Adsorption of heavy metals by *Lycium barbarum* branch-based adsorbents: raw, fungal modification, and biochar

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ABSTRACT

The present study reports on the adsorptive removal of heavy metals (Cr³⁺, Cd²⁺, and Cu²⁺) from water by a series of *Lycium barbarum* branch-based adsorbents: *Lycium barbarum* branch (denoted as LB), fungal fermented LB (FLB), LB biochar (LBB), FLB biochar (FLBB), alkaline modified LBB (ALBB), and alkaline modified FLBB (AFLBB). The six adsorbents were characterized in terms of FTIR, SEM, surface area and pore size as well as Zeta potential. Adsorptive potential of these adsorbents was tested under varying conditions – pH, contact time, initial concentration, and temperature. Adsorption results were well fitted with Langmuir, Freundlich, and Temkin models. The maximum adsorption capacity (qₘ) was calculated to be 6.29 mg/g for Cr³⁺ by FLB, 11.53 mg/g for Cd²⁺ by LB, and 7.27 mg/g for Cu²⁺ by LB. Pseudo-second-order kinetic equation better described the adsorption process. Based on the thermodynamics parameters, the adsorption of heavy metals was endothermic but not spontaneous for biochars. The experimental results offer a new way for recycling and reutilizing LB in wastewater treatment.

Key words: adsorption, biochar, fermentation, heavy metal, *Lycium barbarum* branch

HIGHLIGHTS

- *Lycium barbarum* branch (LB) was used to adsorb Cu²⁺, Cr³⁺, and Cd²⁺.
- LB was further modified with fungal fermentation and O₂-free pyrolysis.
- Isotherm, kinetic, and thermodynamic of adsorption were fitted and analyzed.
- Modified LB-based adsorbents showed varied adsorption capacity and behavior.
- LB and FLB are novel and promising adsorbents.

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1. INTRODUCTION

Anthropogenic activities, i.e., leather, mining, textile, electroplating, battery, and pesticide processing/production as well as e-waste dumping are thought to be the dominant contributors for heavy metals in wastewater (Song & Li 2015). Although awareness in environmental protection has been increasingly reinforced worldwide, high concentrations of heavy metals can be still detected in natural waters. Luo et al. (2021) investigated a series of lakes along Yangtse River and revealed the heavy metals in sediments (mg/kg): Cr (90.8), Cu (60.1), Hg (0.06), Zn (102), Cd (0.89), Pb (42.7), and As (6.01). Heavy metals normally enter into water as ions, which not only jeopardize aquatic lives but also through food chains build up in human bodies, causing organ failure and even cancer (Balali-Mood et al. 2021).

Relatively fewer research has been conducted towards Cr$^{3+}$ due to its low toxicity, which, however, could be enhanced by 100-fold when oxidized into Cr$^{6+}$ in environment, thus posing great threat to environmental ecology and human health (Jin et al. 2020). Presence of Cd$^{2+}$ within the concentrations ranging from 0.18 to 50 μM could cause malformations, delay and arrest of development in a dose dependent manner, with P. wall as a testing subject (Calevro et al. 1998). Even though at low concentration Cu$^{2+}$ could foster the formation of red blood cells and maintaining nervous system and immune functions, the overdose, however, could do great harm to human body by damaging kidney, brain, nervous and blood system (Vardhan et al. 2019).

To achieve efficient removal of heavy metal from water, a pile of methods has been thoroughly examined, among which adsorption technique stands out for its obvious advantages, e.g., flexible design, easy operation, and cost-effectiveness (Wong et al. 2018; Chai et al. 2021). Using lignocellulosic wastes as green adsorbents is gaining interest among researchers all over the world (Mo et al. 2018; Sahmoune 2019). Oiltea shell proves to possess the maximum adsorption capacity of 22.4 (Pb$^{2+}$), 12.1 (Cu$^{2+}$), and 14.2 mg/g (Cd$^{2+}$), respectively (Liu et al. 2019). Pretreatments of agro-wastes, e.g., modification of rice straw with Comamonas testosteroni FJ17 (Xue et al. 2020), can further improve the adsorptive capacity. Besides, activated carbons and biochars derived from agro-wastes have been widely tested as adsorbents as well (Wong et al. 2018; Deng et al. 2019).

Lycium barbarum (denoted as LB in this study) represents a typical Chinese herb and cash crop owing to its pharmaceutical/food trait, whose planting area covers 82,000 hectares in northwest China (Masci et al. 2018; Alam et al. 2021). Periodic trimming and clipping of LB as well as berry harvesting co-produce a large quantity of branch wastes, amounting to 0.2 million tons in a single year. The majority of these wastes are piled in processing factories and basically burnt, which apparently does bad to air quality and to global zero-carbon emission goal. It is of great practical significance to...
reutilize LB biomass for its high availability. High content of cellulosic component in LB makes it possible as adsorbent (Mo et al. 2018) or as feedstock to produce biochar/activated carbon (Danish & Ahmad 2018).

In this study, LB branch was evaluated with respect to its adsorptive potential for Cr^{3+}, Cd^{2+}, and Cu^{2+} from water. To find out the most efficient adsorbent, LB branch was treated in different ways, including fungal fermentation and pyrolysis as well as alkaline modification. To the best of our knowledge, this is the first study using such LB branch as adsorbents.

2. MATERIALS AND METHODS

2.1. Lycium barbarum branch and reagents

*Lycium barbarum* branches (LB) were provided by a local farm in Ningxia Hui Autonomous Region, China. LB was aired dried and grounded into powder for further use. Metal ions were made in solution using CuCl_{2}·2H_{2}O, CdCl_{2}·5/2H_{2}O, Cr(NO_{3})_{3}·9H_{2}O, respectively. These metal salts and other chemicals such as HNO_{3} (65–68%), HCl, and NaOH were all purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of adsorbents

The powdered LB collected from above was passed through an 80-mesh screen and oven-dried at 80 °C to constant weight, which was directly used as adsorbent or further treated to prepare modified adsorbents. Some of the LB was taken and mixed with water at ratio of 1:4 and put in glass petri dish (Φ = 9 cm) for sterilization at 121 °C and 0.12 MPa for 20 min. Afterwards, one piece of fungal dish of *Pleurotus ostreatus* was cut and inoculated right in the center of autoclaved and cooled petri dish (Liu et al. 2018). The cultivation was lasted for 7 days at static condition and 30 °C to allow complete spreading of fungal mycelia on the matrix. The fermented matrix was then soaked into deionized water for 4 h under shaking condition, followed by separation of solid using vacuum filtration. The separated solid was oven-dried at 80 °C as described above and labelled as FLB. LB and FLB were then subjected to pyrolysis for 2 h at 700 °C with the inlet gas of N_{2}. The biochars unloaded from the tube furnace was washed with 0.1 M HCl to clean the impurities on surface and then further washed with deionized water to neutral. After oven-dried at 80 °C, the prepared biochars were termed LBB and FLBB, respectively. LBB and FLBB were further modified with alkaline by immersing 6 g of them into 100 mL NaOH solution (2 mol/L) for 6 h in 80 °C water bath (Liu et al. 2020). The alkaline modified biochars were separated from solution and washed with deionized water to neutral and oven-dried at 80 °C, and the obtained solids were named as ALBB and AFLBB, respectively. All told, six adsorbents were prepared as adsorbents in this study – LB, FLB, LBB, FLBB, ALBB, and AFLBB.

2.3. Adsorbent characterization

Chemical composition, i.e., cellulose, hemicellulose, lignin, and ash, of raw and fungal treated LB was analyzed using National Standards: GB/T 6434-2006, GB/T 6433-2006, GB/T6432-1994. Brunauer-Emmett-Teller (BET) method was adopted to determine the specific surface area, total pore volume, and average pore size (Liu et al. 2018). Surface morphology of six different adsorbents was obtained with scanning electronic microscopy (SEM). FTIR spectra of adsorbents was recorded within a range of 400–4,000 cm\(^{-1}\). Zeta potential of adsorbents were obtained at pH = 6 with an instrument of Malvern Zetasizer Nano ZS90. COD and chromaticity of the solution where adsorption was carried out by different adsorbents (dosage 2 g/L, 12 h) were examined according to previous reports (He et al. 2018; Jing et al. 2018).

2.4. Effect of pH, temperature, and metal concentration on adsorption

To study the effect of pH value on adsorption, metal solution was adjusted with 0.1 mol/L NaOH and/or HNO_{3} within the range of pH 3–7. The adsorption was conducted in a system containing adsorbent 2 g/L and metal ion 10 mg/L in 10 mL solution in a glass flask, which was stabilized on a rotatory shaker (160 rpm) at room temperature for 12 h. After the adsorption was finished, the solution was passed through a 0.45 μm filter and concentration of metal ion in the filtrate was determined by ICP-MS (iCAP Q, Thermo, USA). Three replication of each adsorption experiment was conducted and the mean values were adopted for plotting with the standard deviation lower than 5%.
Through Equation (1) and (2), metal removal rate $R$ (%) and amount of sorbed metal by adsorbent $q$ (mg/g) was calculated:

$$ R(\%) = \frac{C_0 - C_e}{C_0} \times 100 $$

(1)

$$ q \text{ (mg/g)} = \frac{(C_0 - C_e)V}{m} $$

(2)

where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentration of the ion, respectively; $q$ (mg/g) is the amount of ion sorbed by adsorbent; $V$ (L) is the initial volume of solution; and $m$ (g) is the weight of the adsorbent.

### 2.5. Isotherms and dynamics of adsorption

In the reaction system stated above, initial metal concentration was adjusted to 2, 4, 6, 8, 10, 14, 18, 28, and 36 mg/L. The reaction was conducted at room temperature (25 ± 0.5 °C) for 12 h. Using the values calculated from Equations (1) and (2), Langmuir, Freundlich, and Temkin model was fitted through Equation (3), (4), and (5), respectively (Zhang et al. 2021).

$$ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} $$

(3)

$$ \lg q_e = \frac{1}{n} \lg C_e + \lg K_F $$

(4)

$$ q_e = \frac{RT}{B_T \ln A_T} + \frac{RT}{B_T \ln C_e} $$

(5)

where $K_L$ (L/mg) is the Langmuir adsorption constant and $q_m$ (mg/g) is the maximum dye amount of adsorption corresponding to complete monolayer coverage on the surface, $q_e$ (mg/g) is the amount of dye adsorbed by sorbent at equilibrium, and $C_e$ (mg/L) is the equilibrium concentration of dye solution. $K_F$ is an indicator of adsorption capacity (mg/g) and $1/n$ is the adsorption intensity.

Using the following Equation (6) separation factor $R_L$ was calculated, where $C_0$ was initial metal concentration (mg/L).

$$ R_L = \frac{1}{1 + K_L C_0} $$

(6)

In the reaction system and condition stated above, initial metal concentration was adjusted to 10 mg/L, and the reaction was conducted at room temperature (25 ± 0.5 °C) for varying duration —5, 10, 20, 40, 60, 120, 240, 360, and 720 min. After the adsorption, instant ($q_t$) and equilibrium adsorption capacity ($q_e$) were calculated as above stated. The data were then fitted with Lagergren’s pseudo-first-order model (7), Ho’s pseudo-second-order model (8), and intraparticle diffusion model (9) (Liu et al. 2018).

$$ \lg (q_e - q_t) = \lg q_e - \frac{K_1 t}{2.303} $$

(7)

$$ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} $$

(8)

$$ q_t = K_3 \sqrt{t} + c $$

(9)

where $q_e$ is equilibrium adsorption amount (mg/g); $q_t$ is adsorption amount (mg/g) at contact time t (h or min); $K_1$ is the equilibrium rate constant of the first order sorption (min⁻¹); $K_2$ is the equilibrium rate constant of the second order sorption (g/mg·min). $K_3$ is intraparticle rate constant (mg/g·min¹/2); $C$ is film diffusion extent (mg/g).

### 2.6. Thermodynamic analysis

Adsorbent at dosage of 2 g/L was added into a glass flask containing 10 mL metal solution (pH = 6, 10 mg/L) to start the reaction. The adsorption was carried out at 298 K, 308 K, and 318 K on a rotator at 160 rpm for 12 h. Afterward, the solution was passed
through a 0.45 μm filter for metal quantification, from which final metal concentration ($C_e$) and adsorption capacity ($q_e$) were calculated. The change in free energy ($\Delta G^\circ$) was calculated using the following equation to study the thermodynamic nature:

$$\Delta G^\circ = -RT \ln(q_e/C_e)$$ (10)

where $R$ is the gas constant (8.3143 J/mol K), and $T$ is the absolute temperature, $q_e$ is equilibrium adsorption amount (mg/g); $C_e$ is equilibrium ion concentration (mg/L).

From the plot of $\Delta G^\circ$ vs. $T$, the value of enthalpy $\Delta H^\circ$ and entropy $\Delta S^\circ$ can be calculated as follows (Liu & Lee 2014).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$ (11)

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

As shown in Table 1, the content of cellulose, hemicellulose, and lignin in raw LB was 25.5, 14.3, and 31.5%, respectively, which was reduced to 21.1, 13.8, and 29.6% in fungal treated LB (i.e., FLB), respectively. This indicates that LB, as an agro-waste, has great potential in serving as a novel matrix for fungal growth. Once fungal growth occurred, fungal fermentation-based modification of biosorbents would become possible due to changes in chemical composition, and as a result, the adsorptive capacity might be enhanced or behavior altered (Liu et al. 2016; Liu et al. 2018). Fungal modification has another advantage – it produces value-added co-product, namely ligninolytic enzymes that find broad application in wastewater treatment (Wang et al. 2019).

Physical properties of the six adsorbents were characterized and the results are shown in Table 2. Drastic variation in specific surface area (SSA) was observed among adsorbents. Raw LB held the smallest SSA of 0.086 m$^2$/g, which was elevated to 0.109 m$^2$/g for fungal treated LB (i.e., FLB). Pyrolysis of LB and FLB led to a steep increase in SSA of LBB and FLBB, reaching 18.963 m$^2$/g and 19.958 m$^2$/g, respectively. Alkaline treatment of biochars made further increase in SSA of ALBB and AFLBB, reaching 27.174 m$^2$/g and 28.225 m$^2$/g, respectively, suggesting the feasibility of using alkaline to modify carbon-based materials (Zhao et al. 2020). An increasing trend was also observed for total pore volume (cm$^3$/g) with the order of LB, FLB, LBB, FLBB, ALBB, AFLBB. An opposite trend was found with average pore size (APS), that was decreased along with the various treatments. Carbonization via pyrolysis downsized APS (∼350 nm) of LB and FLB to approximately 20 and 35 nm of biochars. Zeta potential for LB, FLB, LBB, FLBB, ALBB, and AFLBB at pH 6.0 was measured as: -18.40, -17.57, -24.07, -25.80, -24.80, and -26.70 mV, respectively, which were in good accordance with other reports (Kong et al. 2014; Liu et al. 2018; Zhang et al. 2021).

Functional groups on the surface of the six adsorbents are revealed by FTIR spectra in Figure 1. LB as well as FLB was found rich in typical absorbance peaks on the surface, which was reduced significantly after pyrolysis for preparation of biochars. The phenomenon of attenuation of numerous functional groups in biochars has been reported (Zhao et al. 2021). Stretching band of O-H at wavenumber of 3,600–3,150 cm$^{-1}$ in LB and FLB indicated the vibration of hydroxyl group present in cellulose, hemicellulose, and lignin (Hashem et al. 2020). Dehydration at high temperature during pyrolysis would lead to a reduction in hydroxyl group in biochars. A small peak at 2,930 cm$^{-1}$ and 2,860 cm$^{-1}$ corresponding to C-H was observed in LB and FLB (Zhang et al. 2020). Peak at 1,740 cm$^{-1}$ corresponded to ester C=O structure, while peak at 1,620 cm$^{-1}$ correlated with phenolic C=O functional group (Xu et al. 2020). Strong stretching vibration of C-O at 1,040 cm$^{-1}$ could be caused by hemicellulose and lignin (Gan et al. 2016), which accounted for a higher intensity in LB and FLB than that in four biochars. Moreover, weak bending vibration of C-H at 780 cm$^{-1}$ and 690 cm$^{-1}$ in LB and FLB was enhanced in FLBB.

| Table 1 | Chemical composition of Lycium barbarum branch (LB) and fermented Lycium barbarum branch (FLB) |
| Material | Component (%) | Cellulose | Hemicellulose | Lignin | Ash |
| LB | 25.5 | 14.3 | 31.5 | 6.5 |
| FLB | 21.1 | 13.8 | 29.6 | 14.0 |
Figure 2 portrays the SEM images of adsorbents at magnification of ×1,000. From the micro-structures in these graphs, it was relatively smooth on the surface of raw LB, with few ravines and cavities being seen (Figure 2(a)). Fungal treatment clearly damaged the smoothness of raw LB surface and increased the heterogeneous morphology (Ighalo & Adeniyi 2020), i.e., more ridged ravines and cavities (Figure 2(b)). As for biochars derived from biomasses, very tiny flaky particles, which looked like impurities and were inferred to mean the possible presence of cavities by some authors (Ighalo & Adeniyi 2020), appeared on the surface of LBB and FLBB (Figure 2(c) and 2(d)). In addition, more ruptured surface with cracks and crevices on biochars has been observed. With further treatment of alkaline, these particles on biochars were partly removed, which made the surface look much cleaner, presumably exposing more micro-structures for the increasement in SSA and pore volume of ALBB and AFLBB (Figure 2(e) and 2(f) and Table 2).

3.2. Effect of several parameters on adsorption

Profiles of metal adsorption by the six adsorbents at varying conditions are unfolded in Figure 3. pH value could significantly impact adsorption by adjusting the degree of ionization of metals as well the distribution of surface charge on adsorbent. Within the pH range 3–7, a general trend that higher pH value led to higher metal removal rate was observed among six adsorbents (Wang et al. 2015). Comparatively, an order of removal efficiency can be seen: LB/FLB > ALBB/AFLBB > LBB/FLBB. At pH 3, abundant H⁺ in the solution would compete with metal ions on adsorption sites, thus resulting in a low removal rate. When pH of the solution was increased to 7, a steep increase in metal removal took place, largely due to the formation of precipitable hydroxides (Zhao et al. 2020). On the other hand, the charge on adsorbents became more negative when pH was increased from 3 to 6, facilitating the electrostatic attraction between metal cations and the negatively charged surface (Kong et al. 2014). This is especially significant for LB and FLB (Figure 3) because they had more functional groups (i.e., -COOH) than the biochars (Figure 1). Reaction solution was therefore adjusted to pH = 6 in the following experiments.

| Adsorbent | Specific surface area (m²/g) | Pore volume (cm³/g) | Median pore width (nm) | Zeta Potential (mV) |
|-----------|-----------------------------|---------------------|------------------------|----------------------|
| LB        | 0.086                       | 0.001               | 357.275                | −18.40               |
| FLB       | 0.109                       | 0.002               | 340.807                | −17.57               |
| LBB       | 18.963                      | 0.014               | 29.824                 | −24.07               |
| FLBB      | 19.958                      | 0.015               | 19.859                 | −25.80               |
| ALBB      | 27.174                      | 0.040               | 28.288                 | −24.80               |
| AFLBB     | 28.225                      | 0.035               | 49.535                 | −26.70               |

Figure 1 | FTIR spectra of six different adsorbents.
As demonstrated in Figure 4, contact time notably influenced the metal removal rate. Similar to the results in most literature, over half of adsorption was finished in the beginning of the process, e.g., 10 min for the adsorption of Cr$^{3+}$ and Cd$^{2+}$ by LB and FLB, indicating rapid occupation of available adsorptive sites. Along with reaction proceeded, equilibrium was gradually achieved due to the decreased number of adsorptive sites. Adsorption reached equilibrium after 120 min, which was therefore chosen as contact time in the other adsorption studies. Removal rate by biochars (LBB and FLBB) was apparently lower than that by LB and FLB when the reaction was just initiated, possibly due to aggregation of biochars in solution. After a short while, the removal rate bounced to normal, probably because metals were re-adsorbed on adsorption sites following a transient desorption.

Initial metal ion concentration also affected adsorption by adsorbents in a severe manner (Figure 5). It was in a general trend among six adsorbents that metal removal rate would constantly descent as initial metal concentration ascended gradually. For instance, at initial concentration of 2 mg/L, the removal rate for Cr$^{3+}$ by LB, FLB, LBB, FLBB, ALBB, and AFLBB was 85.59, 91.42, 41.23, 50.23, 62.93, and 77.29%, respectively, which was reduced to 24.75, 27.24, 11.04, 13.17, 19.48, and 24.16%, correspondingly, when initial concentration was increased to 36 mg/L. Similar trend was found for Cd$^{2+}$ and Cu$^{2+}$.

By the contrast, with increasing initial metal ion concentration, adsorption capacity ($q_e$) at equilibrium showed an increasing momentum (see inserted figures in Figure 5). With respect to removal of Cr$^{3+}$, Cd$^{2+}$, and Cu$^{2+}$, LB and FLB performed better than alkaline modified biochars (ALBB and AFLBB), which were better than biochars (LBB and FLBB).

### 3.3. Isotherms of adsorption

Langmuir, Freundlich, and Temkin model were applied in this study and the corresponding parameters were calculated in Table 3. For adsorption of Cr$^{3+}$, Langmuir model yielded a higher $R^2$ than Freundlich model, suggesting the monolayer adsorption of Cr$^{3+}$ on six adsorbents. Similar has been reported using biomass pine as adsorbent (Zhao et al. 2021). As for Cd$^{2+}$, on the contrary, Freundlich model fit well with the adsorption than Langmuir, implying the occurrence of adsorption on heterogeneous surfaces (Xu et al. 2015). Both Langmuir and Freundlich models could well describe the adsorption of Cu$^{2+}$ on the six adsorbents. Separation factor $K_L$ in Langmuir model was less than 1, indicating the adsorption of Cr$^{3+}$, and Cd$^{2+}$, and Cu$^{2+}$ was favorable ($0 < K_L < 1$). In the Freundlich model, values of $1/n$ for the three ions were all $< 1$, suggesting that the adsorption of heavy metals by six adsorbents was very feasible. Further, Temkin models for six adsorbents generated high $R^2$ of 0.92, indicating the existence of strong intermolecular force in the process of adsorption (Zhang et al. 2021).

Generally, raw LB and fungal fermented LB (i.e., FLB) showed better adsorption performance towards three heavy metals. Pyrolysis of LB into biochars did not enhance adsorption, whilst further alkaline modification of biochars seemed to improve slightly. According to Langmuir model, the maximum adsorption capacity ($q_m$) was calculated to be 6.29 mg/g for Cr$^{3+}$ by FLB, 11.53 mg/g for Cd$^{2+}$ by LB, and 7.27 mg/g for Cu$^{2+}$ by LB. Comparison of maximum adsorption capacity of heavy metals by different agro-adsorbents in previous reports and in this study has been made (Table 4). For the raw LB, its

![Figure 2](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2022.067/1009612/wst2022067.pdf)
adsorption capacity fell well in the range of previously reported results among various agro-wastes. As for fungal pretreatment of LB (i.e., FLB), it was apparently better than some of raw agro-/industrial wastes, e.g., poplar and pine, and comparable to some modified ones, such as modified peanut hush. This reveals LB and FLB have the great potential as adsorbent to remove heavy metals from water. From the perspective of removal efficiency and energy input, more research should be carried out with biochars and even alkaline-modified biochars.

3.4. Dynamics of adsorption
Three kinetic models, namely pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD), were applied to fit the adsorption process and the related parameters are listed in Table 5. By comparing the values
of $R^2$ for all the adsorption experiments, PSO ($R^2 > 0.958$) better explained the adsorption process, suggesting the adsorption of these heavy metals on six adsorbents belonged to chemical adsorption. Furthermore, the calculated capacity ($q_{ec\, cal}$) based on PSO model was closer to the experimental results ($q_{ec\, exp}$). Comparatively, raw LB showed high $R^2$ values for PFO model but still lower than those for PSO model, which was not found in the other five LB-based adsorbents. Many adsorption processes using agro-wastes can be well described with both PFO and PSO.
models (Lee & Choi 2018). Using cow manure-derived biochars as adsorbents for Cu$^{2+}$ removal, adsorption process can be well fitted with both PFO and PSO models (Zhang et al. 2021), which is slightly different from our results of LB-based biochars. Diffusion process of metals transferred from aqueous solution onto adsorbents can be described by IPD model. Some of the adsorptions could be well described by IPD model based on $R^2$ values, such as Cr$^{3+}$ by AFLBB, Cd$^{2+}$ by FLB, LB, and ALBB, and Cu$^{2+}$ by FLB, FLBB, and AFLBB, while the others had very poor fitting. Taking adsorption of Cu$^{2+}$ by AFLBB as an example, such processes might be separated into three phases (Zhang et al. 2021): diffusion phase ($K_{d1} = 0.03$), adsorption phase ($K_{d2} = 0.014$), and equilibrium ($K_{d3} = 0.001$), thus further verifying the saturation of free electric potential on adsorbents.

Figure 5 | Effect of initial concentration on heavy metal removal (pH = 6, sorbent 2 g/L, 25 °C, 160 rpm, 12 h). Each inserted figure is the equilibrated adsorption capacity (mg/g) following 12 h contact at different initial metal concentration.
### 3.5. Thermodynamics of adsorption

In the profile of temperature effect on adsorption (figure not shown), elevated removal rate and adsorption capacity were observed at higher temperature. The reason for such phenomenon might be ascribed to increased odds of collision between metal ions and adsorbents as well as more exposed adsorption sites on adsorbent surface at higher temperature. The nature of endothermic or exothermic inclination, spontaneity, randomness, and the temperature favorability for sorption process can be identified with thermodynamic analysis (Mahmoud et al. 2021). Free Gibbs energy ($\Delta G^\circ$) was calculated based on Equation (10) and plotted vs. temperature, from which enthalpy change $\Delta H^\circ$ and entropy change $\Delta S^\circ$ were obtained according to Equation (11) and these values are summarized in Table 6. The negative values of $\Delta G^\circ$ supports the favorability of the adsorption process. With a few exceptions (adsorption with LB and FLB), most adsorptions in this study generated positive $\Delta G^\circ$ values, meaning the adsorption processes by these adsorbents were not spontaneous. Adsorption of heavy metals ions by green adsorbents has been reported to be spontaneous in most cases ($\Delta G^\circ < 0$) (Sahmoune 2019). In addition, a decreasing trend had been found for $\Delta G^\circ$ along with an increasing temperature in all adsorption scenarios, implying extra heat in solution might favor the adsorption. $\Delta H^\circ$ and $\Delta S^\circ$ for all the adsorption processes were found to be positive, in the range of 6.9 to 44.9 kJ·mol$^{-1}$ and 0.013 to 0.157 kJ·mol$^{-1}$·K$^{-1}$, respectively. Adsorption of Cd$^{2+}$ by Cynara scolymus derived biochar showed values of $\Delta G^\circ$ (−6.28 kJ/mol), $\Delta H^\circ$ (13.47 kJ/mol), and $\Delta S^\circ$ (59.6 kJ·mol$^{-1}$·K$^{-1}$), respectively (Mahmoud et al. 2021). The positive values of $\Delta G^\circ$ together with positive values of $\Delta H^\circ$ strongly indicate that the sorption of heavy metals by these adsorbents was nonsensational and endothermic. The positive values of $\Delta S^\circ$ suggest varied affinity of heavy metals toward different adsorbents and the increased randomness at the solid-solution interface (Lim et al. 2016).

### 3.6. Adsorption mechanism

The order of adsorption capacity has been determined as: LB&FLB > ALBB&AFLBB > LBB&FLBB, which is supposed to be the result of combined effects of several factors – SSA, pore volume, pore size, zeta potential, and functional groups. Although LB and FLB have the lowest SSA (∼0.1 m$^2$/g), their average pore width is the largest (∼350 nm). Besides, the
most abundant functional groups are present on the surface of LB and FLB, which could increase the possibility of chelating with heavy metal ions. AFLBB, holding the biggest SSA (28.225 m²/g) and pore volume (0.035 cm³/g) and highest negative zeta potential (−26.7 mV) but the lest functional groups, eventually exhibited median adsorption capacity among six adsorbents. LBB and FLBB have less functional groups and median SSA and pore size and finally exhibit the poorest adsorption capability. It follows that functional groups, such as -COOH and -OH, might play a dominant role in adsorption of heavy metal ions from water which is accompanied with other minor factors, such as zeta potential and pore size.

### Table 4 | Comparison of maximum adsorption capacity of heavy metals by different adsorbents in previous reports and in this study

| Metal ion | Adsorbent | $q_{\text{max}}$ (mg/g) (T °C)/pH | References |
|-----------|-----------|---------------------------------|------------|
| Cr³⁺      | Modified peanut husk | 7.67 (25/4) | Li et al. (2007) |
|           | Poplar    | 5.52 (25/4)        | Wang et al. (2015) |
|           | Pine      | 1.14 (25/4)        | Zhao et al. (2021) |
|           | FLB       | 6.29 (25/6)        | This study |
| Cd²⁺      | Persimmon leaf | 22.59 (25/6)       | Lee & Choi (2018) |
|           | Coffee husk | 6.90 (25/4)        | Oliveira et al. (2008) |
|           | Linden    | 3.50 (room temperature/5.1) | Božić et al. (2009) |
|           | LB        | 11.53 (25/6)       | This study |
| Cu²⁺      | Modified peanut husk | 10.15 (25/4) | Li et al. (2007) |
|           | Poplar    | 6.59 (25/4)        | Li et al. (2007) |
|           | Persimmon leaf | 19.42 (25/6) | Lee & Choi (2018) |
|           | LB        | 7.27 (25/6)        | This study |

### Table 5 | Parameters of pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic adsorption models by six different adsorbents

| Adsorbent | PFO $q_e$ exp (mg/g) | $K_1$ (min⁻¹) | $q_e$ cal (mg/g) | $R^2$ | PSO $q_e$ exp (mg/g) | $K_2$ (g/mg min⁻¹) | $q_e$ cal (mg/g) | $R^2$ | IPD $K_3$ (mg/g h⁻¹/²) | $C$ (mg/g) | $R^2$ |
|-----------|---------------------|----------------|-----------------|-------|---------------------|---------------------|-----------------|-------|----------------------|-----------|-------|
| LB-Cr     | 3.60                | 0.0074         | 1.31            | 0.9194| 0.0258              | 3.64                | 0.9993          | 0.0369 | 2.67                  | 0.7458    |       |
| FLB-Cr    | 3.37                | 0.0075         | 1.12            | 0.8325| 0.0294              | 3.41                | 0.9998          | 0.0166 | 2.94                  | 0.9555    |       |
| LBB-Cr    | 1.28                | 0.0090         | 0.27            | 0.7005| 0.1510              | 1.29                | 0.9999          | 0.0041 | 1.18                  | 0.8174    |       |
| FLBB-Cr   | 1.29                | 0.0034         | 0.18            | 0.1686| 0.1318              | 1.28                | 0.9990          | 0.0111 | 1.00                  | 0.9294    |       |
| ALBB-Cr   | 2.43                | 0.0124         | 1.79            | 0.9640| 0.0137              | 2.53                | 0.9945          | 0.0406 | 1.44                  | 0.5493    |       |
| AFLBB-Cr  | 2.64                | 0.0113         | 0.58            | 0.8157| 0.0694              | 2.66                | 0.9998          | 0.0024 | 2.57                  | 0.9607    |       |
| LB-Cd     | 3.26                | 0.0064         | 0.84            | 0.9483| 0.0323              | 3.28                | 0.9992          | 0.0286 | 2.54                  | 0.751     |       |
| FLB-Cd    | 3.39                | 0.0075         | 0.82            | 0.8669| 0.0437              | 3.41                | 0.9998          | 0.0103 | 3.11                  | 0.9881    |       |
| LBB-Cd    | 1.38                | 0.0047         | 0.57            | 0.9500| 0.0397              | 1.40                | 0.9974          | 0.0162 | 0.95                  | 0.9934    |       |
| FLBB-Cd   | 1.02                | 0.0053         | 0.13            | 0.5408| 0.2694              | 1.02                | 0.9998          | 0.0021 | 0.96                  | 0.7464    |       |
| ALBB-Cd   | 1.23                | 0.0033         | 0.42            | 0.7128| 0.0508              | 1.23                | 0.9954          | 0.0177 | 0.75                  | 0.9994    |       |
| AFLBB-Cd  | 1.42                | 0.0021         | 0.86            | 0.8939| 0.0149              | 1.40                | 0.9582          | 0.0383 | 0.35                  | 0.9140    |       |
| LB-Cu     | 3.13                | 0.0041         | 1.23            | 0.9047| 0.0149              | 3.16                | 0.9940          | 0.0584 | 1.63                  | 0.8728    |       |
| FLB-Cu    | 2.16                | 0.0040         | 0.41            | 0.4349| 0.0706              | 2.16                | 0.9992          | 0.0132 | 1.80                  | 0.9913    |       |
| LBB-Cu    | 1.15                | 0.0066         | 0.38            | 0.5566| 0.0709              | 1.17                | 0.9992          | 0.0091 | 0.92                  | 0.9116    |       |
| FLBB-Cu   | 1.20                | 0.0070         | 0.48            | 0.6927| 0.0556              | 1.21                | 0.9989          | 0.0058 | 1.04                  | 0.9773    |       |
| ALBB-Cu   | 1.50                | 0.0047         | 0.41            | 0.6281| 0.0666              | 1.30                | 0.9985          | 0.0068 | 1.10                  | 0.6378    |       |
| AFLBB-Cu  | 1.14                | 0.0098         | 0.21            | 0.7568| 0.1798              | 1.15                | 0.9998          | 0.0010 | 1.40                  | 0.9908    |       |
3.7. COD and chromaticity of the adsorption solution

Direct use of agro-wastes as adsorbents may be accompanied with organic & nutrient-leaching problem, thus increasing the contamination risk to aquatic systems (Kong et al. 2014). COD and chromaticity of the adsorption solution using six adsorbents were shown in Figure 6. With dosage of 2 g/L, LB (raw) generated COD and chromaticity of 99 mg/L and 420, while FLB (with fungal modification) significantly reduced the values to 43 mg/L and 93, respectively, showing the advantage of FLB as adsorbent for metal removal with less introduction of organics from adsorbent. Comparatively, all the biochars as well as alkaline modified ones did not exhibit such problem because no COD and chromaticity were detected in the adsorption solution. For practical application, adsorption efficiency, energy input, potential leaching contamination, etc, should be taken into consideration.

4. CONCLUSIONS

High availability of LB together with the experimental results make it possible to be utilized as novel adsorbent in its raw or modified form for removing heavy metals from water. By comparing the adsorption capacity, LB and FLB (fungal treatment) outcompete the others (biochars) even though the latter seem to have enhanced specific surface area and pore volume resulted from pyrolysis. It can be deduced that active sites might govern the adsorption of heavy metal ions in a greater manner because LB and FLB apparently possess more functional groups on the surface than do the corresponding biochars. Through the potential contamination leaching test, FLB proved be more advantageous relative to LB because the former release less COD and chromaticity into aqueous system. In addition, it is economically feasible to manufacture FLB as adsorbent as the fungal treatment normally co-produces value-adding enzymes.

Table 6 | Parameters of Thermodynamic of adsorption by six different adsorbents

| Adsorbent \( T/\text{K} \) | \( \Delta G^\circ/\text{(kJ mol}^{-1}\text{C}_0 \text{)} \) | 298 | 308 | 318 | \( \Delta H^\circ/\text{(kJ mol}^{-1}\text{C}_0 \text{)} \) | 298 | 308 | 318 | \( \Delta S^\circ/\text{(kJ mol}^{-1}\text{K}^{-1}\text{C}_0 \text{)} \) |
|-----------------|-----------------|---|---|---|-----------------|---|---|---|-----------------|
| LB-Cr | -2.318 | -2.650 | -5.168 | 44.927 | 0.157 |
| FLB-Cr | -1.867 | -2.409 | -2.874 | 16.025 | 0.060 |
| LBB-Cr | 3.003 | 2.785 | 2.566 | 6.949 | 0.013 |
| FLBB-Cr | 3.154 | 2.352 | 2.175 | 15.663 | 0.042 |
| ALBB-Cr | 2.595 | 2.396 | 2.118 | 7.561 | 0.017 |
| AFLBB-Cr | -0.277 | -0.441 | -0.861 | 9.234 | 0.032 |
| LB-Cd | -1.321 | -1.750 | -2.378 | 16.766 | 0.061 |
| FLB-Cd | -1.786 | -2.617 | -2.982 | 19.084 | 0.070 |
| LBB-Cd | 3.416 | 2.885 | 2.405 | 16.075 | 0.042 |
| FLBB-Cd | 3.738 | 2.922 | 2.522 | 19.397 | 0.053 |
| ALBB-Cd | 3.195 | 2.730 | 2.362 | 13.222 | 0.034 |
| AFLBB-Cd | 2.880 | 2.692 | 2.344 | 8.530 | 0.019 |
| LB-Cu | -1.197 | -1.836 | -2.194 | 15.889 | 0.057 |
| FLB-Cu | 0.794 | 0.408 | 0.234 | 8.941 | 0.027 |
| LBB-Cu | 3.268 | 2.704 | 2.171 | 17.434 | 0.048 |
| FLBB-Cu | 3.192 | 2.833 | 2.239 | 15.112 | 0.040 |
| ALBB-Cu | 2.747 | 2.487 | 2.071 | 10.724 | 0.027 |
| AFLBB-Cu | 3.016 | 2.616 | 2.255 | 12.110 | 0.031 |

3.7. COD and chromaticity of the adsorption solution

Direct use of agro-wastes as adsorbents may be accompanied with organic & nutrient-leaching problem, thus increasing the contamination risk to aquatic systems (Kong et al. 2014). COD and chromaticity of the adsorption solution using six adsorbents were shown in Figure 6. With dosage of 2 g/L, LB (raw) generated COD and chromaticity of 99 mg/L and 420, while FLB (with fungal modification) significantly reduced the values to 43 mg/L and 93, respectively, showing the advantage of FLB as adsorbent for metal removal with less introduction of organics from adsorbent. Comparatively, all the biochars as well as alkaline modified ones did not exhibit such problem because no COD and chromaticity were detected in the adsorption solution. For practical application, adsorption efficiency, energy input, potential leaching contamination, etc, should be taken into consideration.
CONSENT TO PARTICIPATE
Not applicable.

CONSENT TO PUBLISH
Not applicable.

AUTHORS CONTRIBUTIONS
JG carried out the experiments, analyzed the data, and drafted the manuscript. CH helped analyze the metal concentration using ICP-MS. JZ provided the adsorbent materials and proposed the idea. QH and JL designed and supervised the experiments as well as edited/revised the manuscript. All authors read and approved the final manuscript.

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COMPETING INTERESTS
The authors declare that they have no competing interests.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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