**Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from
KMnO₄ treated hickory wood**

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Abstract

In this work, a novel approach was developed to prepare an engineered biochar from KMnO_4 treated hickory wood through slow pyrolysis ($600\text{ }^\circ\text{C}$). Characterization experiments with various tools showed that the engineered biochar surface was covered with MnO_x ultrafine particles. In comparison to the pristine biochar, the engineered biochar also had more surface oxygen-containing functional groups and much larger surface area. Batch sorption experiments showed that the engineered biochar had strong sorption ability to Pb(II) , Cu(II) , and Cd(II) with maximum sorption capacities of 153.1, 34.2 and 28.1 mg/g, respectively, which were significantly higher than that of the pristine biochar. Batch sorption experiments also showed that the dosage, initial solution pH, and ionic strength affected the removal of the heavy metals by the biochars. The removal of the metals by the engineered biochar was mainly through surface adsorption mechanisms involving both the surface MnO_x particles and oxygen-containing groups.

Keywords: biochar; lead; copper; cadmium; heavy metals; biosorption

1. Introduction

With the rapid development of industrial activities, a large amount of industrial effluents containing heavy metals are released into surface and underground water, which has resulted in a number of environmental problems(Barakat, 2011). Heavy metals such as lead, copper, and cadmium are toxic and non-biodegradable; they can accumulate in living organisms, and may thus pose a threat to human health(Kumar et al., 2014).Therefore, it isvery important to develop effective technologies to treat heavy metal pollutedwastewater before their discharge into natural environment.

Although advanced water treatmenttechnologiesprovide many good solutions to remove heavy metals, most of them may be associated with high operating cost and/or sludge disposal problems(Fu & Wang, 2011).Adsorption is considered a cost-effective choice for heavy metal removal from wastewater, especially at medium or low ion concentrations because it is economical, easy to handle and highly efficient(Hu et al., 2015; Inyang et al., 2012).Many studies have suggested biosorbents derived from waste biomass such as agricultural residues are a promising alternative agent for the treatment of heavy metals while reducing both preparation and running costs(Demirbas, 2008; Zhou et al., 2014).

Biochar, a pyrogenic carbon material derived from biomass, is one of the biosorbents that has received increased attention recently because of its strong affinity for various contaminants in water(Wang et al., 2015b; Yao et al., 2012; Zhou et al., 2014). Biochars produced from

waste biomass such as agricultural and forestry residues have shown good sorption ability to a variety of heavy metal ions in aqueous solutions (Ahmad et al., 2014; Mohan et al., 2014). Recently, techniques have been developed to produce engineered biochars with enhanced sorption ability to heavy metals as well as other contaminants in water. The engineered biochars are prepared through either surface modification of pristine biochars or direct pyrolysis of pretreated biomass feedstocks (Wang et al., 2015a; 2015b; Zhang et al., 2013b; 2012). These two methods, particularly the later, are not only facile and cost-effective, but also suitable for large-scale productions and can thus provide high-efficiency adsorptions for the treatment of heavy metals in water. Wang et al. (2015b) prepared a magnetic biochar by pyrolyzing wood pretreated with hematite. The engineered biochar not only has a strong magnetic property, but also shows much greater ability to remove As(V) from aqueous solution than the pristine biochar. Similarly, engineered biochars have been produced from various metal ion treated biomass and can be used as effective adsorbents for heavy metals as well as other contaminants in water (Yao et al., 2013; Zhang & Gao, 2013; Zhang et al., 2013a).

In this work, for the first time, a novel engineered biochar was synthesized through direct pyrolysis of hickory wood pretreated with potassium permanganate (KMnO_4) for the removal of heavy metals from water. Because KMnO_4 is not only a strong oxidizing agent but also a precursor of manganese oxide (MnO_x) (Zou et al., 2006), the oxidation reaction may promote the incorporation of the precursor into the feedstock, forming the novel engineered biochar after

pyrolysis. A range of experiments was conducted to evaluate the sorption ability of the biochar to Pb(II), Cu(II), and Cd(II) in aqueous solutions. The objectives of this work were as follows:

1) prepare and characterize the engineered biochar; 2) assess the adsorption ability of the biochar to lead, copper, and cadmium; and c) determine the effects of initial solution pH, sorbent dosage, and ionic strength on the adsorption of the heavy metal onto the biochar.

2. Materials and Methods

2.1. Materials

All chemicals and reagents used in this work were of analytical grades and solutions were prepared using deionized (DI) water (18.2 MΩ) (Nanopure water, Barnstead). Lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), potassium permanganate (KMnO_4) were purchased from Fisher Scientific. Hickory chips were collected from a local farm in Gainesville, FL to be used as the feedstock biomass. Dried hickory chips were milled to obtain powders between 0.5 mm and 1 mm prior to use.

2.2. Biochar production

To make the engineered biochar, 20g of the biomass feedstock were immersed in 100 mL of a 0.1 mol/L KMnO_4 solution under ultrasonic irradiation for 2 h. The mixture was then oven dried

at 80°C for 24h. The KMnO_4 -treated biomass was then pyrolyzed in a tube furnace under N_2 flow at a temperature of 600°C for one hour. The obtained biochar sample (MHB) was rinsed with DI water several times, oven dried at 80°C, and placed in an air-tight container prior to use. Unmodified hickory biochar (HB) was prepared from untreated biomass for comparison.

2.3. Biochar characterization

Carbon (C), hydrogen (H), and nitrogen (N) contents in the samples were analyzed using a CHN Elemental Analyzer (Carlo-Erba NA-1500). Surface areas of the samples were determined with a Quantachrome Autosorb-1 surface area analyzer using Brunauer-Emmett-Teller (BET) method. Surface morphology of the samples was determined using scanning electron microscopy (SEM) (JEOL JSM-6400, Japan) equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford Instruments Link ISIS) for analyzing surface elements. In addition, surface elemental composition was determined by using XPS with a PHI 5100 series ESCA spectrometer (Perkin Elmer). A computer-controlled X-ray diffractometer (XRD) (Philips APD 3720) equipped with a stepping motor and graphite crystal monochromator was used to investigate the crystalline Mn minerals in char samples.

2.4. Adsorption kinetics and isotherms

Adsorption kinetics of Pb(II), Cu(II) and Cd(II) onto the biochar samples were investigated by adding 0.05 g of each adsorbent to 68 mL digestion vessels (Environmental Express) containing 25 mL of each heavy metal solution at room temperature (22 ± 0.5 °C). Pb(II), Cu(II) and Cd(II) concentrations were 100, 30, and 30 mg/L, respectively. The vessels were then shaken at 50 rpm in a mechanical shaker. At different time intervals (0, 0.5, 1, 2, 4, 8, 12, 24 and 48 h), vessels were withdrawn and the mixtures were subsequently filtered through 0.22 μ m pore size nylon membrane filters (GE cellulose nylon membrane). Heavy metal concentrations in the filtrates were determined by using inductively coupled plasma-atomic emission spectrometry ((ICP-OES, Optima 2300, Perkin-Elmer SCIEX, USA). The amounts of heavy metals sorbed onto the biochar samples were calculated based as the differences between initial and final aqueous concentrations.

Adsorption isotherms of Pb(II), Cu(II) and Cd(II) onto the biochar samples were determined by adding 0.05 g adsorbent to 68 mL digestion vessels (Environmental Express) containing 25 mL of each heavy metal solution at room temperature (22 ± 0.5 °C). Pb(II) concentration in the digestion vessels ranged from 2 to 500 mg/L, while Cu(II) and Cd(II) concentrations ranged from 2 to 250 mg/L. The vessels were shaken in the mechanical shaker for 24 h at room temperature, and the samples were then withdrawn and subsequently filtered to determine Pb(II), Cu(II) and Cd(II) concentrations in the filtrate by the same method. Some of the post-adsorption

adsorbents were collected, rinsed with deionized water, and dried at 80 °C for further characterization tests.

The kinetic and isotherm experiments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference of more than 5%.

2.5. Effects of dosages, pH, and ionic strength

The effect of adsorbent dosage on Pb(II), Cu(II), and Cd(II) adsorption was studied by adding different amounts of biochar (1, 2, 4, 10, and 20 g/L) to 68 mL digestion vessels containing 25 mL of each heavy metal solution. At the adsorbent dosage of 2 g/L, the pH and ionic strength effects were determined by varying solution pH (2-7) and NaCl concentration (0-0.1 M), respectively. Pb(II), Cu(II), and Cd(II) concentrations in the system were 100, 35, and 30 mg/L, respectively. After 24 h shaking in the mechanical shaker at room temperature, the same procedures were then used to determine metal concentrations in filtrates.

3. Results and Discussion

3.1 Physiochemical properties

The C, H, and N contents of engineered biochar were 66.10%, 1.49%, and 0.03%, respectively; these were all lower than that of the pristine biochar (81.81%, 2.17%, and 0.73%,

respectively). The reduction of CHN in the biochar after the pretreatment might be due to the strong oxidating effect of KMnO_4 on the feedstock. On the other hand, loading of MnO_x particles onto the surface of the engineered biochar might also reduce the proportion of other elements, which is similar to the findings of previous studies of biochar-base composites (Inyang et al., 2015; Wang et al., 2015b). SEM-EDS analysis confirmed the occurrence of Mn on the surface of the engineered biochar (as ultrafine particles), as the EDS spectra showed a strong peak of Mn (Figure S1, Supplementary Materials). Previous studies have shown that, under high temperature conditions, KMnO_4 can be converted into MnO_x particles (Hebeish et al., 2011; Zou et al., 2006). The XRD analysis confirmed that the Mn on the surface of the engineered/modified biochar was in various forms of MnO_x . Although the engineered biochar showed poor crystallinity (Figure S2, Supplementary Materials), its XRD peaks at $d=4.931, 3.048, 1.538, \text{ and } 1.439 \text{ \AA}$ were assigned to $\alpha\text{-MnO}_2$, and at $d=2.489, 1.570, 1.279 \text{ \AA}$ were corresponding to Mn_3O_4 (Cantu et al., 2014; Feng et al., 2014; Tang et al., 2006), indicating that pyrolysis of the KMnO_4 -treated biomass produced MnO_x -biochar composites.

The XPS analysis also showed the abundance of Mn on the engineered biochar surface (Figure S3, Supplementary Materials). In comparison to the pristine biochar, the surface C content of the engineered biochar decreased, which is consistent with the elemental composition analysis. The O content on the surface, however, increased greatly after the modification, probably because the KMnO_4 treatment process introduced MnO_x particles and/or additional

oxygen containing groups on the engineered biochar surface. A detailed XPS scan of the Mn2p of the engineered biochar sample showed two peaks at the binding energy of around 641.65 and 653.5 eV (Figure S4, Supplementary Materials). The locations of the two peaks and their separation (~11.8 eV) suggested the Mn exhibited oxidation state between Mn^{3+} and Mn^{4+} , which is consistent with the XRD data and findings from previous studies (Song et al., 2014). A detailed XPS scan of the C1s of the biochar samples showed three peaks (Figure S5, Supplementary Materials), corresponding to the graphite C (284.89/284.95 eV), C-O (286.48/286.34 eV), and O=C-O (288.76/288.48 eV) (Datsyuk et al., 2008; Xia et al., 2015). After the modification, the atomic contents of C-O and O=C-O on the engineered biochar surface increased from 22.32 % to 23.34% and 5.81% to 8.81%, respectively, indicating the increase in both hydroxyl and carboxyl functional groups on the biochar surface is due to the oxidating effect of $KMnO_4$ (Xia et al., 2015). These results suggested that the engineered biochar would probably have better metal sorption ability than the pristine biochar because both MnO_x and oxygen-containing functional groups have strong bonding affinity to heavy metal ions in aqueous solution (Chen et al., 2011).

After the modification, the BET surface area of the biochar doubled. The engineered biochar had a surface area of 205 m^2/g , much higher than that of the pristine biochar (101 m^2/g). Previous studies have shown that both the presences of metal oxide particles and oxidation of feedstock can increase of the surface area of biochar (Zhang et al., 2012). In general, biochars with higher surface area tend to have larger sorption capacity to contaminants (Wang et al.,

2015c). The characterization data indicated that potassium permanganate modification improved the surface properties of the biochar for its application as an adsorbent for environmental applications.

3.2. Adsorption kinetics and isotherms

Pb(II), Cu(II), and Cd(II) sorption kinetics on the engineered and pristine biochars showed two distinct phases: a rapid initial phase over the first few hours and a much slow sorption phase to reach equilibrium (Figure 1). For all the tested metal cations, about 50% sorption occurs within the first few hours. The sorption of metals on the engineered biochar was faster and higher than that of the pristine biochar. Pseudo-first-order, pseudo-second-order, Elovich, and Ritchie n -th-order models were used to simulate the sorption kinetics data (Table 1). Pb(II) and Cd(II) sorption on the engineered biochar was best fitted by the n -th-order model with $R^2 > 0.98$ (Table 1). For copper sorption, the Elovich models fitted the data slightly better than other models (Table 1). The modeling results suggested that the adsorption of heavy metals onto the engineered biochar might be controlled by multiple mechanisms. This was probably because both the metal oxides and functional groups on biochar surface can serve as adsorption sites for the metals. Based on the best-fit parameters of the Ritchie n -th-order model, the adsorption rate constant (k) of Pb(II) and Cd(II) of engineered biochar were more than 4892 and 3 times greater than that of pristine biochar, respectively. For Cu(II), the initial adsorption rate (α) of the Elovich

model of the engineered biochar was 563 times greater than that of pristine biochar. The model results showed that the engineered biochar had greater affinity to the three metals than the pristine biochar.

Adsorption isotherms of Pb(II), Cu(II), and Cd(II) onto the biochars were all typical “L” shape and showed plateaus at high equilibrium concentrations (Figure 2). For all the metals, the engineered biochar showed much higher sorption capacity than the pristine biochar, indicating the KMnO₄ treatment of the feedstock increased the sorptive ability of the biochar. Three commonly used isotherm equations were used to describe the experimental isotherms (Table 1). The Langmuir maximum sorption capacities of the engineered biochar to Pb(II) was above 150mg/g, which was about 2.1 times greater than that of pristine biochar. In addition, the maximum Cu(II) and Cd(II) sorption capacity of engineered biochar were also about 2.8 and 5.9 times greater than that of pristine biochar, respectively (Table 1). These results confirmed that the modification enhanced the sorption ability of the biochar to heavy metals in aqueous solutions. The maximum sorption capacities of the engineered biochar are similar or even higher than that of many other commonly used adsorbents reported in the literature (Table S1, Supplementary Materials), indicating the KMnO₄ modified biochar can be used as an effective adsorption for heavy metal remediation. Among all three of the isotherm models, the Redlich-Peterson models reproduced the adsorption isotherm data (Table 1), which also suggests that the sorption of heavy metals on the engineered biochar might be governed by multiple mechanisms.

3.3. Effects of sorbent dosage, pH, and ionic strength

The rates of heavy metal removal all increased with increasing biochar dose at a constant Pb(II), Cu(II), and Cd(II) concentration (Figure 3). For Pb(II), the removal rate increased from 91.8% to 98.5% when the engineered biochar dose went from 1 to 2 g/L, and with continued increment in dosage, the removal rate increased marginally. For Cu(II) and Cd(II), their removal rates increased from 63.1% to 93.2% and 79.1% to 95.9%, respectively, when the engineered biochar dose went from 1 to 2 g/L. A similar stable trend was observed for the removal rate from aqueous solution when continuing to increase the dose. Based on these results, the appropriate dose of the engineered biochar for the heavy metal removal was found to be 2 g/L.

Changes in initial solution pH significantly affected Pb(II), Cu(II), and Cd(II) sorption onto both the engineered and pristine biochars (Figure 4). In general, the removal of the metals by the biochars increased gradually with increasing pH. When the pH was beyond 6, the metal removal rates by the engineered biochar reached peaks and did not change much with pH. This result is similar to the findings of Inyang et al. (2012) that, when the initial solution pH is above 7, it has little effect on the removal of heavy metal ions from aqueous solutions by biochars derived from anaerobically digested biomass. At low solution pH values, both MnO_x particles and oxygen containing groups (e.g., carboxyl and hydroxyl) on the engineered and pristine biochar surfaces might be positively or neutral charged, which hindered the adsorption of positively charged

metal ions. As a result, increasing in pH promoted the removal the heavy metals in this work. Previous studies have shown that pH-dependent surface charges play an important role in controlling the surface adsorption of heavy metal ions through electrostatic interactions (Ahmad et al., 2014; Wang et al., 2015b). When the pH was higher than 6, Pb(II), Cu(II), and Cd(II) were almost completely removed, indicating other mechanisms such as precipitation might affect the heavy metal removal process. Previous studies have shown that precipitation can play an important role in controlling the removal of heavy metal ions from aqueous solution by biochars (Inyang et al., 2012; 2011). Furthermore, lead and copper start precipitating (as Pb(OH)₂ and insoluble tenorite), when solution pH is higher than 5.8 (Tiwari et al., 2011).

When solution ionic strength increased, the removal rates of metal ions by the biochars decreased (Figure 5). For Pb(II) sorption, the removal rate by the engineered biochar decreased from 96.0 to 91.2% as the ionic strength increased from 0.01 to 0.1 mol/L. The removal of Cu(II) and Cd(II) by the engineered biochar also dramatically decreased with the increasing of ionic strength from 0.01 to 0.1 mol/L. These might be attributed to the fact that metal ions and sodium ions may compete for the same adsorption sites. For specific adsorption sites, cationic metals are preferentially adsorbed over the sodium ion. When the specific adsorption sites become saturated, however, exchange reactions dominate and competition for these sites between metal ions and sodium ions become important (Liu et al., 2014; Sone et al., 2009). Previous studies have demonstrated that adsorption of Cr(II) or Cu(II) onto clay mineral decreased in the presence of

0.5-5.0% of KCl, NaCl, and NH_4Cl , due to competition between metal ions with Na^+ , K^+ , NH_4^+ for adsorption sites (El-Bayaa et al., 2009).

3.6. Adsorption mechanisms

The XRD spectra of the post-adsorption engineered biochar loaded with Pb(II) showed no evidence of precipitates in the MnO_x -loaded biochar (Figure S6, Supplementary Materials), suggesting that the precipitation was not an important mechanism for Pb(II) removal. Compared with pristine biochar, the amount of oxygen-containing groups such as hydroxyl groups, phenolic hydroxyl and carboxyl functional groups increased significantly on the surface of the engineered biochar after the KMnO_4 pretreatment of the feedstock. In addition, the engineered biochar surface was also covered with ultrafine manganese oxide ($\text{MnO}_2/\text{Mn}_3\text{O}_4$) particles. In this work, both the functional groups and the MnO_x particles could serve as the main adsorption sites for heavy metal ions in aqueous solutions. As a result, the engineered biochar showed much stronger binding affinity to the three heavy metal ions than the pristine biochar.

4. Conclusions

A novel engineered biochar was derived from biomass feedstock pretreated with KMnO_4 . The pretreatment not only introduced ultrafine MnO_x particles on the carbon surface within the biochar matrix, but also increased the amount of oxygen-containing surface functional groups.

As a result, the engineered biochar showed much better sorption ability to Pb(II), Cu(II) and Cd(II) than the pristine biochar. Although dosage, pH, and ionic strength affected the removal rates, the engineered biochar effectively removed all three heavy metals under all of the tested conditions.

The pretreatment method thus can be used to prepare high-efficiency biochars from biochar for heavy metal remediation.

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Table 1. Best-fit parameters for kinetics and isotherm models of heavy metal sorption onto the biochar samples.

Adsorbate	Kinetics and Isotherm models/Equations*	Biochar	Parameter-1	Parameter-2	Parameter-3	R^2
Pb(II)	First-order	HB	$k_1=6.4475$	$q_e=23.911$	-	0.196
	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	MHB	$k_1=9.354$	$q_e=51.353$	-	0.435
	Second-order	HB	$k_2=0.438$	$q_e=24.873$	-	0.550
	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	MHB	$k_2=0.577$	$q_e=52.132$	-	0.835
	Elovich	HB	$\alpha=5241262$	$\beta=0.702$		0.943
	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	MHB	$\alpha=4.028 \times 10^{17}$	$\beta=0.819$		0.940
	Richie	HB	$k_n=2.565 \times 10^{-6}$	$q_e=31.896$	$N=7.328$	0.891
	$\frac{dq_t}{dt} = k_n(q_e - q_t)^N$	MHB	$k_n=0.0125$	$q_e=54.775$	$N=4.424$	0.98
	Langmuir	HB	$K=0.00201$	$S_{\max}=71.43$		0.882
	$q_e = \frac{KS_{\max}C_e}{1 + KC_e^n}$	MHB	$K=0.00508$	$S_{\max}=153.109$		0.974
	Freundlich	HB	$K_f=0.865$	$n=0.597$		0.908
	$q_e = K_f C_e^n$	MHB	$K_f=3.809$	$n=0.552$		0.931
	Redlich-Peterson	HB	$K_r=17800$	$S_{\max}=0.865$	$n=0.403$	0.908
	$q_e = \frac{K_r C_e}{1 + a C_e^n}$	MHB	$K_r=0.000179$	$S_{\max}=3302.23$	$n=1.484$	0.981
Cu(II)	First-order	HB	$k_1=0.622$	$q_e=7.001$		0.842
		MHB	$k_1=2.326$	$q_e=13.725$		0.526
	Second-order	HB	$k_2=0.117$	$q_e=7.603$		0.907
		MHB	$k_2=0.264$	$q_e=14.454$		0.794
	Elovich	HB	$\alpha=31.968$	$\beta=0.879$		0.936
		MHB	$\alpha=17991.69$	$\beta=0.866$		0.951
	Richie	HB	$k_n=8.614 \times 10^{-5}$	$q_e=11.91$	$N=6.175$	0.941
		MHB	$k_n=1.014 \times 10^{-5}$	$q_e=19.994$	$N=7.095$	0.948
	Langmuir	HB	$K=0.029$	$S_{\max}=12.297$		0.945

Cd(II)	Freundlich	MHB	$K=0.0182$	$S_{\max}=34.205$		0.966
		HB	$K_f=1.631$	$n=0.352$		0.874
		MHB	$K_f=2.574$	$n=0.443$		0.959
	Redlich-Peterson	HB	$K_r=0.00137$	$S_{\max}=151.395$	$n=1.447$	0.965
		MHB	$K_r=0.0964$	$S_{\max}=10.206$	$n=0.79$	0.973
	First-order	HB	$k_1=4.178$	$q_e=6.788$		0.539
		MHB	$k_1=3.165$	$q_e=14.274$		0.596
	Second-order	HB	$k_2=1.737$	$q_e=6.931$		0.780
		MHB	$k_2=0.465$	$q_e=14.747$		0.893
	Elovich	HB	$\alpha=3.335 \times 10^{10}$	$\beta=4.088$		0.947
		MHB	$\alpha=3.335 \times 10^{10}$	$\beta=1.913$		0.935
	Richie	HB	$k_n=0.0158$	$q_e=8.494$	$N=8.857$	0.947
		MHB	$k_n=0.0471$	$q_e=16.298$	$N=4.254$	0.972
	Langmuir	HB	$K=0.119$	$S_{\max}=4.748$		0.932
		MHB	$K=0.0363$	$S_{\max}=28.104$		0.932
	Freundlich	HB	$K_f=1.644$	$n=0.196$		0.714
		MHB	$K_f=4.159$	$n=0.338$		0.815
	Redlich-Peterson	HB	$K_r=0.0170$	$S_{\max}=17.420$	$n=1.247$	0.990
		MHB	$K_r=0.00104$	$S_{\max}=560.295$	$n=1.551$	0.977

*: k_1 , k_2 , and k_n are the first-order, second-order, and Richie apparent adsorption rate constants (h^{-1}), respectively. α is the initial adsorption rate ($mg\ kg^{-1}$) and β is the desorption constant ($kg\ mg^{-1}$). K , K_f , and K_r represent the Langmuir bonding term related to interaction energies ($L\ mg^{-1}$), the Freundlich affinity coefficient ($mg^{(1-n)}\ L^n\ g^{-1}$), and the Redlich–Peterson isotherm constants, respectively, $S_{\max}$ denotes the Langmuir maximum capacity ($mg\ g^{-1}$), C_e is the equilibrium solution concentration ($mg\ L^{-1}$) of the sorbate, n is the Freundlich linearity constant, and N ($L^N \cdot mg^{-N}$) is the Redlich–Peterson isotherm constant.

Figure captions

Figure 1. Sorption kinetics data and fitted models of heavy metals onto the pristine (HB) and engineered (MHB) biochars: a) Pb(II), b) Cu(II), and c) Cd(II).

Figure 2. Sorption isotherm data and fitted models of heavy metals onto the pristine (HB) and engineered (MHB) biochars: a) Pb(II), b) Cu(II), and c) Cd(II).

Figure 3. Effect of adsorbent dosages on heavy metal adsorption onto the pristine (HB) and engineered (MHB) biochars: a) Pb(II), b) Cu(II), and c) Cd(II).

Figure 4. Effect of solution pH on heavy metal adsorption onto the pristine (HB) and engineered (MHB) biochars: a) Pb(II), b) Cu(II), and c) Cd(II).

Figure 5. Effect of solution ionic strength on heavy metal adsorption onto the pristine (HB) and engineered (MHB) biochars: a) Pb(II), b) Cu(II), and c) Cd(II).

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5