

Evaluation of Green Waste and Popular Twigs Biochar Produced at Low and High Pyrolytic Temperature for Efficient Removal of Metals from Water

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Abstract Biomass-derived biochar is considered as a promising heavy metal adsorbent, due to its favorable physicochemical properties, from aqueous solution as compared with other adsorbents. However, there is a limited number of studies on the effects of biochar produced from different feedstocks and pyrolytic temperatures on metal removal from metal-contaminated water. So in this study, the removal of the most prevalent heavy metals [lead (Pb(II)), cadmium (Cd), and chromium (Cr)] by green waste biochar (GWB) and popular twigs biochar (PTB), produced at different pyrolytic temperatures, i.e., low 350 and high 650 °C, has been investigated, following the determination of physical and chemical properties of biochar. The efficiency of heavy metals removal of biochar was studied at different

concentrations of heavy metals (10 and 100 $\mu\text{g mL}^{-1}$), biochar types and treatment duration (3, 6, 9, and 12 h) at isothermic condition of aqueous solution. Results revealed that both feedstock type and pyrolytic temperature to produce biochar significantly affected its metal sorption capacity. The maximum sorption capacities of all three metals, i.e., Pb (II), Cd, and Cr were determined in the GWB produced at low pyrolytic temperature 350 °C after 9 h of treatment duration at both high and low metal concentrations. This highest sorption capacity of all metals by low pyrolytic temperature produced GWB was due to its better physicochemical properties especially high surface area, cation exchange capacity, and oxygen-containing functional groups as compared with woody feedstock based high pyrolytic temperature produced PTB. Conclusively, low pyrolytic temperature produced GWB was evaluated as a potential adsorbent to efficiently reduced heavy metal concentration in metal-contaminated water.

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1 Introduction

Wastewater contains industrial as well as sewage wastewater and is used in the urban and semi urban areas to irrigate vegetables (30% of total wastewater), fodder, and food crops (Qadir et al. 2000). According to an estimate, in Pakistan, almost 32.5 thousand hectare area out of total 22 million hectare cultivated area is irrigated

through wastewater (Ensink et al. 2004). Farmers mostly use wastewater because of its continuous availability, rich source of plant nutrients, water scarcity problems, and cost-effective availability (Shah 2000; Lone et al. 2003; Qadir et al. 2010). Besides these beneficial aspects, there are also many detrimental effects of wastewater irrigation for agricultural crops, animals, and human beings (Järup 2003). Both industrial and sewage wastewater contains a vast variety of organic and inorganic pollutants. Among inorganic pollutants, heavy metals are of major concern because of their persistence, toxicity, and non-biodegradable nature (Khan et al. 2008). It is investigated that all the four sewage drains of Faisalabad had chromium (Cr) concentration 2–10 times higher than permissible limit ($0.05 \mu\text{g mL}^{-1}$) set by environment protection agency (EPA) (Hussain et al. 2006). Similarly, concentration of cadmium (Cd) in sewage drains of Faisalabad is 3 times higher than the permissible limit ($0.01 \mu\text{g mL}^{-1}$) of EPA (Qadir et al. 2000). It is also reported that concentration of three metals, i.e., Cd, Cr, and lead (Pb (II)) reached phytotoxic levels in vegetables irrigated with wastewater (Qadir et al. 2000).

Heavy metals not only affect the plant growth and yield but also cause many life threatening diseases in human beings when they eat heavy metal-contaminated food crops. Toxic metals can enter the human body by the consumption of heavy metal-contaminated food crops, water, and inhalation of dust. It is estimated that 70% of these toxic metals enter into the human body via consumption of food crops (Murtaza et al. 2010). In food crops, mostly wastewater irrigated crops are major source of heavy metals intake. These toxic metals cause many diseases, e.g., cardiovascular problems, kidney and nervous diseases, immunological defense and growth retardation, constipation and anemia, bone diseases, and many other problems in humans (Cadmium 1992; Järup 2003; Türkdoğan et al. 2003). So, it has become crucial to prevent the entry of these toxic metals in food crops irrigated with heavy metal-contaminated wastewater and thus decrease their risk to human health.

Many methods have been adopted to treat heavy metal-contaminated wastewater, i.e., chemical (e.g., precipitation, ion exchange, and electro-coagulation), physical (e.g., membrane filtration, packed-bed filtration), and biological methods (e.g., bioremediation approaches) (Akbal and Camcı 2011; Boudrahem et al. 2011; Malamis et al. 2011). Most of these methods and technologies, however, may be associated with high

operational cost, sludge disposal problems, less efficient and short-term effect (Sud et al. 2008). These disadvantages have increased the need to develop alternative, long-term and low-cost treatment technologies for heavy metal contaminants. Bio-sorbents therefore, have been suggested to be a potential candidate to satisfy this need for remediation of toxic metals in wastewater. The use of biochar as a low-cost bio-sorbent to remove metallic contaminants from aqueous solutions is an emerging and promising treatment technology (Uchimiya et al. 2010b; Park et al. 2011; Ahmad et al. 2014).

Biochar is a pyrogenic carbon (C) rich material, derived from thermal decomposition of biomass in a closed system with little or no oxygen (Lehmann et al. 2003). The most important mechanisms by which biochar remove the heavy metals from wastewater are electrostatic outer-sphere complexation due to metal exchange with sodium (Na) and potassium (K) available on biochar surface, co-precipitation and inner-sphere complexation of metals with organic matter and mineral oxides of biochar, surface complexation with active oxygen-containing functional groups especially carboxyl, lactonic, and hydroxyl functional groups of the biochar (Uchimiya et al. 2011a), surface precipitation of metals with PO_4^{3-} , CO_3^{2-} , and Cl present in the biochar, e.g., PO_4^{3-} and CO_3^{2-} react with Pb (II) and form stable minerals (e.g., cerrusite, hydrocerrusite, and pyromorphite) that precipitate on the biochar surface (Inyang et al. 2012).

The properties of biochar which make it more suitable for heavy metals removal from wastewater are high surface area ($> 400\text{--}1500 \text{ m}^2 \text{ g}^{-1}$), pH of biochar (wide range of pH value from 6 to 10), high cation exchange capacity (CEC) ($> 40 \text{ cm mole}_c \text{ kg}^{-1}$), long-term stability (10–100 times of organic matter) and functional groups present on its surface especially oxygen-containing functional groups (Uchimiya et al. 2010a; Park et al. 2011; Ahmad et al. 2014). These characteristics of biochar depend upon the type of feedstock used as well as pyrolysis conditions during biochar production (Ahmad et al. 2014). Biochar is considered as a promising heavy metals adsorbent, due to its favorable physicochemical properties. However, there are a limited number of studies on the effects of various biochars produced from different feedstocks and pyrolytic temperatures on metals removal from wastewater.

Thus, overall objectives of this study were characterization of biochar produce from different feedstocks and pyrolytic temperatures, evaluation and selection of most

efficient biochar produced from different feedstocks and pyrolytic temperatures for remediation of heavy metal-contaminated wastewater.

2 Materials and Experimental Methods

2.1 Biochar Production and Characterization

Two feedstocks, i.e., green waste (GW) and popular twigs (PT), were selected for biochar production. Green waste consisting of Bermuda grass (*Cynodondactylon*) cuttings, were collected from the lawns of University of Agriculture, Faisalabad (UAF). Two hundred grams of each crushed feedstock was pyrolyzed in a laboratory setup as described by Sánchez et al. (2009). Muffle furnace (Gallonghop, England) was used to carry on the pyrolysis process. The increase in furnace temperature per unit time was adjusted at 8–9 °C min⁻¹. After attaining the maximum pyrolytic temperature (350 and 650 °C temperature for each feedstock), 20 min residence time was maintained.

Surface areas of biochars were measured in duplicate by nitrogen adsorption isotherms at 77 K using a NOVA 2000 surface area analyzer (Quantachrome, Boynton Beach, FL). Volatile matter was determined as the weight loss after heating the char in a covered crucible to 950 °C and holding for 7 min. Ash was defined as the remaining mass after subsequently heating in an open crucible to 750 °C and holding at this temperature until sample weight stabilized. After the determination of moisture, ash, and volatile matter, fixed carbon was calculated by difference (Uchimiya et al. 2011a). Biochar yield was calculated by the following equation:

$$\text{Biochar yield(\%)} = \frac{\text{Weight of biochar collected after pyrolysis(kg)}}{\text{Weight of feedstock used for pyrolysis(kg)}} \times 100$$

The pH of biochar was measured by using 1:20 solid to solution ratio, after shaking for 90 min in deionized water on mechanical shaker. The CEC of biochar was measured by a modified ammonium acetate compulsory displacement method (Gaskin et al. 2008). The surface acidic oxygen-containing functional groups (carboxylic, lactonic, and phenolic groups) were determined by Boehm titration (Boehm 1966). The carbon (C),

hydrogen (H), nitrogen (N), and sulfur (S) content in different biochars were analyzed on Vario Micro CHNS-O Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). The percentage of oxygen content was determined by difference method (Aon et al. 2015):

$$\text{Oxygen(\%)} = 100 - (\text{Ash} + \text{carbon} + \text{hydrogen} + \text{nitrogen})\%$$

The results obtained from CHNS-O analyzer were used to calculate molar ratios, i.e., H:C and O:C.

2.2 Treatment of Heavy Metal-Polluted Water with Biochar in a Batch Experiment

The purpose of this experiment was to select the biochar type and time required to treat heavy metal-polluted water with biochar on the basis of maximum sorption of heavy metals from the heavy metal-spiked solution. This was a completely randomized design (CRD) 2 factorial batch experiment conducting in the soil fertility and plant nutrition laboratory, Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad. 1st factor is the biochar types (green waste biochar produced at 350 °C pyrolysis temperature, GWB350 °C, green waste biochar produced at 650 °C pyrolysis temperature, GWB650 °C, popular twigs biochar produced at 350 °C pyrolysis temperature, PTB350 °C, popular twigs biochar produced at 650 °C pyrolysis temperature, PTB650 °C) and 2nd factor is the treatment durations (3, 6, 9, and 12 h) of metal solution with different biochar types.

Metal solutions (10 and 100 µg mL⁻¹) of lead (Pb (II)), cadmium (Cd), and chromium (Cr) were prepared in the laboratory by artificially spiking the deionized water with lead nitrate, cadmium nitrate, and potassium dichromate ultra-pure salts, respectively, and their pH was adjusted 7 by using NaOH and HCl. Then the prepared heavy metals solutions were treated with above mentioned four types of biochars at the rate of 2 g L⁻¹ for four different times (3, 6, 9, and 12 h) on a mechanical shaker at constant temperature, i.e., 25 °C. After shaking, the solutions were centrifuged, and filtered the supernatants by using centrifuge machine and Whatman#42 filter paper, respectively. The concentration of heavy metals, i.e., Pb (II), Cd, and Cr in the filtrate was analyzed by using inductively coupled plasma atomic emission

spectrometry (ICP-AES) (ICP-OES optima 5300 DV) having limit of detection ($3 \mu\text{g kg}^{-1}$) and limit of quantification ($9 \mu\text{g kg}^{-1}$). The pH and electrical conductivity (EC) of the filtrates were also analyzed. Water soluble PO_4^{3-} and CO_3^{2-} contents were determined using ion chromatography (Waters 2690 Separations Module, Waters Corporation, USA) (Cao and Harris 2010).

2.3 Statistical Analysis

Statistical analysis and data computations of biochar characterization and batch experiment were made on Microsoft Excel 2013[®] (Microsoft Corporation, Redmond, WA, USA) and Statistix 8.1[®] (Analytical Software, Tallahassee, USA). However, significantly different means in case of biochar characterization were compared with LSD (least significant difference) test at $P \leq 0.05$ (Steel and Dickey 1997) while in case of batch experiment, significantly different treatment means were separated by using Tukey's multiple comparison test ($P \leq 0.05$).

3 Results

3.1 Characterization of Biochar

3.1.1 Elemental Characteristics

There was a significant ($P \leq 0.05$) effect of feedstock and pyrolytic temperature on elemental characteristics of biochar (Table 1). The maximum concentration of N, O, H, and S were determined in biochar produced at low pyrolytic temperature $350 \text{ }^\circ\text{C}$ as compared with biochar produced at high pyrolytic temperature $650 \text{ }^\circ\text{C}$ from both feedstocks, i.e., green waste (GW) and popular twigs (PT). While carbon (C) content was significantly ($P \leq 0.05$) higher in the biochar produced at high pyrolytic temperature $650 \text{ }^\circ\text{C}$ as compared with biochar produced at low pyrolytic temperature $350 \text{ }^\circ\text{C}$ from both feedstocks. Among feedstocks green waste biochar (GWB) showed significantly ($P \leq 0.05$) higher concentration of all nutrients as compared with popular twigs biochar (PTB) produced at both high and low pyrolytic temperatures (Table 1) but C content was maximum in biochar produced from PT at both low and high pyrolytic temperature.

3.1.2 Molar Ratio

There was a significant ($P \leq 0.05$) effect of feedstock and pyrolytic temperature on molar ratio of elements in biochar (Table 1). Table 1 shows that maximum value of O:C and H:C ratio was calculated in the biochar produced at low pyrolytic temperature $350 \text{ }^\circ\text{C}$ as compared with high pyrolytic temperature $650 \text{ }^\circ\text{C}$ in both GW and PT feedstocks. Among feedstocks, GWB showed significantly ($P \leq 0.05$) higher molar ratio of O:C and H:C as compared with PTB produced at both high and low pyrolytic temperatures.

3.1.3 Physicochemical Characteristics

There was a significant ($P \leq 0.05$) effect of feedstock and pyrolytic temperature on biochar physicochemical properties, i.e., pH, surface area and CEC (Table 1). There was a significant ($P \leq 0.05$) increase in surface area and pH of biochar, produced from both feedstocks GW and PT, when pyrolytic temperature was enhanced from 350 to $650 \text{ }^\circ\text{C}$. The significantly ($P \leq 0.05$) highest value of surface area and pH, i.e., $309.58 \text{ m}^2 \text{ g}^{-1}$ and 10.34 , respectively, were measured in GWB $650 \text{ }^\circ\text{C}$. The maximum values of CEC were measured when the feedstocks were pyrolyzed at low temperature $350 \text{ }^\circ\text{C}$ as compared with high temperature $650 \text{ }^\circ\text{C}$. The significantly ($P \leq 0.05$) highest value of CEC, i.e., $43.74 \text{ c mol}_c \text{ kg}^{-1}$ was determined in GWB $350 \text{ }^\circ\text{C}$. Among feedstocks, GWB showed higher values of pH, surface area, and CEC as compared with PTB produced at both high and low pyrolytic temperatures.

3.1.4 Proximate Composition

It can be easily identified from the Table 1 that ash and fixed carbon (FC) contents were increased significantly ($P \leq 0.05$) by increasing the pyrolytic temperature in both GW and PT feedstocks. While the biochar yield and volatile matter (VM) was higher when biochar produced at low pyrolytic temperature $350 \text{ }^\circ\text{C}$ as compared with high temperature $650 \text{ }^\circ\text{C}$. The maximum amounts of ash and volatile matter were determined when biochar produced from GW at both low ($350 \text{ }^\circ\text{C}$) and high ($650 \text{ }^\circ\text{C}$) pyrolytic temperature but yield and FC content were higher when biochar produced from

Table 1 Characterization of biochar

	Units	Biochar types			
		Green waste biochar		Popular twigs biochar	
		350 °C	650 °C	350 °C	650 °C
Elemental characteristics					
C	%	39.30 ± 2.40 c	49.40 ± 2.40 b	46.70 ± 3.20 b	66.70 ± 3.20 a
H	%	3.96 ± 0.40 a	1.96 ± 0.40 c	3.16 ± 0.27 b	1.23 ± 0.17 d
O	%	19.10 ± 1.80 a	9.07 ± 1.80 c	14.10 ± 2.10 b	5.74 ± 0.35 d
N	%	1.47 ± 0.10 a	0.77 ± 0.10 b	0.53 ± 0.16 c	0.30 ± 0.07 d
S	g kg ⁻¹	8.65 ± 1.30 a	0.98 ± 0.27 bc	5.65 ± 1.30 b	2.31 ± 0.56 c
Cd	mg kg ⁻¹	0.03 ± 0.01 b	0.08 ± 0.02 a	0.04 ± 0.01 b	0.09 ± 0.02 a
Pb (II)	mg kg ⁻¹	0.07 ± 0.03 a	0.11 ± 0.05 a	0.06 ± 0.02 a	0.09 ± 0.02 a
Cr	mg kg ⁻¹	0.47 ± 0.17 b	0.83 ± 0.19 a	0.33 ± 0.12 b	0.49 ± 0.16 b
Water soluble PO ₄ ³⁻	mg kg ⁻¹	53.70 ± 9.50 a	16.30 ± 4.50 bc	19.00 ± 4.00 b	5.30 ± 2.50 c
Water soluble CO ₃ ²⁻	%	1.23 ± 0.06 b	1.86 ± 0.14 a	0.90 ± 0.19 c	1.39 ± 0.12 b
Molar ratio					
H:C ratio		1.22 ± 0.20 a	0.48 ± 0.13 c	0.81 ± 0.06 b	0.22 ± 0.03 d
O:C ratio		0.36 ± 0.04 a	0.14 ± 0.03 c	0.23 ± 0.02 b	0.07 ± 0.00 d
Physicochemical characteristics					
Surface area	m ² g ⁻¹	23.80 ± 2.80 c	309.6 ± 18.60 a	19.30 ± 2.60 c	215.90 ± 6.30 a
CEC*	c mol _c kg ⁻¹	43.70 ± 5.20 a	30.40 ± 2.40 b	31.25 ± 4.40 b	27.90 ± 3.30 b
pH		8.01 ± 0.16 c	10.34 ± 0.45 a	7.38 ± 0.20 d	9.38 ± 0.19 b
Proximate composition					
Ash content	%	27.26 ± 2.80 b	39.60 ± 1.80 a	9.98 ± 2.30 c	13.31 ± 1.29 c
Fixed carbon	%	24.62 ± 2.43 d	35.02 ± 1.77 c	55.11 ± 2.09 b	69.77 ± 3.99 a
Volatile matter	%	41.27 ± 1.96 a	16.20 ± 2.94 c	31.27 ± 2.06 b	11.60 ± 1.57 c
Yield	%	40.31 ± 2.95 b	27.64 ± 1.68 c	51.59 ± 2.70 a	41.59 ± 2.70 b
O-Containing Functional groups					
Carboxylic	meq g ⁻¹	0.12 ± 0.003 a	0.06 ± 0.002 c	0.09 ± 0.006 b	0.04 ± 0.005 c
Lactonic	meq g ⁻¹	0.13 ± 0.004 a	0.04 ± 0.002 b	0.12 ± 0.009 a	0.03 ± 0.011 b
Phenolic	meq g ⁻¹	0.13 ± 0.005 a	0.04 ± 0.003 c	0.10 ± 0.005 b	0.03 ± 0.003 c

Values are mean of the three replicates ± standard deviation ($n = 3$). Different letters within a column indicate significance between treatment at $\alpha = 0.05$ according to LSD test

*Cation exchange capacity

woody feedstock, i.e., PT at both low and high pyrolytic temperature.

3.1.5 Oxygen-Containing Functional Groups

The significantly ($P \leq 0.05$) highest concentration of oxygen-containing functional groups, i.e., carboxylic, lactonic, and phenolic groups concentration was measured in low pyrolytic temperature 350 °C produced biochar as compared with high

temperature 650 °C produced biochar from both GW and PT feedstock (Table 1). Similarly, among feedstocks, GWB showed significantly ($P \leq 0.05$) higher concentration of oxygen-containing functional groups as compared with PT produced biochar at both high and low pyrolytic temperatures. The maximum values of carboxylic, lactonic, and phenolic functional groups, i.e., 0.121, 0.130, and 0.130, respectively, were determined in GWB350 °C.

3.2 Batch Experiment

3.2.1 Heavy Metals (HM) Removal from Metal Solutions by Using Biochar

There was a significant ($P \leq 0.05$) difference in Pb (II), Cd, and Cr removal (%) from their 100 and 10 $\mu\text{g mL}^{-1}$ solutions by changing the biochar type and treatment duration as can be seen in Table 2. The significantly ($P \leq 0.05$) higher removal of Pb (II), Cd, and Cr from both 100 and 10 $\mu\text{g mL}^{-1}$ solutions were calculated when these solutions were treated with biochar produced at low pyrolytic temperature 350 °C as compared with high pyrolytic temperature 650 °C produced biochar from both GW and PT feedstocks. Among feedstock types, biochar produced from GW feedstock showed higher removal of metals, i.e., Pb (II), Cd, and Cr as compared with biochar produced from PT feedstocks from their 100 and 10 $\mu\text{g mL}^{-1}$ solutions. It was also showed on the Table 2 that metals removal from their 100 and 10 $\mu\text{g mL}^{-1}$ solutions were also significantly ($P \leq 0.05$) increased by increasing the treatment duration of metals spiked solution with biochar and statistically ($P \leq 0.05$) maximum removal was noted after 9 hours of treatment duration. The maximum removal of Pb (II) up to 90%, Cd up to 60%, and Cr up to 53% was determined when HM spiked solution was treated with GWB 350 °C after 9 h of treatment duration followed by PTB 350 °C that remove 73, 46, and 36%, respectively, from their 100 $\mu\text{g mL}^{-1}$ solution.

3.2.2 Heavy Metals Sorption Capacity of Biochar

Heavy metals (Pb (II), Cd, and Cr) sorption capacities of different biochars were significantly ($P \leq 0.05$) different when the artificially heavy metal-spiked solution of different concentration, i.e., 100 and 10 $\mu\text{g mL}^{-1}$ were treated with biochar for various time intervals (Table 3). There was significantly ($P \leq 0.05$) increased in the heavy metals sorption capacities of all four types of biochar by increasing the treatment duration of artificially heavy metal-spiked solutions, i.e., both 100 and 10 $\mu\text{g mL}^{-1}$ solution. The maximum sorption capacities of all three metals, i.e., Pb (II), Cd, and Cr were calculated for GWB350 °C and PTB350 °C after 9 hours of treatment duration of both their 100 and 10 $\mu\text{g mL}^{-1}$ solutions while the minimum values were recorded for GWB650 °C and PTB650 °C. It

was also noted that the sorption capacities of all four types of biochars for all three metals (Pb (II), Cd, and Cr) were decreased when we used these biochars to treat 10 $\mu\text{g mL}^{-1}$ solution as compared with 100 $\mu\text{g mL}^{-1}$ solution.

3.2.3 Electrical Conductivity and pH of Metal Solutions

Figure 1a and b shows the effect of different biochar types and treatment duration on pH and EC of artificially spiked metal solutions of 100 and 10 $\mu\text{g mL}^{-1}$, respectively, after treatment. There was non-significant ($P \leq 0.05$) change in pH and EC of metal solution of both 100 and 10 $\mu\text{g mL}^{-1}$ after treatment with GWB350 °C and PTB350 °C at all treatment durations while in case of higher temperature produced biochars, i.e., GWB650 °C and PTB650 °C showed significant ($P \leq 0.05$) changed in solution pH and EC after treatment. There was significant ($P \leq 0.05$) increase in pH and EC of metal solutions (both 100 and 10 $\mu\text{g mL}^{-1}$) by increasing the treatment duration with higher pyrolytic temperature produced biochar, i.e., 650 °C. The highest value of pH and EC in both 100 and 10 $\mu\text{g mL}^{-1}$ metal solutions was measured after treatment with GWB650 °C while the minimum values were measured after treatment with PTB350 °C.

3.2.4 Phosphate and Carbonate Concentration of Metal Solutions

There was a significant effect of biochar type and treatment duration on phosphate and carbonate concentration of artificially spiked metal solutions of both 100 and 10 $\mu\text{g mL}^{-1}$ after treatment (Fig. 2a and b). Solution phosphate concentration (both 100 and 10 $\mu\text{g mL}^{-1}$) was significantly ($P \leq 0.05$) decreased in case of low pyrolytic temperature produced biochar treatment, i.e., GWB350 °C and PTB350 °C while non-significant change in phosphate concentration was measured after treatment with high temperature produced biochar, i.e., GWB650 °C and PTB650 °C treatment. Carbonate concentration was also significantly ($P \leq 0.05$) decreased in both biochar types produced at high and low pyrolytic temperature. Similarly, phosphate and carbonate concentration was significantly ($P \leq 0.05$) decreased by increasing the treatment duration as showed in the Fig. 2a and b of both metal solution, i.e., 100 and 10 $\mu\text{g mL}^{-1}$, respectively.

Table 2 Lead, cadmium and chromium removal (%) from their 10 and 100 µg mL⁻¹ solutions by using different types of biochar (2 g/L)

Treatment Duration	Biochar types											
	Green waste biochar		Popular twigs biochar		Green waste biochar		Popular twigs biochar					
	350 °C	650 °C	350 °C	650 °C	350 °C	650 °C	350 °C	650 °C				
	Lead removal (%) from 10 µg mL ⁻¹ solution						Lead removal (%) from 100 µg mL ⁻¹ solution					
3 h	49.67 ± 3.51c	19.33 ± 4.04 g	33.00 ± 2.65ef	17.67 ± 4.04 g	56.67 ± 2.52e	32.00 ± 3.00i	46.00 ± 2.00 g	26.00 ± 3.00j				
6 h	77.56 ± 3.50b	37.00 ± 5.00d-f	44.67 ± 4.04 cd	30.67 ± 3.51f	77.33 ± 3.51b	52.23 ± 3.15f	61.50 ± 2.78d	37.70 ± 1.87 h				
9 h	88.33 ± 2.08a	42.33 ± 4.50c-e	71.67 ± 2.52b	36.67 ± 4.04d-f	84.96 ± 1.65a	56.63 ± 2.27e	66.16 ± 2.25c	43.93 ± 2.30 g				
12 h	94.67 ± 2.52a	44.33 ± 4.04 cd	76.33 ± 3.06b	39.00 ± 2.65d-f	88.83 ± 1.45a	59.73 ± 2.05de	69.73 ± 2.50c	46.60 ± 2.12 g				
	Cadmium removal (%) from 10 µg mL ⁻¹ solution						Cadmium removal (%) from 100 µg mL ⁻¹ solution					
3 h	29.00 ± 7.55e-g	16.67 ± 3.51hi	23.33 ± 2.52 g-i	15.00 ± 4.00i	33.33 ± 2.52ef	20.33 ± 3.05 hi	27.00 ± 3.61f-h	17.33 ± 3.51i				
6 h	47.00 ± 4.00 bc	26.00 ± 5.00f-h	38.20 ± 3.70c-e	23.33 ± 2.52 g-i	51.00 ± 2.00b	32.33 ± 2.52ef	38.67 ± 3.06c-e	24.00 ± 2.00 g-i				
9 h	56.33 ± 4.51ab	31.67 ± 5.03e-g	44.67 ± 3.51 cd	27.00 ± 3.00 fg	58.33 ± 2.52a	36.00 ± 2.00e	43.33 ± 2.52 cd	27.00 ± 3.00f-h				
12 h	61.33 ± 4.51a	35.33 ± 3.51d-f	47.33 ± 2.08bc	30.33 ± 3.51e-g	59.43 ± 2.83a	37.90 ± 2.42de	44.73 ± 2.06bc	28.78 ± 2.38 fg				
	Chromium removal (%) from 10 µg mL ⁻¹ solution						Chromium removal (%) from 100 µg mL ⁻¹ solution					
3 h	19.67 ± 3.51f-h	12.33 ± 3.05 h	18.67 ± 3.51f-h	11.00 ± 4.00 h	28.67 ± 2.52de	15.67 ± 2.52gh	22.83 ± 1.76ef	12.73 ± 1.91 h				
6 h	41.33 ± 3.51 cd	19.67 ± 3.06f-h	34.00 ± 4.00de	16.00 ± 5.00 gh	44.33 ± 1.53b	25.00 ± 2.00d-f	31.23 ± 2.43 cd	18.67 ± 2.52f-h				
9 h	51.00 ± 3.00ab	24.33 ± 2.52 fg	42.67 ± 3.51b-d	19.67 ± 2.08f-h	51.00 ± 3.00ab	29.33 ± 2.52c-e	35.90 ± 1.65c	21.46 ± 1.94 fg				
12 h	56.67 ± 2.52a	27.00 ± 1.00ef	45.00 ± 1.00bc	22.67 ± 2.08 fg	53.13 ± 3.67a	30.53 ± 2.11 cd	36.17 ± 2.28c	22.76 ± 1.75ef				

Values are mean of the three replicates ± standard deviation (n = 3). Different letters within a column indicate significance between treatment at α = 0.05 according to Tukey's-HSD test

Table 3 Lead, cadmium, and chromium sorption capacity (mg g^{-1}) of different biochars from 10 and 100 $\mu\text{g mL}^{-1}$ metal solutions

Treatment Duration	Biochar types							
	Green waste biochar		Popular twigs biochar		Green waste biochar		Popular twigs biochar	
	350 °C	650 °C	350 °C	650 °C	350 °C	650 °C	350 °C	650 °C
	Pb (II) sorption capacity (mg g^{-1}) from 10 $\mu\text{g mL}^{-1}$ solution							
3 h	2.48 ± 0.18c	0.97 ± 0.20 g	1.65 ± 0.13ef	0.88 ± 0.20 g	28.33 ± 1.25e	16.00 ± 1.50i	23.00 ± 1.00 g	13.00 ± 1.50j
6 h	3.88 ± 0.18b	1.85 ± 0.25d-f	2.23 ± 0.20 cd	1.53 ± 0.18f	38.67 ± 1.76b	26.11 ± 1.58f	30.75 ± 1.39d	18.85 ± 0.93 h
9 h	4.42 ± 0.10a	2.12 ± 0.23c-e	3.58 ± 0.13b	1.83 ± 0.20d-f	42.48 ± 0.83a	28.31 ± 1.14e	33.08 ± 1.13c	21.96 ± 1.15 g
12 h	4.73 ± 0.13a	2.22 ± 0.20 cd	3.82 ± 0.15b	1.95 ± 0.13d-f	44.42 ± 0.73a	29.87 ± 1.03de	34.87 ± 1.25c	23.30 ± 1.06 g
	Cd sorption capacity (mg g^{-1}) from 10 $\mu\text{g mL}^{-1}$ solution							
3 h	1.45 ± 0.38e-g	0.83 ± 0.18hi	1.67 ± 0.13 g-i	0.75 ± 0.20i	16.67 ± 1.26ef	10.16 ± 1.53hi	13.50 ± 1.80f-h	8.77 ± 1.76i
6 h	2.35 ± 0.20bc	1.30 ± 0.25f-h	1.91 ± 0.19c-e	1.17 ± 0.13 g-i	25.50 ± 1.00b	16.17 ± 1.26ef	19.33 ± 1.53e-e	12.00 ± 1.00 g-i
9 h	2.81 ± 0.23ab	1.58 ± 0.25e-g	2.23 ± 0.18 cd	1.35 ± 0.15 fg	29.17 ± 1.26a	18.00 ± 1.00e	21.67 ± 1.25 cd	13.50 ± 1.50f-h
12 h	3.07 ± 0.23a	1.76 ± 0.18 d-f	2.37 ± 0.10bc	1.52 ± 0.18e-g	29.72 ± 1.41a	18.95 ± 1.21de	22.37 ± 1.03bc	14.39 ± 1.19 fg
	Cr sorption capacity (mg g^{-1}) from 100 $\mu\text{g mL}^{-1}$ solution							
3 h	0.98 ± 0.18f-h	0.62 ± 0.15 h	0.93 ± 0.18f-h	0.55 ± 0.20 h	14.33 ± 1.26de	7.83 ± 1.26gh	11.42 ± 0.88ef	6.37 ± 0.96 h
6 h	2.06 ± 0.18 cd	0.98 ± 0.15f-h	1.70 ± 0.20de	0.80 ± 0.25gh	22.17 ± 0.76b	12.50 ± 1.00d-f	15.61 ± 1.22 cd	9.33 ± 1.26f-h
9 h	2.55 ± 0.15ab	1.22 ± 0.13 fg	2.13 ± 0.18b-d	0.98 ± 0.10f-h	25.50 ± 1.50ab	14.67 ± 1.26c-e	17.95 ± 0.83c	10.73 ± 0.97 fg
12 h	2.83 ± 0.13a	1.35 ± 0.05ef	2.25 ± 0.05bc	1.13 ± 0.10 fg	26.57 ± 1.83a	15.27 ± 1.06 cd	18.08 ± 1.14c	11.38 ± 0.88ef

Values are mean of the three replicates ± standard deviation ($n = 3$). Different letters within a column indicate significance between treatment at $\alpha = 0.05$ according to Tukey's-HSD test

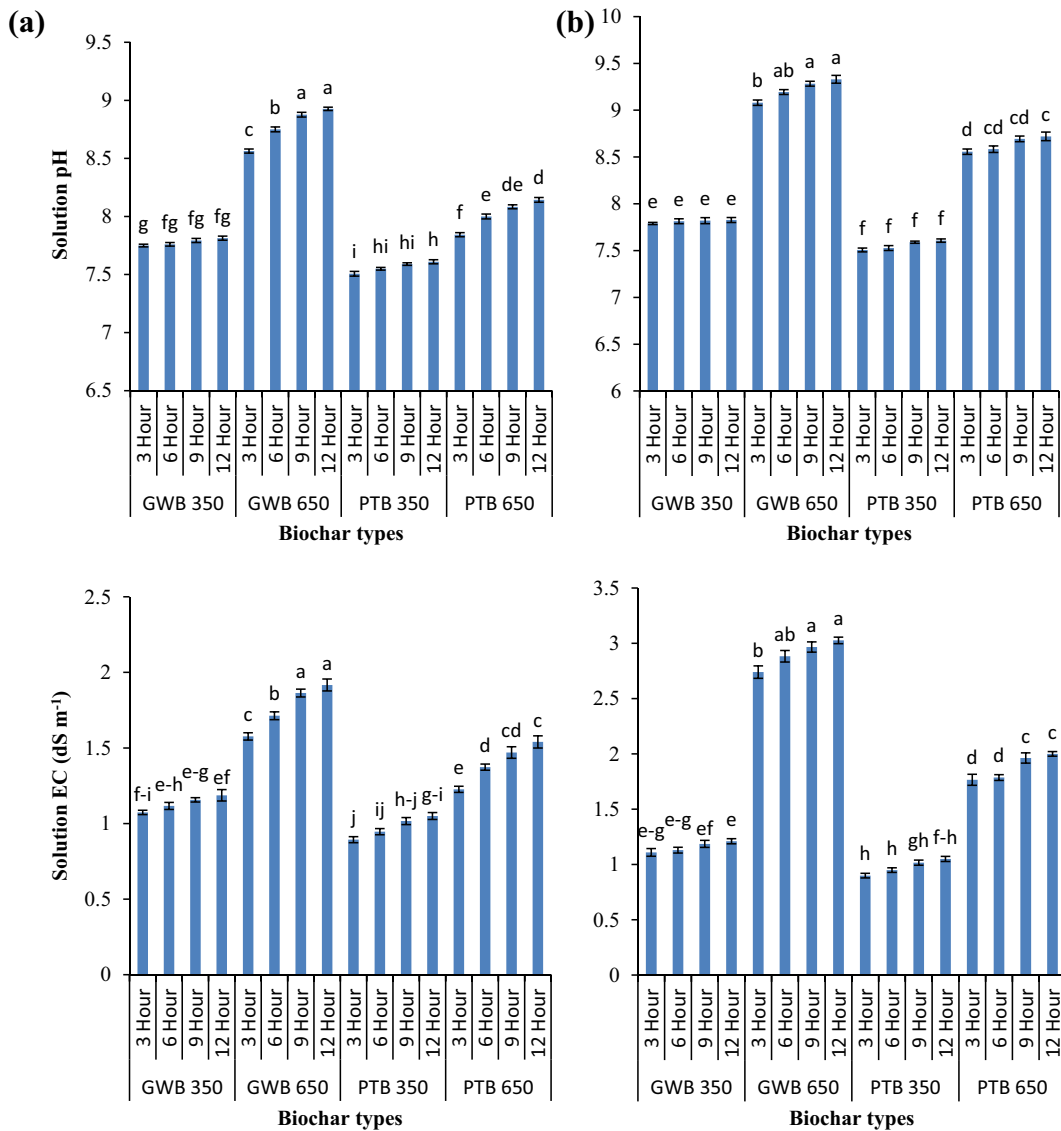


Fig. 1 pH and EC of 100 µg mL⁻¹ (a) and 10 µg mL⁻¹ (b) solutions of lead, cadmium and chromium after treatment with different types of biochar (2 g L⁻¹) for different durations

4 Discussion

In this study we produced four different biochars by using two feedstocks, i.e., green waste (GW) and popular twigs (PT), and two pyrolytic temperatures, i.e., 350 and 650 °C. There was significant difference in the elemental characteristics and molar ratio, physiochemical properties, and oxygen-containing functional groups present in all four types of biochar (Table 1). The statistically higher concentration of N was measured in the biochar produced at low pyrolytic temperature in case of both feedstocks, i.e., GW and PT (Table 1). Most of the

nutrients in feedstock become volatilized at high pyrolytic temperature, e.g., N starts to become volatilize ~ 200 °C (Steiner et al. 2008). Low pyrolytic temperature favors higher N (Baldock and Smernik 2002) because N is the most sensitive for heating (Tryon 1948). In the current study, to get maximum benefit from the elemental characteristics of both biochar feedstocks, low pyrolysis temperature (350 °C) was used for biochar production. Similarly, biochar produced from GW feedstock showed significantly higher concentration of nutrients, i.e., N, S, and O (Table 1) as compared with biochar produced from PT at both low and high

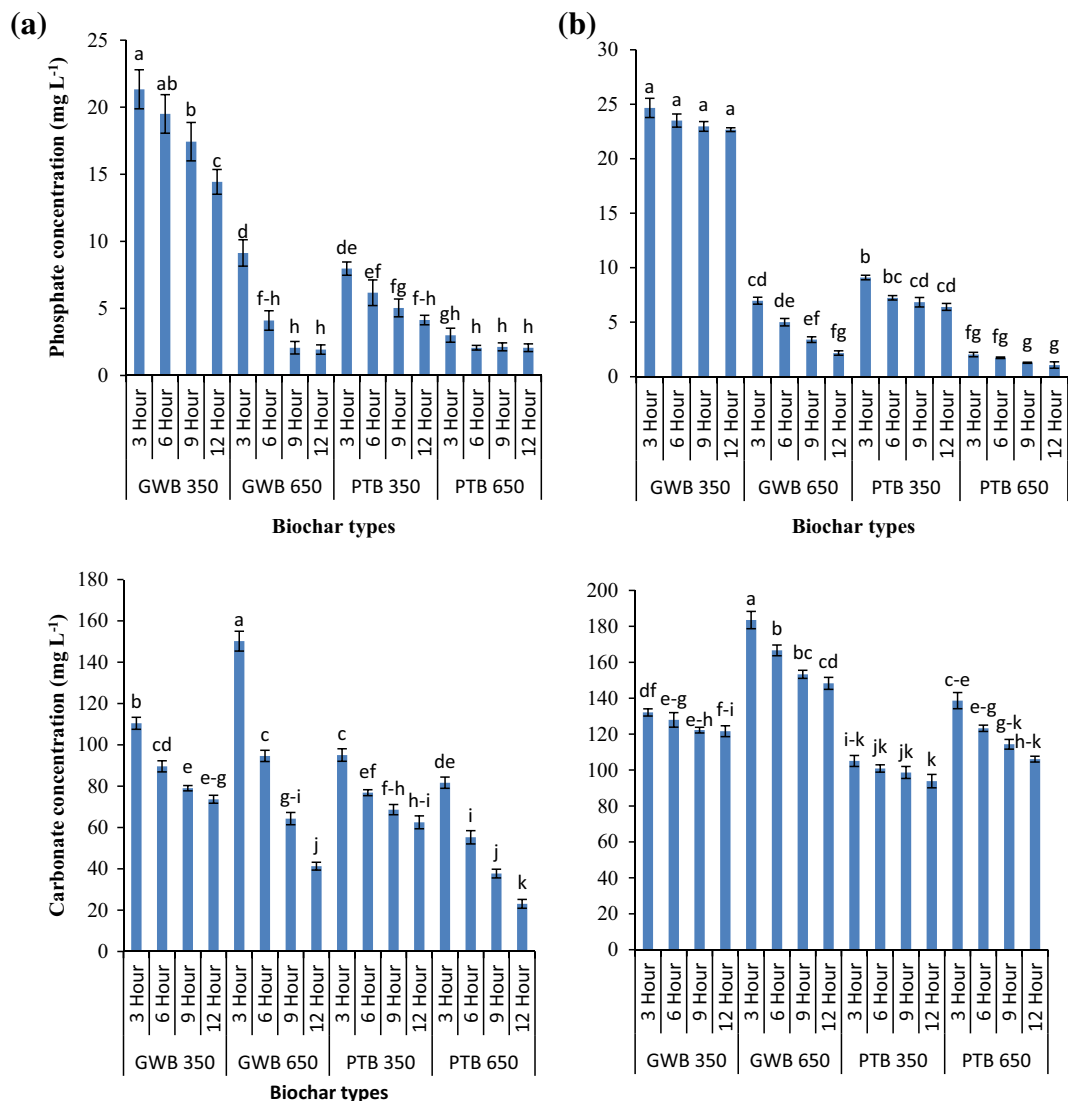


Fig. 2 Phosphate and carbonate concentration after treatment of $100 \mu\text{g mL}^{-1}$ (a) and $10 \mu\text{g mL}^{-1}$ (b) solutions of lead, cadmium, and chromium solution with different types of biochar (2 g/L) for different durations

pyrolytic temperatures. According to Deluca et al. (2015), biochar composition is varied with feedstock type, as in the present study of biochar characterization.

The elemental composition of each feedstock was used to calculate atomic ratios as a predictor of their polarity and potential interaction with water. One would expect that a biochar possessing higher H:C and O:C molar ratios to be more interactive with polar compounds (Wang et al. 2005). The atomic ratios of the biochars, because of dissimilar O and H losses, varied considerably (Table 1). Spokas (2010) suggested that O:C molar ratio is the most reliable predictor of biochar stability. As in this study of biochar characterization,

PTB650 °C (with O:C ratio 0.07) produced at high pyrolytic temperature (650 °C) with short residence time (20 min), may have a very long half-life (100–1000 years). Recently, Schimmelpennig and Glaser (2012) proposed the combined use of H:C and O:C molar ratios as a tool to assess the stability of biochar, with threshold limits of H:C (<1.4) and O:C (<0.7). In the present study, all four types of biochars (GWB350 °C, GWB650 °C, PTB350 °C, and PTB650 °C) had H:C and O:C molar ratios within abovementioned threshold limits. Physicochemical properties of all four types of produced biochars were also significantly varied (Table 1). The pH of biochar

depends upon feedstock type and pyrolysis conditions (Shinogi and Kanri 2003). In our case, pH and surface area of biochars produced at high pyrolytic temperature (650 °C) were high as compared with biochar produced at low pyrolytic temperature (350 °C) (Table 1). Increasing temperature has been found to decrease acidity and increase basicity of the biochar (Chun et al. 2004). In the same way, biochar produced at high pyrolytic temperature 650 °C had high pH which may be due to less concentration of oxygen and hydrogen (Table 1) and ultimately lower concentration of oxygen-containing functional groups (Table 1) which resulted in high pH. According to Uchimiya et al. (2010b), biochar produced at low pyrolytic temperature had low pH as compared with biochar produced at high pyrolytic temperature due to its high oxygen-containing acidic functional groups. Another reason of high pH of high pyrolytic temperature produced biochar was its high ash contents (Shinogi and Kanri 2003). According to Joseph and Lehmann (2009), surface area of biochar was increased by increasing the pyrolytic temperature because at high pyrolytic temperature, volatile matter that condense on micro pores become volatilized and thus increase the overall porosity and surface area of the biochar. Among the feedstock GWB showed high pH and surface area as compared with PTB at both high and low pyrolytic temperatures. Green waste biochar has more nutrients and ash content as compared with PTB which resulted in high pH. Similarly, according to Uchimiya et al. (2011b), woody feedstock contains more lignin content which cannot easily break down during pyrolysis as compared with non-woody feedstock, resulted produced biochar is not fine and has low surface area. Cation exchange capacity (CEC) of biochar was significantly decreased by increasing the pyrolytic temperature and its highest values were measured in case of biochar produced at low pyrolytic temperature 350 °C (Table 1). Oxidized functional group on biochar particles could lead to high CEC and charge density to retain cations (Liang et al. 2006). The highest CEC of biochars at low temperature (350 °C) might be due to high oxygen-containing functional groups (Table 1) (Wu et al. 2012). Similarly, GWB showed higher values of CEC as compared with PTB at both low and high pyrolytic temperature (Table 1). This might be due to more surface area and more concentration of oxygen-containing functional groups present GWB as compared with PTB (Table 1).

Presence of oxygen-containing functional groups is very important property of biochar regarding

remediation of heavy metal-contaminated water system (Uchimiya et al. 2011a). Concentration of oxygen-containing functional groups depends on feedstock type and pyrolytic temperature used for biochar production. In the present study of biochar characterization, it can be seen that feedstock type and pyrolytic temperature significantly affect the concentration of oxygen-containing functional groups (Table 1). Concentration of oxygen-containing functional groups (carboxylic, lactonic, and phenolic groups) was significantly high when biochar produced at low pyrolytic temperature 350 °C as compared with biochar produced at high pyrolytic temperature 650 °C from both feedstocks, i.e., GW and PT (Table 1). According to Uchimiya et al. (2011a, b), at high pyrolytic temperature, oxygen become volatilized which results in decrease the concentration of oxygen-containing functional groups as can be seen from Table 1. Further, it was confirmed by Han et al. (2013) that most of the oxygen-containing functional groups were volatilized at high pyrolytic temperature for biochar production.

After production and characterization of different biochars, a batch experiment was conducted to select the most effective biochar for water system on the basis of maximum removal of heavy metals (HM), i.e., Pb (II), Cd, and Cr from water system. It was determined after batch experiment that low pyrolytic temperature produced biochars, i.e., GWB350 °C and PTB350 °C showed significantly higher removal of all three HM, i.e., Pb (II), Cd, and Cr from their artificially spiked metal solutions, i.e., both 100 and 10 $\mu\text{g mL}^{-1}$ HM solutions and has higher sorption capacities as compared with high pyrolytic temperature produced biochar, i.e., GWB650 °C and PTB650 °C at all treatment durations (Tables 2 and 3). Further, removal of HM from metal solutions was significantly increased by increasing the treatment duration and statistically maximum removal of Pb (II), Cd, and Cr from metal solutions were measured after 9 hours of treatment duration with low pyrolytic temperature produced biochars. It may be due to complexation that is attraction between HM and oxygen-containing functional groups present in biochar (Choppala et al. 2012). Because oxygen-containing functional groups were present in high concentration in low pyrolytic temperature produced biochars as compared with high pyrolytic temperature produced biochars (Table 1). So, complexation may be the dominant mechanism for HM removals from metal solutions. According to Inyang et al. (2012), low pyrolytic

temperature produced biochar shows higher removal of heavy metals from HM polluted wastewater as compared with high pyrolytic temperature produced biochar due to its high oxygen-containing functional groups. Surface precipitation of HM with different compounds present on the biochar surface, e.g., water soluble phosphate and carbonates is also another mechanism of HM removal from aqueous solution (Cao and Harris 2010). Water soluble phosphate content was present in high concentration in low pyrolytic temperature produced biochars (Table 1) and was decreased significantly from the metal solution with increasing treatment duration (Fig. 2) that might be due to precipitation of HM with phosphate compounds. According Muthusamy et al. (2014), oxygen-containing functional groups donate π electrons to chromium (VI) and reduced it to chromium (III) which sorb on the biochar surface. Low pyrolytic temperature produced biochar showed high concentration of oxygen-containing functional groups (Table 1). So, greater concentration of chromium (VI) reduced into to chromium (III) and sorbed on biochar surface as compared with high pyrolytic temperature produced biochar. Greater removal of HM from metal solution by increasing the biochar treatment duration may be due to high exposure and contact of HM with biochar (Sun et al. 2014; Inyang et al. 2012). According to Ahmad et al. (2014), feedstock type to produce biochar is also very important for HM removal from metal-polluted wastewater. In this study of batch experiment, GWB showed higher removal of heavy metals from aqueous solution as compared with PTB (Table 2).

It was observed that pH and EC of metal solutions (i.e., 100 and 10 $\mu\text{g mL}^{-1}$) were significantly increased by treatment of artificially metals, i.e., Pb (II), Cd, and Cr spiked solutions with high pyrolytic temperature produced biochars, i.e., GWB650 °C and PTB650 °C as compared with low pyrolytic temperature produced biochar (Fig. 1 a, b). This may be due exchange of cations, e.g., Ca, K, Na, etc. present on the biochar surface with HM present in the metal solution (Inyang et al. 2012). So, exchange of metals with cations present on the biochar surface may be a mechanism of the metals removal from aqueous solution of high pyrolytic temperature produced biochar. Similarly, Lu et al. (2012) determined that Pb (II) removal from aqueous solution by using biochar was due to altering pH of the solution. According to Lu et al. (2012), Pb (II) solubility was decreased by increasing the pH of solution. In our study, pH and EC of the metals solutions were

significantly high when treated with high pyrolytic temperature produced biochar as compared with low pyrolytic temperature produced biochar (Fig. 1 a, b). So, this may be another mechanism of metals removal from high pyrolytic temperature produced biochar treated metals solutions. Similarly, carbonate contents were present in high concentration in high pyrolytic temperature produced biochar (Fig. 2 b) which precipitated the heavy metals present in metal-spiked solutions (Xu et al. 2013).

5 Conclusion

It was confirmed from this batch experiment that low pyrolytic temperature produced biochars showed higher removal of heavy metals from water as compared with high pyrolytic temperature produced biochars. Similarly, green waste biochar showed significantly higher removal of HM from aqueous solution as compared with woody feedstock produced biochar due to its better physiochemical properties especially surface area and CEC, and oxygen-containing functional groups characteristics.

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