NB
WC-300	4.14	8.02	6.55	11.55
WC-400	3.39	5.34	4.66	6.98
WC-500	2.52	3.11	3.01	3.69
WC-600	2.90	3.45	3.31	3.90
WC-700	3.11	3.58	3.61	4.05
AC	2.85	3.53	3.56	4.16

isotherms are of a typical concave-downward shape at low solute concentrations, indicating the dominance of an adsorption process. The isotherms with WC-300 and WC-400 are noticeably less concave at low  $C_e/C_s$  and rise more rapidly at high  $C_e/C_s$  than those with other chars, a result due likely to a concurrent solute partition into the residual organic phase of the former char samples. Braidia et al. (24) reported benzene adsorption by a wood char derived from pyrolysis at 400 °C. While they focused on desorption hysteresis, the adsorption isotherm was similar to that of WC-400 with a continuous rise at high  $C_e/C_s$ , although solute partition was not discussed. The rapid rise at high  $C_e/C_s$  with AC may be ascribed to solute condensation instead of solute partition.

The partition effect is further evidenced by a comparison of the surface area normalized benzene uptake values in Table 3, obtained from the uptake data at two relative concentrations divided by the char surface areas. The normalized sorption values for both the sorbates with WC-500, WC-600, WC-700, and AC are relatively constant ( $2.82 \pm 0.29 \times 10^{-4}$  and  $3.31 \pm 0.30 \times 10^{-4}$   $\text{mL}/\text{m}^2$  for benzene;  $3.35 \pm 0.24 \times 10^{-4}$  and  $3.93 \pm 0.24 \times 10^{-4}$   $\text{mL}/\text{m}^2$  for nitrobenzene at  $C_e/C_s$  of 0.1 and 0.3, respectively), as these char samples are essentially organic-free and exhibit a

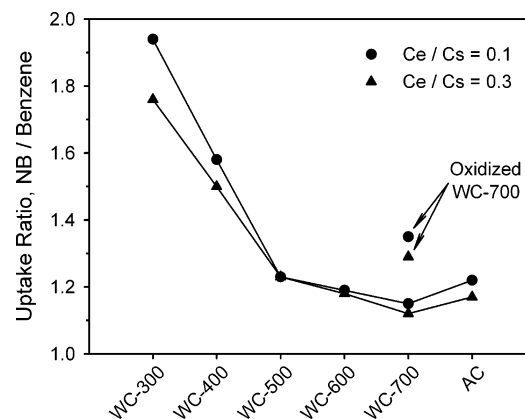


FIGURE 4. Uptake ratios of nitrobenzene (NB) to benzene at two relative concentrations.

comparable total acidity/basicity as well as surface functional group density. The sorption of benzene and nitrobenzene with WC-300 and WC-400 higher than with other chars and AC is due apparently to a concomitant solute partition, since without this effect the uptake with these two chars would have been lower because of the hydrophilic nature of their polar functional groups on the surfaces. A somewhat larger partition effect for nitrobenzene with the chars is expected, because nitrobenzene, due to its polar nature, should partition more effectively than benzene into the organic phase of the chars. Toward this effect, we obtained the linear isotherms for the partition of benzene and nitrobenzene from water into the organic precursor of the chars (i.e., wheat residue) (Figure 3). The measured partition coefficient ( $K$ ) of nitrobenzene is 12.9 L/kg, which is greater than 7.3 L/kg for benzene. Calculation indicates that the contribution of nitrobenzene partition at  $C_e/C_s$  of 0.1 to the total uptake was <5%. As such a small partition cannot fully account for the enhanced nitrobenzene uptake over that of benzene with WC-300 and WC-400 (Table 3), the sorption of nitrobenzene may also result from additional contributions.

Relative to the surface area (porosity) effect, the surface functionality of chars can be equally important in the NOC uptake. The hydrophilicity of oxygen-containing surface groups may reduce the surface area accessible to NOCs because of the interference by the adsorbed water (50, 51). It may also affect differently the adsorptive competition of different NOCs against water for carbon surfaces. In this respect, it is possible for polar NOCs (e.g., nitrobenzene) to engage in specific interactions with polar surface groups, thus mitigating the competition of water, while the adsorption of nonpolar NOCs (e.g., benzene) will be more effectively reduced by the affinity of water for polar surface groups. To see if this selectivity occurs, Figure 4 presents the ratios of nitrobenzene to benzene uptakes with respective char samples at  $C_e/C_s$  of 0.1 and 0.3. Such ratios should eliminate the surface-area effect as well as most of the mentioned small solute partition effect, thus bringing out the specific interaction effect, if any, on the NOC uptake. For the samples of WC-500, WC-600, WC-700, and AC, which possess similar quantities of surface oxygen groups and virtually no organic phase, the ratios are about 1.18. This magnitude is well in line with the fact that nitrobenzene has a somewhat higher molar volume and polarizability per unit volume than benzene (52), which according to the Polanyi adsorption theory should give a somewhat higher adsorbed volume for nitrobenzene than for benzene at the same  $C_e/C_s$  (i.e., adsorption potential). The ratios are about 1.55 for WC-400 and 1.90 for WC-300. The noted differences for high- and low-temperature chars are more than those estimated for the different partition effects of nitrobenzene and benzene with the residual organic phase. The results thus suggest the

occurrence of certain specific interactions between nitrobenzene and char surface polar groups.

The hypothesis for solute-surface specific interactions was further evaluated by an experiment using the WC-700 sample. When WC-700 was oxidized in concentrated (96%) H<sub>2</sub>SO<sub>4</sub> at 210 °C for 3 h, the total acidity/basicity increased from 0.59 to 1.70 mmol/g and the carboxyl acidity from 0.17 to 0.89 mmol/g. Although the individual uptakes of both nitrobenzene and benzene with the oxidized char were reduced, the ratios of nitrobenzene to benzene uptakes increased to 1.35 and 1.29 at C<sub>e</sub>/C<sub>s</sub> of 0.1 and 0.3, respectively (Figure 4). The respective increases by 17% and 15% in the ratios with the oxidized WC-700 as compared to the original WC-700 are supportive of the specific interaction effect.

**Environmental Significance.** The compositions, surface characteristics, and sorptive properties of combustion-derived chars depend strongly on the formation conditions. The chars produced from wheat residue precursors at high temperatures are nearly completely carbonized and exhibit a relatively high surface area, little organic carbon, low oxygen content, and low content of polar surface groups. In contrast, the chars obtained at low temperatures are only partially carbonized and show the opposite surface properties in each of the above respects. The carbonized surface adsorbs NOCs, while the residual organic matter acts as a partition medium. The surface polar groups reduce the uptake of nonpolar NOCs from water, because of the enhanced competitive adsorption of water. Polar NOCs may compete more efficiently than nonpolar NOCs against water for their uptake from water. However, the net uptake of a given NOC by a char in natural aquatic systems would depend not only on the NOC and char properties but also on other factors such as the char mass, the relative concentrations of individual NOCs, and the adsorptive competition between multiple NOCs for a given char (6, 7) and between the char and other sorbents (such as clay minerals) (53–55).

Our results show that pyrolysis yielded a char being 10–27% of the original weight of wheat residue (data not shown), depending on the temperature. On the basis of the average production of wheat biomass of ca. 6000 kg/ha, assuming that the char arising from the burning of wheat residue is mixed with a soil of furrow slice (~15 cm deep), calculations show that each burning would result in a char content of 0.024–0.066% (by weight) in the soil. A higher char level may occur in agricultural soils because the char is usually refractory under environmental conditions and thus may accumulate in the soils following each burning. At such levels, the char in agricultural soils could act as a potential uptake medium for NOCs.

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