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This study examined the ability of two sugarcane bagasse biochars to remove lead from water. The sorption of lead by biochars made from raw (BC) and anaerobically digested sugarcane bagasse (DBC) was compared with a commercial activated carbon (AC) using batch sorption experiments. DBC was a more effective sorbent of lead from water than AC, and far more effective than BC. The maximum lead sorption capacity of DBC ($653.9\,mmol\,kg^{-1}$) was about double that of AC ($395.3\,mmol\,kg^{-1}$) and about twenty times higher than that of BC ($31.3\,mmol\,kg^{-1}$). Post-sorption characterizations using X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that the enhanced sorption of lead by DBC was at least partly related to a precipitation mechanism, while surface adsorption was the principal mechanism of sorption of lead onto BC. These results suggest that biochars made from bagasse and other agricultural residues may be effective alternative, low-cost environmental sorbents of lead or other metals. In addition, the enhanced lead sorption ability of the digested bagasse biochar introduces the possibility of developing a novel carbon production method to use anaerobic digestion as a means of biological activation to create high-efficiency sorbents.

Keywords   anaerobic digestion; biochar; lead; low-cost sorbent; sugarcane bagasse

INTRODUCTION

Heavy metal pollution in wastewater has become a pressing environmental concern and presents a great challenge to remediation efforts (1). Lead is a highly toxic heavy metal which may be introduced to a water body from various sources ranging from battery to ammunition industries (2). Lead poses a risk to public health when consumed in drinking water, even at very low concentrations due to bioaccumulation (3–7).

Various methods have been employed to remove lead from wastewater including ion exchange, chemical precipitation, membrane filtration, electrodialysis, and granular filtration (8–12). Most of these methods, however, have high operational costs (13–15). It is therefore desirable to develop alternative, low-cost lead removal technologies.

Biochar is a black carbon derived from the thermal treatment of carbon-rich biomass (e.g., agricultural residues and organic waste) in an inert atmosphere (pyrolysis). The use of biochar to remove contaminants such as metals or organic contaminants from aqueous solutions is a relatively novel and promising wastewater treatment technology. Several studies have recently reported the effective removal of lead by biochar sorbents (16–19). For example, Cao et al. (16) reported that biochar made from animal manure was six times more effective than activated carbon in adsorbing lead and had a sorption capacity of up to 680 mmol/kg. And Sekhar et al. (19) showed biochar made from coconut shell and commercial activated carbon to have a similar lead sorption capacity of about 145 mmol/kg. These authors have attributed the effective lead removal by biochar sorbents to either precipitation of lead onto the biochar surface or electrostatic interactions between lead species and negatively charged functional groups on biochar's surface (16,18). Like many other traditional sorbents, the high affinity for lead and other metal ion species bound by biochar may be controlled by other mechanisms as well, including complexation, chelation, and ion exchange (20,21).

Studies have attempted to improve the metal sorption abilities of biochar from pyrolyzed agricultural residues such as bagasse (22), pine wood and rice husk (17). The presence of cellulose, hemicellulose, proteins, sugars, and lipids in these materials provide a variety of functional groups that can be physically activated through pyrolysis and further steam or CO_2 treatment to enhance their uptake of compounds such as lead. There has also been

notable work on the chemical activation of agricultural residue derived biochar for lead sorption (23). To our knowledge, however, only little research has explored the use of anaerobic digestion as a means of biological activation to enhance the sorption ability of agricultural residue-derived biochar (24,25).

This study investigated the enhanced removal of lead by an anaerobically digested sugarcane bagasse biochar. Raw and digested sugarcane bagasses were pyrolyzed into biochar at 600°C in the laboratory. Bench-scale batch sorption and desorption experiments were conducted to compare the lead sorption ability of the digested bagasse biochar to that of the undigested bagasse biochar and a commercial activated carbon. Mathematical models and material characterization techniques were used to aid the experimental data interpretation. Our goal was to understand the effect of anaerobic digestion on the ability of bagasse biochar to remove lead from water, and thus, to develop a biological activation technology.

The objectives were to:

a. compare the sorption kinetics of lead onto digested and undigested bagasse biochar and activated carbon,
b. compare the equilibrium sorption of lead onto these sorbents, and
c. identify the mechanisms governing lead sorption onto the biochar samples.

MATERIALS AND METHODS
Materials

Sugarcane bagasse (sized 0.5–1 mm) was obtained from Florida Crystals, Okeelanta, Florida. Digested bagasse residues were obtained by aerobically digesting the raw bagasse samples in a laboratory thermophilic digester at a constant temperature of 55°C. Biochar samples were obtained by pyrolyzing the feedstock materials (digested bagasse residues and undigested bagasse) for 1.5 hours at 600°C in a N_2 environment. The two biochars were crushed and sieved to a size fraction of 0.5–1 mm. Detailed information about the anaerobic digestion of bagasse and biochar production can be found in Inyang et al. (26). Physicochemical properties of the biochar samples were reported previously (26), and are shown in Table 1.

Granulated activated carbon (AC, from steam activated coconut shell) was also obtained from Fisher Scientific and was crushed and sieved to the same size as the biochar samples. A range of physicochemical properties, including pH, surface potential, surface area, cation exchange capacity (CEC), and anion exchange capacity (AEC), of the AC were determined using methods detailed in Inyang et al. (26). Lead solution was prepared from lead nitrate (certified A.C.S) from Fisher Scientific.

Sorption

Sorption kinetics of lead onto the three sorbents were determined by mixing 50 mL $Pb(NO_3)_2$ (20 ppm) solutions with 0.1 g of each sorbent in 60 mL plastic vials at room temperature (22 ± 0.5°C). The vials were then shaken at 200 rpm in a mechanical shaker. Over the course of 24 h, the vials were withdrawn at time intervals and the mixtures were immediately filtered through 0.1 μm pore size nylon membranes (GE cellulose nylon membrane). Equilibrium sorption isotherm experiments were conducted similarly using $Pb(NO_3)_2$ solutions with initial Pb concentrations ranging from 5 to 200 ppm and apparent sorption equilibrium times of 24 h. Following the experiments, the solids were collected, washed with deionized water, and dried at 100°C in an oven before post-sorption characterizations as described below. The Pb concentrations of the liquid phase samples were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200). The solid phase Pb (i.e., sorbed Pb) concentration was calculated based on the difference between Pb in the initial and final aqueous solutions. Blank controls containing sorbents and solutions with no Pb were tested in parallel with each kinetic and isotherm experiment and Pb release was below the detention limit of the ICP-AES. All the experimental treatments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 10%.

Kinetic and equilibrium sorption models were used to understand the interaction mechanisms between lead and the sorbents. The model parameters were calibrated to fit the experimental data using inverse analysis techniques (27).

TABLE 1
Summary of physicochemical properties of the adsorbents studied

Sample	pH	Zeta potential (mV)	BET surface area (m^2/g)	CEC (cmol/kg)	AEC (cmol/kg)
DBC	10.9	−61.7	17.7	14.3	11.2
BC	7.7	−28.1	14.1	4.2	6.6
AC	9.5	−33.9	1100.0	19.3	6.4

Post-Sorption Characterizations

X-ray diffraction (XRD) analysis was carried out on the chars before and after Pb sorption. This was done using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Scanning electron microscope (SEM) imaging of DBC and BC after Pb sorption was carried out using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4000) with maximum resolution of 1.5 nm. The accelerating voltage of the instrument was maintained at 10 kv.

Fourier transform infrared (FTIR) spectrographic analysis of BC and DBC before and after sorption was carried out to characterize the samples' surface functional groups and to investigate any possible interaction with the Pb ion. Samples were ground and mixed with KBr to approximately 0.1 wt.% and pressed into a pellet manually using a mechanical vice. Spectra were collected on a Bruker Vector 22 FTIR with OPUS 2.0 software.

Desorption

Desorption of lead from the lead-laden sorbents was investigated by conducting Pb stripping experiments using an acid solution. Duplicates of 0.1 g sorbents were reacted for 24 h with 50 mL of 80 ppm Pb solution. After filtration (as above), aqueous Pb concentrations in the filtrates were used to determine sorbed Pb concentrations using the method described above. The solids on the filters were rinsed three times with 50 mL of distilled water to remove any residual Pb. The rinsed samples were then transferred into plastic vials and mixed with 30 mL of 0.1 M HCl. These mixtures were agitated for 0.5 h using a mechanical shaker, filtered, and the aqueous Pb concentration was measured in the filtrate. The desorption rate of each sorbent was calculated based on the ratio of the amount of Pb released to the initial amount of Pb adsorbed. Samples without sorbed Pb were also treated with the acid solution followed the same procedures to test for pre-existing Pb in the sorbents.

RESULTS AND DISCUSSION
Physiochemical Properties

The physicochemical properties of the two biochar samples that may influence their sorption abilities have been reported previously (26,28) and are compared with those of AC in Table 1. The N_2-BET surface areas of both DBC and BC were below $20 \, m^2 \, g^{-1}$, much less than that of activated carbon ($1100 \, m^2/g$). These data suggest that, if surface adsorption dominates Pb sorption onto these materials, DBC and BC should have much lower sorption capacity than AC. Low specific surface areas are commonly reported for biochars derived from agricultural residues (21,29–32).

The CEC and AEC of all the sorbents were comparable to those of natural soils (Table 1). DBC and AC had a much higher CEC than BC, while DBC had the highest AEC compared to BC and AC. These data suggest the possibility of using at least some biochars as ion exchangers that may sequester both positively and negatively charged ions from water. The zeta potential of all the samples were negative (Table 1), with that of DBC the lowest value (−61.7 mV), indicating strongly negatively charged surfaces that might facilitate the deposition of cations such as Pb onto these sorbents.

Sorption Kinetics

The sorbents showed different lead sorption kinetic behaviors (Fig. 1). Both DBC and AC reached sorption equilibrium within several minutes. Lead sorption onto BC, however, was much slower and reached equilibrium after about 5 hours. A rate-limited, first-order (pseudo-first-order) kinetic model was used to simulate the experimental data:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

where q_t and q_e are the amount of lead sorbed at time t and at equilibrium (mmol kg^{-1}), respectively, and k_1 is the first-order apparent sorption rate constant (h^{-1}). This model reproduced the kinetic data closely (Fig. 1), with correlation coefficients (R^2) exceeding 0.98 for the three sorbents tested. Because there was no obvious difference in results for DBC and AC, the same model simulations are shown for both in Fig. 1. The model-estimated sorption first-order rate constants (k_1) for DBC, BC, and AC were 320.25, 0.55, and 320.25 hr^{-1}, respectively, suggesting that the anaerobic digestion can chemically modify bagasse such that its biochar has sorption characteristics similar to commercial activated carbons.
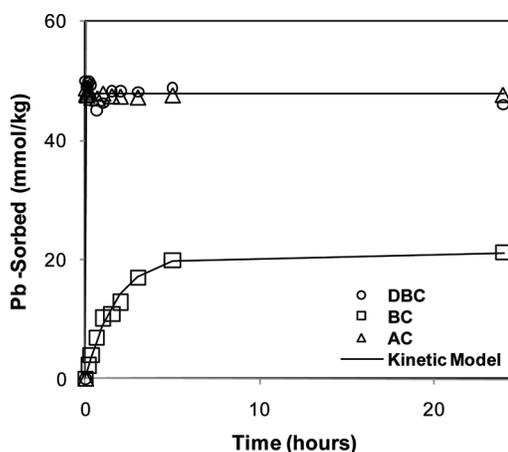

FIG. 1.   Lead sorption kinetics.

Previous studies on the kinetic behaviors of metal sorption onto microporous sorbents showed that intraparticle surface diffusion may be important to the sorption process (33,34). In this study, the sorption of lead onto DBC and AC reached equilibrium rapidly with no indication of a rate limiting diffusion step. This might indicate that the pores in the two sorbents were relatively large compared to some other microporous sorbents, or a different "sorption" method altogether (i.e., precipitation). The lead sorption kinetics of BC, however, was slower and the pre-equilibrium (i.e., before 5 h) lead sorption showed a strong linear dependency ($R^2 = 0.98$) on the square root of time (Fig. 2). This result suggests that intraparticle surface diffusion may play an important role in controlling the sorption of lead onto the undigested bagasse biochar samples.

Sorption Isotherms

The maximum observed Pb sorption onto DBC was much greater than that of AC or BC (Fig. 3) despite its lower surface area suggesting mechanisms other than surface adsorption may be involved in the sorption process. Because all the isotherms are "L" type, the classic Langmuir model was used to simulate the sorption isotherms:

$$q_e = \frac{KQC_e}{1 + KC_e} \qquad (2)$$

where K represents the Langmuir bonding term related to interaction energies (L $mmol^{-1}$), Q denotes the Langmuir maximum capacity (mmol kg^{-1}), and C_e is the equilibrium solution concentration (mmol L^{-1}) of the sorbate. Simulations using the Langmuir model fit all the isotherm data well (Fig. 3), with R^2 exceeding 0.84. The best-fit values of the bonding term (K) for DBC, BC, and AC were 189.45, 13.54, and 13.52 L $mmol^{-1}$, respectively. These results suggest that the digested bagasse biochar has much stronger

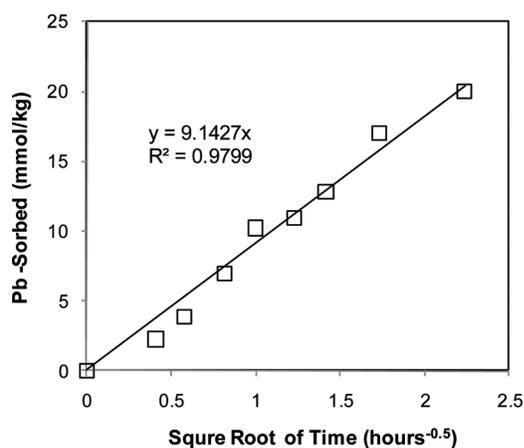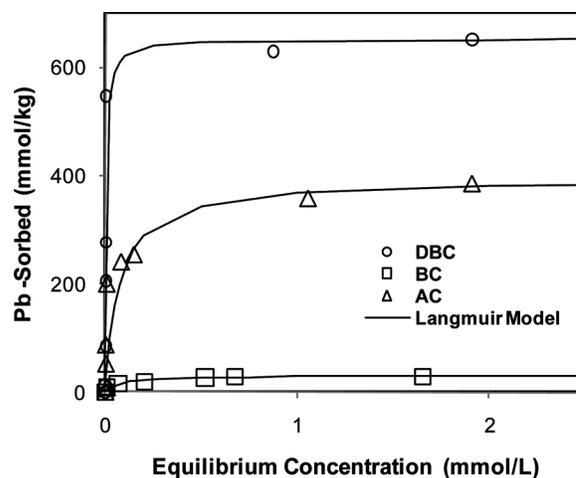FIG. 3.   Lead sorption isotherms.

bonding ability for lead than the undigested bagasse biochar and AC. The DBC also had the highest sorption capacity (653.9 mmol kg^{-1}), about double that of AC (395.3 mmol kg^{-1}) and about twenty times higher than that of BC (31.3 mmol kg^{-1}). Thus, anaerobic digestion of sugarcane bagasse prior to pyrolysis created a biochar with increased sorption strength and sorption capacity for lead. Although BC had a much lower lead sorption capacity than AC, the K values of the two sorbents were almost identical suggesting their sorption of lead could be controlled by similar mechanisms.

Sorption Mechanisms

The enhanced sorption of lead by DBC may be related to a precipitation mechanism such as that proposed by Cao et al. (16) for Pb sorption to biochar made from animal manure. The XRD analysis identified lead minerals on the DBC surface as hydrocerrusite –[$Pb_3(CO_3)_2(OH)_2$] and cerrusite – [$PbCO_3$] (Fig. 4). This was further confirmed by SEM images which clearly showed mineral crystals on the DBC surface at a magnification of 10000 X after the sorption experiments (Fig. 5). The mineral crystals were neither found on the original biochars nor of the other biochars following Pb sorption. The precipitation of hydrocerrusite and cerrusite on the surface of DBC might be attributed to a collective contribution from its high pH (Table 1) and specific surface functional groups (16). Comparisons of the FTIR spectra between fresh DBC and Pb-laden DBC reveals an almost complete disappearance of the O=C=O band at wave number 2343 cm^{-1} after Pb sorption (Fig. S3a, supplementary data). This suggests that the O=C=O functional groups on the digested bagasse biochar surface played an important role in the Pb precipitations onto this biochar. This corresponds to the results obtained from the XRD analyses of the cerrusite on the

FIG. 2.   Relation between Pb sorbed onto BC and square root of time before equilibrium.
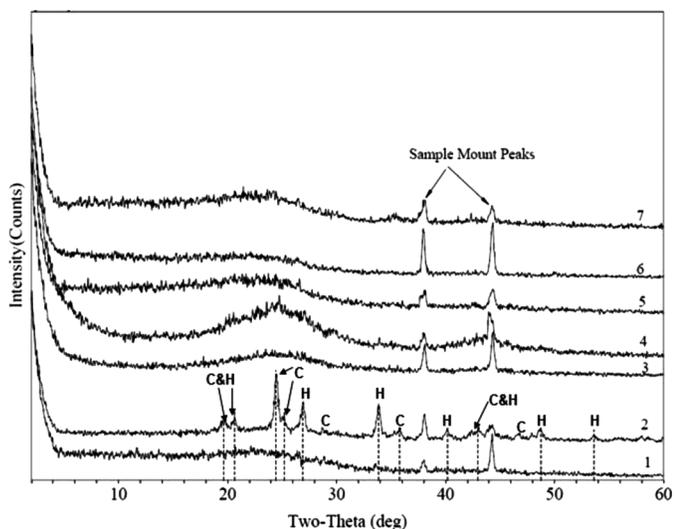
FIG. 4. XRD patterns of (1) fresh DBC, (2) post-adsorption DBC, (3) fresh AC, (4) post-adsorption AC, (5) fresh BC, (6) post-adsorption BC, and (7) background signal. Minerals were only detected in the post-adsorption DBC with peak labeled as H for hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) and C for cerrusite ($PbCO_3$).

surface of post-sorption DBC. Additional investigation is needed to further explore the role of the O=C=O functional groups in controlling the precipitation of lead onto biochars.

Previous studies have concluded that the sorption of lead onto activated carbon is mainly through a surface adsorption mechanism (16,35). In this study, both BC and AC showed no change in XRD patterns before and after Pb sorption, providing no evidence of mineral precipitation. In addition, Langmuir model simulations indicated that the bonding energy (i.e., K) of lead onto BC and AC were almost the same. These results suggest that the sorption of lead onto BC was probably also governed by a surface
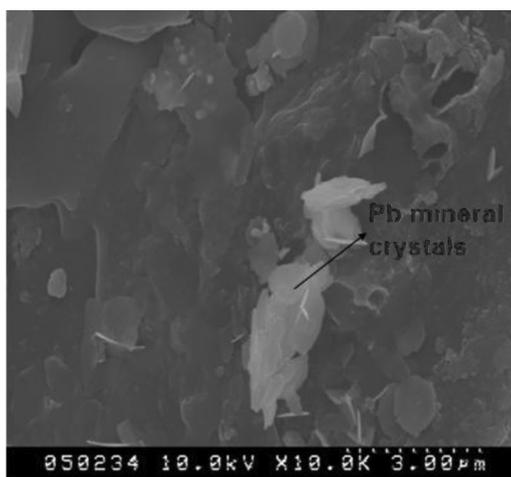
adsorption mechanism instead of precipitation. The FTIR analysis of BC indicated a disappearance of the OH band at wave number $1080\,cm^{-1}$ after Pb sorption (Fig. 6b), suggesting that the deposition of lead onto the bagasse biochar surfaces was probably through coordination of a Pb d-electron to a hydroxyl group, producing a -O-Pb bond (16). The FTIR spectrum of the fresh BC also showed the strongest signal at wave number 1080, indicating that OH functional groups were abundant (Fig. 6b). Despite this abundance, the total number of the OH functional groups on the biochar surface, however, may have been limited by its lower surface area (Table 1). As a result, the undigested bagasse biochar showed lower lead removal ability, on a mass basis, compared to the AC.

Desorption Rate

Most of the sorbed Pb could be retrieved from the DBC (77.4%), BC (73.0%), and AC (77.0%) samples using the 0.1M HCl. This result suggests that acid solution can be used to clean up the two biochar sorbents as well as the activated carbon after they are saturated with Pb ions. Acid washing has also been commonly used in cleaning up other sorbents to recover metal ions (36). The release of lead from BC and AC samples by acid washing might be controlled by similar surface desorption mechanisms.
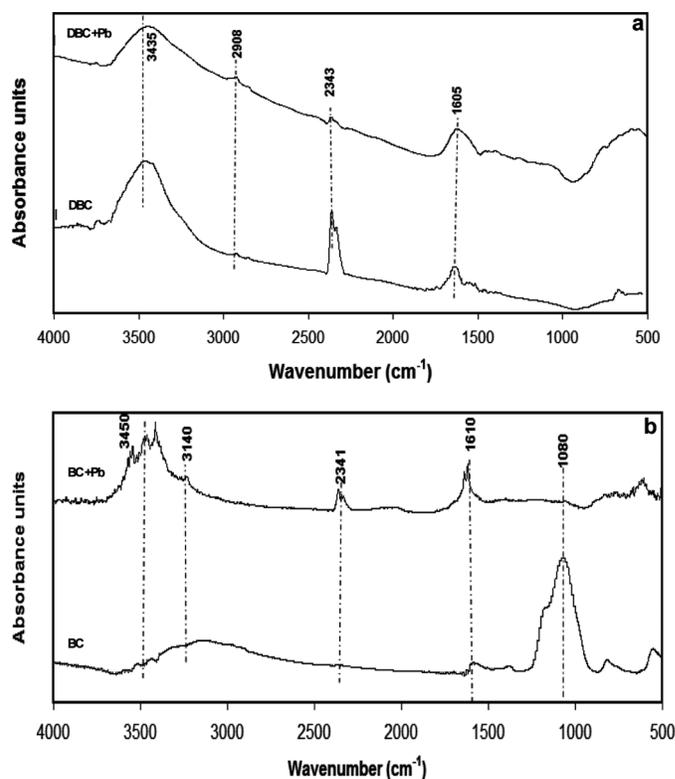

FIG. 6. FTIR spectra of (a) fresh and post-adsorption DBC and (b) fresh and post-adsorption DBC.

FIG. 5. SEM image of the post-adsorption DBC.

However, for DBC, Pb release likely involves the dissolution of the precipitated Pb minerals (i.e., hydrocerrusite and cerrusite) on the biochar surface.

CONCLUSIONS

Both digested and undigested sugarcane bagasse biochars effectively removed lead from water. Digested bagasse biochar showed a much greater sorption capacity than a commercially activated carbon. As bagasse is an abundant agricultural waste material, bagasse-based biochar could be produced at low cost. In addition, Pb-laden biochars can also be "cleaned" with acid solution with Pb recovery rates higher than 70%. Biochars should therefore be considered a promising alternative water treatment or environmental remediation technology for lead removal.

Biochar converted from the anaerobically digested sugarcane bagasse showed superior Pb sorption characteristics to undigested biochar made from bagasse and a commercial carbon sorbent, suggesting the possibility of using anaerobic digestion as a means of biological activation to produce high quality carbon-based sorbents. Biological activation of carbon through anaerobic digestion is much lower in cost and may be more effective compared to the traditional physical or chemical activation methods. Although further testing of its universal applicability (using other biomass types and adsorbing other metals) is required, biological activation of biochar can provide new opportunities for the carbon industry to develop novel products to solve environmental problems.

ACKNOWLEDGEMENTS

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