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pH-Dependence of Pesticide Adsorption by Wheat-Residue-Derived Black Carbon

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The potential of black carbon as an adsorbent for pesticides in soils may be strongly influenced by the properties of the adsorbent and pesticides and by the environmental conditions. This study evaluated the effect of pH on the adsorption of diuron, bromoxynil, and ametryne by a wheat (*Triticum aestivum* L.) residue derived black carbon (WC) as compared to a commercial activated carbon (AC). The pH drift method indicated that WC had a point of zero charge of 4.2, much lower than that of 7.8 for AC. The density of oxygen-containing surface functional groups, measured by the Boehm titration, on WC was 5.4 times higher than that on AC, resulting in a pesticide adsorption by WC being 30–50% of that by AC, due to the blockage of WC surface by the waters associated with the functional groups. A small decrease (5.5%/unit pH) in diuron adsorption by WC with increase in pH resulted from increased deprotonation of surface functional groups at higher pH values. A much larger decrease (14–21%/unit pH) in bromoxynil adsorption by WC with increase in pH resulted from the deprotonation of both the adsorbate and surface functional groups of the adsorbent. The deprotonation reduced the adsorptive interaction between bromoxynil and the neutral carbon surface and increased the electrical repulsion between the negatively charged WC surface and bromoxynil anions. Deprotonation of ametryne with increase in pH over the low pH range increased its fraction of molecular form and thus adsorption on WC by 15%/unit pH. Further increase in pH resulted in a 20%/unit pH decrease in ametryne adsorption by WC due primarily to the development of a negative charge on the surface of WC. The pH-dependent adsorption of pesticides by black carbon may significantly influence their environmental fate in soils.

Introduction

The environmental fate of pesticides in soils is strongly influenced by the sorption process. While black carbon (BC) was recognized three decades ago to be widely present in natural solids,¹ only recently has it been confirmed as a potential adsorbent for soil organic pollutants such as pesticides.^{2–4} A paucity of understanding of BC surface and adsorptive properties has stimulated great interest in BC identification, isolation, surface characteristics, and adsorptive properties. BC is believed to be generated through the thermal carbonization of various organic materials and eventually deposited in soils and sediments.^{1,4} As such, BC may resemble activated carbon in some manner as a surface adsorbent for organic pollutants.^{1–4} As a prevalent method of immediate land clearing, the field burning of crop residues is practiced worldwide and may thus be the major source of BC in agricultural soils.⁵ Hilton and Yuen⁶ postulated that BC-containing chars arising from the burning of sugarcane

trash were responsible for the retained sorptivity of Hawaiian soils for substituted ureas and *s*-triazines following the oxidative removal of organic matter from the soils by H₂O₂. Toth et al.⁷ found that the phytotoxicity of herbicides was reduced due to adsorption to ash carbon arising from the burning of crop residues and grass. Our recent studies have indicated that the carbon fraction of a char resulting from the burning of wheat residue was the predominant adsorptive component of the char and showed competitively reduced diuron adsorption in the presence of a competing solute (atrazine) or dissolved soil organic matter.^{8,9}

While surface area is a key indicator of the adsorptive power of activated carbon, surface functionality often plays a dominant role in determining the surface heterogeneity and hence the adsorptive characteristics of the carbon.^{10–13} BC produced under natural conditions without an activation process is expected to have a much more heterogeneous surface than that of activated carbon. As the most abundant heteroatom, the oxygen atoms primarily contribute to the surface functionality of carbon.^{14,15} Oxygen

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is present on the carbon surface in various functional groups (such as carboxyl, phenolic, and ketonic groups).^{14–17} These functional groups possess acidity/basicity and, thus, are hydrophilic in nature and act as water adsorption sites.^{18–20} The hydrophilicity of oxygen-containing surface functional groups may reduce the surface area accessible to pesticides because of blockage by adsorbed water.^{10,13} It may also reduce the adsorptive competition between pesticides and water for carbon surface.

Due to the acidity/basicity of surface functional groups, the carbon surface may have a net charge resulting from protonation/deprotonation of surface functional groups and, thus, an electrical double layer,¹⁵ depending on solution pH. Ionizable pesticides may exist in neutral, positively charged, or negatively charged species. At a given pH, the carbon surface and the adsorbate species may coexist in a complex system, in which the same or opposite charges may be present, resulting in some widely different adsorption schemes. A simple case was studied by Yamane and Green,²¹ who reported the adsorption of ametryne, an ionizable pesticide, by an oxisol in the presence and absence of a commercial charcoal. Higher adsorption of ametryne by the (charcoal-free) soil at low pH values than at high pH values was in accord with the fact that ametryne was largely protonated (positively charged) at low pH values. Addition of the commercial charcoal to the soil masked the effect of soil pH, resulting in a higher ametryne adsorption at high pH values when ametryne was in the molecular form.

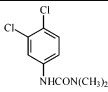
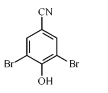
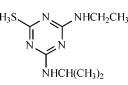
In this study, we measured the adsorption of diuron, bromoxynil, and ametryne at various pHs by a crop-residue-derived BC as compared to a commercial activated carbon. The three pesticides have different charge properties. The two carbon samples have widely different surface properties. The objectives of this study were to investigate the influence of surface functionality of BC on pesticide adsorption, to determine the adsorption of ionizable pesticides in relation to the charge properties of both carbon surface and pesticides, and to evaluate the pH dependence of pesticide adsorption by crop-residue-derived BC.

Experimental Section

Pesticides. Diuron (with a purity of 99%), bromoxynil (99.5%), and ametryne (98.5%) were purchased from ChemService (West Chester, PA) and used as received. Diuron is an electroneutral molecule. Bromoxynil is mostly neutral at pH < 4.06 and becomes deprotonated (anionic) at pH > 4.06. Ametryne is mostly protonated (cationic) at pH < 4.1 and neutral at pH > 4.1. The three pesticides have similar log K_{ow} values, indicating a similar hydrophobicity. The selected physicochemical properties of these pesticides are listed in Table 1.²²

BC Adsorbents. A commercial 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 BC. Wheat (*Triticum aestivum* L.) carbon was obtained by purifying charred wheat residue as follows. Wheat straw, one of the most frequently burned crop residues worldwide, was collected from the Arkansas Agricultural Re-

Table 1. Selected Physicochemical Properties of Pesticides Used in This Study²²

Pesticide	Structure	Water solubility (mg/L)	pK _a	log K _{ow} (25°C)
Diuron		40 (20°C)	---	2.58
Bromoxynil		130 (25°C)	4.06	2.80
Ametryne		185 (20°C)	4.10	2.63

search and Extension Center at Fayetteville, AR. To simulate the field burning of the crop residue, air-dried wheat straw was burned in the air on a stainless steel plate (1 m × 1 m) in an open field under natural conditions. The resulting char was demineralized with acids to remove silica and other metal salts.⁸ The char (10 g) was treated with 200 mL of 1 M HCl four times and in 200 mL of HCl–HF (1 M/1 M) four times, followed by a thorough washing with distilled water four times. Such purification has proven effective in removal of Si and salts and in enrichment of wheat carbon.⁸ Elemental analysis of the wheat carbon showed that carbon, oxygen, and hydrogen accounted for ~98% of sample weight, confirming the effectiveness of the purification. The activated carbon and wheat carbon are referred to as commercial activated carbon (AC) and wheat-residue-derived black carbon (WC), respectively.

The surface areas of WC and AC were measured with N₂ adsorption at liquid nitrogen temperature determined by a Gemini 2360 Micromeritics surface area analyzer. The BC samples (~0.2 g) were outgassed overnight (~15 h) at 105 °C under a helium gas flow at 20 mL/min prior to N₂ adsorption. The molecular surface area of 16.2 Å² for N₂ and the BET (Brunauer–Emmett–Teller) equation were used to calculate the surface areas of the samples.

The points of zero charge (pH_{PZC} values) of WC and AC were determined by the pH drift method. The method, originally developed for activated carbon, provides a quick yet reliable determination of pH_{PZC}.^{23,24} The method is presumed to be suitable for WC because any potential side effects on the pH drift from the dissolution processes of salts in wheat char have been eliminated during the WC enrichment. A solution of 0.005 M CaCl₂ was boiled to remove dissolved CO₂ and then cooled to room temperature. The pH was adjusted to a value between 2 and 10 using 0.5 M HCl or 0.5 M NaOH. AC or WC (0.06 g) was added into 20 mL of the pH-adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the pH_{initial} = pH_{final} line is taken as pH_{PZC}.

Oxygenated surface functional groups of WC and AC were determined by Boehm's titration method.^{16,17} The method provides an accurate quantification of several categories of surface functional groups for activated carbon and is presumed to be suitable for WC. Again, the WC enrichment has eliminated any potential side effects from the dissolution of salts on the titration. Prior to measurement, the BC samples were equilibrated with dilute HCl solution at pH 2 for 3 days, followed by a thorough washing with deionized water until they were free of Cl[–] as detected by AgNO₃. The dried samples (0.1–0.5 g) were mixed with 20 mL of 0.05 M solution of NaHCO₃, Na₂CO₃, NaOH, or HCl. The sample suspensions were shaken for 24 h. The excess of base or acid in 5 mL of the filtrates was titrated with 0.01 M HCl or NaOH. Surface acidity or basicity was calculated based on the assumption that NaHCO₃ neutralizes carboxyl groups only, Na₂CO₃ neutralizes carboxyl and lactonic groups, NaOH

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neutralizes all acidic groups including carboxyl, lactonic, and phenolic groups, and HCl neutralizes all basic groups.

Adsorption Isotherms. Pesticide adsorption by WC and AC was measured at different pH values between 2.2 and 6.6 by the batch equilibration technique. Adsorption of diuron was measured at two pH values while those of bromoxynil and ametryne were measured at three pH values. The pH of the 0.005 M CaCl_2 solution was adjusted to targeted values using 1 M HCl and 1 M NaOH. Various quantities of pesticides in the pH-adjusted 0.005 M CaCl_2 solutions were added into 25-mL Corex glass centrifuge tubes containing carbon adsorbents with a constant mass between 1.5 and 6.0 mg. Due to the high adsorptivity of AC, adsorption of diuron to AC was measured in 120-mL glass tubes. The mass of adsorbents was adjusted to allow for >40% of added pesticide to be adsorbed. Additional pH-adjusted 0.005 M CaCl_2 solution was added to bring the total liquid volume to 10 mL, except that the total volume was 60 mL for the diuron adsorption by AC and 20 mL for the bromoxynil adsorption by AC. Buffer solution was not used to avoid any possible side effects on the carbon surface. The tubes were closed with Teflon-lined screw caps and rotated (40 rpm) at room temperature ($\sim 25^\circ\text{C}$) for 24 h. Previous measurements have shown that diuron adsorption by WC reached apparent equilibrium within 24 h.⁸ To evaluate adsorption kinetics with bromoxynil and ametryne, the adsorption of the two pesticides on WC was measured at various adsorption times over an extended period at given pH values by rotating a mixture of 40.6 mg of WC and 100 mL of bromoxynil or 61.5 mg of WC and 100 mL of ametryne. Initial concentrations of bromoxynil and ametryne were 35.6 mg/L and 42.8 mg/L, respectively.

After the establishment of adsorption equilibrium, adsorbents and aqueous phases were separated by centrifugation at 6000 rpm (relative centrifugal force = 5210g) for 30 min. For the diuron adsorption by AC, supernatants were obtained by filtering through Acrodisc syringe filter (13 mm). The supernatant pH values were found shifted (upward or downward depending on the initial pHs) during the adsorption with up to one pH unit; the equilibrium pHs of supernatants were therefore measured. The average equilibrium pH value of the supernatants comprising each isotherm was reported, with the difference being generally <0.1 pH unit. The pesticide concentrations in supernatants were analyzed by direct injection of 20 μL into a Hitachi reversed-phase high-performance liquid chromatograph (Hitachi High-Technologies Co., Tokyo, Japan) fitted with a UV-visible detector set at the maximum absorption wavelength for each pesticide (252 nm for diuron, 250 nm for bromoxynil, and 225 nm for ametryne). A Phenomenex Prodigy C18 column was used (Alltech Assoc., Deerfield, IL). The mobile phase was a mixture of acetonitrile and water at a flow rate of 1.0 mL/min with the percent of acetonitrile between 40 and 55 (v%). All measurements were in triplicate with a variation generally <5%, and the average data with error bars were reported. The amount of pesticide adsorbed was calculated as the difference between the amount initially added and that remaining in equilibrium solution. The measurements with blanks not containing adsorbents found that glass tubes did not adsorb pesticides and no processes other than adsorption contributed to the loss of solution-phase pesticides. Adsorption isotherms were plotted as the amount of pesticide adsorbed by WC or AC (mg/g) against the equilibrium concentration (mg/L) in water.

Results and Discussion

Adsorption Kinetics. As diuron adsorption by WC reached apparent equilibrium within 24 h,⁸ it is rational to assume that the adsorption of the molecular form of bromoxynil and ametryne reaches equilibrium within 24 h. Figure 1 shows the adsorption of the two pesticides in their ionic forms with time over a period of more than 1

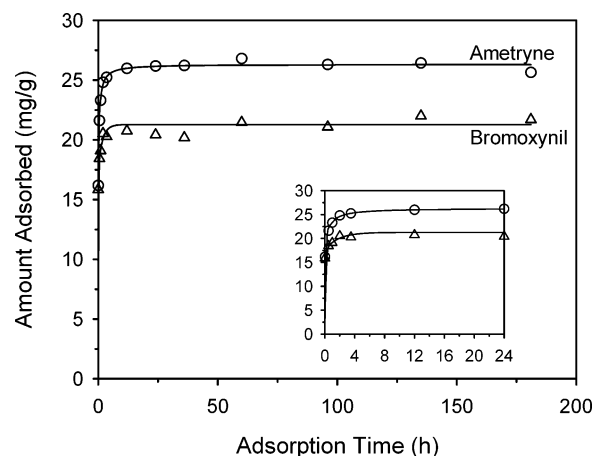


Figure 1. Kinetics of adsorption of bromoxynil and ametryne from water by wheat carbon (WC) at pH values of 7.20 and 2.19, respectively.

week. The measured pH values at various sampling times were consistently 7.20 ± 0.07 and 2.19 ± 0.05 for bromoxynil and ametryne, respectively, at which the former pesticide was mostly in its anionic form and the latter was in its cationic form. The concentrations of the two pesticides decreased initially with time and were 27.0 and 27.3 mg/L for bromoxynil and ametryne, respectively, at 12 h. After 12 h, no further decreases in pesticide concentration were detectable; an apparent adsorption equilibrium was thus attained within 12 h for both pesticides (Figure 1 inset). Selection of 24 h for the measurement of equilibrium adsorption of all pesticides at various pH values in this study was thus warranted.

Adsorbent Characteristics and General Adsorption Results. Table 2 presents the measured surface areas of WC and AC. As a commercial activated carbon, AC has a large surface area, which reflects the fine-pore structure of the sample created under the well-controlled activation conditions. WC sample, produced under natural conditions without an activation process, has a significantly lower surface area, $\sim 40\%$ of that of AC. However, the surface area of WC is sufficiently high that it may be a potential adsorbent for pesticides when present in agricultural soils. Adsorption of diuron, bromoxynil, and ametryne by WC and AC at different pH values is presented in Figures 2–4. All isotherms are of a Langmuir-type, suggestive of the surface adsorption mechanism. Although the adsorptive power of WC is lower than that of AC, which is in agreement with the surface area measurements, adsorption by WC is substantial, confirming the high adsorptivity of WC for pesticides. The adsorption data in the figures will be further analyzed in later discussion.

Although the surface area of BC is a key factor for pesticide adsorption, the surface functional groups may play an equally important role.^{10–13} Heteroatoms are known to be present in manufactured activated carbon. Oxygen, the most abundant heteroatom, is fixed on the carbon surface during the making of activated carbon in the form of polar functional groups, resulting in an apparent surface acidity/basicity of the carbon.^{14,15} Similar properties are expected for the WC sample. The acidic surface groups on the carbon surface include carboxylic acid

Table 2. Surface Areas and Surface Acidity/Basicity of Activated Carbon (AC) and Wheat Carbon (WC)

sample	surface area (m^2/g)	surface acidity/basicity (mmol/g)						density of groups (group/ nm^2)
		base	carboxyl	lactonic	phenolic	acid	total	
AC	776	0.34	0.10	0.06	0.11	0.27	0.61	0.47
WC	310	0.18	0.49	0.36	0.28	1.13	1.31	2.55

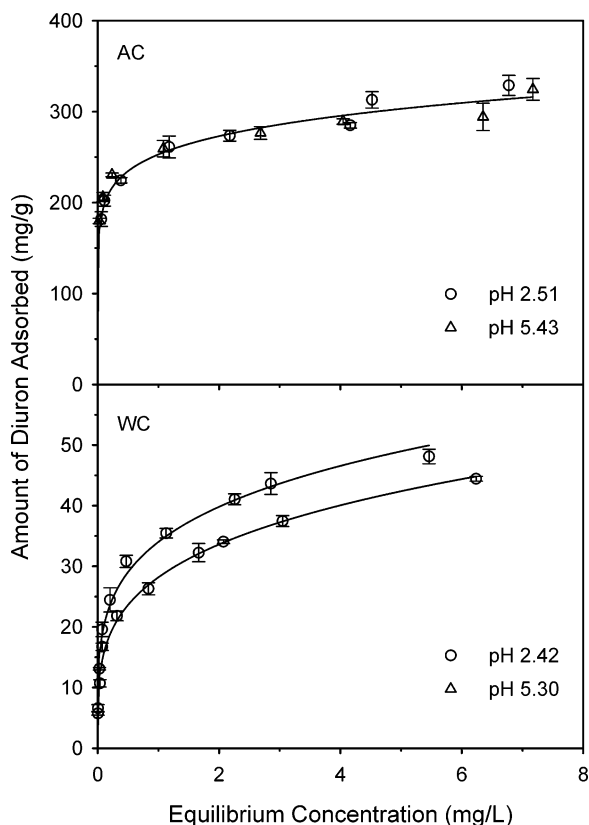


Figure 2. Adsorption of diuron from water by activated carbon (AC) and wheat carbon (WC) at two pH values.

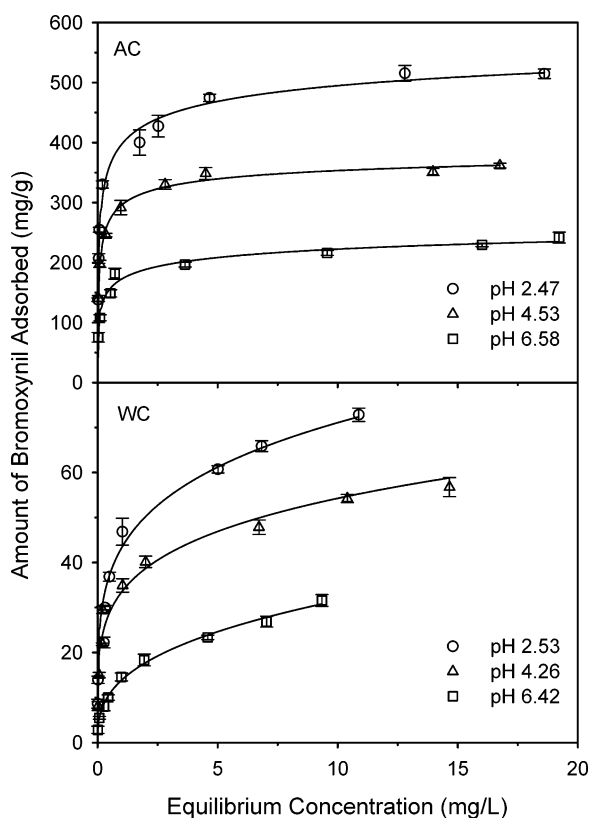


Figure 3. Adsorption of bromoxynil from water by activated carbon (AC) and wheat carbon (WC) at three pH values.

groups, derivatives of carboxyl acid groups such as lactone and lactol groups, and phenolic groups. These acidic groups have acid dissociation constants differing by several orders of magnitude.²⁵ According to Boehm,^{16,17} it is assumed

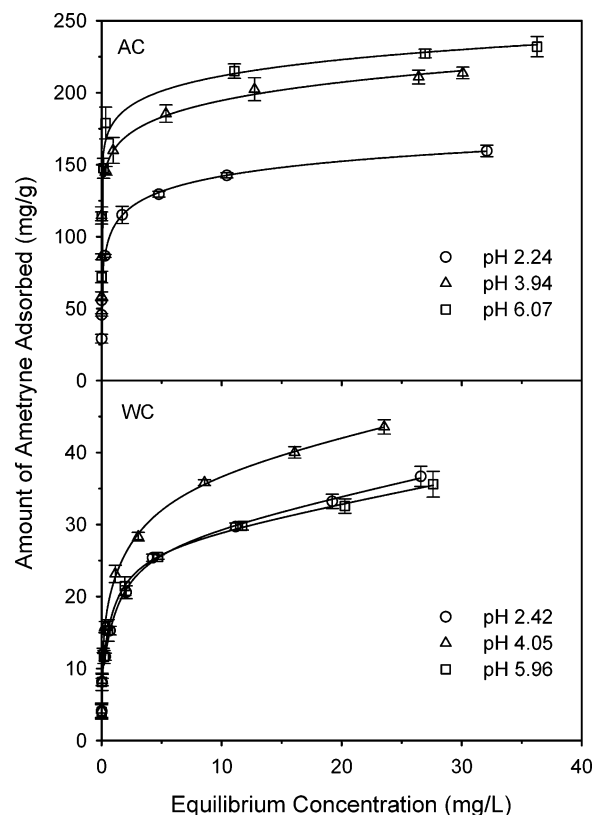


Figure 4. Adsorption of ametryne from water by activated carbon (AC) and wheat carbon (WC) at three pH values.

that only the strongly acidic carboxyl species with a $pK_a < \sim 4.4$ are neutralized by NaHCO_3 , whereas Na_2CO_3 neutralizes the acidic groups with a $pK_a < \sim 8.4$ (carboxyl, lactone, and lactol groups). The weakly acidic phenolic groups react only with strong alkali reagents such as NaOH . Stepwise neutralization using bases of different strengths allows the quantitative characterization of the surface acidic functional groups in carbons. The basic surface groups on the carbon surface include oxygen-containing species such as ketone. The basic properties may also come from the π electron system of carbon basal planes. Total basicity may be measured by neutralization with HCl . Table 2 presents the Boehm titration results for WC and AC. WC had a higher surface acidity in each category and a higher total acidity than did AC. The total acidity for WC was shown to be 4.2 times higher than that for AC. As the strongest acidic species, the carboxyl acidity displayed a similar result, being 4.9 times higher for WC than for AC. Although the basicity for WC was lower than that for AC, the total surface functionality for WC remained approximately twice that for AC. Because the adsorption of pesticides on carbons occurs as a surface process, the density of surface functional groups may be a more descriptive parameter in expressing the surface heterogeneity of carbons. From the calculation using the surface areas, the density of surface functional groups for WC was ~ 5.4 times higher than that for AC (Table 2), indicating a much more heterogeneous surface for WC.

Effect of Surface Functionality on Adsorption. Oxygen-containing functional groups are known to be hydrophilic and act as water adsorption sites to facilitate the formation of water clusters on the carbon surface.^{19,20} This suggests that WC would have a higher surface affinity

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Table 3. Surface Area Normalized Adsorption Values (Q_{SA}) for Diuron, Bromoxynil, and Ametryne Adsorption to Activated Carbon (AC) and Wheat Carbon (WC) under Different pH Values at a Relative Equilibrium Concentration of 0.05

pesticide	AC		WC		$Q_{SA}(WC)/Q_{SA}(AC) \times 100$
	pH	Q_{SA} (mg/m ²)	pH	Q_{SA} (mg/m ²)	
diuron	2.51	0.36	2.42	0.13	36
	5.43	0.36	5.30	0.11	31
bromoxynil	2.47	0.62	2.53	0.21	34
	4.53	0.45	4.26	0.16	36
	6.58	0.28	6.42	0.086	31
ametryne	2.24	0.18	2.42	0.093	52
	3.94	0.25	4.05	0.12	48
	6.07	0.27	5.96	0.092	34

for water than would AC. The hydrophilic nature of oxygen-containing surface groups may reduce the surface area accessible to pesticides because of the blockage by adsorbed water.^{10,13} The hydrophilic effect is also expected to reduce the adsorptive competition of pesticides against water for carbon surfaces. Table 3 presents the adsorption, Q_{SA} (mg/m²), of diuron, bromoxynil, and ametryne by WC as compared to AC at the relative concentration (C_e/C_s = equilibrium concentration/water solubility) of 0.05 (selected as an example concentration), at which the adsorption of the three pesticides at all pH values approached saturation. The Q_{SA} values are obtained by normalization of the adsorption data in Figures 2–4 to the surface areas of respective BCs. At this C_e/C_s , the equilibrium concentrations of diuron, bromoxynil, and ametryne were 2.0, 6.5, and 9.25 mg/L, respectively. The normalization to surface area eliminates the surface area effect, thus bringing out the surface functionality effect. To avoid complication from pesticide ionization, adsorption is compared among the pesticides in their molecular forms. According to their pK_a values (acid dissociation constants) (Table 1), diuron is electroneutral at both experimental pHs (2.51 and 5.43). Bromoxynil and ametryne are mostly neutral at pH 2.47 and 6.07, respectively. As seen in Table 3, the Q_{SA} values for WC were consistently lower than those for AC, clearly indicating the effect of surface functionality. The ratios of the Q_{SA} values for WC to those for AC at similar pHs (2.42 vs 2.51 and 5.30 vs 5.43 for diuron, 2.53 vs 2.47 for bromoxynil, and 5.96 vs 6.07 for ametryne) in Table 3 indicate that the adsorption of neutral pesticides by WC was 31–36% of that by AC. Assuming that the lower adsorption per unit surface area with WC was due primarily to its higher surface functionality, the ratios suggest that the surface functionality played a significant role in reducing pesticide adsorption by BCs.

Points of Zero Charge. The effect of surface functionality on pesticide adsorption may be complicated by the charge characteristics of the carbon surface. Over the range of experimental pH values from 2.2 to 6.6, a portion of surface functional groups (including carboxyl, lactonic, and basic groups) should become deprotonated with increasing pH. This results in a less positively or more negatively charged carbon surface at higher pH than at lower pH. The comprehensive influence of all functional groups determines pH_{PZC} , the pH at which the net charge on the carbon surface is zero.²⁶ At $pH < pH_{PZC}$, the carbon surface has a net positive charge, whereas at $pH > pH_{PZC}$, the surface has a net negative charge. Figure 5 shows the

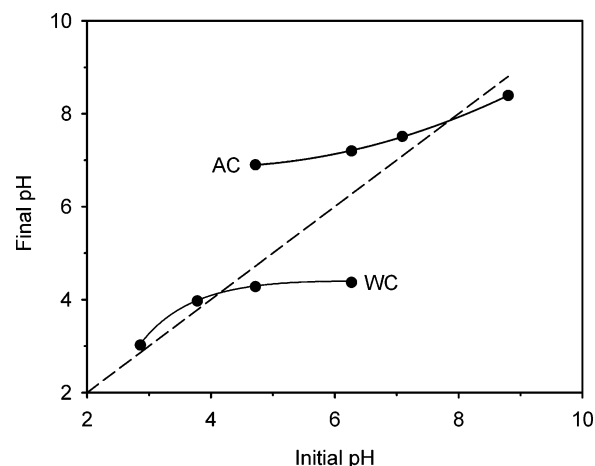


Figure 5. Determination of the points of zero charge of activated carbon (AC) and wheat carbon (WC) by the pH drift method.

pH drift tests, from which the pH_{PZC} values of 7.8 and 4.2 for AC and WC were obtained, respectively. The pH_{PZC} values indicate that over the experimental pH range the surface of AC consistently had a net positive charge while a charge reversal from positive to negative on the surface of WC occurred with increasing pH. Such charge properties of the carbon surfaces would be expected to have a dramatic effect on the adsorption of ionizable pesticides.

Adsorption of Diuron. Figure 2 shows the adsorption of diuron by WC and AC at low and high pH. No obvious pH effect with AC was observed. Because the London forces associating adsorbate and adsorbent do not change with pH ,²⁷ the interaction of a neutral adsorbate such as diuron with the electroneutral surface of an adsorbent should result in an adsorption independent of the solution pH. The lack of a pH effect on diuron adsorption by AC was thus apparently due to the low density of functional groups (i.e., a negligible charge) on the surface of the adsorbent, as indicated in Table 2. On the other hand, an increase in pH from 2.42 to 5.30 resulted in a small decrease in diuron adsorption by WC. Clearly, the deprotonation of surface functional groups over the pH range sufficiently altered the surface charge properties of WC and caused the adsorption to decrease. Using the Q_{SA} values in Table 3, at the C_e/C_s of 0.05, the decrease with WC was ~16% over the experimental pH range, or the average decrease is ~5.5%/unit pH.

Adsorption of Bromoxynil. A change in solution pH may also change the charge properties of ionizable pesticide molecules and, hence, their adsorption. With a pK_a of 4.06 (Table 3), bromoxynil is present in solution primarily in the molecular form at $pH < 4.06$ and as an anionic species at $pH > 4.06$ because of the deprotonation of phenolic hydroxyl groups. Figure 3 illustrates the adsorption of bromoxynil by WC and AC at various pH values. Generally, the adsorption of bromoxynil significantly decreased with increasing pH. Over the equilibrium concentration range, the adsorption by both carbon samples at the intermediate pH (4.53 and 4.26 for AC and WC, respectively) was 72–75% of that at the low pH (2.47 and 2.53, respectively). At the high pH (6.58 and 6.42, respectively), the adsorption was further reduced to 40–45% of that at the low pH. As the diuron adsorption by AC was not affected by pH (Figure 2), the decrease in bromoxynil adsorption by AC with increasing pH was

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apparently a result of the deprotonation of bromoxynil. Although the deprotonation may have slightly enhanced the electrical attraction between anionic bromoxynil and the net positive charge on the AC surface, it should have significantly reduced the adsorptive interaction of anionic bromoxynil with the neutral carbon surface. Examinations using the Q_{SA} values in Table 3 show that, at the C_e/C_s of 0.05, the average decrease in bromoxynil adsorption by AC was $\sim 13.5\%$ /unit pH with an increase in pH from 2.47 to 4.53 and $\sim 18.5\%$ /unit pH from 4.53 to 6.58. Calculations indicate that bromoxynil molecules are 97.3% neutral at pH 2.5 but 63.5% deprotonated at pH 4.3 and 99.5% deprotonated at pH 6.4. The larger adsorption decrease per unit pH over the range of the higher pH (from 4.53 to 6.58) suggests that the adsorption was dominated by the interaction between bromoxynil and AC surface over that by the adsorbate–adsorbent electrical attraction. It also suggests a weaker interaction of carbon surface with deprotonated (anionic) bromoxynil than with its molecular form, consistent with earlier studies.^{21,28}

As the adsorption of diuron by WC slightly decreased with increasing pH (Figure 2), due to the higher density of surface functional groups for WC as compared to AC, a similar effect was expected to contribute to the adsorption of bromoxynil by WC. At the C_e/C_s of 0.05, the calculated average decreases in bromoxynil adsorption by WC were $\sim 14\%$ /unit pH over the pH range from 2.53 to 4.26 and $\sim 21\%$ /unit pH from 4.26 to 6.42. These values are similar to those with bromoxynil adsorption by AC, indicating that deprotonation of bromoxynil played a dominant role in the adsorption decrease. Slightly higher decrease in bromoxynil adsorption over the higher pH range (from 4.26 to 6.42) with WC ($\sim 21\%$) than that with AC ($\sim 18.5\%$) may have been a result of the enhanced repulsion at high pH values between anionic bromoxynil and the net negative charge of the WC surface.

Adsorption of Ametryne. The adsorption of ametryne by AC and WC is illustrated in Figure 4. Due to the protonation of isopropylamine and ethylamine groups at low pH, ametryne molecules are present in solution mostly in positively charged (cationic) species at pH < 4.1 and largely in molecular form at pH > 4.1. By calculations, 98.0% of ametryne is protonated (positively charged) at pH 2.4 and 50.0% at pH 4.1 while 98.8% is neutral at pH 6.0. In direct contrast to the bromoxynil adsorption by AC (Figure 3), the adsorption of ametryne by AC increased with increasing pH from 2.24 to 3.94, followed by a further but smaller increase from pH 3.94 to 6.07 (Figure 4). Once again, due to the lack of a pH effect on the diuron adsorption by AC (Figure 2), the increase in ametryne

adsorption by AC with increasing pH was apparently a result of the deprotonation of the pesticide. The reduced electrical repulsion between the positive AC surface and cationic ametryne may also have contributed to the increase. Calculations indicate that the average increase in ametryne adsorption by AC with an increase in pH from 2.24 to 3.94 was $\sim 22\%$ /unit pH. A much smaller increase of $\sim 4\%$ /unit pH from 3.94 to 6.07 was observed. Initial deprotonation of ametryne over the low pH range thus played a dominant role in adsorption increase.

While the adsorption of ametryne by WC increased with increasing pH from 2.42 to 4.05, it decreased with a further increase in pH from 4.05 to 5.96 (Figure 4), in contrast to the observation with the ametryne adsorption by AC. The initial increase in adsorption over the low pH range (from 2.42 to 4.05) appeared to be a net result of the adsorption increase due to the deprotonation of ametryne and the adsorption decrease due to the deprotonation of surface functional groups. The adsorption increase may also have resulted from the reduced adsorbate–adsorbent repulsion at pH 4.05. A smaller average increase of $\sim 15\%$ /unit pH with WC as compared to $\sim 22\%$ /unit pH with AC in adsorption over the pH range from 2.42 to 4.05 was further evidence of the effect of the deprotonation of surface functional groups. As the increase in ametryne adsorption by AC from pH 3.94 to 6.07 was relatively small, the $\sim 20\%$ /unit pH decrease in ametryne adsorption by WC from pH 4.05 to 5.96 was primarily caused by the deprotonation of surface functional groups of WC.

In summary, the surface of crop-residue-derived BC may be highly heterogeneous due to the presence of surface functional groups. The hydrophilicity of surface functional groups reduces the potential of BC in adsorbing pesticides due to reduced accessible surface area. Protonation/deprotonation of surface functional groups results in a charged carbon surface. Thus, the adsorption of ionizable pesticides by BC may be greatly influenced by pH at which the adsorption occurs. For example, assuming that bromoxynil and ametryne coexist in a soil containing crop-residue-derived BC, bromoxynil would be taken up in a greater amount than would ametryne under very acidic conditions (pH ~ 2.5), whereas more ametryne may be adsorbed at near neutral pH. This selective adsorption may greatly influence the mobilization and retention of pesticides in agricultural soils.

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