Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22414

118 (2018) 195–204
June

Adsorption of Cd(II) and Pb(II) on biochars derived from grape vine shoots

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Received 4 September 2017; Accepted 28 April 2018

ABSTRACT

Grape vine shoots were utilized as the biomass feedstock and pyrolyzed under temperatures ranging in 300°C–600°C with nitrogen atmosphere to produce biochars. The surface properties of the as-obtained biochars were characterized, followed with the careful investigation of the adsorption of lead and cadmium removal in aqueous environments. All as-prepared biochars had weak alkali characteristics and large amount of mineral species, which can greatly improve the adsorption performance. Outstanding storing capacities of 250.81, 327.31, 377.36 mg g^{-1} for Cd^{2+} and 156.12, 237.25, 258.86 mg g^{-1} for Pb^{2+} were exhibited by biochar pyrolyzed under 300°C, 450°C and 600°C, respectively. The adsorption equilibrium could be reached about 7 h and the suitable solution pH should be above 3. Both Langmuir and Freundlich models fitted the data well and precipitation was found to be the dominant mechanism for the adsorption of both metals. Overall, grape vine shoots are confirmed to be a promising feedstock to produce biochar sorbents of heavy metals in wastewater with excellent performance, economic cost, and easy process.

Keywords: Biochar; Heavy metals removal; Grape vine shoots; Pyrolysis temperature; Precipitation; Minerals

1. Introduction

Water contamination with toxic heavy metals has become a worldwide environmental problem nowadays. Lead and cadmium, as two of the most 10 poisonous chemicals in the World Health Organization's list, are well known for their fatal impact on human beings and other living species. Lead is found to be a highly poisonous metal that can affect almost every organ and system in the body, especially the nervous system, while cadmium can cause significant damage to kidney [1]. Unfortunately, these two metals are non-biodegradable, resulting in easy accumulation in the environment and ecosystem [2], and then easily enter into humans and other living organisms through contaminated water and food chain, causing irreversible damage [3,4]. Thus, removal of heavy metals like lead and cadmium has become an important and urgent issue to secure the environment and living creatures.

Although lots of approaches including chemical precipitation, solvent extraction, reverse osmosis, ion exchange, electrochemical techniques, filtration, and membrane separation have been developed during the past decades [5,6], those traditional methods are suffering from expensive costing due to the utilization of specialized reagents and complicate apparatus [7,8]. Taking into account the necessities of highly effective, low-cost, easy available and environmental friendly, immobilizing the heavy metal ions via adsorption should be a promising way to remove contaminates from polluted water or soil [9,10], which raises a high demand

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1944-3994/1944-3986

for effective, economic, and environmental benign adsorbent materials.

Recently, carbon rich materials derived from biomass, also referred as biochars, are being developed as effective adsorbents for wastewater treatment. The easy conversion and abundant resources guarantees the economic cost, while the rich surface chemicals can benefit the adsorption capacity, and the native resources from bioproducts ensures the harmless nature to environment, all of which make biochars promising adsorbents for heavy metals removal with easy process, saving cost, and good performance. The adsorption mechanism of various heavy metals on biochars has been clarified to be molecular forces, surface complexation, precipitation, and π-interaction, which is significantly controlled by the biochar properties and the type of metals. It is reported that the primary adsorption mechanism of lead on biochar is precipitating with minerals, which also plays important role in cadmium stabilization. Thus, developing the content and species of minerals should be a good way to improve the storing capacities of lead and cadmium on biochars.

However, unlike the other functional characteristics such as surface oxygen containing groups and aromatic structures that can be easily enhanced by postactive processes, the contents and species of minerals are greatly depended on the biomass that is used as feedstock. For example, biochars produced from celery biomass are featured by high content of alkaline minerals, which show excellent lead adsorption capacity of 288 and 304 mg g^{-1} [11]. Biochars derived from peanut shell and Chinese medicine material residues with the same pyrolysis conditions show different adsorption capacities toward lead ions despite the same adsorption mechanism was observed [12]. Therefore, selecting an appropriate biomass becomes a key role in the developing of biochar adsorbents for lead and cadmium clearance.

Grape is a nonclimacteric fruit that can be eaten raw or used for food and beverage producing. Today, the area for grape cultivation in China is larger than 0.8 million hectares [13] and huge quantity of grape vine shoots (GVSs, henceforth) are generated as a result of the pruning works carried out yearly in all vineyards after the grape harvest, causing serious problems in both environment and disposal. It has been reported that grape wastes generated from wine production can be applied as adsorbent for heavy metals removal due to the enrichment of functional compounds like polyphenolic [14,15]. Besides, with abundant amount of cellulose and lignin, grape wastes can be utilized as precursor to prepare activated carbon and then used to immobilize organic pollutants [16–21] and heavy metal ions in aqueous solutions [13,22,23]. Nevertheless, the former has dubious adsorption performances while the latter requires for chemical agents and complicate posttreatments, which will largely increase the financial cost and energy consumption. Thus, new approaches like carbonizing GVS into biochars need to be explored to diversify the applications of this agricultural residue from the standpoints of economic and environmental.

With these premises, the present study is focused on the feasibility of converse GVSs into biochars to obtain effective adsorbents through pyrolysis. Various reaction temperatures were applied to study the impact of temperature on the characteristics and properties of those biochar products. The particle size and morphology, the crystal structure, the elements component, the surface area, as well as the ingredient of organic groups of the as-prepared biochars were analyzed, following with the evaluation of the adsorption potential of lead and cadmium ions on the adsorbents. The influence of several parameters such as sorbents dosage, metal concentration, contact time, and initial pH on the sorption capacity was investigated to determine the adsorption details and kinetics and isotherms. Besides, the postadsorption analysis of crystal structures and functional compounds was carried out to clarify the adsorption mechanisms of lead and cadmium on GVS biochars.

2. Experimental

2.1. Preparation of GVS-based biochars

GVSs were obtained from a vineyard nearby. The raw GVS were washed for several times and then dried in an oven at 100°C until constant weight achieved. After that, the dehydrated GVS were chopped and pulverized into small powder, followed with pyrolysis in a tube furnace under temperature of 300°C, 450°C, and 600°C for 4 h with atmosphere protection of nitrogen. Finally, the tube furnace was cooled naturally and black products of biochars were obtained. For convenience, the obtained biochars are named as B300, B450, and B600.

2.2. Characterization

The elements contents and surface area of the three samples were analyzed via an elemental analyzer (Vario Micro cube, Elementar, Germany) and N_2 sorption 77 K based Brunauer–Emmett–Teller (BET) experiments (Gemini VII 2390 Surface Area Analyzer), respectively. 1 g of the sample was mixed with 20 mL of distilled water and then shaken on a mechanical shaker for 24 h for pH value determination through a pH meter (Lei-ci PHS-3C, Inesa Instruments Co., Shanghai, China) [12]. The particle size and morphology of the obtained biochars were determined via scanning electron microscopy (SEM) measurement (JSN-6380LV instrument). The crystal structure and the component of organic groups of the three biochars before and after adsorption were characterized by X-ray diffraction (XRD) analysis (XRD-6000, SHIMADZU, Japan) and Fourier transform infrared (FT-IR) (Spectrum 65, PE, USA), respectively. The adsorption amounts of lead and cadmium ions were analyzed through a frame atomic absorption spectrophotometer (FAAS) (Z-2000 HITACHI, Japan).

2.3. Adsorption experiments

Batch adsorption experiments were conducted in 50 mL glass bottle at room temperature under environmental pressure. Lead nitrate $Pb(NO_3)_2$ and cadmium nitrate $Cd(NO_3)_2{\cdot}4H_2O$ were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China) with analytical purity and used as received. Working solutions with a concentration of 2,000 mg L^{-1} of Pb^{2+} and Cd^{2+} ions were prepared by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2{\cdot}4H_2O$ in distilled water and then diluted to appropriate concentrations. All adsorption experiments were performed in triplicate and average results were reported, with blank solution measured for quality control. Typically, settled amount of biochar adsorbents were added into metal ions solutions with designed concentrations and specific volumes. Then the mixtures were shaken at 150 rpm in a mechanical shaker for 3 h except the contact time examination. After that, the mixtures were withdrawn and subsequently vacuum filtered. The filtrates were analyzed directly to determine the metal ions concentrations after adsorption by FAAS and the postadsorption adsorbents were collected, rinsed, and then dried at 80ºC for further XRD and FT-IR examinations.

Gradient amounts of 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15 and 0.2 g of biochars were added to 25 mL Cd^{2+} solution with concentration of 300 mg L^{-1} and Pb^{2+} solution with concentration of 600 mg L^{-1} to investigate the effect of biochar dosage on the adsorption first. Then the influence of the contact time was studied by adding 0.1 g of each biochar sample into 25 mL Cd^{2+} (300 mg L^{-1}) and Pb^{2+} (600 mg L^{-1}) solutions and shaken in the mechanical shaker for various durations of 0.083, 0.33, 0.5, 1, 2, 3, 6, 12 and 24 h. Gradient concentrations of both Cd^{2+} (10, 20, 50, 100, 200, 300, 400, 500, 750, and 1,000 mg L^{-1}) and Pb^{2+} (20, 50, 100, 200, 400, 600, 800, and 1,000 mg L^{-1}) solutions were utilized to analyze the impact of metal amount on the adsorption with constant biochar dosage set of 0.1 g and volume of 25 mL. The effect of pH on the adsorption was finally investigated by adjusting the pH level of Pb^{2+}- and Cd^{2+}-bearing solutions through 1 M HNO_3 and NaOH solutions before adding the adsorbent. The initial metal concentrations for the pH influence experiments were 300 mg L^{-1} for Cd^{2+} and 600 mg L^{-1} for Pb^{2+}, and the biochar dosage was 0.1 g.

The adsorption capacity Q (mg g^{-1}) and the removal efficiency E%, were calculated according to the following equations, respectively:

$$Q = \frac{\left(C_e - C_0\right) \times V}{m} \tag{1}$$

$$E\% = \frac{C_e - C_0}{C_0} \times 100\% \tag{2}$$

where C_e and C_0 are the equilibrium and the initial metal concentrations (mg L^{-1}), respectively. V is the volume of solution (mL) and m is the weight of added biochar (g).

According to the adsorption test results of contact time and metal concentration, kinetic and isotherm parameters were calculated based on pseudo-first-order (PF-order) and pseudo-second-order (PS-order) models, Langmuir and Freundlich models. Details are listed as follows:

$$\text{PF-order: } Q_t = Q_e\left(1 - e^{k_1 t}\right) \tag{3}$$

$$\text{PS-order: } Q_t = \frac{Q_e^{\,2} k_2 t}{1 + Q_e k_2 t} \tag{4}$$

where Q_t (mg g^{-1}) is the amount of metal ions adsorbed at time t (min), k_1(min^{-1}) is the rate constant of PF-order adsorption, k_2 (g·(mg min$)^{-1}$) is the rate constant of PS-order adsorption, and Q_e (mg g^{-1}) is the maximum amount of metal ions adsorbed per mass of the material at equilibrium.

$$\text{Langmuir isotherm: } Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{5}$$

$$\text{Freundlich isotherm: } Q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where Q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the equilibrium concentration after the adsorption; $Q_{\max}$ (mg g^{-1}) is the maximum sorption capacity, K_L is a Langmuir constant, K_F is the Freundlich constant, and $1/n$ (dimensionless) is the intensity of adsorption.

3. Results and discussion

3.1. Characteristics of biochars

The chemical elemental compositions and atomic ratios of the as-prepared biochars were first examined; results are presented in Table 1, combined with the overall solid yields (defined as the percentage of the original precursor weight that remains after pyrolysis process), pH values, and BET surface areas. Apparently, the content of carbon increased, while contents of oxygen and hydrogen decreased with the elevation of temperature, resulting in lower molar ratios of O/C, H/C, and (O + N)/C. Higher carbon content and lower H/C ratio indicates higher carbonization degree of the raw biomass, since hydrogen is primarily associated with the organic matter [24]. Higher temperature could promote the decomposition of the organics and polysaccharides, during which large quantity of volatile small molecular materials were formed. As a result, lots of oxygen and hydrogen were stripped, left in carbon rich products. These results were in accordance with the obtained yields, which were also reduced quickly with the increase of the pyrolysis temperature. On the other hand, the drop of O/C and (O + N)/C ratio suggested the loss of polar functional groups, which was also reported in previous works [25,26].

The pH examination results turned out that all three biochars had weak alkali characteristics, which is also widely

Table 1
Overall solid yields, pH values, elemental composition, and BET surface areas of the B300, B450, and B600 biochars

Sample	Yields (%)	Elements composition (%, mass based)				Atomic ratio			pH	S_{BET} (m^2 g^{-1})
		C	H	O	N	O/C	H/C	(O + N)/C		
B300	45.70	66.34	3.79	25.32	0.50	0.38	0.06	0.39	8.35	24.06
B450	33.99	71.36	3.12	20.29	0.23	0.28	0.04	0.29	10.08	11.90
B600	29.31	80.25	1.51	12.93	0.31	0.16	0.02	0.16	10.06	155.18

happened to most of the biochars produced through pyrolysis [27,28]. The alkali properties of three biochars can enhance the pH of the wastewater and then promote the formation of hydroxide precipitations of heavy metals, finally develop the adsorption process. Nevertheless, the surface areas based on nitrogen adsorption of three as-obtained biochars were quite low, especially when compared with activated carbon (the most commonly used carbon-based sorbent with high surface area that is usually larger than 800 $m^2 g^{-1}$). According to the adsorption mechanism of heavy metals on biochar, huge surface area and abundant porous structure are the crucial impact factors on physical adsorption [24]. The poor porosity of three samples indicates that the physical attraction should not be the main process contributing to the heavy metals removal on biochars pyrolyzed from GVS.

SEM technique was used to investigate the apparent morphology and microstructure changes of biochar pyrolyzed under different reaction temperatures. Fig. 1 depicts the surface morphologies of B300, B450, and B600 with different magnifications. It can be seen from Figs. 1(a) and (d) that B300 retained most of the original hollow configuration of raw fibers, but had a relatively glossy surface without voids. The structure of this sample is similar to the typical lingocellulosic creature, suggesting that the construct of the raw GVS was not damaged during the pyrolysis process under this low temperature of 300°C. The smooth surface of this material certificates the dreadful porosity of the biochar, which is in agreement with the small surface area of 24 $m^2 g^{-1}$. A heterogeneous surface consists of smaller rods and cracked pieces were found for sample B450, indicating that the construct of the GVS started to collapse under this temperature. When the pyrolysis temperature increased to 600°C, much smaller particles with irregular shapes were obtained, and no cracked tube-like fragments of the original GSV had been detected, implying the complete decomposition of hemicellulose, cellulose, and lignin components.

3.2. Adsorption studies

3.2.1. Effect of adsorbent dosage on Cd^{2+} and Pb^{2+} removal

Adsorbent dose is one of the most strongly effective parameters that affects the adsorption process in the aqueous solution, since the storage capacity of the adsorbate with a given initial concentration on the adsorbent can be determined [25]. Thus, gradient amounts of biochars were added into Cd^{2+} and Pb^{2+} solutions, respectively, to study the effect of sorbent dose on the removal of each metal (Fig. 2). Apparently, for both metal ions on all three biochars, increasing the adsorbent dose resulted in a decrease of the adsorption capacity but an increase of the removal efficiency. As seen in Fig. 2, outstanding Cd^{2+} adsorption capacities of 250.81, 327.31, and 377.36 mg g^{-1} (25 mL/300 mg L^{-1}) were exhibited for B300, B450, and B600, respectively; and high Pb^{2+} adsorption capacities of 156.12, 237.25, and 258.86 mg g^{-1} (25 mL/600 mg L^{-1}) were depicted by B300, B450, and B600, respectively; all of which demonstrates that biochars pyrolyzed from GVSs have excellent adsorption properties of heavy metals like cadmium and lead. The capacities dropped with the adding of sorbents, but the removal efficiencies were greatly enhanced. Especially for the biochar pyrolyzed at 600°C, strengthened Cd^{2+} and Pb^{2+} removal efficiencies of 97.06% and 98.03% were observed, indicating the complete adsorption of these two metal ions on B600 at the current condition. Obviously, biochars obtained under higher pyrolysis temperature showed better adsorption properties, which might be attributed to higher contents of minerals formed on the surface of this biochar. It has been confirmed that

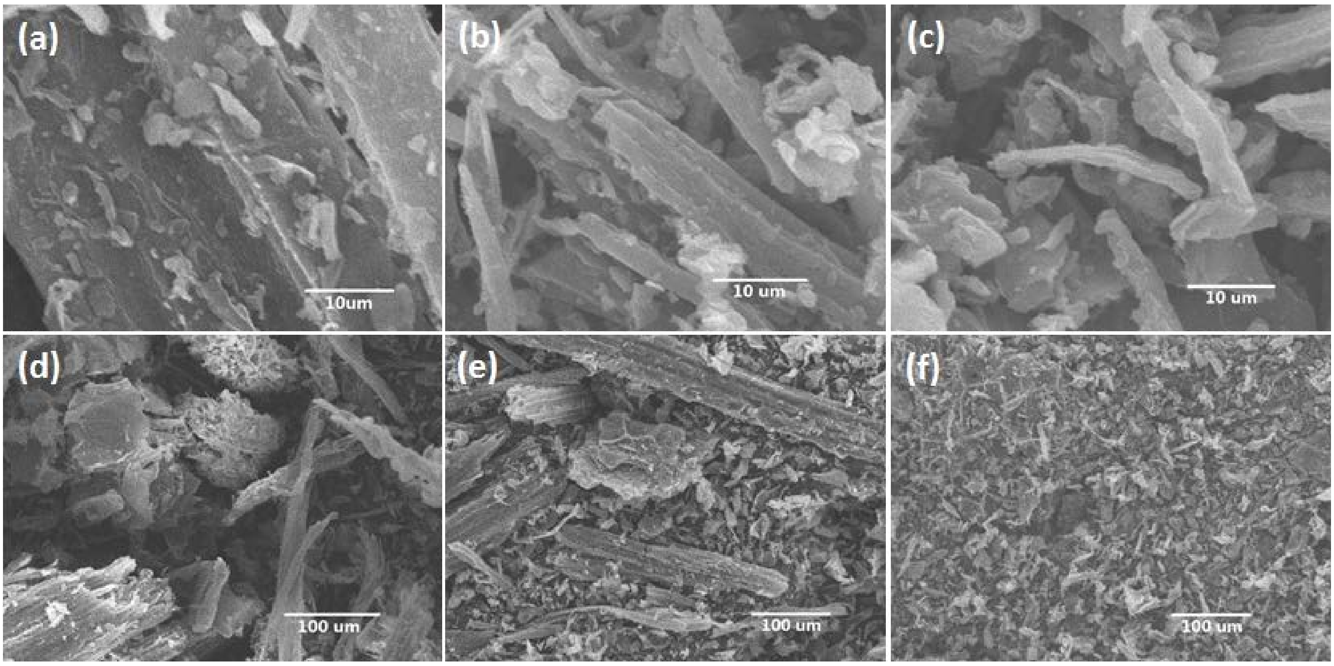

Fig. 1. SEM images of (a) and (d) B300, (b) and (e) B450, and (c) and (f) B600 with lower (bottom) and higher (up) magnification.

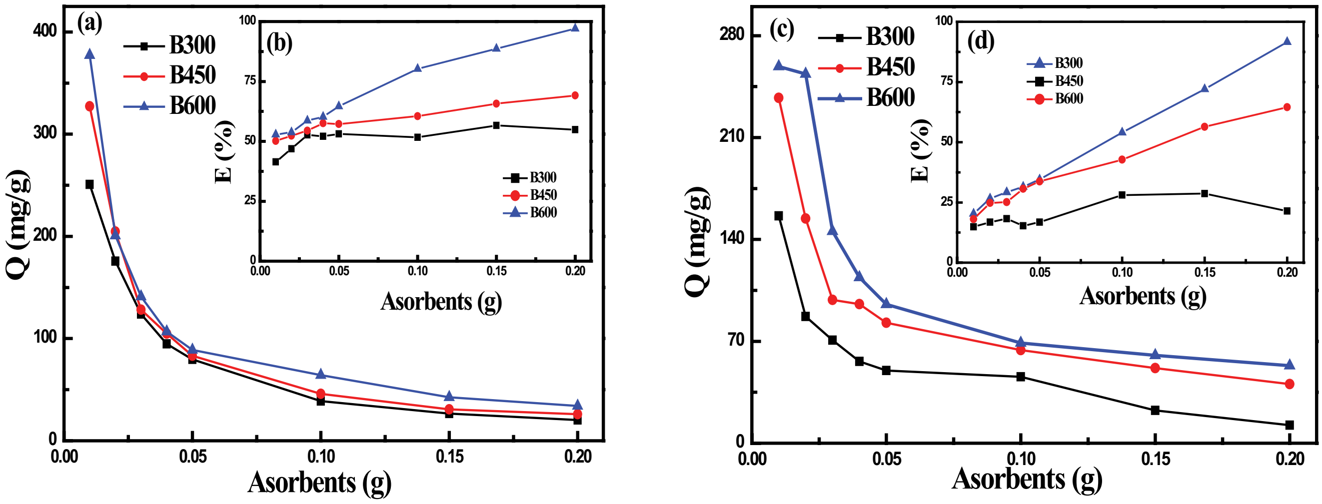

Fig. 2. Effect of adsorbent dosage on (a) Cd^{2+} and (c) Pb^{2+} removal, insets are adsorption efficiency of (b) Cd^{2+} and (d) Pb^{2+} on biochars.

precipitate with minerals is a common mechanism to store heavy metals on biochars, since anion groups such as CO_3^{2-}, PO_4^{3-}, and SO_4^{2-} are mineral fractions that can react with heavy metal ions and form solid precipitations [12].

3.2.2. *Effect of the initial pH on Cd^{2+} and Pb^{2+} removal*

The pH value of the aqueous solution is another controlling parameter that affects the heavy metal adsorption process, since the degree of ionization, the surface charge of the adsorbent and especially the speciation of the heavy metals are dominated by the amount of protons in the solution [29]. The pH study was carried out in weak acidic environment (range 2–7), since Cd^{2+} and Pb^{2+} ions started to form hydroxide precipitation when the pH value rose above 7. As shown in Fig. 3, the uptake of heavy metals was quite low at lower pH. Especially for lead, nearly no adsorption happened at pH 2. Similar situation was reported in previous literatures [30], and the affection should be attributed to the high content of H^+ ions that competed for the surface active sites on the biochars. Besides, large amount of protons could impede the formation of precipitation of the heavy metals, which was depicted to be the key mechanism of the adsorption on biochars. With increasing pH value, obvious enhancements in adsorption were recorded for all GVS-based biochars, and the Cd^{2+} and Pb^{2+} removal efficiencies reached 93.6%, 90.1%, 88.7% and 93.6%, 90.1%, 88.7% at pH 6 for B600, B450, and B300, respectively. The increase in pH resulted in lower hydrogen ion concentration, decreasing the protonation degree on the surface of the adsorbents and weakening the competitive adsorption of H^+ protons toward the fixation sites [25]. Therefore, more anionic functional groups on the surface of biochars were set free and exaggerated the number of binding sites available for the adsorption of metal ions. As mentioned earlier, couple of ionized anions such as OH^-, CO_3^{2-}, PO_4^{3-}, and SO_4^{2-} can stabilize heavy metal ions by precipitation. However, those sediments can only be stable when the pH is above 4.0. This should be another

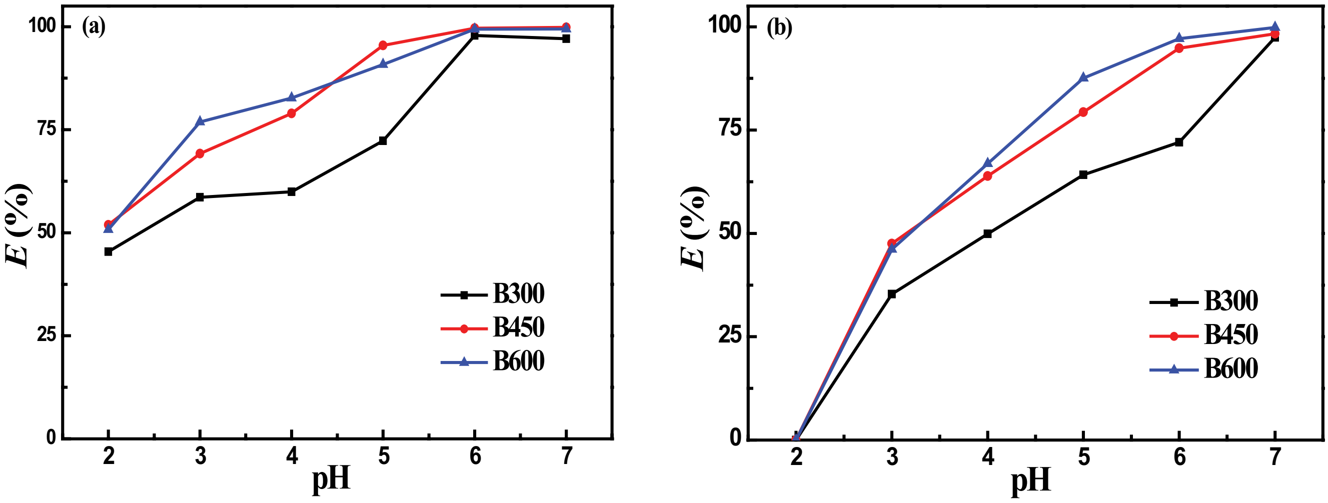

Fig. 3. Effect of pH on (a) Cd^{2+} and (b) Pb^{2+} removal.

reason that the heavy metal removal efficiency had been greatly enhanced when the testing pH increased above 4.0, since precipitation reactions with the surface minerals might be the main attractions between the heavy metals and the biochars derived from GVSs.

3.2.3. Effect of contact time and kinetic models

To address the effect of contact time on the adsorption of heavy metals on the GSV-based biochars, 0.1 g biochar samples were added into Cd^{2+} and Pb^{2+} solutions and the adsorption processes were performed within various durations, respectively, results are shown in Fig. 4. For cadmium removal, typical kinetic curves with an initial rapid increase within the first 3 h were obtained for all three biochars, and then reached equilibrium within 24 h. Analogical detections had been found for lead adsorption, except that the time consumed to get close to equilibrium were about 7 h. The fast adsorption during the initial stages should be attributed to the abundant vacant surface sites. But after a lapse of time, the large occupancy of those sites would greatly reduce the availability and increase the repulsive forces between solid molecules in bulk and solid phases. At last, the speed of the adsorption would slow down and finally reach the equilibrium. Two kinetic equations of PF-order and PS-order were utilized to analyze the kinetic quantitatively, and the corresponding parameters are listed in Table 2. According to the values of the regression coefficient (R^2), the PS-order model describes the kinetic sorption data better than the PF-order model does. It is well known that the PS-order model correlates well with kinetic data when chemical sorption between the adsorbate and the adsorbent is the rate-limiting step. From the experimental results, one can safely grant that the binding behavior of GSV-derived biochars toward these two metal ions were chemical sorption processes.

3.4. Effect of initial metal concentration and isotherm models

Cd^{2+} and Pb^{2+} solutions with gradient concentrations from 5 to 1,000 mg L^{-1} were employed to investigate the effect of the initial concentration of metal ions on the adsorption, results are presented in Fig. 5. With the increase of the initial content of cadmium and lead in the aqueous solution, the quantities of the adsorbed Cd^{2+} and Pb^{2+} on three biochar samples enlarged rapidly and no obvious equilibrium stages were detected even with a high metal ion concentration of 1,000 mg L^{-1}, confirming the outstanding adsorption performance of those biochars. Apparently, B600 gave the best heavy metal storage property among those three samples, which is consistent with former results. It is reported that higher pyrolysis temperature has positive effect on the formation of minerals while negative effect on the existence of surface organic groups [31], the better adsorption performance of B600 indicates the primary adsorption mechanism of these two metal ions on GVS biochars shall be precipitation.

Isotherm models (Langmuir and Freundlich) were used to better understand the adsorption isotherm of those biochars. The fitting parameters and the correlation coefficients of model predictions versus experimental observations are listed in Table 3. Almost all the correlation coefficients that obtained were larger than 0.99 (the only exception is 0.989), from which it can be concluded that both the Langmuir and Freundlich models described the adsorption process very well. Hence, the adsorption of cadmium and lead onto GSV-derived biochars should be occurred mainly through single molecular adsorption.

Based on the Langmuir model, the dimensionless separation parameter R_L ($R_L = 1/(1 + K_L \cdot C_0)$, where K_L is the Langmuir constant and C_0 is the initial concentration of heavy metal ions) can be numerated, which is usually used to describe the characteristics of the adsorption isotherm of the Langmuir model [32]. The value of R_L is a judgment parameter that can determine whether the sorption process is a thermodynamically favorable process or not: the conditions are unfavorable when $R_L > 1$; linear conditions prevail when $R_L = 1$; the conditions are favorable when $1 > R_L > 0$; and the reaction is irreversible when $R_L = 0$. In the present study, the calculated values of R_L were all in the range of 0–1, implying that both the cadmium and lead adsorption by all biochars are thermodynamically favorable processes. The calculated maximum

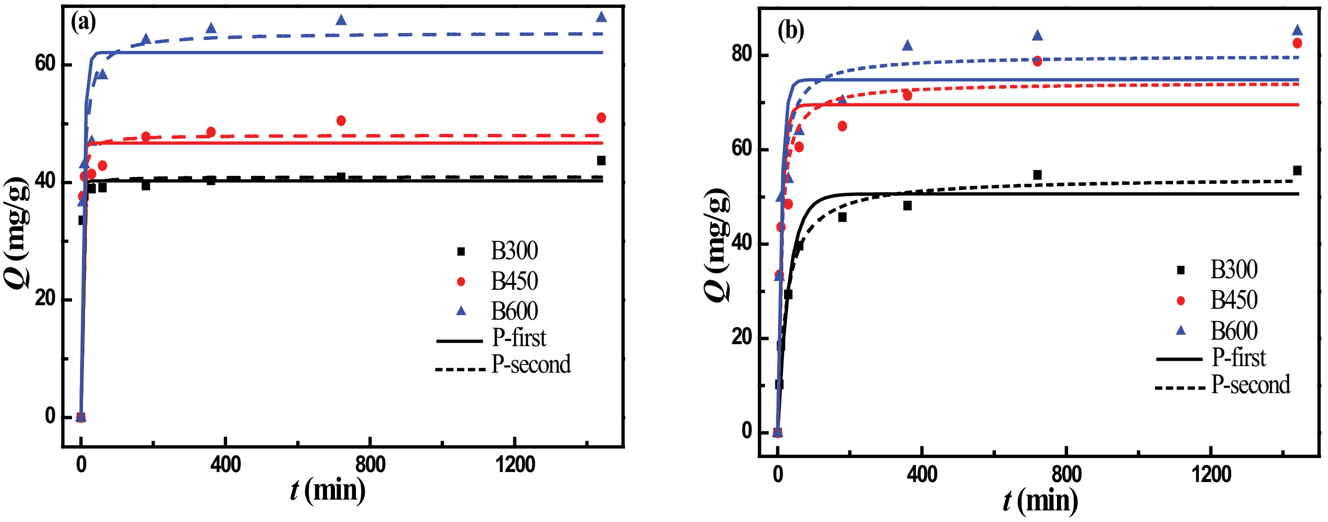

Fig. 4. Effect of adsorbent time on (a) Cd^{2+} and (b) Pb^{2+} removal and sorption kinetics.

Table 2
Kinetic parameters of Pb^{2+} and Cd^{2+} on the B300, B450, and B600 biochars

Metal	Sample	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$Q_{e,cal}$ (mg g^{-1})	R^2	k_1 (g mg^{-1} min^{-1})	$Q_{e,cal}$ (mg g^{-1})	R^2
Cd	B300	0.345	40.261	0.986	0.022	40.93	0.991
	B450	0.296	46.70	0.946	0.012	48.05	0.971
	B600	0.034	56.375	0.939	7.74E-4	60	0.980
Pb	B300	0.031	50.64	0.960	8.01E-4	54.18	0.990
	B450	0.090	69.55	0.852	0.002	74.34	0.937
	B600	0.094	74.85	0.874	0.001	80.05	0.950

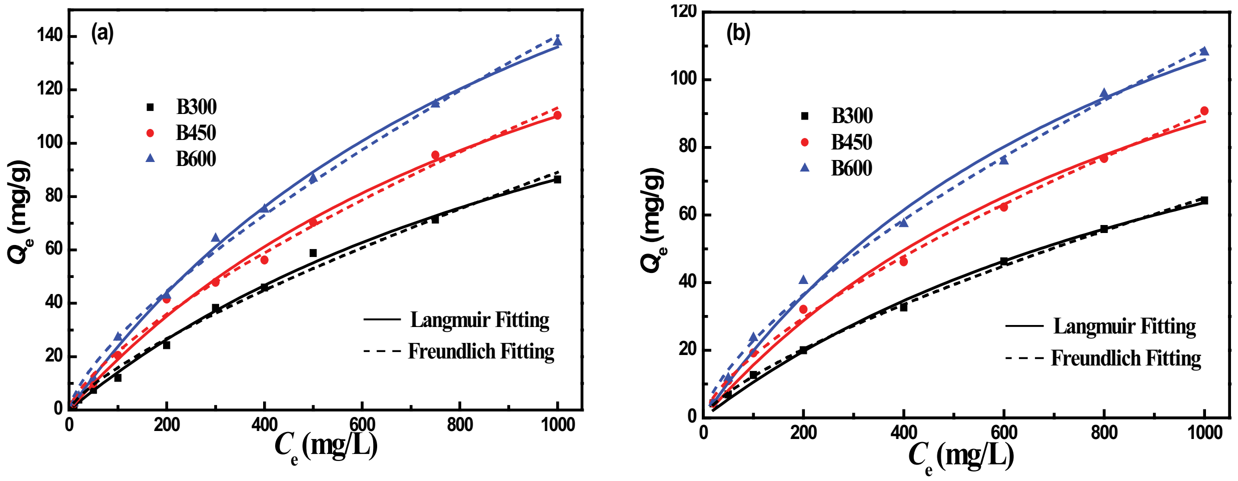

Fig. 5. Effect of initial metal concentrations on (a) Cd^{2+} and (b) Pb^{2+} removal and sorption isotherm.

Table 3
Langmuir and Freundlich constants and correlation coefficients (R^2) for Pb^{2+} and Cd^{2+} adsorption on GVS biochars

Metal	Sample	Langmuir			Freundlich		
		$Q_{e,cal}$ (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L mg^{-1})	R^2
Cd	B300	200.40 ± 18.077	7.599 ± 1.025	0.996	1.337 ± 0.072	0.509 ± 0.131	0.990
	B450	236.01 ± 24.857	8.753 ± 0.00014	0.993	1.402 ± 0.063	0.821 ± 0.167	0.992
	B600	286.30 ± 15.673	9.059 ± 0.00008	0.998	1.40 ± 0.049	1.02 ± 0.164	0.995
Pb	B300	144.16 ± 16.142	7.907 ± 1.385	0.995	1.383 ± 0.030	0.441 ± 0.045	0.999
	B450	179.71 ± 25.712	9.523 ± 0.00023	0.989	1.448 ± 0.042	0.762 ± 0.099	0.998
	B600	204.51 ± 23.674	0.001 ± 2.158	0.992	1.470 ± 0.061	0.994 ± 0.181	0.995

adsorption capacities Q_{max} of Cd^{2+} and Pb^{2+} on B300, B450, and B600 are 200.40, 236.01, 286.30 mg g^{-1} and 144.16, 179.71, 204.51 mg g^{-1}, respectively, further confirming the excellent adsorption performance of those GVS-derived biochars. Besides, all factors "$1/n$" obtained according to Freundlich isotherm model were smaller than 0.5, indicating that cadmium and lead can be easily adsorbed on three biochars [33].

3.3. Adsorption mechanism

Heavy metals sorbed on biochars are usually through following chemical reactions: ion exchange, surface complexation, precipitation, and π-coordination. To address the possible chemical attraction between the metal ions and GSV-based biochars, XRD and FT-IR analysis were carried out to observe the further insight of the crystal structures and functional groups present on the surface of the samples before and after metals loading.

Fig. 6 depicts the crystal structures of the obtained three biochars and heavy metals loaded sorbents. For all three samples, broad peaks around 22° were presented, which should be indexed to the disordered graphite (002) diffraction plane [34], suggesting that all as-prepared biochars were amorphous carbon rich materials. Distinct crystal peaks corresponding to calcite ($CaCO_3$), aragonite ($CaCO_3$), and magnesium phosphate ($Mg_3(PO_4)_2$) were detected, illustrating

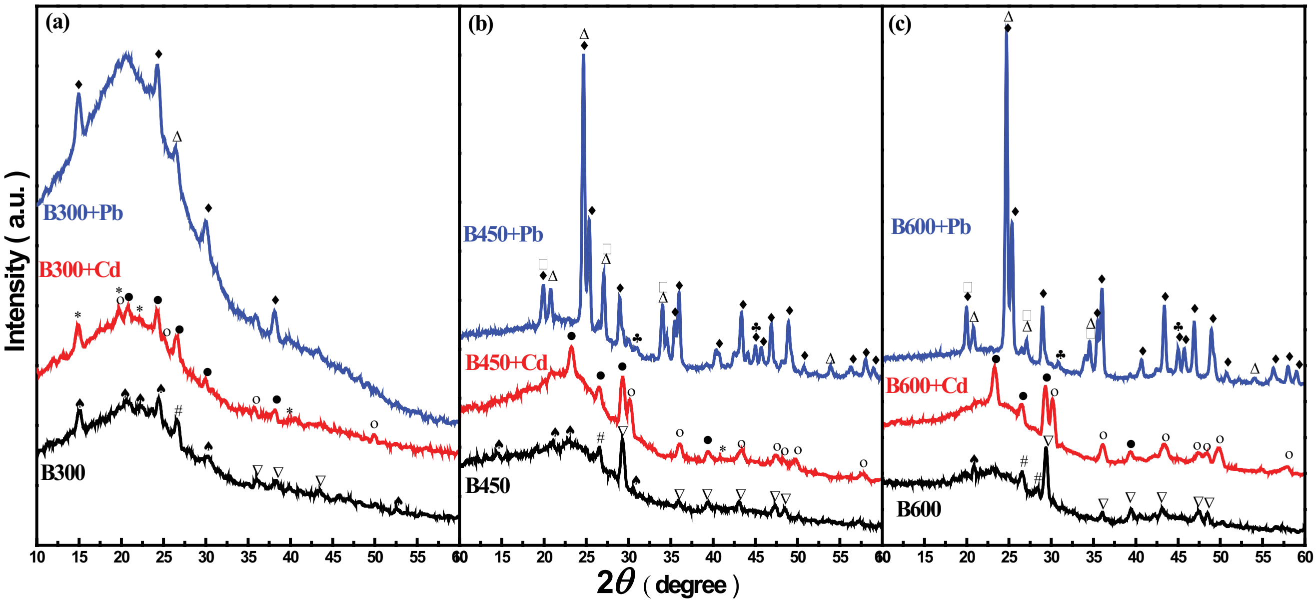

Fig. 6. XRD patterns of the (a) B300, (b) B450, and (c) B600 biochars before and after Pb^{2+} and Cd^{2+} adsorption. ▽. Calcite, $CaCO_3$; #. Aragonite, $CaCO_3$; ♠. Magnesium, $Mg_3(PO_4)_2$; ○. Otavite, $CdCO_3$; *. Cadmium phosphate, $Cd(PO_3)_2$; ●. Cadmium phosphate, $Cd_3(PO_4)_2$; □. Lead carbonate hydroxide hydrate, $3PbCO_3{\cdot}2Pb(OH)_2{\cdot}H_2O$; ♦. Cerussite, $PbCO_3$; △. Hydrocerussite, $Pb_3(CO_3)_2(OH)_2$; ♣. Pyromorphite-OH, $Pb_5(PO_4)_3OH$.

that there were plenty of minerals that had been formed in the as-obtained biochars. The existence of these mineral salts could benefit the ion exchange and precipitate processes, and then improve the adsorption performance. Consequently, peaks indexed to $CaCO_3$ and $(Mg_3(PO_4)_2$ disappeared, while typical peaks indexed to cadmium and lead carbonate, hydroxide and phosphate emerged after the adsorption procedure, confirming the formation of Cd^{2+} and Pb^{2+} containing precipitations. Apparently, chemical reactions such as cationic ion exchange and precipitation with anion groups had taken place during the adsorption process.

On the other hand, with the increase of the pyrolysis temperature, sharper peaks with larger intensity corresponding to carbonate and phosphate were detected, indicating that more minerals were formed with higher pyrolysis temperature. Larger content of minerals can precipitate more Cd^{2+} and Pb^{2+} in solution, and then promote the coprecipitation reactions. As a result, the XRD patterns of cadmium- and lead-loaded B450 and B600 were well-defined crystalline files of carbonates and phosphates of cadmium and lead. It can be concluded that the coprecipitation was the dominant procedure of the adsorption of heavy metals like cadmium and lead on GVS-derived biochars.

To further confirm the chemical reactions happened between the heavy metal ions and the as-prepared biochars, FT-IR analysis were performed to detect the change of the surface functional groups before and after adsorption. Fig. 7 depicts the FT-IR spectra of the original biochars (black lines), the Cd^{2+} sorbed biochars (red lines), and the Pb^{2+} sorbed biochars (blue lines). As shown in Fig. 7(a), a broad absorption peak around 3,422 cm^{-1}, related to H-bonded hydroxyl groups from carboxyls, phenols, and chemisorbed water, was observed in the spectrum of the biochar B300 before adsorption (Fig. 6(a)). Combined with the detection of bands assigned to $–CH_2$ or CH_3 groups in carboxylic acid at approximately 2,927, 2,855 and 1,378 cm^{-1}, and bands represent the C=O (C–O) stretching vibration of carboxyl groups at 1,710 and 1,615 cm^{-1}, confirms the existence of large amount of acidic oxygen containing functional groups on the surface of this biochar. However, after the adsorption of cadmium and lead, those bands had been largely reduced, indicating that chemical reactions like ion exchange and surface complexation had taken place. Biochars pyrolyzed under 450°C and 600°C exhibited similar FT-IR files but with much weaker intensities, representing that less content of oxygen containing functional groups were formed with the increase of the pyrolysis temperature. This is a common situation and reasonable since large amount of oxygen and hydrogen had been wiped away with the small molecular volatile materials due to the decomposition of polysaccharides. The reduction of surface functional groups should weaken the ion exchange or surface complexation reactions, and then slow down the adsorption process. However, according to the previous adsorption studies discussed earlier, the biochar sample pyrolyzed under 600°C displayed the best heavy metal removal performance among all the three products, suggesting that the ion exchange or surface complexation might not be the dominant mechanism of heavy metals sorbed on the GVS-derived biochars.

Additionally, other functional species such as CO_3^{2-} and PO_4^{3-} also showed appearance as broad band with strong intensity assigned to the vibration of O–C–O located at 1,090 cm^{-1} and sharp peaks according to the vibration of P–H (2,350 cm^{-1}) and P–O (1,090 cm^{-1}) had been detected in the FT-IR files of three biochars. These results are in well accordance with the XRD files, further confirms the existence of mineral fractions. Similar to those acidic functional groups, mineral groups were consumed by heavy metal ions during

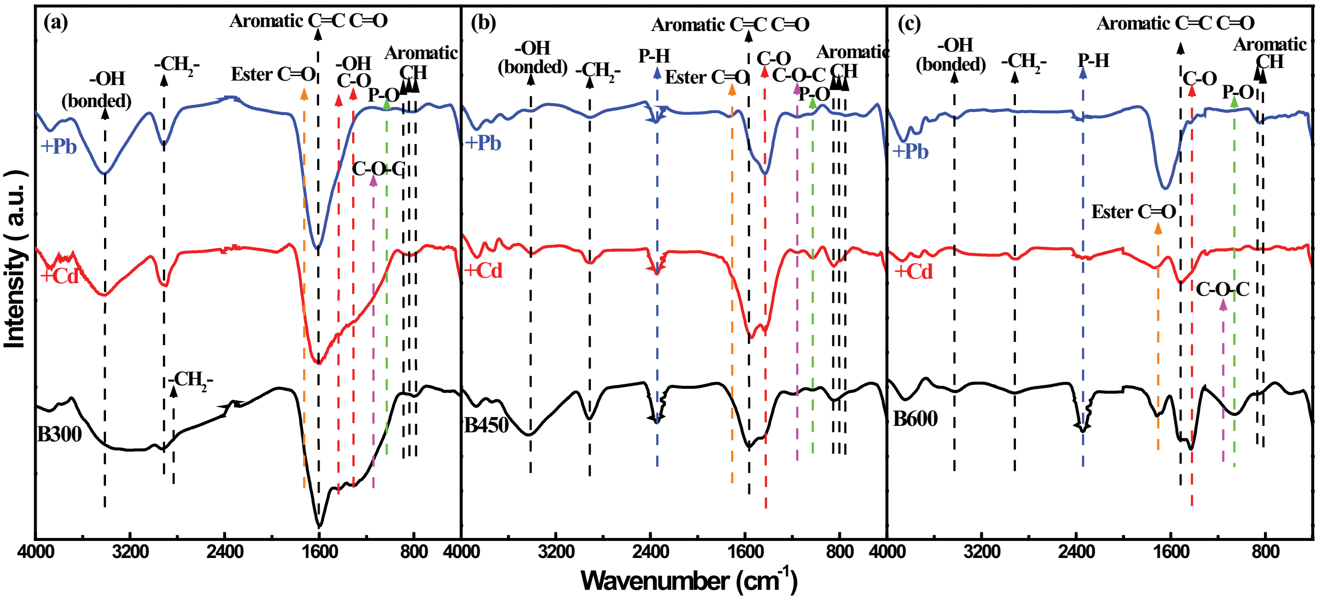

Fig. 7. FT-IR spectra of the (a) B300, (b) B450, and (c) B600 biochars before and after Pb^{2+} and Cd^{2+} adsorption.

the adsorption as well, since corresponding peaks were weakened after the cadmium adsorption and even disappeared after lead loading. The consumption of those mineral fractions by heavy metal ions demonstrates that mineral species on the surface of biochars had been largely participated into the removal of heavy metals, verifying the dominant control of the coprecipitation reactions during the adsorption.

4. Conclusion

GVSs were employed as raw materials to prepare biochars via pyrolyzation under various temperatures 300°C, 450°C, and 600°C. The produced biochars had smooth surfaces and poor porosities, resulting in low surface areas. The content of carbon increased and O/C and H/C ratio decreased with the increase of pyrolysis temperature, and the acidic oxygen containing surface functional groups reduced consequently. The obtained biochars had excellent storage capabilities for both cadmium and lead ions, and the adsorption capacities of Cd^{2+} were 250.81, 327.31, 377.36 mg g^{-1} and that of Pb^{2+} were 156.12, 237.25, 258.86 mg g^{-1} for biochars pyrolyzed under 300°C, 450°C, and 600°C, respectively. Ion exchange and surface complexation reactions participated in the adsorption process, but coprecipitation between the minerals and heavy metals should be the dominant mechanism. The adsorption procedure was complex, and should be a cooperation of a series of chemical reactions. It is confirmed that the GVSs are precious biomass feedstock and biochars pyrolyzed from GVS can be effective adsorbents for removal of heavy metals like cadmium and lead in wastewater.

Acknowledgment

The authors would like to acknowledge the financial support from Chinese National Natural Science Foundation (no. 21402063), China Postdoctoral Science Foundation (no. 2016M592427), Hunan Natural Science Foundation (nos. 2016JJ3065, 2015JJ6091), and Hunan provincial key laboratory for germplasm innovation and utilization of crop (nos. 15KFXM06, 15KFXM20).

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