

Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine

XINDE CAO,^{*,†,‡} LENA MA,[‡] BIN GAO,[§]
AND WILLIE HARRIS[‡]

School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China, Soil and Water Science Department, and Agricultural and Biological Engineering Department, University of Florida, Gainesville, Florida 32611

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Biochar (BC) produced from agricultural crop residues has proven effective in sorbing organic contaminants. This study evaluated the ability of dairy-manure derived biochar to sorb heavy metal Pb and organic contaminant atrazine. Two biochar samples were prepared by heating dairy manure at low temperature of 200 °C (BC200) and 350 °C (BC350). The untreated manure (BC25) and a commercial activated C (AC) were included as controls. Sorption of Pb by biochar followed a dual Langmuir–Langmuir model, attributing to Pb precipitation (84–87%) and surface sorption (13–16%). Chemical speciation, X-ray diffraction, and infrared spectroscopy indicated that Pb was precipitated as β - $\text{Pb}_9(\text{PO}_4)_6$ in BC25 and BC200 treatment, and as $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ in BC350. Lead sorption by AC obeyed a single Langmuir model, attributing mainly to surface sorption probably via coordination of Pb d-electron to C=C (π -electron) and —O—Pb bonds. The biochar was 6 times more effective in Pb sorption than AC, with BC200 being the most effective (up to 680 mmol Pb kg⁻¹). The biochar also effectively sorbed atrazine where atrazine was partitioned into its organic phase, whereas atrazine uptake by AC occurred via surface sorption. When Pb and atrazine coexisted, little competition occurred between the two for sorption on biochar, while strong competition was observed on AC. Results from this study indicated that dairy manure can be converted into value-added biochar as effective sorbent for metal and/or organic contaminants.

Introduction

Various sorbents have been developed to remove contaminants from wastewater (1). However, they are often expensive and mostly effective in removing one single metal or organic contaminant. In practice, wastewater often consists of both heavy metals and organic pollutants (2). It would be desirable to develop a cost-effective sorbent that can remove both metals and organics.

Biochar refers to carbonaceous residues of incomplete burning of carbon-rich biomass (3–5). It has shown strong sorption affinity for organic compounds and may play an important role in controlling organic pollutants in the

environment (4). Biochar is generally obtained under low temperatures (<500 °C) and thus is not fully carbonized (6–8). The relative carbonized and noncarbonized fractions determine its sorption behavior (9). Sorption of contaminant by carbonized phase is characterized by nonlinear Langmuir (L)-type isotherms and uptake competition exists between solutes; whereas the sorption on noncarbonized phase follows partitioning mechanism which is characterized by linear isotherms and a lack of competition between coexisting solutes (10–12). The sorption of aromatic hydrocarbons to a wood char is assisted by π -electron interactions (13) and proceeds with a pore-filling mechanism (14, 15).

Much work has been done on plant-residue derived biochar for sorbing organic pollutants (9–16). For example, Chen et al. (9) reported that pine-needle derived biochar was effective in removing naphthalene, nitrobenzene, and *m*-dinitrobenzene from water; Sheng and Yang (12) showed that soil amended with rice- or wheat-straw derived biochar enhanced sorption of diuron and atrazine. However, to our knowledge, few data are available for metal and/or organic sorption by animal-waste derived biochar as well as the associated underlying mechanisms.

Our previous work indicated that the biochar produced from dairy-manure has a potential to sorb both heavy metals and organics (17). The objective of this study was to demonstrate such ability. Atrazine and Pb were chosen as model organic and heavy metal contaminant, respectively. Lead has long been considered as one of the priority pollutants and its contamination continues to be a serious problem worldwide (18). Atrazine is a toxic herbicide that has been widely used to control broadleaf weeds in agriculture. Leaching of atrazine and its metabolites has led to serious surface water and groundwater contamination (19). The sorption characteristics of Pb and atrazine onto the manure-based biochar were further compared with that of a commercial activated carbon (AC). The mechanisms responsible for contaminant removal were elucidated using sorption isotherms, chemical speciation model, and solid phase spectroscopy.

Experimental Section

Preparation of Biochar and Sorbates. Briefly, the biochar was produced by heating air-dried dairy manure under O₂-limited condition at ≤ 350 °C for 4 h. The biochars generated at 200 and 350 °C were referred to as BC200 and BC350. The manure without heat treatment and dried at 25 °C (BC25), and a commercial activated carbon (AC) were included as controls. The AC (<150 μm) was made from woody plants (JT Baker Chemical Co.). More details on biochar preparation and characterization can be found in Cao and Harris (17). Selected physicochemical properties of the biochar and AC are given in Tables S1 in the Supporting Information (SI).

A stock solution of 5 mM Pb was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Thermo Fisher Scientific Inc.) in 0.01 M NaNO_3 solution as background electrolyte. Atrazine (with a purity of >99%) was purchased from AccuStandards (New Haven, CT). Atrazine is neutral (pH 6.2–6.8) with a water solubility of ~ 34 mg L⁻¹ (12). A stock solution of 20 mg L⁻¹ atrazine was prepared in 0.01 M NaNO_3 solution containing 0.2% methanol.

Lead Sorption. The experiment was conducted in 60-mL polypropylene tubes by mixing 0.25 g of biochar or AC with 50 mL of 0.01 M NaNO_3 containing 0–5 mM Pb. The mixture was then agitated on a reciprocating shaker at 60 rpm for 4 h. Preliminary experiment showed that Pb sorption reached equilibrium after 0.5 h (Figure S1).

* Corresponding author phone: +86 (21) 3420-2841; fax: +86 (21) 5474-0825; e-mail: xdc@sjtu.edu.cn.

[†] Shanghai Jiao Tong University.

[‡] Soil and Water Science Department, University of Florida.

[§] Agricultural and Biological Engineering Department, University of Florida.

After equilibrium, solid and liquid phases were separated by centrifugation at 4000 rpm for 15 min and the solution was filtered through a 0.22- μm Millipore filter. The filtrate was immediately acidified to $\text{pH} < 2$ with concentrated HNO_3 for chemical analysis. Concentrations of Pb, Ca, and Mg in the filtrate were determined by atomic absorption spectroscopy (AAS) and that of P was determined by colorimetry method (20). The solids retained on the filter, referred to as "residual solids", were collected and washed with deionized (DI) water and air-dried. To elucidate the sorption mechanism, a portion of the dried residual solid was heated at 550 $^\circ\text{C}$ for 4 h to increase the crystallinity of potential minerals. The residual and heat-treated solids were examined using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) (SI).

Lead Speciation Modeling. Fifty mL of 0.01 M NaNO_3 solution containing 1 mM Pb was mixed with 0.25 g of biochar or AC. After being shaken for 4 h, solid and liquid separation and liquid filtration were conducted as done in the Pb sorption experiment. Half of the filtrate was collected for dissolved organic C (DOC) measurement using organic C analyzer and for anions (PO_4 , SO_4 , Cl , NO_3 , and CO_3) analysis using ion chromatography (21). Remaining filtrate was acidified to $\text{pH} < 2$ with HNO_3 prior to analysis of Pb, Cu, Zn, Ca, Mg, Fe, Al, Mn, Na, and K using AAS. The analytical results including pH, DOC, anions, and cations were used in the speciation model Visual MINTEQ (version 2.53) to calculate Pb species in solid phase.

Atrazine Sorption. The experiment was conducted in 25-mL Corex glass centrifuge tubes by mixing 0.2 g of biochar or 0.01 g of AC with 20 mL of 0.01 M NaNO_3 solutions containing 0–20 mg L^{-1} atrazine. Different amounts of the absorbents were used to ensure that $>40\%$ of atrazine was sorbed (22). NaN_3 was added into the solution at 200 mg L^{-1} to inhibit microbial degradation. The mixture was shaken at 60 rpm for 4 d. Preliminary tests showed that atrazine sorption on AC and biochar reached equilibrium within 1 and 3 d, respectively (data not shown). After equilibrium, solid and liquid separation and the liquid filtration were conducted as done in the Pb sorption experiment. The atrazine concentrations in the filtrate were analyzed using high-performance liquid chromatography (HPLC) (SI).

Lead and Atrazine Sorption in a Binary-Solute System. Both Pb and atrazine were mixed with biochar or AC in 0.01 M NaNO_3 solution containing 1 mM Pb and 10 mg L^{-1} atrazine. After 4 d of shaking, solid and liquid separation and the liquid filtration were conducted as done in the Pb sorption experiment. The Pb and atrazine in the filtrate were analyzed using AAS and HPLC, respectively.

Quality Control. All sorption experiments were conducted at ambient temperature and included three controls: DI water, Pb and/or atrazine solution, and biochar + DI water. Three replicates were used for each treatment. Solution pH was not controlled but recorded at the beginning and the end of the equilibration. Sorption of Pb or atrazine was calculated from the difference between initial and final solution concentrations after taking controls into account. Actually, the control effect was negligible.

Results and Discussion

Lead Sorption. The Pb sorption capacity of the manure-derived biochar and commercial AC was determined by plotting the amount of Pb sorbed onto the biochar or AC against equilibrium Pb concentration in solution. All sorption isotherms were of L-type (Figure 1) (23).

Sorption of metal ion from aqueous solution is generally governed by surface chemistry and surface area of the sorbent or by precipitation reactions (24). The Pb sorption capacity of the biochar was much higher than that of AC (Figure 1) despite its lower specific surface area (Table S1), suggesting

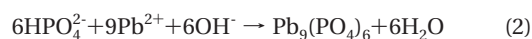
the Pb sorption by the biochar was not controlled by its surface area. Compared to AC, the biochar reduced equilibrium Pb concentrations to near the detection limit of 0.05 mg L^{-1} from initial Pb concentrations of up to 1.0 mM (Figure 1a–c). Isotherms that have similar equilibrium concentrations for different amounts of metal added reflect a precipitation mechanism (24). Therefore, we infer that Pb uptake by the biochar may be attributed to a combined sorption–precipitation mechanism. In light of these results, we evaluated Pb sorption on the biochar using the Langmuir–Langmuir (L–L) model, which accommodates precipitation (eq 1):

$$q = q_a + q_p = \frac{k_a Q_a C_e}{1 + k_a C_e} + \frac{k_p Q_p C_e}{1 + k_p C_e} \quad (1)$$

where q_a and q_p represent sorption and precipitation amount per unit mass (mmol kg^{-1}) of biochar, respectively; Q_a and Q_p denote the maximum capacity (mmol kg^{-1}) of sorption and precipitation, respectively; k_a and k_p stand for the Langmuir bonding term (L mmol^{-1}) related to sorption and precipitation energy, respectively; and C_e is the equilibrium concentration (mmol L^{-1}) of Pb in solution.

Little difference was observed between L and L–L isotherms for Pb uptake by AC (Figure 1d), indicating that surface sorption may be responsible. However, Pb uptake by the biochar was better fitted to L–L model than L model (Figure 1a–c), with R^2 generally >0.015 higher in L–L model than that in L model (Table 1). Dual models have been successfully used to describe metal sorption isotherms involving multiple sorption processes, e.g., surface adsorption, precipitation, and complexation (25). Das et al. (25) indicated that mercury sorption on *Aspergillus versicolor* biomass followed the Langmuir–Freundlich model. The calculated maximum capacity between two models was similar for biochar and AC (Table 1). However, Q_p was much higher than Q_a in the L–L model, indicating that precipitation was mainly responsible for Pb retention by the biochar (84–87%). The remaining 13–16% of sorption (Q_a) was attributed to surface sorption, probably via complexation of Pb with surface functional group such as carboxyl (Table S1) (1). For AC, surface sorption dominated Pb retention, accounting for 95% (Table 1). Overall, the biochar consistently retained much more Pb (up to 6 times) than AC, with BC200 having the maximum sorption capacity of up to 680 mmol kg^{-1} , corresponding to 15% Pb (w/w) in the biochar solid.

Elemental analysis shows that the biochar was rich in P, with as much as 2.5% in BC350 (Table S1). We have previously shown that addition of P induces formation of insoluble Pb phosphate minerals in Pb-contaminated water and soils (21). We hypothesized that higher Pb removal by the biochar may be attributed to formation of Pb-phosphate precipitate, which was confirmed by XRD and FTIR analysis (Figures 2 and 3). XRD shows precipitation of poorly crystalline $\beta\text{-Pb}_9(\text{PO}_4)_6$ in BC25 and BC200 after reaction with aqueous Pb. Heat treatment of the residual solids confirmed the presence of more crystallized $\beta\text{-Pb}_9(\text{PO}_4)_6$ (top patterns in Figure 2a and b) (26). FTIR analysis shows decrease or disappearance of PO_4^{3-} bands at $\sim 1095 \text{ cm}^{-1}$ after Pb sorption, compared to control biochar BC25 (Figure 3a and b). Higher sorption by BC200 than BC25 was attributed to the higher P (Table S1). The Pb–P precipitation can be described as follows:



In spite of the highest total P in BC350, soluble P was the lowest (Table S2). The low soluble P was probably due to the association of stable P–Ca–Mg at elevated temperature (17). Contrary to BC25 and BC200, higher pH (pH ~ 10) and

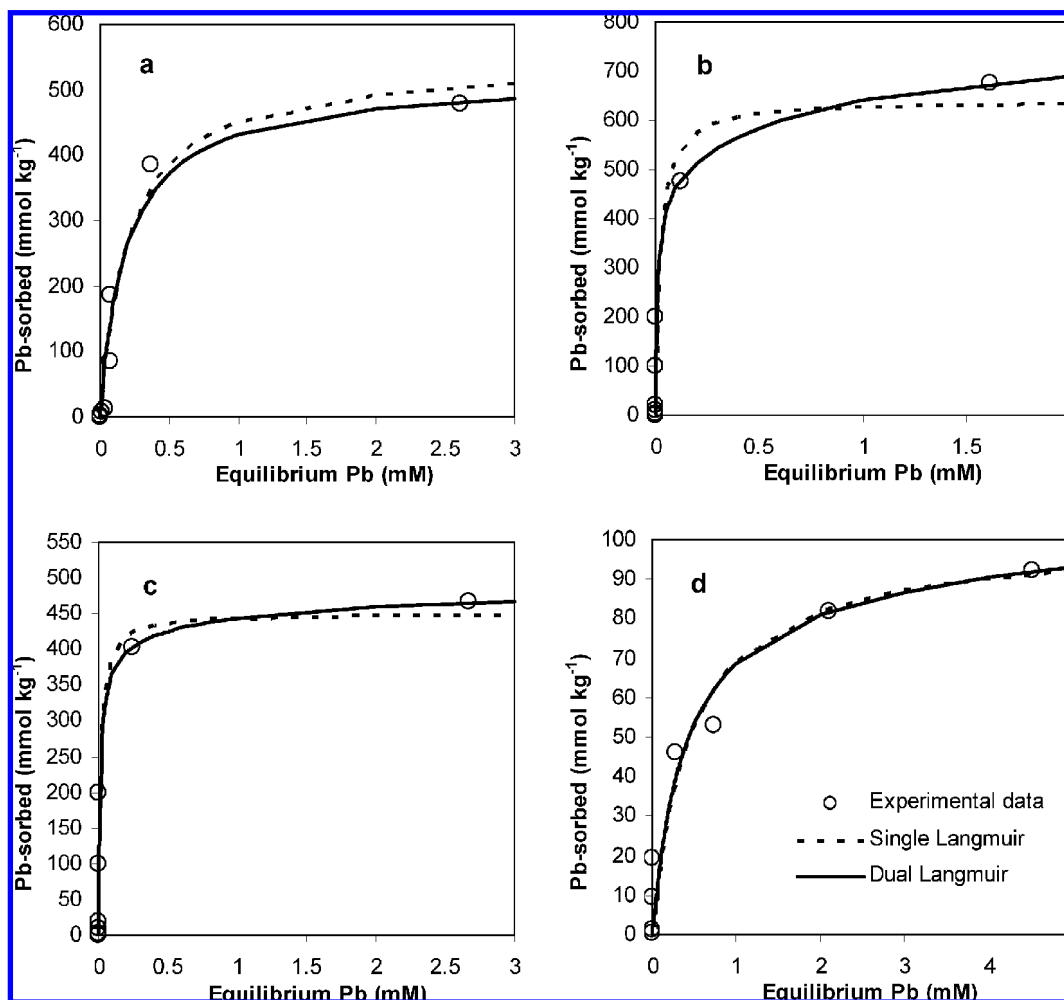
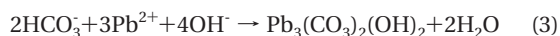


FIGURE 1. Sorption isotherms of Pb on (a) BC25, (b) BC200, (c) BC350, and (d) AC. Dashed line represents Langmuir isotherm, and solid line represents Langmuir–Langmuir isotherm.

TABLE 1. Sorption Constant, Maximum Sorption Capacity, and Regression Coefficient for Pb Isotherm Based on Langmuir and Langmuir–Langmuir Models

	Langmuir			Langmuir–Langmuir						
	k L mmol ⁻¹	Q mmol kg ⁻¹	R^2	k_a L mmol ⁻¹	Q_a mmol kg ⁻¹	k_p L mmol ⁻¹	Q_p mmol kg ⁻¹	$Q_a + Q_p$ mmol kg ⁻¹	R^2	
BC25	4.81	528	0.936	1.14	65.1	5.72	438	503	0.952	
BC200	43.9	641	0.934	1.21	97.2	87.3	583	680	0.953	
BC350	61.3	452	0.902	0.91	78.3	69.3	413	491	0.916	
AC	2.17	101	0.932	2.74	89.3	0.13	5.21	93.8	0.938	

carbonate concentrations (Table S2) allowed for precipitation of hydrocerussite $Pb_3(CO_3)_2(OH)_2$ in BC350, which was evidenced by XRD analysis (Figure 2c). FTIR shows the disappearance of CO_3^{2-} band at 1480 cm^{-1} after Pb sorption (Figure 3c). The precipitation can be described as follows:



The Visual MINTEQ speciation model predicted precipitation of hydroxypyromorphite in the solid phases of BC25 and BC200 (Table 2), contrary to XRD results showing precipitation of $Pb_9(PO_4)_6$ (Figure 2). This was possibly because the latter phase was kinetically favored. Nevertheless, both the model and XRD data showed Pb precipitated as phosphate minerals. In the BC350 solid phase, Pb was precipitated as hydrocerussite (Table 2), consistent with XRD analysis (Figure 2). The model indicated that more than 99.5% of Pb was precipitated in

all biochar systems (Table 2). Nearly complete precipitation of Pb in the biochar was consistent with the isotherm observation that almost no Pb was detected in equilibrium solution even with initial Pb concentration of 1 mM (Figure 1a–c).

Precipitation of Pb as phosphate and carbonate compounds from Pb uptake by the biochar was further supported by changes in solution P, Ca, and Mg concentration. In BC25 and BC200, solution P decreased with increasing Pb concentration due to formation of Pb phosphate (Figure S2a). Solution Ca and Mg remained unchanged at lower initial Pb concentration range ($Pb < 1\text{ mM}$ for BC25 and $Pb < 0.1\text{ mM}$ for BC200); Beyond the low Pb concentration range, increasing initial Pb increased solution Ca and Mg (Figure S2b and c). This probably resulted from dissolution of solid phosphate phase (e.g., Ca–Mg–P association), which provided more P for more Pb precipitation. The greater increase in soluble Ca

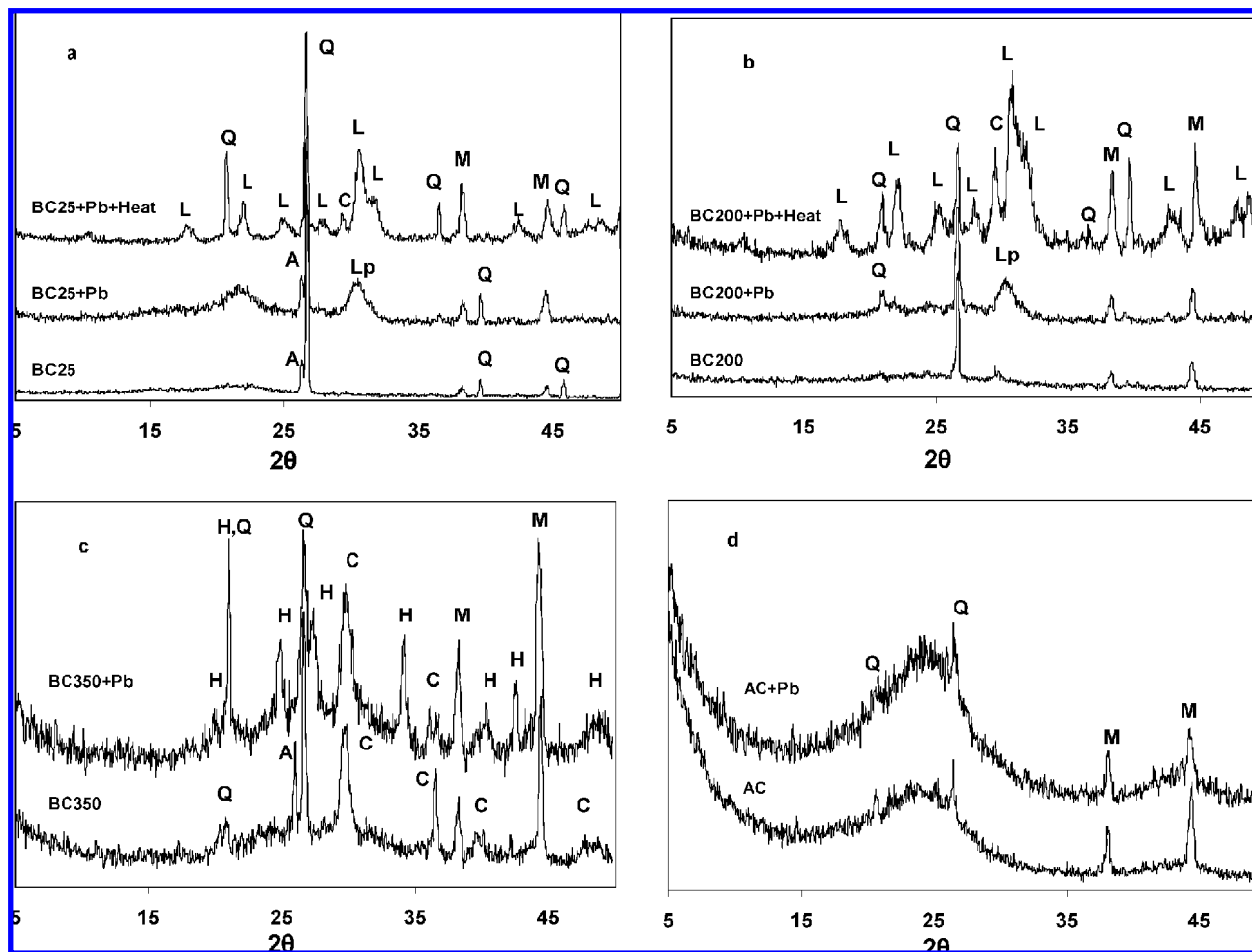
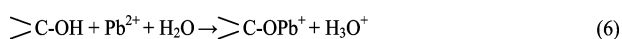
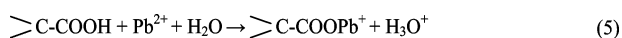
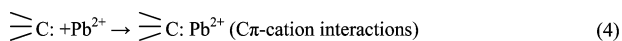


FIGURE 2. X-ray diffraction patterns of (a) BC25, (b) BC200, (c) BC350, and (d) AC before and after reaction with aqueous Pb. Top patterns in (a) and (b) are for the Pb-sorbed solids with heating treatment. Minerals with peak labeled: Lp, poorly crystalline β - $\text{Pb}_9(\text{PO}_4)_6$; L, β - $\text{Pb}_9(\text{PO}_4)_6$; Q, quartz; A, aragonite; C, calcite; H, hydrocerussite; M, X-ray mount background.

and Mg found with BC200 (Figure S2b and c) was due to more Pb phosphate precipitation. For BC350, solution P was lower and remained unchanged (Figure S2a). Solution Ca and Mg remained unchanged until Pb > 0.5 mM where Ca and Mg increased with increasing Pb (Figure S2b and c), probably due to dissolution of some Mg-substituted calcite (17), which provided more carbonate for hydrocerussite precipitation.

No Pb minerals were detected by XRD in the AC solid after Pb sorption (Figure 2d), as indicated by the speciation model (Table 2). FTIR shows reduction of the bands at 1514 and 1265 cm^{-1} , attributing to the lignin C=C stretching and the phenolic -OH stretching vibration, respectively. This indicated that Pb sorption by AC was probably through a surface sorption mechanism via coordination of Pb d-electron to C=C (π -electrons) bond and -O-Pb bond. Complexation of metals with ionized O-containing groups (e.g., $-\text{COO}^-$ and $-\text{O}^-$) or C=C (π -electrons) bond has been proposed to be the major mechanism for metal sorption by AC (27). The possible mechanisms can be described schematically as follows:



Atrazine Sorption. Sorption isotherms of atrazine by the biochar and AC were normalized to the C content of the biochar and AC and plotted against the equilibrium

concentration in solution (Figure 4). Sorption of atrazine onto the biochar displayed a linear isotherm (Figure 4a), showing characteristics of solute partitioning (9–12) (Table S3). Since the biochar was rich in organic (Table S1), atrazine partitioning into the organic phase probably dominated atrazine sorption. Many studies have demonstrated that sorption of organic contaminants on the biochar produced at low temperatures is controlled mainly by the partitioning mechanism (9–12). Partitioning of atrazine is positively related to biochar C content. Higher sorption by BC200 than BC350 was due to higher C in BC200 (31%) than that in BC350 (26%). In spite of highest C (37%) in BC25, however, lowest sorption of atrazine was observed. Chen et al. (9) indicated that this specific sorption behavior may be related to the polymer aliphatic fraction in the biochar, which increased from BC25 to BC200 and promoted compatibility of the atrazine with partition phase of biochar. When the heating temperature increased to 350 °C (BC350), the aliphatic partition phase decreased; thus, the partition medium changed from a more flexible aliphatic phase to a more rigid and condensed aromatic phase ($\text{H}/\text{C} < 0.8$, see Table S1), making the partition less favorable. The lowest sorption of atrazine observed in BC 25 may also be due to suppression of high DOC in solution (Table S2). Kilduff and Wigton (28) indicated that preloaded humic substances on biochar significantly reduced the sorption of trichloroethylene, attributing to the effects of size-exclusion and a pore blockage of DOC.

Atrazine sorption on AC displayed the characteristics of L-type isotherm (Figure 4b), suggesting a surface sorption

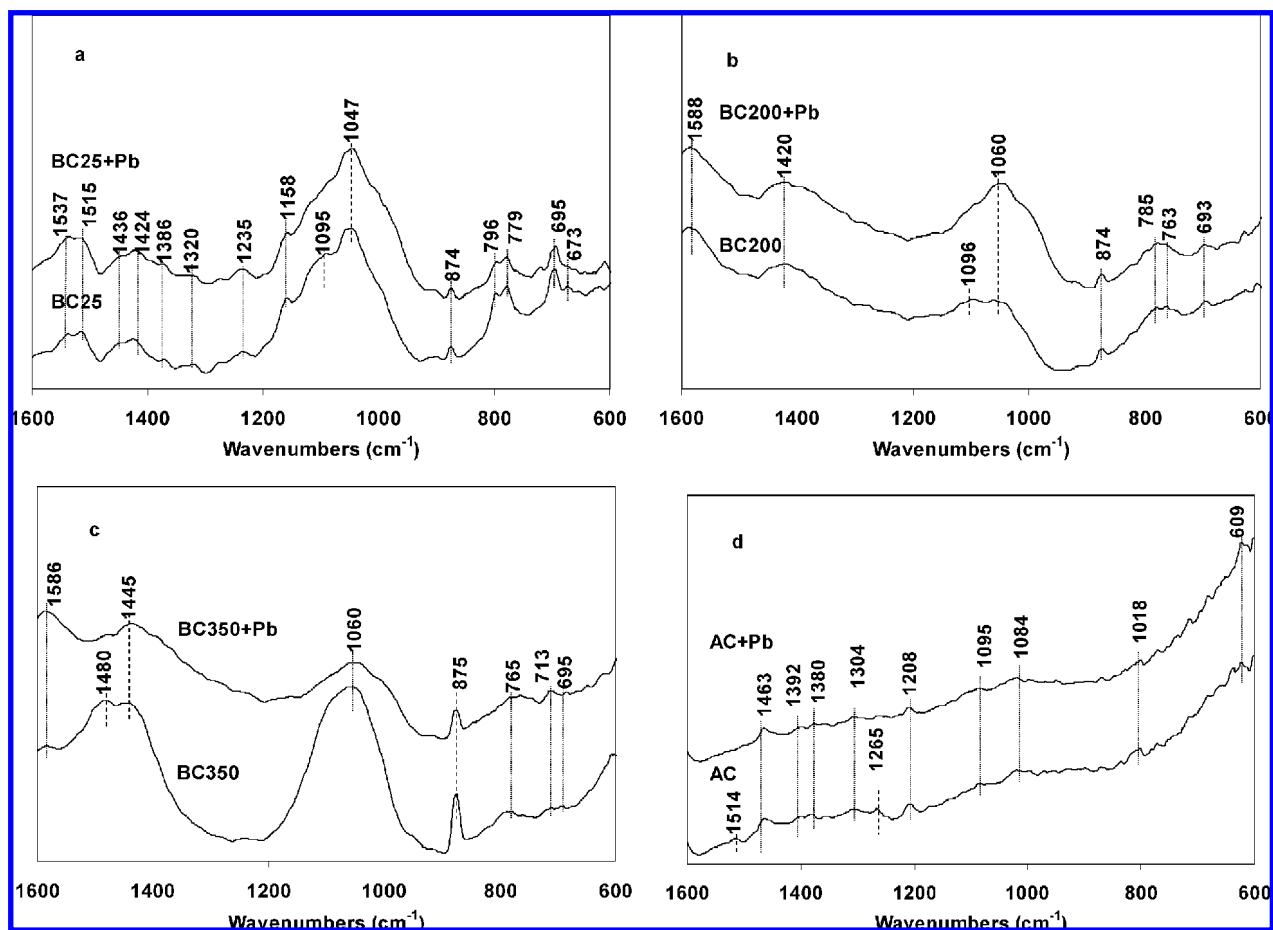


FIGURE 3. FTIR analysis of (a) BC25, (b) BC200, (c) BC350, and (d) AC before and after reaction with aqueous Pb. Note, the infrared absorbance was only presented here within the wavenumber range of 800–1600 cm^{-1} , beyond which there was little difference with or without Pb sorption.

TABLE 2. Lead Precipitation and Speciation in the Solid Phase After Reaction of Aqueous Pb with Biochar and Activated Carbon Based on Visual MINTEQ Model (Electrolyte: 0.01 M KNO_3 , $\text{Pb} = 1.0 \text{ mM}$)

	$\text{Pb}_5(\text{PO}_4)_3\text{OH}$ (mmol kg^{-1})	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (mmol kg^{-1})	Pb precipitation (%)
BC25	0.20		99.6
BC200	0.20		99.9
BC350	<0.01	0.33	99.5
AC	<0.01		0.48

mechanism. Atrazine can be sorbed onto AC surfaces through specific interactions of atrazine molecules with an abundance of polar groups in AC (e.g., carboxyl groups, phenolic hydroxyl groups) (12). Fitting to the L isotherm (eq 1) gave the maximum sorption of 123 g kg^{-1} ($r^2 = 0.960$) (Table S3), attributing to AC's high surface area ($356 \text{ m}^2 \text{ g}^{-1}$) (Table S1).

Sorption of Pb and Atrazine in a Binary-Solute System.

Sorption of Pb and atrazine on biochars was similar in both single- and binary-solute systems (Table 3), indicating limited sorption competition between Pb and atrazine. This was because precipitation and partitioning were respectively responsible for Pb and atrazine sorption by the biochar. In contrast, compared to the single-solute system, Pb and atrazine sorption by the AC in the binary-solute system was reduced by 35% and 55%, respectively (Table 3). As discussed previously, sorption of both Pb and atrazine on the AC was via surface sorption. Competition for the same surface sites likely reduced their individual sorption capacities. In a study

determining the effect of metals on organics sorption onto maple-wood derived charcoal, Chen et al. (2) indicated that addition of Cu at 50 mg L^{-1} decreased sorption of 2,4-dichlorophenol, 1,2-dichlorobenzene, and naphthalene by 30–60%. They assumed the surface complexation of Cu^{2+} to form hydration shells of dense water, which directly compete with organics for sorption surface area.

Environmental Implication. Results from this study indicated that dairy manure can be converted into biochar as a unique sorbent for both metals and organics, implying that manure can potentially serve as a remediation amendment. In the United States, ~350 billion tons of manure are generated annually (29). Land application of manure to fertilize soil as a common method for managing dairy manure has caused a serious environmental issue, i.e., high levels of P accumulated in the soils receiving long-term manure applications led to P enrichment and water quality deterioration in aquatic systems (30). Therefore, turning dairy manure into biochar as a sorbent is a “win-win” solution via improving waste management and protecting the environment.

Several studies have successfully converted animal waste into activated carbon (AC) as sorbent for environmental remediation (31). However, production of AC needs higher temperature and additional activation processing, which require more energy and higher production cost. In comparison, biochar can be produced at low temperature for direct use, consuming less energy. Furthermore, previous work consistently shows that biochar generated from other sources such as crop residues, peat, and wood is only effective in sorbing organic contaminants (12), whereas most contaminated sites contain both heavy metals and organic

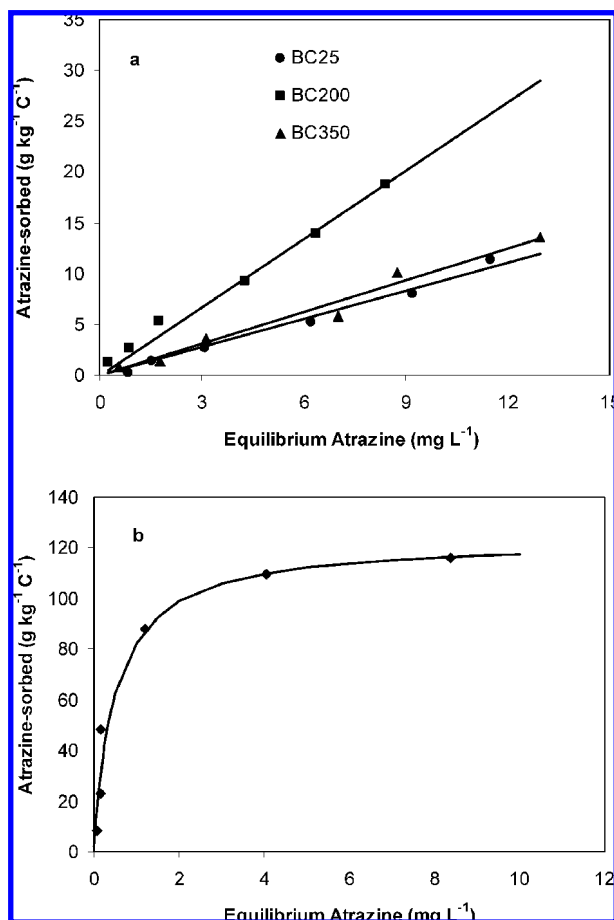


FIGURE 4. Sorption isotherms of atrazine on (a) biochar and (b) activated C.

TABLE 3. Comparison of Pb and Atrazine Sorption on Biochar and Activated Carbon in Single- and Binary-Solute Systems (Initial Concentrations: Pb = 1.0 mM, Atrazine = 10 mg L⁻¹)

	Pb sorbed (mmol kg ⁻¹)		atrazine (g kg ⁻¹ C ⁻¹)	
	single	binary	single	binary
BC25	185	172	5.25	4.94
BC200	211	198	9.51	8.82
BC350	199	187	5.75	5.80
AC	52.9	34.2	89.8	40.2

pollutants. Therefore, it is advantageous to produce a sorbent such as manure-derived biochar, which can remove both metals and organics. High content of P in the biochar is mainly responsible for Pb retention via formation of stable phosphate minerals, with less contribution from surface sorption, whereas atrazine sorption is attributed to its partitioning into the noncarbonized organic phase. However, more studies are needed to verify remediation efficacy of the biochar for sorption of other heavy metals (e.g., Cd and Hg) and organic contaminants (e.g., PAHs and PCBs).

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Supporting Information Available

Four tables and two figures. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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