

# Comparison of Heavy Metal Adsorption by Peat Moss and Peat Moss-Derived Biochar Produced Under Different Carbonization Conditions

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Received: 27 August 2014 / Accepted: 11 December 2014  
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**Abstract** Biochar has attracted recent research interest as a metal adsorbent. The heavy metal adsorption capacity of biochar can be controlled by the carbonization of biochar. The adsorption characteristics of heavy metals (Pb, Cu, and Cd) by peat moss-derived biochars produced under different carbonization conditions were investigated by a series of batch experiments. Biochars were produced by the pyrolysis of peat moss over a temperature range of 400–1000 °C for 30–90 min. Biochar produced at 800 °C for 90 min was the most efficient for the removal of Pb and Cu, when weight loss ratio was considered. The pseudo-second-order and Langmuir models adequately described kinetics and isotherms, respectively, of heavy metal adsorption on peat moss-derived biochar, indicating that heavy metal ions were chemically adsorbed on the adsorption sites as uniform monolayer. The peat moss-derived biochar showed the highest maximum adsorption capacity for Pb (81.3 mg/g), followed by Cd and Cu, which were 39.8 and 18.2 mg/g, respectively. This study shows that peat moss-derived biochar is an effective adsorbent to remediate heavy metal-contaminated water.

**Keywords** Heavy metals · Peat moss · Biochar · Adsorption · Kinetics · Isotherm

## 1 Introduction

Rapid industrialization has increased the release of hazardous pollutants, which transport through various channels and contaminate the surrounding environments. Heavy metals do not degrade in the environment, and they remain in soil and contaminate water bodies. Heavy metals introduced in the environment can accumulate in plants and animals and may cause serious illness (Greener and Kochen 1983; Strubelt et al. 1996). Several remediation techniques are available for metal-contaminated water including chemical precipitation, ion exchange, solution extraction, and biological treatment. However, these remediation techniques are not often cost-effective, require long time to reach remediation goal, and may cause secondary contamination (Seo et al. 2006). Sorption techniques have been broadly used to remove heavy metals from water. Bailey et al. (1999) suggested the use of low-cost materials as a metal adsorbent, requiring little processing, abundant in nature, or a by-product or a waste material from industry. Examples of low-cost adsorbents include bark, lignin, chitin, dead biomass, seaweed, zeolite, clay, fly ash, and peat moss. Peat moss has been reported as an inexpensive adsorbent with high metal sorption capacity (Babel and Kurniawan 2003). However, naturally occurring peat moss is acidic and may decrease pH when mixed with soil, thereby releasing heavy metals.

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Furthermore, secondary organic contaminants may be released by peat moss in water (Inbar et al. 1990). Therefore, peat moss needs to be modified for the remediation of metal-contaminated water and soil.

In recent years, biochar has attracted research interest as a sorption material because of its high sorption capacity for heavy metals. Biochar is a carbon-rich product produced by the carbonization of various waste materials (Altland and Locke 2012; Bonelli et al. 2001; Rajkovich et al. 2012). Choi et al. (2013) tested the heavy metal (Pb, Cu, Cd, and Zn) sorption capacity of biochar produced from sesame seed by-product in metal-contaminated wastewater. Tong et al. (2011) showed that biochar prepared from straws of peanut (*Arachis hypogaea*), soybean (*Glycine max*), and canola (*Brassica napus*) adsorbed Cu through the formation of surface complexes. The maximum sorption capacity of Cu by these biochars was greater than that of a commercially activated carbon (Beesley et al. 2011; Cao and Harris 2010).

The physicochemical properties of biochars vary depending on the raw materials and conditions of biochar production, thus affecting the metal sorption capacity of biochars. Therefore, the identification of the optimum production condition for the heavy metal sorption is critical for the production of biochars. The objectives of this research were to find out the optimal production conditions of peat moss-derived biochar for the heavy metal sorption and to evaluate their adsorption capacity for metals (Pb, Cu, and Cd) in aqueous solution.

## 2 Materials and Methods

### 2.1 Production and Characterization of Biochar

Peat moss was purchased from Russia, and then air-dried, grounded, and sieved (<2 mm). A crucible (50 mL capacity) was filled with 3 g of peat moss and purged with nitrogen for 5 min. The peat moss-derived biochar was produced under various pyrolysis temperatures (400, 600, 800, and 1000 °C) and times (30, 60, and 90 min). The weight loss in peat moss during the carbonization was calculated using Eq. 1 to determine the optimal carbonization condition of peat moss. The structure and morphology of the produced biochars were examined by scanning electron microscopy (SEM, JSM-6701F, JEOL, Tokyo, Japan). The physicochemical properties of the produced biochars under various pyrolysis conditions were assessed by analyzing ash content and C, H,

N, O, and S contents using an elemental analyzer (Flash 2000 Series, Thermo Fisher Scientific). The functional groups of biochars were identified using Fourier transform infrared (FTIR) spectroscopy.

Weight loss of peatmoss (%)

$$= \frac{\text{weight of peat moss} - \text{weight of biochar}}{\text{weight of peat moss}} \times 100 \quad (1)$$

### 2.2 Adsorption of Heavy Metals by Biochars Produced Under Various Carbonization Conditions

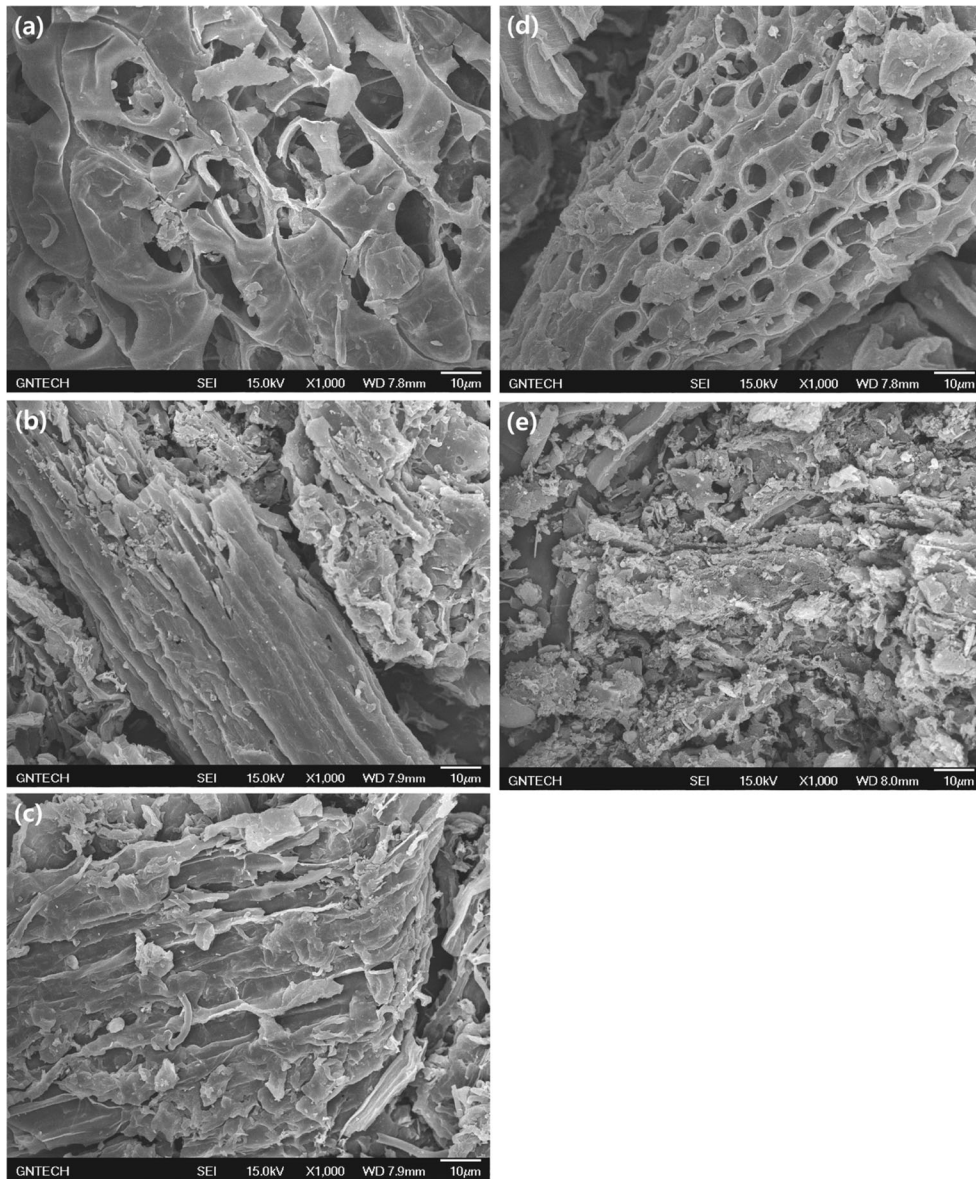
Adsorption of Pb and Cu by peat moss-derived biochar was tested to determine the optimal carbonization condition to produce biochar. Pb and Cu stock solutions (1000 mg/L) were prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> in Milli-Q water, respectively. Working solution (100 mg/L) was prepared by diluting the stock solutions. The sorption equilibrium was attained by shaking 0.2 g of biochar in 200 mL of working solution at 200 rpm in an orbital shaker at 20±1 °C for 48 h. Initial pH was adjusted to pH 5±0.1 by 0.1 M NaOH or HNO<sub>3</sub> solution. After the adsorption, the solution was filtered through a 0.2-µm syringe filter (Advantec MFS, Dublin, USA), diluted with 1 % HNO<sub>3</sub> and Pb and Cu concentrations were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, 8300DV, Perkin Elmer, USA). For the kinetics studies, 200 mL of working solution was added to 0.2 g of biochar in a 250-mL flask and shaken in an orbital shaker for 0, 5, 10, 30, 60, 90, 120, 240, 360, 480, 720, 1440, and 2880 min. Pb, Cu, and Cd stock solutions (1000 mg/L) were prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and Cd(NO<sub>3</sub>)<sub>2</sub> in Milli-Q water, respectively, and working solutions (100 mg/L) were prepared by diluting the stock solutions. For the isotherm studies, 0.2 g of biochar in a 250-mL flask was mixed with 200 mL of Pb, Cu, and Cd solution (10, 30, 50, 100, 200, and 400 mg/L). After shaking the flask for 48 h, the solution was filtered through a 0.2-µm syringe filter and diluted with 1 % HNO<sub>3</sub> solution. The remaining Pb, Cu, and Cd concentrations were analyzed using ICP-OES. The amount of heavy metal adsorbed ( $q_t$ ) at time  $t$  was calculated by Eq. 2.

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (2)$$

where  $C_0$  and  $C_t$  are concentrations of metal ions in the initial solution and aqueous phase at time  $t$  (mg/L),

**Table 1** Effect of carbonization conditions on weight loss of peat moss

Carbonization conditions		400 °C	600 °C	800 °C	1000 °C
30 min	Loss of weight (g)	2.05±0.02	2.31±0.04	2.46±0.04	2.60±0.06
	Loss ratio (%)	68.2±0.8	77.2±1.6	81.9±1.9	86.5±2.5
60 min	Loss of weight (g)	2.22±0.09	2.45±0.11	2.48±0.08	2.68±0.07
	Loss ratio (%)	74.0±3.7	81.7±4.8	82.7±3.6	89.2±2.9
90 min	Loss of weight (g)	2.29±0.09	2.55±0.08	2.54±0.02	2.76±0.02
	Loss ratio (%)	76.2±3.7	84.9±3.5	84.7±0.9	92.0±1.2

**Fig. 1** Scanning electron microscopy (SEM) images of peat moss (a) and peat moss-derived biochars at different carbonization temperatures (b 400 °C, c 600 °C, d 800 °C, e 1000 °C)

respectively.  $V$  is the volume of the solution (L) and  $W$  is the dry weight of biochar added (g). The kinetic analysis of the adsorption data was conducted based on the reaction of Lagergren’s pseudo-first-order kinetic model (Eq. 3), and the pseudo-second-order kinetic model (Eq. 4) (Ho 2006; Lagergren 1898).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{3}$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

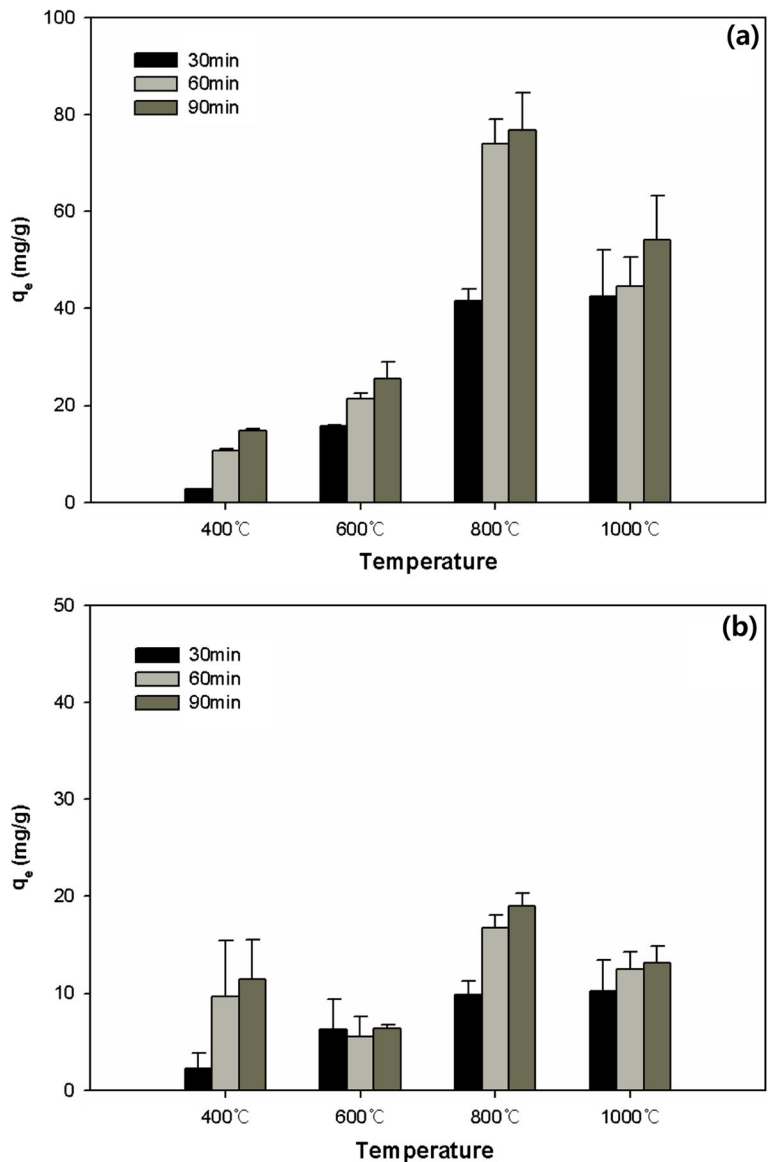
where  $q_e$  is the amounts of metal adsorbed onto adsorbent at equilibrium (mg/g), and  $k_1$  (1/min) and  $k_2$  (g/mg min) are the rate constants of the first-order and second-order kinetics, respectively.

Adsorption isotherm models are widely used to describe adsorption mechanisms. The experimental isotherm data were analyzed by the Langmuir (Eq. 5) and Freundlich (Eq. 6) isotherm models.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

**Fig. 2** Effect of carbonization temperature and time on heavy metal adsorption (a Pb, b Cu). Data presented are mean values with standard deviation ( $n=3$ )



**Table 2** Properties of peat moss (P) and peat moss-derived biochar (CP)

Adsorbent type	Elemental composition (%)						pH	EC (dS/cm)
	C	H	N	S	O	Ash		
P	45.0	5.5	0.8	0	46.4	2.3	3.7±0.2	0.13±0.02
CP	75.3	1.3	0.6	0	13.5	9.3	9.2±0.2	0.44±0.04

where  $C_e$  is the heavy metal concentration in the solution at equilibrium.  $Q^0$  and  $b$  are the maximum adsorption capacity (mg/g) based on the Langmuir isotherms and constant related to the affinity of the binding sites, respectively.  $K_F$  and  $n$  are the measurement of the sorption capacity (mg/g) based on the Freundlich isotherms and the adsorption intensity, respectively (Ünlü and Ersoz 2006). All experiments were conducted in triplicate and data presented are mean values with standard deviation.

### 3 Results and Discussion

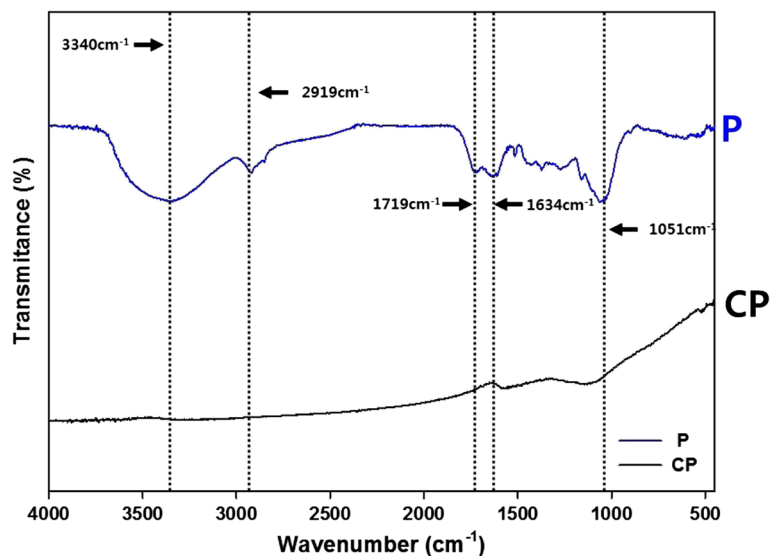
#### 3.1 Characteristics of Biochars Produced Under Various Carbonization Conditions

Table 1 shows the effect of carbonization conditions on the weight loss of peat moss. The weight loss ratio increased with increasing carbonization temperature and time. Hossain et al. (2011) also showed that biochar yield decreased with increasing carbonization temperature from 300 to 700 °C. Increasing weight loss with increasing carbonization temperature and time is

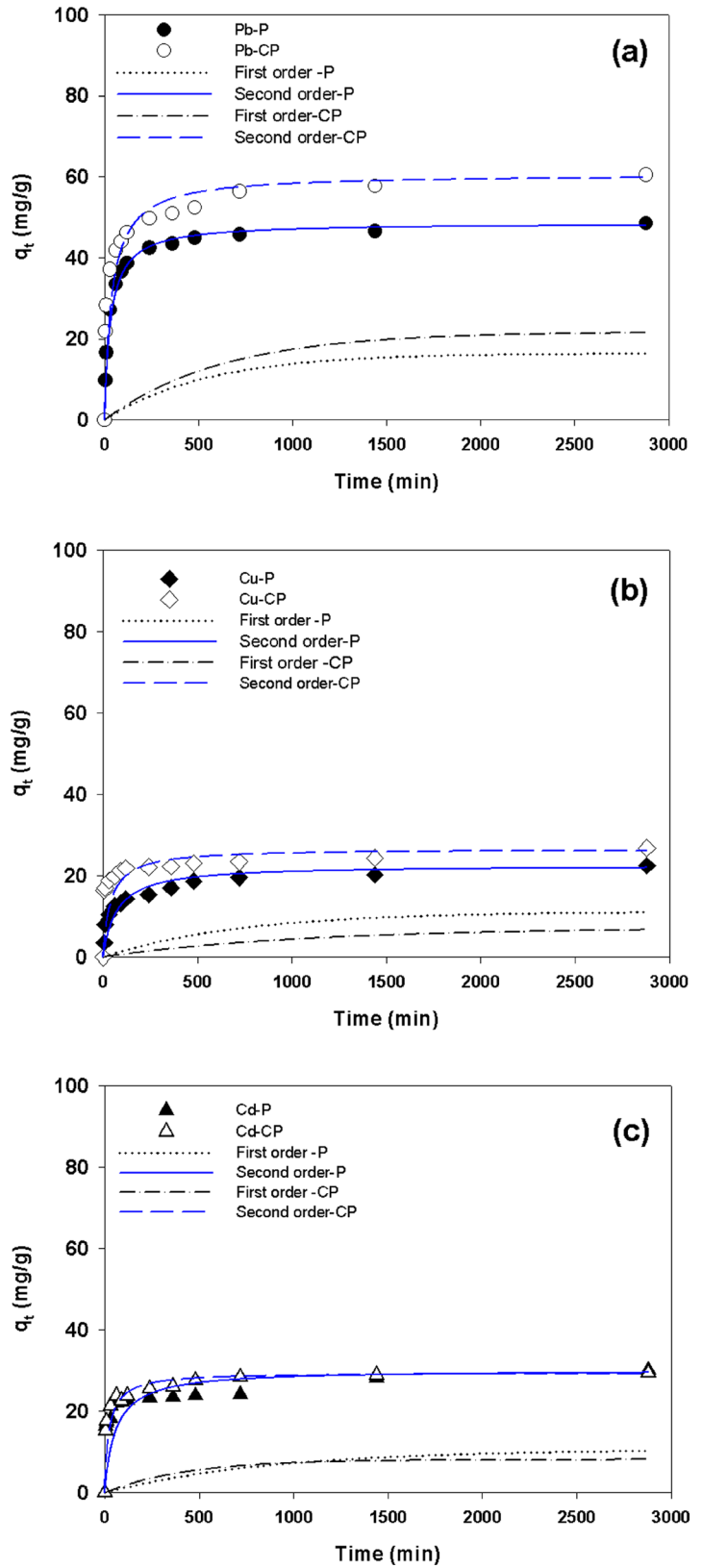
attributed to increasing amount of combustible organic contents. The optimum production conditions should be determined by considering the weight loss because of the cost effectiveness of biochar for heavy metal adsorption. Too high carbonization temperature and long carbonization time are not favorable for the sorption material in terms of weight loss.

The most widely recognized property of peat moss is its highly porous structure (Kim and Kim 2011). The SEM images showed the porous structure of peat moss and peat moss-derived biochars produced under different carbonization temperatures (Fig. 1). Observed structure of peat moss is an assemblage of decayed plant cellular structures interconnected with less decayed fibers (Girardello et al. 2013). The peat moss-derived biochars produced at 400 and 600 °C did not show well-developed porous structure. Lu et al. (1995) also showed that pore structure was not evolved at 650 °C during the carbonization. Yang et al. (2010) showed that tar remained on the surface of biochar and blocked micropores at 400–500 °C, whereas biochar produced at 700 °C presented well-developed pore structure. Tar was decomposed or volatilized and pore size increased at 700 °C. Lee et al. (2010)

**Fig. 3** Fourier transform infrared (FTIR) spectra of peat moss (P) and peat moss-derived biochar (CP)



**Fig. 4** First- and second-order plots for heavy metal adsorption onto peat moss (*P*) and peat moss-derived biochar (*CP*) (**a** Pb, **b** Cu, **c** Cd).  $q_e$  amounts of metal adsorbed onto adsorbent at equilibrium (mg/g)



and Ahmad et al. (2012) also reported that volatile materials were removed by the thermal decomposition, and the surface area increased at relatively high carbonization temperature. Our study confirmed that carbonization of peat moss at 800 °C evolved well-developed porous structures. The peat moss-derived biochar produced at 1000 °C showed micropores; however, most of pore structures were destroyed and contracted.

Lu et al. (1995) and Song (2009) showed that the pore size changed from mesopores to micropores in biochars with increasing carbonization time. The development of micropore during the carbonization is important for the adsorption of heavy metals because it increases the absorption surface area (Lu et al. 1995; Song 2009). Therefore, the carbonization at 800 °C will be the optimal temperature for biochar production as an adsorbent.

Metal adsorption capacity of biochar produced under various carbonization conditions is the most important factor to determine optimal carbonization condition. Figure 2 shows Pb and Cu adsorption capacity of biochars produced under various carbonization conditions. Metal adsorption capacity of biochars increased with increasing carbonization temperature up to 800 °C and time, but decreased at 1000 °C. Therefore, biochar produced at 800 °C for 90 min was the most efficient for the removal of Cu and Pb, when weight loss was considered. This result can be related to well-developed micropores and high surface area of biochar produced at 800 °C as shown in Fig. 1.

### 3.2 Properties of Biochar Produced Under Optimum Carbonization Condition

Characteristics of the biochar produced under optimum carbonization condition (800 °C, 90 min) are compared

with peat moss (Table 2). The carbonization of peat moss increased the pH from 3.65 to 9.15 and electrical conductivity (EC) from 0.13 to 0.44 dS/cm. Increase in pH and EC can be explained by the separation of C and alkali metal salts according to Shinogi and Kanri (2003) and Cao and Harris (2010). Yuan et al. (2011) also reported increased pH of biochars produced from the crop residues compared to feed materials with increased pyrolysis temperature, indicating that carbonate and functional groups such as  $-\text{COO}^-$  and  $-\text{O}^-$  present in the biochars were the major alkaline components, thus contributing to the high pH of the biochar.

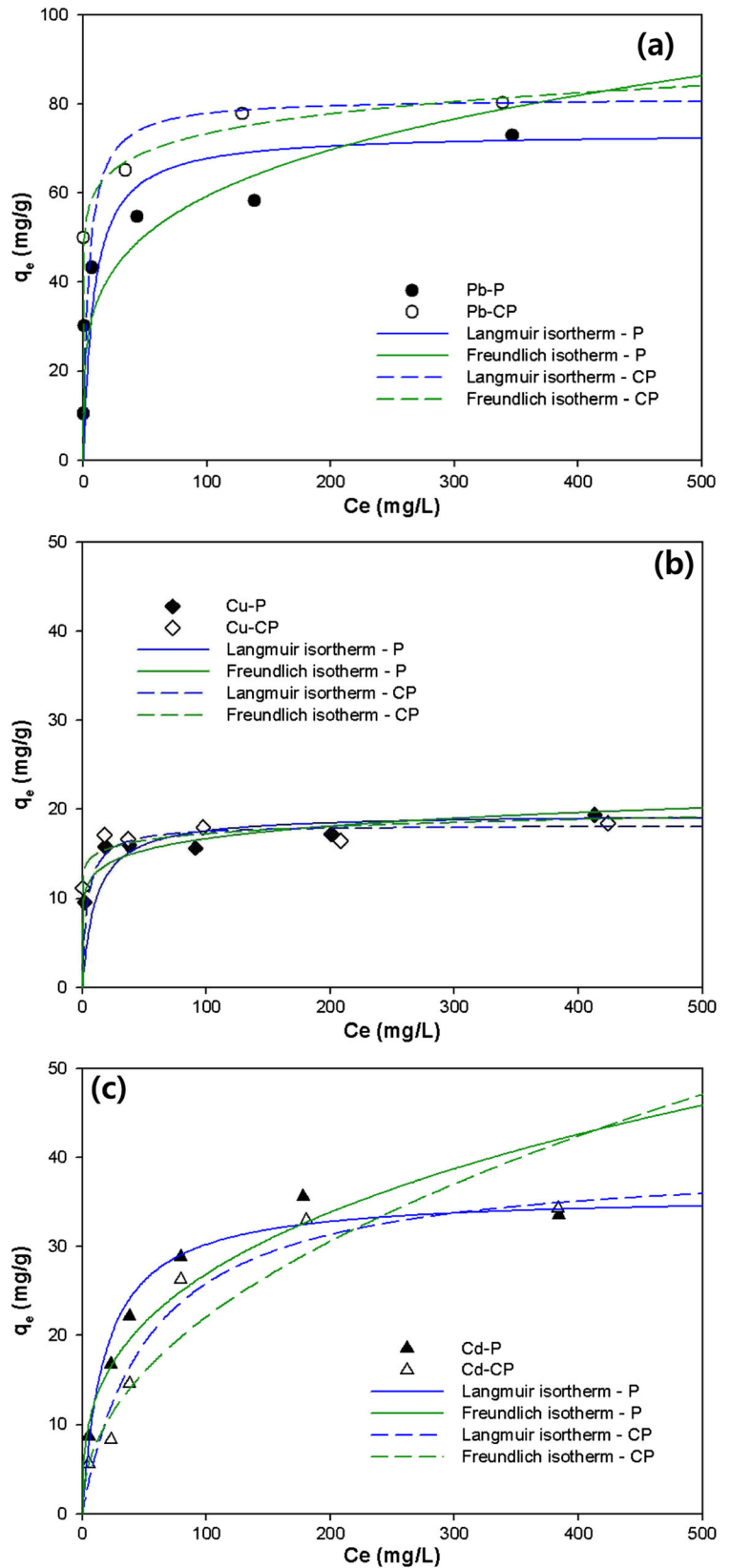
The elemental analysis (C, H, N, S, and O) of biochar showed that C content of biochar increased, and the ratio of H, N, and O in biochar decreased in comparison to peat moss (Table 2). Similarly, Abdullah and Wu (2009) indicated that the carbonization of mallee wood (*Eucalyptus polybractea*) increased C content from 60.3 % at 300 °C to 85.5 % at 500 °C and decreased other elemental contents (H, N, S, and O) than that of raw material. N and H were removed by the loss of volatile species, and the transformation of organic N in the form of amine functionalities to pyridine-like structure at low temperature, increased the basicity of the surface (Bagreev et al. 2001).

The nature of the functional groups in the peat moss and peat moss-derived biochar was identified by the FTIR spectroscopy (Fig. 3). The FTIR spectrum of peat moss-derived biochar showed peaks at 1634 and 1051  $\text{cm}^{-1}$ , indicating lignite aromatic C=C and polysaccharides C–O absorption bands, respectively, which were also present in the FTIR spectra of the peat moss. The absorption peaks at 3340  $\text{cm}^{-1}$  in peat moss spectra indicate the presence of hydroxyl ( $-\text{OH}$ ) group in the humic substance. The IR absorption peaks at 2912 and

**Table 3** First-order and second-order kinetic parameters for the adsorption of Pb, Cu, and Cd onto peat moss (P) and peat moss-derived biochar (CP)

Heavy metal	Adsorbent	$q_e(\text{exp.})$ (mg/g)	First-order rate constants			Second-order rate constants		
			$k_{\text{ad}}$ (1/min)	$q_e(\text{cal.})$ (mg/g)	$R^2$	$k_2$ (g/mg·min)	$q_e(\text{cal.})$ (mg/g)	$R^2$
Pb	P	48.4	0.0018	16.5	0.7077	0.0006	48.5	0.9997
	CP	60.5	0.0016	21.8	0.8311	0.0004	60.6	0.9991
Cu	P	22.5	0.0014	11.2	0.8057	0.0006	22.5	0.9968
	CP	26.8	0.00092	7.18	0.7505	0.0009	26.6	0.9973
Cd	P	30.2	0.0012	10.6	0.8619	0.0005	30.1	0.9954
	CP	29.4	0.0023	8.12	0.8994	0.001	29.5	0.9998

**Fig. 5** Adsorption isotherms of heavy metals onto peat moss (*P*) and peat moss-derived biochar (*CP*) (**a** Pb, **b** Cu, **c** Cd).  $q_e$  amounts of metal adsorbed onto adsorbent (mg/g),  $C_e$  heavy metal concentration in the solution at equilibrium





1719  $\text{cm}^{-1}$  represent C–H and C=O, respectively. The disappearance of these peaks in the biochar spectrum can be attributed to the loss of cellulosic content (Herbert et al. 2012). The FTIR spectroscopic results of the peat moss correspond to polymethylenic ( $-\text{CH}_2$ ), carboxyl ( $-\text{COOH}$ ), lignite aromatic C=C, and polysaccharides C–O functional groups (Lee 2005).

### 3.3 Heavy Metal Adsorption Characteristics of Peat Moss and Peat Moss-Derived Biochar

The experimental metal adsorption data were fitted to pseudo-first-order (Eq. 3) and pseudo-second-order (Eq. 4) kinetic models. The adsorption of Pb, Cu, and Cd reached to equilibrium within 240 min (Fig. 4). Both the peat moss and peat moss-derived biochar showed the highest adsorption capacity of 48.4 and 60.5 mg/g, respectively for Pb at equilibrium. The adsorption of Cu by the peat moss-derived biochar (26.8 mg/g) was slightly higher than that of the peat moss (22.4 mg/g), but there was no significant difference in Cu adsorption. In addition, the adsorption of Cd by peat moss (30.2 mg/g) and peat moss-derived biochar (29.4 mg/g) was not significantly different. The adsorption of Cu and Cd is not much affected by the pH increase of biochar while Pb adsorption is sensitive to pH, and Pb easily precipitates at alkaline pH. The experimental value of the adsorption at equilibrium ( $q_e$  (exp.)) was very close to that of the calculated value ( $q_e$  (cal.)) from the second-order kinetic model (Table 3).

The correlation coefficient ( $R^2$ ) values of the pseudo-first-order kinetics were 0.831, 0.750, and 0.899 for Pb, Cu, and Cd, respectively. The experimental values of  $q_e$  (exp.) were far from the calculated ones,  $q_e$  (cal.). Correlation coefficient ( $R^2$ ) values of the pseudo-second-

order kinetics were 0.999, 0.997, and 0.999 for Pb, Cu, and Cd, respectively, and were higher than those of the pseudo-first-order kinetics (Table 3). Therefore, the pseudo-second-order model better described the kinetics of Pb, Cu, and Cd adsorption by the peat moss-derived biochar than the pseudo-first-order model, indicating that the adsorption rate of heavy metals by the peat moss and peat moss-derived biochar is determined by the chemical adsorption or chemisorption involving valence forces by sharing or exchange of electrons between the adsorbent and metals rather than physical adsorption (Aksu 2002; Ho and McKay 1999).

The equilibrium data of the peat moss-derived biochar and peat moss were analyzed by the Langmuir and Freundlich isotherm models (Fig. 5). Parameters from the isotherm models are shown in Table 4. The correlation coefficient ( $R^2$ ) values obtained from the Langmuir model were 0.999, 0.996, and 0.977 for Pb, Cu, and Cd adsorption by peat moss-derived biochar, whereas the correlation coefficient ( $R^2$ ) values from the Freundlich model were 0.982, 0.842, and 0.923 for Pb, Cu, and Cd, respectively. Similarly, the correlation coefficient ( $R^2$ ) values from the Langmuir model for Pb, Cu, and Cd adsorption by peat moss were higher than those from the Freundlich model. Therefore, the heavy metal adsorption by biochar and peat moss can be explained better by the Langmuir isotherm. These results indicate that heavy metal ions are chemically adsorbed as uniform monolayer on the adsorption sites of the peat moss and peat moss-derived biochar (Ruthven 1984).

The maximum adsorption capacity of Pb by the peat moss-derived biochar was higher than that by the peat moss, which might be attributed to a higher pH of biochar. Increasing pH increases the negative charges on surface of the adsorbent, thereby increasing the

**Table 4** Langmuir and Freundlich isotherm parameters for the adsorption of Pb, Cu, and Cd on peat moss (P) and peat moss-derived biochar (CP)

Metal	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		$Q^0$	$b$	$R^2$	$K_F$	$n$	$R^2$
Pb	P	73.5	0.117	0.9901	20.3	4.29	0.9809
	CP	81.3	0.229	0.9995	49.7	11.8	0.9828
Cu	P	19.5	0.094	0.9952	9.75	8.57	0.8661
	CP	18.2	0.245	0.9968	12.83	15.6	0.8427
Cd	P	35.8	0.0541	0.9958	5.87	3.02	0.9203
	CP	39.8	0.0185	0.9774	2.53	2.13	0.9230

adsorption of metals. The maximum adsorption capacities of Cu and Cd by the peat moss and peat moss-derived biochar were not significantly different, indicating that Cu and Cd adsorption was not much affected by increasing pH. The maximum adsorption capacities of Pb, Cu, and Cd by peat moss-derived biochar acquired by the Langmuir isotherm were 81.3, 18.2, and 39.8 mg/g, respectively, and were quite higher than the maximum adsorption capacity of biochars produced from other raw materials. Huanliang et al. (2012) showed that the sludge-derived biochar removed Pb from acidic solution with capacities in the range 16.1–30.8 mg/g. Xincal et al. (2011) reported that the maximum adsorption capacities for Cu and Zn by biochars derived from hardwood and corn (*Zea mays*) straw were 12.5 and 11.0 mg/g for corn straw, and 6.79 and 4.54 mg/g for hardwood, respectively. Therefore, peat moss-derived biochar can be used as an effective adsorbent for heavy metals in contaminated water. The metal sorption capacity of the peat moss-derived biochar also implies its possible application for the remediation of metal-contaminated soils.

#### 4 Conclusions

The peat moss-derived biochar produced at 800 °C for 90 min was the most efficient for the removal of heavy metals, when the weight loss ratio and metal adsorption capacity were considered, which might be attributed to a well-developed porous structure. The sorption of Pb, Cu, and Cd on the peat moss and peat moss-derived biochar followed the pseudo-second-order reaction kinetics and Langmuir isotherm models. The removal of Pb by the peat moss-derived biochar was higher than the removal by the peat moss. Comparison of the heavy metal sorption capacity by the peat moss and peat moss-derived biochar showed that biochar enhanced metal adsorption by developing a porous structure and increasing pH. The maximum adsorption capacities of Pb, Cu, and Cd by peat moss-derived biochar were 81.3, 18.2, and 39.8 mg/g, respectively, which were relatively higher than those of biochars produced from other feed materials in the literature. The obtained results confirm that the peat moss-derived biochar can be used as a cost-effective adsorbent to remediate heavy metal-contaminated water.

**Acknowledgements** This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education [No. 2012R1A1A4A01014928] and the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science, ICT and Future Planning of Korea.

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