



Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass

Mandu Inyang^a, Bin Gao^{a,*}, Ying Yao^a, Yingwen Xue^{b,a}, Andrew R. Zimmerman^c, Prapat Pullammanappallil^a, Xinde Cao^d

^a Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States

^b School of Civil Engineering, Wuhan University, Wuhan 430072, China

^c Department of Geological Sciences, University of Florida, Gainesville, FL 32611, United States

^d School of Environmental Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China

ARTICLE INFO

Article history:

Received 21 November 2011

Received in revised form 11 January 2012

Accepted 15 January 2012

Available online xxx

Keywords:

Biochar

Sorption

Heavy metal

Wastewater

Anaerobic digestion

ABSTRACT

This study examined the ability of two biochars converted from anaerobically digested biomass to sorb heavy metals using a range of laboratory sorption and characterization experiments. Initial evaluation of DAWC (digested dairy waste biochar) and DWSBC (digested whole sugar beet biochar) showed that both biochars were effective in removing a mixture of four heavy metals (Pb²⁺, Cu²⁺, Ni²⁺, and Cd²⁺) from aqueous solutions. Compared to DAWC, DWSBC demonstrated a better ability to remove Ni and Cd. Further investigations of lead sorption by the two biochars indicated that the removal was mainly through a surface precipitation mechanism, which was confirmed by batch sorption experiments, mathematical modeling, and examinations of lead-laden biochars samples using SEM–EDS, XRD, and FTIR. The lead sorption capacity of the two biochars was close to or higher than 200 mmol/kg, which is comparable to that of commercial activated carbons.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Heavy metals pose a risk to public health because of their toxic and non-biodegradable nature and widespread occurrence in natural and human-altered environments. They are mainly introduced into the environment from point sources such as discharges from mining, metal plating, battery, and paper industries. Lead, copper, cadmium, and nickel are among the most toxic and carcinogenic heavy metals that could cause serious environmental and health problems. The United States Environmental Protection Agency (USEPA), therefore, has established very strict maximum contaminant level goals for these heavy metals in natural waters (Table S1, Supporting information).

Many methods have been developed to address these stringent environmental regulations which necessitate removal of heavy metal compounds from waste water. Traditional water treatment technologies, such as precipitation, ion exchange, electro-coagulation, membrane filtration, and packed-bed filtration have been found to be effective in reducing heavy metal concentrations (Akbal and Camci, 2011; Boudrahem et al., 2011; Malamis et al., 2011). Most of these technologies, however, may be associated with high operation cost and/or sludge disposal problems (Sud

et al., 2008). These disadvantages have increased the need of developing alternative and low-cost water treatment technologies for heavy metal contaminants. Biosorbents therefore have been suggested to be a potential candidate to satisfy this need to remove toxic metals from wastewater (Demirbas, 2008, 2009). For example, Demirbas (2008) indicated that agricultural by-products and in some cases appropriately modified could be used to develop cost-effective technologies to treat heavy metals in both industrial and municipal wastewater.

Biochar is a pyrogenic carbon-rich material, derived from thermal decomposition of biomass in a closed system with little or no oxygen (Das et al., 2008; Lehmann et al., 2006; Van Zwieten et al., 2010). When cheap biomass, particularly agricultural by-products, is used for biochar produce, the cost of biochar production is mainly associated with the machinery and heating, which is only about \$4 per gigajoule (Lehmann, 2007). The use of biochar as a low-cost sorbent to remove metallic contaminants from aqueous solutions is an emerging and promising wastewater treatment technology, which has already been demonstrated in previous studies (Beesley and Marmiroli, 2011; Liu and Zhang, 2009; Mohan et al., 2007; Uchimiya et al., 2010). Biochars converted from agricultural residues, animal waste, and woody materials have been tested for their ability to sorb various heavy metals, including lead, copper, nickel, and cadmium (Cao et al., 2009; Uchimiya et al., 2011, 2010). In addition, aerobically digested biomass has been

* Corresponding author. Tel.: +1 352 392 1864x285; fax: +1 352 392 4092.

E-mail address: bg55@ufl.edu (B. Gao).

found to be a good feedstock to produce biochars with suitable physicochemical properties to serve as a low-cost sorbent (Inyang et al., 2010; Yao et al., 2011a). A recent study indicated that biochar converted from anaerobically digested sugarcane bagasses is a far more effective sorbent of lead than biochar from undigested bagasses and even more effective than commercial activated carbon (Inyang et al., 2011). It is suggested that anaerobic digestion could be used as new activation method (i.e., 'biological activation') to create high-efficiency carbon-based sorbents for heavy metals (Inyang et al., 2011). In addition, this method may also provide other benefits, such as producing renewable bioenergy through anaerobic digestion and pyrolysis and reducing waste management cost. However, there is still a paucity of data showing the universal applicability of 'biologically activated' biochars to water purifications. Particularly, it is unclear whether biochars converted from other digested biomass types also have superior ability to remove heavy metals from water (Inyang et al., 2011).

Sugar beets and dairy manure are two of the most common biomass types used in anaerobic digesters to produce bioenergy. Sugar beets are traditionally used for sugar production; however, they require rapid processing to maximize sugar extraction and minimize spoilage. Traditionally, dairy waste could be applied directly to agricultural lands as amendment for soils, but there are increasing concerns over the potential risk of surface and groundwater contamination (Hooda et al., 2000). Recent studies suggest that anaerobic digestion could be an effective waste management strategy to reduce the volume of sugar beets and dairy waste as well as to generate bioenergy (Brooks et al., 2008; Fang et al., 2011; Wang et al., 2010). Because most of the bacterial digestion processes cannot utilize all the feedstock materials, it is therefore important to develop methods to handle the residuals. To our knowledge, however, little research has been conducted to develop methods to process anaerobic digestion residuals, particularly with respect to using the digested biomass to make biochar-based sorbents.

The over arching objective of this work was to determine whether biochars converted from anaerobically digested biomass other than sugarcane bagasse can be used as effective sorbents to remove heavy metals from water. Two biochars were produced from anaerobically digested dairy waste and whole sugar beets in the laboratory through slow pyrolysis. Batch sorption experiments were used to examine the sorption behaviors of heavy metals on the biochars and the physicochemical properties of the pre- and post-sorption biochars were determined. Mathematical models were used to help data analysis and interpretation of sorption mechanism. The specific objectives of this work were to: (1) evaluate the removal efficiency of lead, copper, nickel and cadmium from aqueous solution by the two biochars; (2) determine the sorption characteristics of lead on the biochars; and (3) understand the sorption mechanisms of lead on the biochars.

2. Methods

2.1. Materials

Digested dairy waste residue was produced by a single-stage, thermophilic, anaerobic digester at the Dairy Research Unit of the Animal Science Department, University of Florida (UF) in Gainesville, FL. Digested whole sugar beet residue was obtained from a two-stage, thermophilic, high-solids sequencing, anaerobic digester in the Sequential Batch Anaerobic Composting (SBAC) pilot plant at UF. The residues were pressed, de-watered, then stored in air-tight plastic bags, and refrigerated prior to use.

To make the biochars, the residue materials were first dried at 80 °C. About 500 g of the dried feed stocks were converted into biochar through slow pyrolysis at 600 °C for 2 h in a N₂ environment

in a furnace (Olympic 1823HE) following the procedures of Yao et al. (2011a). The resulting biochars are referred to as DAWC (digested animal waste char) and DWSBC (digested whole sugar beet char). The biochar samples were ground and sieved to 0.5–1 mm sized particles. After several rinses with deionized (DI) water to remove impurities such as ash, both DAWC and DWSBC samples were dried at 80 °C for further testing.

All chemical reagents used were of high purity grades from Fisher Scientific (Suwanee, Georgia). Stock solutions of 1000 ppm lead (II) nitrate, cadmium (II) nitrate tetrahydrate, nickel (II) nitrate hexahydrate, and copper (II) nitrate trihydrate were prepared by dissolving appropriate amount of chemicals in DI water.

2.2. Biochar properties

Carbon, hydrogen, and nitrogen contents of the biochars were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of resulting CO₂, H₂ and NO₂ gases. Major inorganic elemental constituents of the biochars were determined using the EPA 200.7 method of acid digestion followed by analysis by inductively coupled plasma with atomic emission spectroscopy (ICP–AES).

The pH of the biochar samples was measured by combining biochar with DI water in a mass ratio of 1:20. The solution was then hand stirred and allowed to stand for 5 min before measurement with a pH meter (Fisher Scientific Accumet Basic AB15).

Biochar surface potential was determined by measuring the zeta potential (ζ) of colloidal biochar suspensions obtained through sonication according to the procedure of Johnson et al. (1996). Charge mobility of each biochar suspension was determined using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY) and Smoluchowski's formula was used to convert the electric mobility into zeta potential.

Specific surface areas of the biochars were determined on a Quantachrome Autosorb1 surface area analyzer. N₂ adsorption isotherms measured at 77 K and interpreted using Brunauer, Emmet, and Teller (BET) theory yielded mesoporous surface area (pores >1.5 nm) and CO₂ adsorption isotherms at 273 K were interpreted using Monte Carlo simulations of the non-local density functional theory and yielded microporous surface area (pores <1.5 nm).

2.3. Sorption of heavy metals

An initial evaluation of the sorption ability of DAWC and DWSBC was performed using a mixed heavy metal solution containing Pb²⁺, Cu²⁺, Cd²⁺, and Ni²⁺. The concentration of each metal in the solution was adjusted to be 0.1 mmol/L. About 0.1 g of the test biochar was added into 68 mL digestion vessels (Environmental Express) and mixed with 50 mL of the heavy metal solution at room temperature (22 ± 0.5 °C). After shaking in a reciprocating shaker for 24 h, the vessels were withdrawn and filtered immediately through 0.1 μm pore size nylon membranes (GE cellulose nylon membranes). The Ni, Cu, Cd, and Pb concentrations in the filtrates were determined using ICP–AES (Perkin Elmer Plasma 3200RL). The sorbed heavy metal concentrations were calculated based on the difference between the initial and final metal concentrations in the supernatant. Vessels without the sorbent (biochar) or the sorbates (metals) were included as experimental controls.

2.4. Sorption of lead

Sorption kinetics of lead on DAWC and DWSBC were determined by mixing 50 mL of 200 ppm Pb²⁺ solution with 0.1 g of each sorbent in the digestion vessels at room temperature, and shaking

over the course of a 24 h period. Sample solutions with their corresponding blank controls were withdrawn at specific time intervals to examine sorption kinetics. The mixtures were immediately filtered and the filtrates were stored for further analysis.

Sorption isotherms were obtained by adding 0.1 g of each biochar to 50 mL of Pb^{2+} solutions with varying concentrations (5–600 ppm) in each vessel and shaken for 24 h. The solutions were then filtered and pH values of the filtrates were recorded. Both the filtrates and lead-laden biochars were collected for further analysis. The lead-laden biochars were washed with DI water several times and oven dried before analysis.

For all lead sorption experiments, blank experiments without the sorbent or sorbate were included as experimental controls, which indicated that no addition or loss of lead in the experiments. Lead concentrations in the filtrates were determined with the ICP–AES. Lead concentrations on the biochars were calculated based on the differences between initial and final aqueous solutions. All the sorption experiments (mixed heavy metals and lead) were performed in duplicate and the average values are reported here. Additional analyses were conducted whenever two measurements showed a difference larger than 5%.

2.5. Post-sorption characterizations

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was used to examine surface morphology and elemental composition of both pre-sorption and post-sorption (lead-laden) DAWC and DWSBC. The tested samples were mounted on carbon stubs using carbon conductive paint. The samples were placed under a JEOL JSM-6330F field-emission SEM equipped with an Oxford EDS. During operation, the accelerating voltage of the instrument was maintained at 10 kV and varying magnifications were used.

X-ray diffraction (XRD) analysis was conducted on both pre- and post-sorption biochar samples to identify possible crystalline structures. A computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator was used.

Fourier transform infra-red (FTIR) analysis was used to characterize functional groups present on the biochar surfaces. The biochar samples were directly mounted on the diamond base of a Nicolet 6700FTIR (Thermo Scientific) and a transparent polyethylene film was used to cover the samples for the FTIR analysis.

3. Results and discussion

3.1. Biochar properties

CHN analysis revealed that DAWC contained much more carbon than DWSBC (Table 1), probably because the feedstocks were from different types of anaerobic digesters. DAWC also had higher nitrogen content but slightly lower hydrogen content than DWSBC (Table 1). Elemental analysis showed that the two biochars had various amounts of inorganic elements and slightly higher amounts of Ca (5.5%) and K (2.3%) were presented in DWSBC and DAWC, respectively (Table 1). These inorganic elements originated

from nutrients rich in plant and animal residues, but the most predominant component in both biochars was carbon.

Previous studies have shown that physicochemical properties of biochars, such as pH, surface potential, and surface area, are important factors controlling their environmental applications (Inyang et al., 2010). Both DAWC and DWSBC were alkaline with a relatively high pH (Table 2), which is similar to the biochars obtained from anaerobically-digested sugarcane bagasse (Inyang et al., 2010). This suggests that the two biochars could be good conditioners for acid soils. The surface potential measurements indicated that DAWC had more negative surface charge than DWSBC which may be related to its higher surface area and pore volume (Table 2). All of these data seems to suggest a greater potential for DAWC to sorb abundant positively charged heavy metals.

3.2. Sorption of mixed heavy metals

Both DWSBC and DAWC showed good ability to remove the mixture of four heavy metals from aqueous phase (Fig. 1). The removal efficiency of the four metals by DWSBC was higher than 97%, indicating this biochar has a strong affinity for all the tested heavy metals. DAWC also showed high removal efficiency for Pb^{2+} (99%) and Cu^{2+} (98%), but relatively low removal efficiency for Cd^{2+} (57%) and Ni^{2+} (26%).

Previous studies indicated that the effectiveness of biochar in the immobilization of heavy metals strongly depends on the metal contaminant type (Uchimiya et al., 2010). The two biochars, however, showed different trends in removal rates (ability) for the four metals in the mixed solution, indicating both metal and biochar type played important roles. Although the differences were very small, the removal ability of DWSBC for the metals followed the order of $Cd > Ni > Pb > Cu$. In contrast, DAWC followed the order of $Pb > Cu > Cd > Ni$, which is consistent with the removal efficiency trend of biochars converted from poultry litter (Uchimiya et al., 2010).

According to Shi et al. (2009), high sorption of Pb^{2+} from solution on sorbents through surface electrostatic attraction could be attributed to its high electronegativity constant (2.33), which results in a high tendency for specific adsorption. However, the electronegativity constants of Ni^{2+} , Cu^{2+} , and Cd^{2+} are 1.93, 1.90, and 0.69, respectively, is not consistent with the heavy metal removal trends for either DAWC or DWSBC. Surface electrostatic interaction, therefore, might not be a dominant heavy metal removal mechanism for these biochars. Other mechanisms, such as precipitation and surface complexation, should also be considered (Cao et al., 2009; Inyang et al., 2011; Uchimiya et al., 2011). In the following sections, sorption of lead on DAWC and DWSBC was examined in greater detail to improve current mechanistic understanding of heavy metal removal by biochars from anaerobically digested biomass.

3.3. Lead sorption kinetics

DAWC and DWSBC sorbents showed similar lead sorption kinetics and reached apparent sorption equilibrium after about 24 h (Fig. 2). There was an initial rapid increase in lead removal followed by a slow down as sorption approached equilibrium.

Table 1

Elemental composition (% mass based) of biochars used in this study.

	C	H	N	P	K	Ca	Mg	Zn	Mn	Cu	Fe	Al	Pb
DAWC	65.42	0.68	3.63	0.36	2.33	1.89	0.55	0.02	0.02	– ^a	0.09	0.16	– ^a
DWSBC	20.15	1.07	0.43	0.54	1.51	0.64	5.50	1.08	0.04	0.01	1.54	1.30	– ^a

^a <0.01.

Table 2
Basic physiochemical properties of biochars used in this study.

	pH	CO ₂ surface area (m ² /g)	N ₂ surface area (m ² /g)	Pore volume (cc/g)	Zeta potential (mv)
DAWC	10.0	555.2	161.2	0.147	-29.18
DWSBC	9.0	128.5	48.6	0.034	-15.85

Pseudo-first-order, pseudo-second-order, and Elovich models were used to simulate the sorption kinetics data collected. The governing equations can be written as (Gerente et al., 2007; Yao et al., 2011b):

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{first-order}, \quad (1.1)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \quad \text{second-order}, \quad (1.2)$$

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad \text{Elovich}, \quad (1.3)$$

where q_t (mmol kg⁻¹) and q_e (mmol kg⁻¹) are the amounts of lead sorbed at time t and at equilibrium, respectively; k_1 (h⁻¹) and k_2 (kg mmol⁻¹ h⁻¹) are the first-order and second order apparent sorption rate constants, respectively; and α (mmol kg⁻¹ h⁻¹) and β (kg mmol⁻¹) are the initial Elovich sorption and desorption rate constant at time t , respectively. The first order, second order and Elovich models reproduced the sorption data closely for both biochars with coefficients of correlation all above 0.94 (Fig. 2). While the Elovich model had the best fit for DWSBC with an R^2 of 0.97, the second-order model was a better fit for DAWC with an R^2 of 0.95 (Table 3). Fittings of the three models to DWSBCPb sorption were slightly better than that of DAWC (Table 3), suggesting that sorption of lead on DAWC was more energetically heterogeneous. Although those models assume different mechanisms (Gerente et al., 2007), comparisons of the fittings did not help reveal the governing mechanisms of lead sorption on the two biochars because there were only slight differences among the simulated results (Fig. 2).

A plot of the pre-equilibrium sorbed Pb amounts against the square root of contact times for both biochar sorbents showed a strong linear dependency with an R^2 of 0.90 and 0.98 for DAWC and DWSBC, respectively (Fig. S1, Supporting information). This strong linear relationship, along with the slow sorption rate prior to reaching equilibrium for both sorbents, suggests diffusion-controlled removal of Pb²⁺ by the two biochars. This diffusion rate could be controlled by each biochar's intrapore dimensions, either for a surface adsorption or precipitation removal mechanism. The

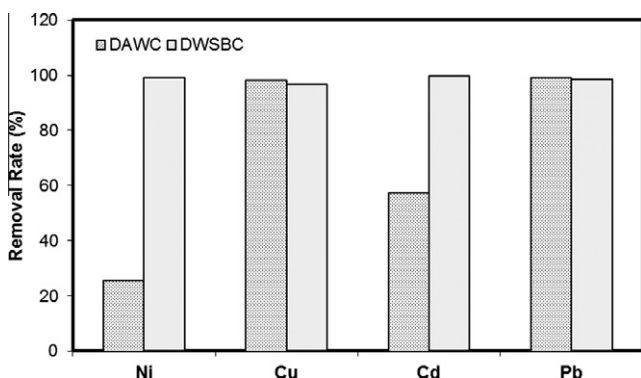


Fig. 1. Removal of heavy metals from aqueous solution by the two biochars converted from anaerobically digested biomass.

more rapid approach to Pb sorption equilibrium by DAWC and its larger pore volume is consistent with this interpretation.

3.4. Lead sorption isotherms

The lead sorption isotherms on the two biochars showed a very rapid increase in solid-phase concentrations, removing close to all the lead at low equilibrium solution concentrations (Fig. 3). Above lead equilibrium solution concentrations of 0.5 mmol/L there was very little additional lead removal. Similar phenomena was observed for lead removal by biochars made from anaerobically digested bagasses, in which precipitation was shown to be the dominant sorption mechanism (Inyang et al., 2011). Previous studies have demonstrated that slow release of negatively charged ions, such as carbonate and phosphate, from biochars can precipitate heavy metal ions, particularly lead (Cao et al., 2009; Inyang et al., 2011). Because Pb²⁺ has strong chemical affinity with those ions, biochar sorbents may completely remove lead from aqueous solutions when its initial concentration is low. When the initial lead concentration is high, however, Pb²⁺ can consume all the available anions in solution and thus the isotherms will reach a plateau.

Comparisons between solution pH before (i.e., before adding biochar) and after sorption for different initial lead concentrations in the isotherm experiment (Fig. 4) support the surface precipitation mechanism of lead removal by the two biochars. When the

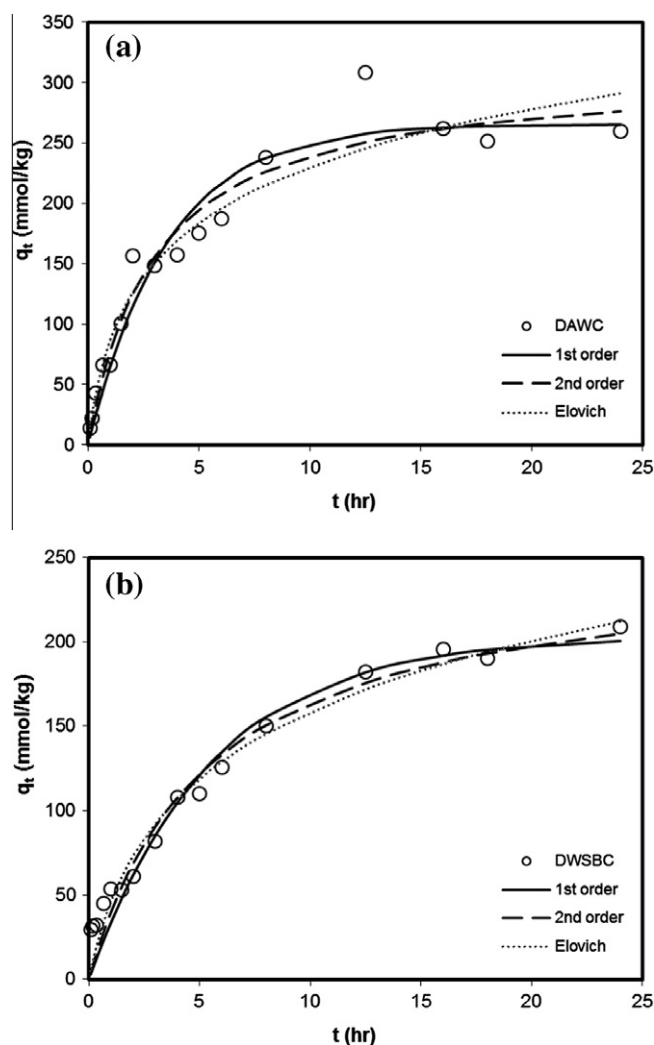


Fig. 2. Kinetics of lead sorption by DAWC (a) and DWSBC (b).

Table 3

Best-fit model parameters of lead sorption on DAWC and DWSBC.

		Parameter 1	Parameter 2	Parameter 3	Parameter 4	R ²
DAWC	First-order	$k_1 = 0.280$	$q_e = 266$	–	–	0.943
	Second-order	$k_2 = 0.00100$	$q_e = 311$	–	–	0.950
	Elovich	$\alpha = 174$	$\beta = 0.0140$	–	–	0.943
	Langmuir	$K = 928$	$S_{\max} = 248$	–	–	0.0594
	Freundlich	$K_f = 248$	$n = 0.0619$	–	–	0.416
	Double Langmuir	$K_1 = 1120$	$S_{\max1} = 234$	$K_2 = 0.00233$	$S_{\max2} = 1.90$	0.122
DWSBC	First-order	$k_1 = 0.181$	$q_e = 203$	–	–	0.951
	Second-order	$k_2 = 0.000760$	$q_e = 250$	–	–	0.960
	Elovich	$\alpha = 67.7$	$\beta = 0.0150$	–	–	0.968
	Langmuir	$K = 266$	$S_{\max} = 197$	–	–	0.930
	Freundlich	$K_f = 189$	$n = 0.140$	–	–	0.808
	Double Langmuir	$K_1 = 351$	$S_{\max1} = 172$	$K_2 = 2.87$	$S_{\max2} = 43.9$	0.944

initial lead concentrations were low, solution pH increased from about 5 to about 10 after the lead was removed, which is consistent with the alkali nature of the biochars (Table 2). This was because initial lead concentration of lead was not high enough to consume all the carbonate and/or phosphate ions (alkali) released by the biochars. Because both carbonate and phosphate have strong buffer capacities, their release from biochars could increase solution pH even if lead precipitation on biochar surfaces might release some H⁺ under certain conditions. When the amount of lead in the solution was greater, the solution pH stayed unchanged or became lower because of the full consumption of these alkali ions (Fig. 4). The fact that final pH reached the minimum at the same solvent concentration at which isotherm curve reached plateau further confirmed the importance of the surface precipitation mechanism (Figs. 3 and 4).

The Langmuir (L), Freundlich (F) and Langmuir–Langmuir (LL) models were used to simulate the sorption isotherms of lead on the two biochars. These governing equations can be written as (Cao et al., 2009; Gerente et al., 2007):

$$q_e = \frac{KS_{\max}C_e}{1 + KC_e} \quad \text{Langmuir,} \quad (2.1)$$

$$q_e = K_f C_e^n \quad \text{Freundlich,} \quad (2.2)$$

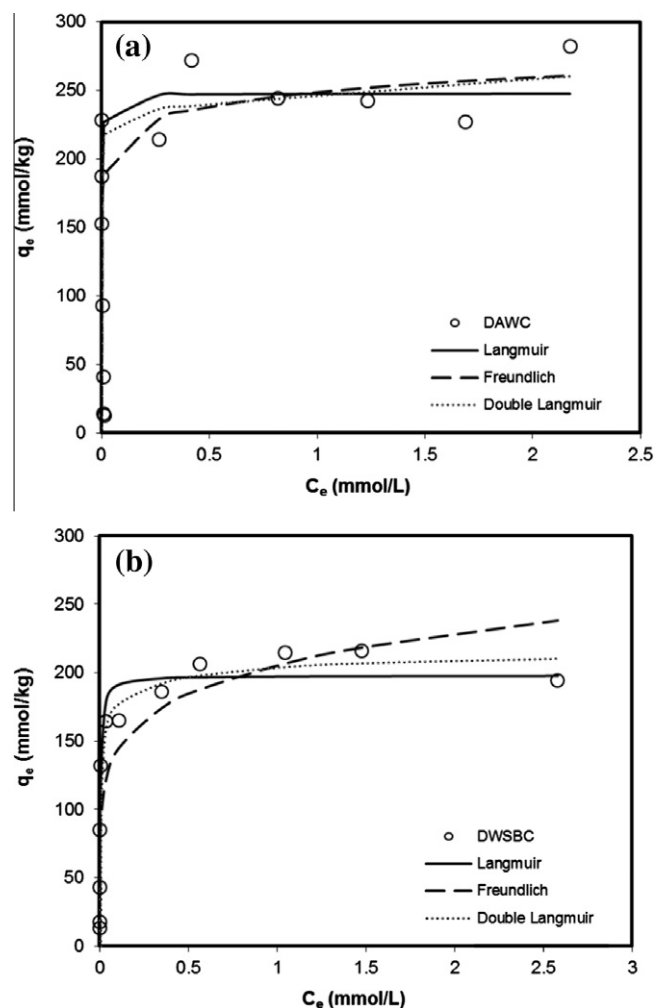
$$q_e = \frac{K_1 S_{\max1} C_e}{1 + K_1 C_e} + \frac{K_2 S_{\max2} C_e}{1 + K_2 C_e} \quad \text{Langmuir – Langmuir,} \quad (2.3)$$

where S_{\max} (mmol kg⁻¹) is the maximum amount of Pb sorbed; K (L mmol⁻¹) and K_f (mmol⁽¹⁻ⁿ⁾ Lⁿ kg⁻¹) are the Langmuir adsorption constant related to the interaction bonding energies and the Freundlich equilibrium constant, respectively; C (mmol L⁻¹) is the equilibrium solution concentration of the sorbate; and n is the Freundlich linearity constant.

The models fit the experimental sorption data of DWSBC well, but failed to describe that of DAWC (Fig. 3). The best-fit model for DAWC isotherm was the Freundlich model, but the r^2 was only 0.416 (Table 3). The failure of these models was probably due to the higher heterogeneity of DAWC, which was converted from digested dairy waste, a highly heterogeneous feedstock, a mixture of components with different compositions.

For lead sorption on DWSBC, the two Langmuir-based models (i.e., L and LL models) simulated the data better ($r^2 > 0.930$) than the Freundlich model ($r^2 = 0.808$) (Table 3). Although Langmuir-based models are developed for weak physical sorption, L or LL model can be used to describe the sorption of metals on biochars through precipitation (Cao et al., 2009; Inyang et al., 2011). Inyang et al. (2011) indicated that precipitation of lead on biochar derived from anaerobically digested bagasses could be modeled with the L model with a large bonding constant ($K = 189 \text{ L mmol}^{-1}$). The Langmuir sorption constant for the

DWSBC tested in this study was also very high ($K = 266 \text{ L mmol}^{-1}$), confirming a strong affinity of lead. The Langmuir sorption capacity of lead sorption on the DWSBC was around 197 mmol kg⁻¹, which is comparable to that of commercial activated carbons (101–395 mmol kg⁻¹) and other biochar sorbents (11–680 mmol kg⁻¹) (Beesley and Marmiroli, 2011; Cao et al., 2009; Inyang et al., 2011; Liu and Zhang, 2009; Mohan et al., 2007; Uchimiya et al., 2010). Although the Langmuir model could not be used, a rough estimation of the lead sorption capacity of DAWC directly from the plateau of the isotherm indicated that it should be even higher (>200 L mmol⁻¹) than that of DWSBC (Fig. 3). This confirms that

**Fig. 3.** Isotherms of lead sorption by DAWC (a) and DWSBC (b).

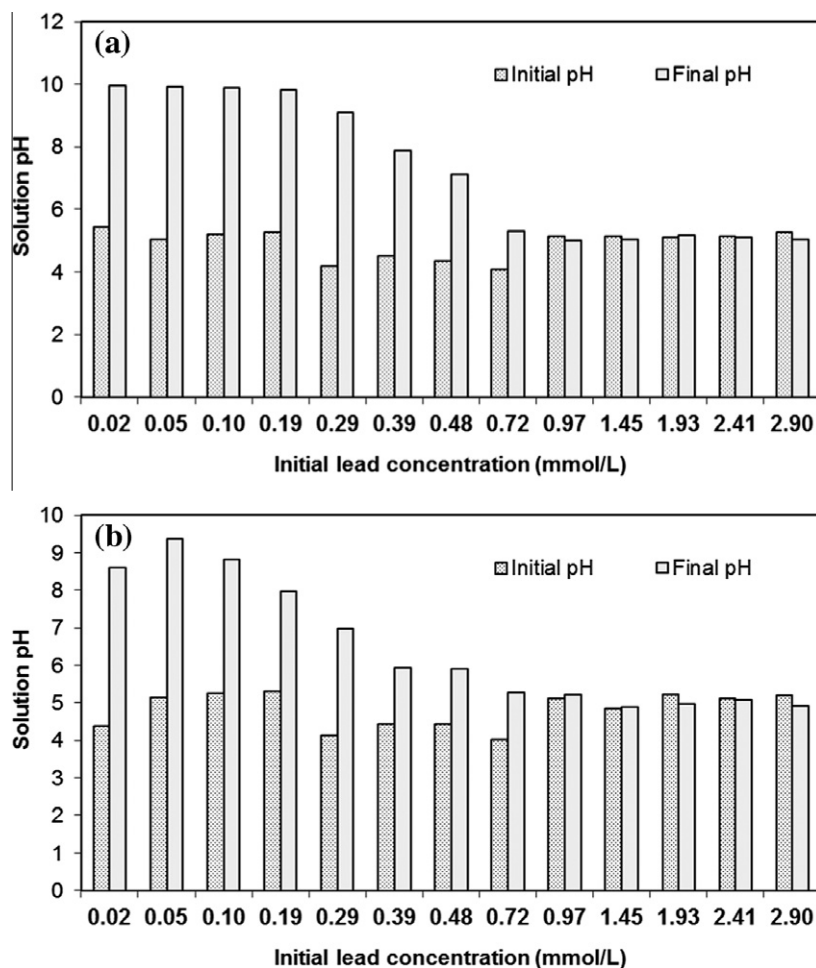


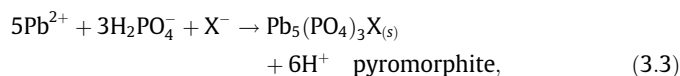
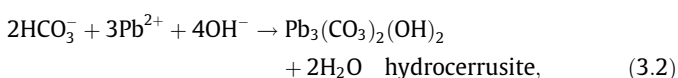
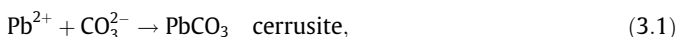
Fig. 4. Changes in solution pH during lead sorption by DAWC (a) and DWSBC (b).

biochars converted from anaerobically digested biomass can be used as effective sorbents to remove lead from aqueous solutions.

3.5. Post-sorption characteristics and sorption mechanisms

SEM image analysis of the post-sorption (Pb-laden) DAWC and DWSBC revealed the presences of many hexagonal and prismatic crystalline structures on their surfaces (Fig. S2). The corresponding EDS spectra of the SEM image focusing area showed very high peaks of lead element, which demonstrated the presence of lead on surfaces of the post-sorption biochars. This strongly suggests the precipitation of lead mineral(s) from aqueous solution onto the biochar surfaces, because both the elemental analysis (Table 1) and the SEM-EDS analysis of pre-sorption biochars (Fig. S3, Supporting information) showed no lead or crystals of this type in the original biochars.

Compared to pre-sorption biochars, XRD spectra of post-sorption biochars showed several new peaks at specific d -values associated with lead minerals, further supporting the precipitation mechanism of lead removal by the two biochars (Fig. S4). As discussed above, carbonate and/or phosphate released from the biochars can react with lead in aqueous solution to form stable minerals on biochar surfaces through following reactions:



where X can be either F^- , Cl^- , Br^- , or OH^- .

Three types of lead minerals, cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), and pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), were identified in the post-sorption DAWC, indicating lead removal by DAWC could be controlled by all the three precipitation mechanisms (i.e., Eqs. (3.1), (3.2), (3.3)). This was probably because DAWC was converted from a complicated feedstock (digested dairy waste) and thus could release both carbonate and phosphate to react with heavy metals in solution. Because of this heterogeneity, the ability of biochar from digested manure to sorb aqueous heavy metals might tend to fluctuate among samples, which may explain why the three sorption models failed to describe the isotherms of lead sorption on DAWC. In spite of the fluctuation, biochar converted from anaerobically digested dairy waste still has an unexceptionable ability to remove heavy metals from water (Figs. 1–3).

Only one lead precipitate (hydrocerussite), however, was found on the post-sorption DWSBC. Similarly, hydrocerussite was also found in a recent study of lead sorption through precipitation on biochar converted from anaerobically digested sugarcane bagasses (Inyang et al., 2011). XRD spectra of the pre-sorption biochars indicated the existence of calcite (CaCO_3) in both DAWC and DWSBC, which could be a source of carbonate release into the solution. Carbonate minerals such as calcite have also been found in other biochars converted from other anaerobically digested biomass (Yao et al., 2011a). Anaerobic digestion may concentrate

exchangeable cations, such as Ca^{2+} , K^+ , Na^+ , into residue materials (Gu and Wong, 2004; Hanay et al., 2008). Those cations may react with the carbon material in the feedstock to form carbonate minerals during slow pyrolysis (Inyang et al., 2010).

Surface organic functional groups of the two biochars converted from anaerobically digested biomass were characterized using FTIR spectroscopy (Fig. S5, Supporting information). Functional group distributions of DAWC and DWSBC were similar to biochars made from other types of digested biomass (Inyang et al., 2010; Yao et al., 2011a). Although the two biochars had relatively high surface area (Table 1), comparisons of pre- and post-sorption FTIR spectra for both DAWC and DWSBC showed high similarity, which provides no evidence of lead adsorption on biochar through interacting with the surface functional groups.

4. Conclusions

This study indicated that biochars produced from anaerobically digested biomass (dairy waste and sugar beets) can effectively remove heavy metals from aqueous solutions. The lead sorption capacity of the two biochars used in this study is comparable to that of commercial activated carbons. Thus, biochar converted from anaerobically digested biomass can be used as an alternative sorbent for activated carbon or other water purifiers to treat heavy metals in wastewater. High metal removal efficiency of biochars from digested feedstock suggests that anaerobic digestion could be used as a means of 'biological activation' to make high quality biochar-based sorbents.

Acknowledgements

This research was partially supported by the USDA T-STAR Program and the NSF through Grant CBET-1054405. The authors also thank the anonymous reviewers for their invaluable insight and helpful suggestions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2012.01.072](https://doi.org/10.1016/j.biortech.2012.01.072).

References

Akbal, F., Camci, S., 2011. Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation. *Desalination* 269 (1–3), 214–222.

Beesley, L., Marmiroli, M., 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environ. Pollut.* 159 (2), 474–480.

Boudrahem, F., Soualah, A., Aissani-Benissad, F., 2011. Pb(II) and Cd(II) removal from aqueous solutions using activated carbon developed from coffee residue activated with phosphoric acid and zinc chloride. *J. Chem. Eng. Data* 56 (5), 1946–1955.

Brooks, L., Parravicini, V., Svardal, K., Kroiss, H., Prendl, L., 2008. Biogas from sugar beet press pulp as substitute of fossil fuel in sugar beet factories. *Water Sci. Technol.* 58 (7), 1497–1504.

Cao, X.D., Ma, L., Gao, B., Harris, W., 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* 43 (9), 3285–3291.

Das, K.C., Garcia-Perez, M., Bibens, B., Melear, N., 2008. Slow pyrolysis of poultry litter and pine woody biomass: impact of chars and bio-oils on microbial growth. *J. Environ. Sci. Health, Part A* 43 (7), 714–724.

Demirbas, A., 2009. Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. *J. Hazard. Mater.* 167 (1–3), 1–9.

Demirbas, A., 2008. Heavy metal adsorption onto agro-based waste materials: a review. *J. Hazard. Mater.* 157 (2–3), 220–229.

Fang, C., Boe, K., Angelidaki, I., 2011. Anaerobic co-digestion of by-products from sugar production with cow manure. *Water Res.* 45 (11), 3473–3480.

Gerente, C., Lee, V.K.C., Le Cloirec, P., McKay, G., 2007. Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review. *Crit. Rev. Env. Sci. Technol.* 37 (1), 41–127.

Gu, X.Y., Wong, J.W.C., 2004. Identification of inhibitory substances affecting bioleaching of heavy metals from anaerobically digested sewage sludge. *Environ. Sci. Technol.* 38 (10), 2934–2939.

Hanay, O., Hasar, H., Kocer, N.N., Aslan, S., 2008. Evaluation for agricultural usage with speciation of heavy metals in a municipal sewage sludge. *B. Environ. Contam. Toxicol.* 81 (1), 42–46.

Hooda, P.S., Edwards, A.C., Anderson, H.A., Miller, A., 2000. A review of water quality concerns in livestock farming areas. *Sci. Total Environ.* 250 (1–3), 143–167.

Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A.R., Cao, X., 2011. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. *Sep. Sci. Technol.* 46 (12), 1950–1956.

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W., Zimmerman, A.R., 2010. Biochar from anaerobically digested sugarcane bagasse. *Bioresour. Technol.* 101 (22), 8868–8872.

Johnson, P.R., Sun, N., Elimelech, M., 1996. Colloid transport in geochemically heterogeneous porous media: modeling and measurements. *Environ. Sci. Technol.* 30 (11), 3284–3293.

Lehmann, J., 2007. A handful of carbon. *Nature* 447 (7141), 143–144.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. *Mitig. Adapt. Strat. Global. Change.* 11, 403–427.

Liu, Z., Zhang, F.-S., 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *J. Hazard. Mater.* 167 (1–3), 933–939.

Malamis, S., Katsou, E., Haralambous, K.J., 2011. Study of Ni(II), Cu(II), Pb(II), and Zn(II) removal using sludge and minerals followed by MF/UF. *Water Air Soil Pollut.* 218 (1–4), 81–92.

Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* 310 (1), 57–73.

Shi, T., Jia, S., Chen, Y., Wen, Y., Du, C., Guo, H., Wang, Z., 2009. Adsorption of Pb(II), Cr(III), Cu(II), Cd(II) and Ni(II) onto a vanadium mine tailing from aqueous solution. *J. Hazard. Mater.* 169 (1–3), 838–846.

Sud, D., Mahajan, G., Kaur, M.P., 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresour. Technol.* 99 (14), 6017–6027.

Uchimiyama, M., Chang, S., Klasson, K.T., 2011. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *J. Hazard. Mater.* 190 (1–3), 432–441.

Uchimiyama, M., Lima, I.M., Klasson, K.T., Chang, S.C., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (Cu-II, Cd-II, Ni-II, and Pb-II) by broiler litter-derived biochars in water and soil. *J. Agric. Food Chem.* 58 (9), 5538–5544.

Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* 327 (1–2), 235–246.

Wang, L., Li, Y., Chen, P., Min, M., Chen, Y., Zhu, J., Ruan, R.R., 2010. Anaerobic digested dairy manure as a nutrient supplement for cultivation of oil-rich green microalgae *Chlorella* sp.. *Bioresour. Technol.* 101 (8), 2623–2628.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011a. Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. *Bioresour. Technol.* 102 (10), 6273–6278.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011b. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. *J. Hazard. Mater.* 190 (1–3), 501–507.