Sorption of lead and methylene blue onto hickory biochars from different pyrolysis temperatures: Importance of physicochemical properties

Zhuhong Ding^{a, b}, Yongshang Wan^c, Xin Hu^{d, b}, Shengsen Wang^b, Andrew R. Zimmerman^e, Bin Gao^{b *},

^a *School of Environment, Nanjing University of Technology, 30 Puzhu Southern Road, Nanjing 211816, P.R. China*

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

^c *South Florida Water Management District, West Palm Beach, FL 33406, United States*

^d *State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering and Center of Material Analysis, 20 Hankou Road, Nanjing University, Nanjing 210093, P.R. China*

^e *Department of Geological Sciences, University of Florida, Gainesville, FL 32611*

* Corresponding author. Tel.: (352) 392-1864x285; fax: (352) 392-4092. Email address: bg55@ufl.edu (B. Gao).

Abstract

Hickory biochars were obtained through slow pyrolysis under 350 °C, 450 °C, and 600 °C. Multiple characterization techniques were used to characterize the biochars and showed pyrolysis temperature affected their O/C ratios, surface areas, cation-exchange capacities, zeta potential, surface acidic groups. As the result, the biochars showed different adsorption ability to Pb(II) and methylene blue in aqueous solutions, which was due to the important roles of the physicochemical properties of the biochars in controlling the sorption processes. This work provided a comprehensive evaluation of biochars, and thus expanded on previous research on effects of pyrolysis temperature on biochar properties.

Keywords: Biochar; heavy metal; organic contaminant; dye; sorption

1. Introduction

Biochar, a product of incomplete biomass combustion in an oxygen-limited environment, has received increasing attention in the scientific community for its many potential applications and environmental benefits such as carbon sequestration, soil fertility improvement, remediation of contaminated soils, and treatment of drinking water and industrial wastewater [1-4]. Understanding of the chemical and physical characteristics of biochar and how they are related to biochar production conditions is crucial to the design of biochar production technologies, which can be employed to optimize the needed biochar characterization for target uses. For example, using biochars for carbon sequestration comes mainly with the realization of the similarity between the relatively enriched carbon (C) in biochar and organic C in soils and sediments while potential environmental applications of biochar as a sorbent for water and wastewater treatment is based on an understanding of the surface property of biochars and their strong sorptive affinity to both organic and inorganic contaminants [4-8]. Biochars have been suggested as low-cost adsorbents for the removal of aqueous metal ions (e.g. Pb^{2+} , Cd^{2+} , Cu^{2+} , and As^{2+}), dyes, phenolics, pesticides, and polynuclear aromatics from contaminated soils and waters [2, 3, 5].

There are a great number of studies in the literature, focusing on biochar characterization using various analytical techniques and sorptive properties with respect to different types of biochar. Previously published data indicate that the adsorption capacity of biochars ranges from a few grams to hundreds of grams per kilogram of biochars, depending on the types of feedstock such as wood materials, crop residues (straw, corn stover, nutshells, coconut shells, and rice husks), bagasse from sugar cane, dairy manure, and sewage sludge [2, 3, 6, 7]. A number of recent studies, have examined the adsorption isotherms, adsorption kinetics and adsorption thermodynamics of pollutants onto biochars [2, 3, 6-8], and revealed that the sorption

1 mechanisms, can be both physisorption and chemisorption. Biochar characterization with some
2
3
4 of the fundamental physicochemical properties such as surface elemental composition and
5
6
7 species, surface functional groups, specific surface area (SE) and cation-exchange capacity (CEC)
8
9
10 has greatly improved our understanding the nature and behavior biochar, especially with respect
11
12
13 to its sorptive affinity to organic and inorganic contaminants [2, 3]. It is generally concluded that
14
15
16 surface properties of biochar are important for the understanding of chemical adsorption and ion
17
18
19 exchange adsorption of pollutants [2, 3].
20

21 The technological factors such as pyrolysis temperature can be controlled to achieve the
22
23 desired sorption capacities in preparation of biochars [9, 10]. Since biochars are obtained through
24
25
26 pyrolysis of feedstocks at a wide range of temperatures [11], the peak pyrolysis temperature is a
27
28
29 key factor determining the physicochemical properties of biochars [2, 3]. For example, Kloss et
30
31
32 al. indicate that pyrolysis temperatures of 400, 460, and 525 °C resulted in the different
33
34
35 physicochemical properties of biochar derived from wheat straw, poplar wood, and spruce wood
36
37
38 [12]. Wang et al. concluded that increasing pyrolysis temperature from 500 to 700 °C resulted in
39
40
41 decrease in biochar yield, total acidic functional groups, cation exchange capacity, and N content
42
43
44 and increase in BET surface area, ash content, pH, and total Ca and P contents [10].
45

46 Although several studies have examined the effects of temperature on the physicochemical
47
48 properties of biochars derived from agricultural and forestry residuals [12-14]; there are still
49
50
51 needs of compressive investigations that examine both physical and chemical properties of
52
53
54 biochars in details and then link them with their sorption ability to contaminants in aqueous
55
56
57 solution. Furthermore, most of the previous studies on the effects of biochar surface properties
58
59
60 on their sorption performance are mainly focused on inorganic contaminants, such as heavy
61
62
63 metals [15-17], it is thus very important to determine the relationships between biochars'
64
65

physicochemical properties and their sorptive performance for both inorganic and organic contaminants. To satisfy these needs, a range of physical and chemical properties of biochars derived from hickory at different pyrolysis temperature were investigated in details in this work. The sorption of organic (methylene blue) and inorganic (lead) contaminants on the biochars were examined in details to expand on previous research on the relationship between physicochemical properties and sorption ability. Hickory is a type of deciduous tree distributed throughout the world. Hickory wood chips are used for charcoal grill and gas grill, as well as for smoking meats, poultry, vegetables, and fish. In this work, biochar was produced from hickory chips at a range of peak pyrolysis temperatures (350°C, 450°C and 600°C). We employed a number of analytical techniques include scanning electron microscope (SEM), thermal analysis, Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), zeta potential analyzer, Boehm titration, and batch sorption experiments to characterizing surface properties of the obtained biochars and their sorption of Pb(II) and methylene blue. The objectives of this study were (1) to reveal the effects of the peak pyrolysis temperature on the physicochemical properties of biochar, and (2) to elucidate the linkage between the physicochemical properties of biochars and their sorption abilities.

2. Experimental

2.1. Chemical reagents

Chemical reagents of analytic grade including methylene blue (MB), NaOH, HNO₃ and Pb(NO₃)₂ were purchased from Fisher Scientific. All solutions were prepared using deionized (DI) water (18 MΩ*cm).

2.2. Preparation of biochars

Dried commercial hickory wood chips were ground in a knife mill (Model No. 4, Arthur H. Thomas Company, Philadelphia, PA) to achieve 0.5-1 mm hickory powders. The hickory powders were placed inside tubular quartz reactors (50 g in 6 cm diameter $\times$ 28 cm length cylinders) and then inserted into a bench-top furnace (Barnstead 1500 M) purged with N₂ gas (10 psi). The pyrolysis furnace temperature was increased at a rate of 20°C/min and then held at 350°C, 450°C, and 600°C for 5h, 3h and 2 h, respectively, with flowing N₂ gas. The biochar samples produced were rinsed with tap water and DI water, and then oven dried at 80°C. The obtained biochars were placed in sealed containers and notated as B350, B450 and B600, respectively.

2.3. Characterization of biochars

Contents of C, H and N in the biochars were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion of 50 mg samples followed by thermal conductivity detection of the resulting gases. Ashing of 0.2 g samples were carried out at 550°C and then the residue was dissolved by using 5% HNO₃. Major mineral elements in the resulting digestion solution were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2100 DV, USA). Specific surface areas were measured on a Quantachrome Autosorb-1 surface area analyzer using N₂ sorption and calculated according to the BET theory. Zeta potential was analyzed following Mukherjee et al. [8] on a Zeta Plus Zeta Potential Analyzer (Brookhaven Instruments Corporation). Cation exchange capacity (CEC) was analyzed using US EPA SW-846 method 9081. Acidic functional group distributions on biochars were determined using a modified Boehm titration method

[18-20]. Thermogravimetric TG and derivative (DTG) curves were obtained using a Mettler TGA/DSC thermogravimetric analyzer (TGA/DSC 1, STARe System, METTLER TOLEDO, USA) at a heating rate of 10 °C/min from 50°C to 900°C under a controlled atmosphere of N₂ (50 ml min⁻¹) with initial mass of 30 mg. The samples were treated by fixation and spray-gold and then a JEOL JSM-6330F field-emission scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) was used to examine and compare surface morphology and elemental composition of the biochars.

Biochar samples were grinded into fine powder as far as possible for the next instrumental characterization. Surface chemistry of biochars was studied by constructing FT-IR spectra recorded in the range 400–4000 cm⁻¹ with 2 cm⁻¹ resolution using a Nicolet 6700 FT-IR (Thermo Scientific) after samples were milled with potassium bromide (KBr) (the mass ratio of the sample to KBr was about 0.01) to form a very fine powder and then compressed into a thin pellet. Crystalline minerals in biochars were detected using XRD (Philips Electronic Instruments) after pressing the fine biochar powders into disks directly. Surface elemental composition and speciation of the fine biochar powder was studied using XPS with a PHI 5100 series ESCA spectrometer (Perkin Elmer).

2.4. Batch sorption experiments

Batch isotherm sorption experiments were carried out at a room temperature (22 ± 2 °C) following Ding et al. [2014]. Briefly, 0.1 g biochars was added to 50 mL Pb(II) or MB solutions of different initial concentrations ranging from 1 to 250 mg L⁻¹ in 100 mL polyethylene centrifuge tubes. Pb(II) and MB were selected in this study for representation of inorganic (heavy metal) and organic (dye) in wastewater. The initial concentrations of Pb(II) and MB were set as 2,

10, 25, 50, 100, and 250 mg L⁻¹ and 5, 10, 25, 50, 100, and 250 mg L⁻¹, respectively. The initial solution pH was set as 5.0±0.1 for Pb(II) and 6.5±0.1 for MB, adjusted using 0.01 M NaOH or HNO₃. The tubes were shaken in a mechanical shaker for 24 h at the room temperature to reach a dynamic equilibrium. The mixture was then centrifuged at 4000 rpm for 10 min. Pb(II) in the supernatant was determined using ICP–OES (Optima 2300, Perkin–Elmer SCIEX, USA) and MB was analyzed using a UV–Vis spectrophotometer Evolution-60 (Thermo Fisher Scientific, USA) at 664 nm. The amount of adsorbed Pb(II) or MB at adsorption equilibrium (q_e) per unit biochar mass were calculated using $q_e = [(C_0 - C_e) V]/m$, where C_0 and C_e are the initial and equilibrium concentrations of Pb(II) or MB (mg L⁻¹), respectively; V is the volume of the solution (L); and m is the mass of biochar sample (g).

3. Results and discussion

3.1. Elemental composition of bulk biochar samples

Pyrolysis of hickory wood at temperature of 350, 450 and 600 °C yielded about 35%, 33% and 21% biochars, consistent with previous reports about decreasing yield with increasing pyrolysis temperature [11]. The raw hickory feedstock contained about 48.2% C, 5.88% H, 0.22% N, 45.5% O, and less than 0.1% other main mineral elements (Ca, K, Mg, Al and Fe). In contrast, the elemental composition of biochars showed relative decrease in O and H and increase in C and mineral elements (N, Ca, K, Mg, Al and Fe) (Table 1). The relative loss of O and H and gain of C and minerals increased with increasing pyrolysis temperature. For example, B600 was the most carbonized biochar with the C mass percentage of 84.7%. Atomic ratios of H/C (0.650→0.259), O/C (0.243→0.100), and (O+N)/C (0.246→0.103) also decreased with increasing pyrolysis temperature, consistent with Keiluweit et al. who noted that when the peak

pyrolysis temperature increased from 100°C to 700°C, atomic ratios of H/C and O/C decreased from 1.59 to 0.21 and 0.63 to 0.05 for biochar derived from Ponderosa pine shavings and from 1.81 to 0.2 and 0.69 to 0.03 for biochar derived from tall fescue straw, respectively [21]. The lower O/C ratio (0.100) in B600 indicated that the biochar surface at high pyrolysis temperature was less hydrophilic [22]. The decreased polarity index [(O+N)/C] (0.246→0.103) reflected a decreased polar-group content with increasing pyrolysis temperature [22].

Table 1 Elemental composition (weight %), specific surface areas (SA, m²/g) and cation-exchange capacity (cmol/kg) of the pristine biochars.

	Fe	Ca	Mg	Al	K	Mn	C	N	H	O	SA	CEC
B350	0.01	0.63	0.17	0.02	0.23	0.03	71.6	0.25	3.88	23.2	<0.5	42.7
B450	0.02	0.77	0.22	0.03	0.27	0.03	77.6	0.27	3.52	17.3	1.60	41.9
B600	0.03	1.17	0.29	0.04	0.28	0.05	84.7	0.30	1.83	11.3	256	45.7

Contents of O were obtain by subtraction method

3.2. Morphology, phase and thermal stability of bulk biochar samples

The morphology of the obtained biochars was observed using SEM under 1000 times magnifications. The results did not show clear regularity or amorphous characteristics (Fig. 1). The different size and shape of biochar particles may be influenced by the sample preparation such as grinding and washing activities. The XRD pattern, however, indicated that carbon in the studied biochars existed mainly in the amorphous form. Compared to B350, quartz and calcite existed in B600 (Fig. 2), which may result from the higher hydrolysis temperature.

Fig. 1 – SEM images of (a) B350, (b) B450 and (c) B600.

Fig. 2 – XRD patterns of biochar B350 and B600.

Fig. 3 – TG/DTG curves of the pristine biochar samples

The TG/DTG curves exhibited obvious differences in thermal stability among biochar samples, varying with pyrolysis temperature (Fig. 3). As expected, B350, B450, and B600 showed strong weight loss above 350 °C, 450 °C, and 600 °C, respectively, with weight loss following the order of B350>B450>B600. The percentage of the final mass at 900°C to the initial mass was 25.7% for B350, 74.7% for B450, 88.9% for B600. Biochar mass loss at varying temperature may be associated with thermal destruction of different functional groups [23]. It was reported that the thermal decomposition of surface functional groups of activated carbon was generally 150–300°C for carboxylic groups, 300–500°C for acid anhydride and lactone and 500–800°C for phenolic hydroxyl and carbonyl groups and ethers [24]. While all biochars samples displayed an initial mass loss up to about 100 °C, attributable to water loss. For B350, B400, and B600, it can be well assumed that some functional groups were destroyed during pyrolysis with major thermochemical decompositions taking place at temperature >350°C, or specifically between 350 to 700 °C (the main peak in DTG curve, Fig. 3).

3.3. Surface properties of biochars influenced by pyrolysis temperature

The surface properties of biochar include the specific surface area, surface charges, surface elemental composition and functional groups. Specific surface areas of biochars increased from <0.5 m²/g for B350 to 256 m²/g for B600 (Table 1). In a literature review, Ahmad et al. reported that specific surface area of 101 biochars under peak pyrolysis temperature from 100 °C to 900 °C ranged from 0 to 490.8 m²/g with a median value of 15 m²/g [2]. They further concluded that an increase of the pyrolysis temperature resulted in a considerable increase of the surface area of

the biochars [2]. Our results were consistent with those reports.

Surface charges of biochar were characterized by using zeta potential and cation exchange capacity. Zeta potential values of the colloidal biochar samples at near neutral pH were -27.5 ± 2.0 mV for B350, -28.8 ± 4.8 mV for B450, and -32.4 ± 1.9 mV for B600, respectively. It seems that zeta potential values decreased with the increasing pyrolysis temperature from 350°C to 600°C. The zeta potential of oak-biochar for a given pH was significantly more electronegative with the increasing temperature from 250°C to 600°C [8], and this is consistent with our results. The CEC values of biochars in our study varied little with increasing peak pyrolysis temperature from 350°C to 600°C (Table 1), supporting the Lehmann's results [25], but contrary to the reports of Gaskin et al. [26] and Singh et al. [6]. The CEC of oak-, pine- and grass-biochar at the pyrolysis temperature of 250, 400 and 650°C, determined using K^+ exchange, ranged between 10.2 and 69.2 cmol kg^{-1} at near neutral pH [8]. The CEC of the straw-, spruce- and poplar- derived biochars ranged from 5.22 to 14.4 cmol kg^{-1} and decreased with increasing pyrolysis temperature from 400°C to 525°C; but their CEC was calculated as the sum of the Na, K, Mg, Ca, Al, Fe, and Mn after a sequential water- BaCl_2 extraction method [12]. Zeta potential and CEC confirmed the surface negative charges of biochars and the electronegative surface will facilitate the adsorption of cations.

Acidic functional groups (carboxyl, lactone and phenol) on biochars were determined by the Boehm titration method with different alkali solutions (NaOH , Na_2CO_3 , and NaHCO_3). Carboxylic groups were the dominant acidic groups for the studied biochars (Table 2). Carboxyl groups and total acidic groups of these biochars became lower as temperature increased [27], confirming the TG/DTG curves. The slight decrease of carboxylic groups as temperature increase suggests carboxylic groups may still remain at temperature of 600 °C, as opposed to the

report of Jaramillo et al [24] about destruction of carboxylic groups below temperature of 350°C.

Table 2 Acidic functional groups determined by Boehm titration (mmol g^{-1}) reported as the mean $\pm$ standard deviation.

	Carboxyl	Lactone	Phenol	Total acidic groups
B350	0.738 ± 0.038	0.113 ± 0.058	0.069 ± 0.038	0.921 ± 0.014
B450	0.721 ± 0.023	0.042 ± 0.032	0.029 ± 0.022	0.791 ± 0.019
B600	0.620 ± 0.015	0.029 ± 0.008	0.046 ± 0.013	0.696 ± 0.015

Fig. 4 – FT-IR spectra of the biochar samples

The changes of surface functional groups of the pristine biochar samples are verified by using FT-IR. B350 and B450 is rich in H and O contents (Table 1), which include OH groups (at $3000\text{--}3700\text{ cm}^{-1}$), CH_2 groups (at $2800\text{--}3690\text{ cm}^{-1}$), C=O for carboxyl groups (at $1700\text{--}1740\text{ cm}^{-1}$), and phenolic -OH (at 1270 cm^{-1}). The band C-O (1040 and 1058 cm^{-1}) represents O-containing function groups (Fig. 4). Peaks at 890 , 820 , and 760 cm^{-1} are assigned to the aromatic C-H banding (Fig. 4). The nonexistence of such peaks in B600 reflects the decrease of surface functional groups with increasing pyrolysis temperature, consistent with the change of contents of O, H and acidic functional groups in biochar samples (Fig. 4).

Surface analysis using XPS indicated that biochars were mainly composed of C, O and small amounts of inorganic matter (Fig. 5). The atomic percentage of surface C increased from 78.9% to 86.7% while surface O decreased from 20.5% to 12.0% with the increasing pyrolysis temperature from 350°C to 600°C (Fig. 5), consistent with the change of their total contents in Table 1. Surface O/C ratio was 0.260 and 0.138 for B350 and B600, respectively, indicating that the high pyrolysis temperature decreased the surface oxygen-containing functional groups. Bulk O/C ratios were 0.243 and 0.100 for B350 and B600, respectively. The fitting of high-resolution XPS spectra of C_{1s} region shows two main peaks in the peak binding energy of ~284.0 eV (68.00–75.28%) and ~286.5 eV (19.49–26.11%) for B350 and B600 (Fig. 6a). According to the XPS database of Thermo Scientific and the NIST X-ray Photoelectron Spectroscopy Database, the binding energy of C_{1s} at ~284.8 eV was assigned to C-C, at ~286 eV to organic C (C–O–C), and at ~288.5 eV to organic C (O–C=O). Therefore, the following species of surface C in biochars were identified as C–C and/or graphite C at 284.75–284.81 eV and C bound to O (C–O) at 286.11–286.58 eV. The amorphous C and/or graphite C were the dominant species of C in the pristine biochars. The increasing pyrolysis temperature from 350 °C to 600 °C increased C and/or graphite C and decreased C–O groups (Fig. 6a), consistent with the TG–DTG analyses and Boehm titration analyses. XPS spectra of O_{1s} region show a peak in the peak binding energy of ~533 eV for B350 and B600 (Fig. 6b). According to the XPS database of Thermo Scientific, the binding energy of O_{1s} at ~533 eV was assigned to organic C=O. Therefore, the binding energy peaks of O_{1s} in B350 and B600 at 532.85–533.11 eV were assigned to C=O (Fig. 6b), suggesting that species of O were not influenced by the pyrolysis temperature. Therefore, the increasing pyrolysis temperature changes the surface contents of C and O, but not their surface species.

Fig. 5 – The XPS spectra of the biochar samples.

Fig. 6 – XPS spectra of C_{1s} (a) and O_{1s} (b) in the biochars.

Fig. 7 – Sorption isotherms for Pb(II) and MB onto biochars.

3.4. Sorption of Pb(II) and methylene blue onto the pristine biochars

The equilibrium adsorption capacities of all the tested biochars increased with increasing equilibrium Pb(II) concentration in the range of 0 to 50 mg L⁻¹ and reached a plateau above that range (Fig. 7), suggesting the Type L (Langmuir) adsorption isotherm for Pb(II). There were great differences on the adsorption isotherm of Pb(II) and MB (Fig. 7). The equilibrium adsorption capacities increased quasilinearly with increasing equilibrium MB concentrations, suggesting the Type C (constant partition) adsorption isotherm for MB. Therefore, only the sorption isotherm data of Pb(II) were fitted by using Freundlich, Dubinin–Radushkevich (D-R) and Langmuir isotherm models and all coefficients of determination (R^2) were > 0.80 , suggesting the good fitting with those isotherm models. The Freundlich model is considered to be an empirical isotherm based on sorption on a heterogeneous surface of varied affinities [28]. The slope of $1/n$ indicates a normal Freundlich isotherm when $1/n < 1$ and cooperative adsorption when $1/n > 1$. $0.1 < 1/n < 0.3$ in the present study (Table 3), ranging between 0.1 and 0.5, indicates easy adsorption. The constants for Dubinin–Radushkevich isotherm model [28, 29], Q_m and K , at a constant temperature of 22 °C are listed in Table 3. The value of coefficient of determination indicates that the Dubinin–Radushkevich isotherm model fit well with the

equilibrium experimental data as compared with the other models considered (Table 3). The maximum adsorption capacities obtained using Dubinin–Radushkevich isotherm model is similar to them obtained using the Langmuir isotherm model (Table 3). The mean free energy of adsorption, E ($E = 1/\sqrt{2\beta}$), gives information about sorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the sorption process takes place chemically, while $E < 8$ kJ/mol suggests the physical sorption process [30]. The E (kJ/mol) value is obtained as 8.25–9.05 kJmol⁻¹ (Table 3), suggesting the chemical sorption process in the present study.

Table 3 Isotherm model parameters for Pb sorption onto biochars

	Langmuir isotherm			Freundlich isotherm			D-R isotherm			
	$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m}$			$\log q_e = \frac{1}{n} \log C_e + \log K_F$			$q_e = q_m \cdot \exp(-\beta(RT)^2 \cdot [\ln(1 + \frac{1}{C_e})]^2)$			
	q_m	K_L	R^2	K_F	$1/n$	R^2	q_m	β	E	R^2
B350	16.3	0.313	0.945	5216	0.239	0.906	16.9	6.54E-09	8.75	0.990
B450	15.1	0.281	0.970	5472	0.213	0.921	15.8	7.34E-09	8.25	0.997
B600	12.2	0.332	0.910	5257	0.171	0.855	12.3	6.10E-09	9.05	0.962

Where q_m : maximum adsorption capacity (mg g⁻¹); K_L : Langmuir constant (L mg⁻¹); R^2 : coefficient of determination; K_F : affinity coefficient related to the bonding energy (mg^(1-1/n) L^{1/n} g⁻¹); n : the heterogeneity factor which represents the bond distribution; β : the isotherm constant (mol/J)²; R : the gas constant (8.314 J/mol K); and T : absolute temperature (K).

Langmuir isotherm is used to describe the monomolecular layer and homogeneous adsorption [28, 29]. Therefore, Langmuir adsorption isotherm confirms the monolayer adsorption of Pb(II) onto the biochar surface (Fig. 7). The dimensionless separation factor, R_L , can be obtained based on the Langmuir constant (K_L) and the initial Pb(II) concentration (C_0) ($R_L = 1/(1 + K_L C_0)$). The value of R_L indicates the type of isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for the adsorption of Pb(II) onto the biochars for all studied initial Pb(II) concentrations were below 1, indicating that the sorption of Pb(II) onto the biochars was a favorable process. Langmuir adsorption

capacities for Pb (II) ranged from 12.2 to 16.3 mg g⁻¹ (Table 3), larger than most of the reported values in the literature such as 4.13/3.00 mg g⁻¹ for pine wood/bark char, 2.62/13.10 mg g⁻¹ for oak wood/bark char [31], 3.89-4.25 mg g⁻¹ for pine wood biochar, and 1.84-2.40 mg g⁻¹ for rice husk biochar [32]. While Ding et al. [33] reported that the maximum sorption capacity of Pb(II) decreased from 21 to 6.1mg g⁻¹ as pyrolysis temperature increased from 250 to 600°C for sugarcane bagasse derived biochar, our results did not show clear difference in sorption capacity between B350 and B450. However, the maximum sorption capacity of B600 was apparently lower than that of B350 or B450. The potential sorption mechanisms for Pb(II) reported in the literature included cation exchange, precipitation, and intraparticle diffusion [33]. The dominant mechanism, however, depended on factors such as the pyrolysis temperature and types of biochar. For example, with dairy-manure derived biochar, which contained high levels of soluble phosphate, Cao et al. demonstrated that precipitation of Pb(II) with phosphate was the predominant sorption mechanism, and this explained why biochar derived at 200° C sorbed more Pb(II) than biochar derived at 350° C [34].

The linkage between sorption behavior and the physicochemical properties of biochars can be complex and needs to be interpreted on a case-by-case basis. Although adsorption phenomenon occurs mostly on the surface of the biochars, our data did not reveal a conclusive correlation between adsorption capacity for Pb(II) with specific surface areas of the studied biochars. For example, specific surface areas of the pristine biochars increased with increasing pyrolysis temperature (Table 1) [8, 21]; yet the adsorption capacity for Pb(II) did not follow the this pattern. Negative zeta potential values were found for all the studied biochars, which were consistent with the previous reports [16, 35]. This indicates that the biochars carried negative charges on their surfaces were more likely to adsorb positively charged ions such as Pb(II). This

is confirmed by the cation-exchange capacity, which reflects the ion exchangeable potential and surface negative charges on biochars. Surface acidic functional groups (carboxyl, lactone and phenol) of biochars analyzed by Boehm titration varied with the peak pyrolysis temperature. The anions of surface functional groups can form surface complexes with Pb(II) on the biochars and thus increased specific adsorption [16, 36]. XPS analyses indicated that C and O were the main surface elements for those studied biochars and they were impacted by the peak pyrolysis temperature (Fig. 5).

4. Conclusions

The pyrolysis temperature has different effects on biochar's elemental composition, physicochemical properties and surface elemental species. Contents of O, atomic ratios of O/C and (O+N)/C and total acidic groups of biochars decreased while C contents, specific surface areas increased with the increasing pyrolysis temperature from 350°C to 600°C. Quartz and calcite were confirmed by XRD analyses in the biochar under the pyrolysis temperature of 600°C. FT-IR verified the changes on surface functional groups of the biochars under different pyrolysis temperature. X-ray photoelectron spectroscopy analyses show that the increasing pyrolysis temperature only changes the surface contents of C and O. The batch equilibrium adsorption of all the tested biochars shows that B350 had higher adsorption capacities of Pb(II) than other biochars. Therefore, bulk elemental composition, specific surface area, surface electronegativity and XPS analyses can effectively characterize and screen the surface properties of biochars for wastewater treatment.

Acknowledgments

This work was partially supported by the Natural Science Fund of Jiangsu Province
(BK20131268) and the NSF (CBET-1054405).

References

- [1] J. Lee, M. Kidder, Evans BR, S. Paik, A.C. Buchanan, C.T. Garten, R.C. Brown, Environ. Sci. Technol., 44 (2010) 7970-7974.
- [2] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok, Chemosphere, 99 (2014) 19-33.
- [3] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman, Bioresource Technol., 160 (2014) 191-202.
- [4] T.M. Abdel-Fattah, M.E. Mahmoud, S.B. Ahmed, M.D. Huff, J.W. Lee, S. Kumar, J. Ind. Eng. Chem., 22 (2015) 103-109.
- [5] S.E. Elaigwu, V. Rocher, G. Kyriakou, G.M. Greenway, J. Ind. Eng. Chem., 20 (2014) 3467-3473.
- [6] B. Singh, B.P. Singh, A.L. Cowie, Aust. J. Soil Res., 48 (2010) 516-525.
- [7] Z.A. Mayer, Y. Eltom, D. Stennett, E. Schroder, A. Apfelbacher, A. Hornung, Environ. Prog. Sustain. Energy, 33 (2014) 490-496.
- [8] A. Mukherjee, A.R. Zimmerman, W. Harris, Geoderma, 163 (2011) 247-255.
- [9] L.W. Low, T.T. Teng, A.F.M. Alkarkhi, N. Morad, B. Azahari, J. Ind. Eng. Chem., 28 (2015) 37-44.
- [10] Y. Wang, Y.T. Hu, X. Zhao, S.Q. Wang, G.X. Xing, Energ. Fuel., 27 (2013) 5890-5899.
- [11] J.J. Manya, Environ. Sci. Technol., 46 (2012) 7939-7954.
- [12] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, J. Environ. Qual., 41 (2012) 990-1000.
- [13] S.S. Wang, B. Gao, A.R. Zimmerman, Y.C. Li, L.N. Ma, W.G. Harris, K.W. Migliaccio, Chemosphere, 134 (2015) 257-262.
- [14] Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen, L. Yang, Chem. Eng. J., 240

(2014) 574-578.

[15] M. Inyang, B. Gao, Y. Yao, Y. Xue, A. Zimmerman, A. Mosa, P. Pullammanappallil, Y. Ok, X. Cao, Crit. Rev. Env. Sci. Tec, 46 (2016) 406-433.

[16] W. Ding, X. Dong, M. Inyang, B. Gao, L.Q. Ma, Chemosphere, 105 (2014) 68-74.

[17] M. Uchimiya, L.H. Wartelle, K.T. Klasson, C.A. Fortier, I.M. Lima, J. Agr. Food Chem., 59 (2011) 2501-2510.

[18] S.L. Goertzen, K.D. Theriault, A.M. Oickle, A.C. Tarasuk, H.A. Andreas, Carbon, 48 (2010) 1252-1261.

[19] A.M. Oickle, S.L. Goertzen, K.R. Hopper, Y.O. Abdalla, H.A. Andreas, Carbon, 48 (2010) 3313-3322.

[20] R.B. Fidel, D.A. Laird, M.L. Thompson, J. Environ. Qual., 42 (2013) 1771-1778.

[21] M. Keiluweit, P.S. Nico, M.G. Johnson, M. Kleber, Environ. Sci. Technol., 44 (2010) 1247-1253.

[22] Z.M. Chen, B.L. Chen, C.T. Chiou, Environ. Sci. Technol., 46 (2012) 11104-11111.

[23] M. Zhang, B. Gao, Y. Yao, Y.W. Xue, M. Inyang, Sci. Total. Environ., 435 (2012) 567-572.

[24] J. Jaramillo, P.M. Alvarez, V. Gomez-Serrano, Appl. Surf. Sci., 256 (2010) 5232-5236.

[25] J. Lehmann, Front. Ecol. Environ., 5 (2007) 381-387.

[26] J.W. Gaskin, C. Steiner, K. Harris, K.C. Das, B. Bibens, T. ASABE, 51 (2008) 2061-2069.

[27] S. Kang, X. Li, J. Fan, J. Chang, Ind. Eng. Chem. Res., 51 (2012) 9023 - 9031.

[28] K.Y. Foo, B.H. Hameed, Chem. Eng. J., 156 (2010) 2-10.

[29] Y. Liu, Y. Liu, Sep. Purif. Technol., 61 (2008) 229-242.

[30] F. Helfferich, McGraw Hill, New York, USA, (1962) 166.

[31] D. Mohan, C.U. Pittman, M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F.

Alexandre-Franco, V. Gomez-Serrano, H. Gong, J. Colloid Interf. Sci., 310 (2007) 57-73.

[32] Z.G. Liu, F.S. Zhang, J. Hazard. Mater., 167 (2009) 933-939.

[33] W.C. Ding, X.L. Dong, I.M. Ime, B. Gao, L.Q. Ma, Chemosphere, 105 (2014) 68-74.

[34] X.D. Cao, L.N. Ma, B. Gao, W. Harris, Environ. Sci. Technol., 43 (2009) 3285-3291.

[35] X.J. Tong, J.Y. Li, J.H. Yuan, R.K. Xu, Chem. Eng. J., 172 (2011) 828-834.

[36] M. Inyang, B. Gao, A. Zimmerman, Y.M. Zhou, X.D. Cao, Environ. Sci. Pollut. R, 22 (2015) 1868-1876.