Removal of heavy metals from wastewater using biochars: adsorption and mechanisms

Qingqing Ye, Qianhui Li and Xin Li

Key Laboratory for Clean Renewable Energy Utilization Technology, Ministry of Agriculture, College of Engineering, China Agricultural University, Beijing, People’s Republic of China

ABSTRACT

The physicochemical properties and heavy metals adsorption capacities of biochars derived from cattle manure (CM) and cherry wood (CW) were systematically investigated and compared. The results showed that the yields, pH and the ash content of cattle manure biochars (CMB) were higher due to high levels of mineral constituents in CM. CMB6 and CWB6 showed higher aromaticity and polarity, whereas CMB4 and CWB4 carried higher oxygen-containing functional groups. CMB6 exhibited the maximum adsorption capacities for Pb\(^{2+}\) (40.8 mg·g\(^{-1}\)), Cd\(^{2+}\) (24.2 mg·g\(^{-1}\)), and Ni\(^{2+}\) (25.1 mg·g\(^{-1}\)), with relatively higher adsorption capacities for Pb\(^{2+}\). The adsorption isotherms fitted Langmuir model, indicating that the heavy metal adsorption occurred via a combination of physical and chemical adsorption mechanisms. The quantitative analysis showed that the interaction with minerals was the dominant mechanism, especially accounting for about 70% in CMB6. This study provides important information for comprehensive recycling utilization of biomass for sustainable development.

1. Introduction

Heavy-metal pollution has become a crucial environmental concern because of the accumulation of non-biodegradable contaminants [1]. The discharge of industrial wastewater with high concentrations of heavy metals can cause serious water and soil pollution. Meanwhile, the livestock farm wastewater also contains a high concentration of heavy metals because of low utilization rate of heavy metals in the animal feed and the cumulative effect in food chain [2]. Among heavy metals, lead (Pb), cadmium (Cd), and nickel (Ni) are the most hazardous contaminants, which can cause serious environmental and health problems even at low concentrations. The results obtained by Tuyarila (2019) showed that compared with the background value, Cd and Pb exceeded the standard in the northwestern and western parts of the North China Plain, southwestern China, and the middle and lower reaches of the Yangtze River [3]. The China National Soil Pollution Survey Bulletin reported that 4.8% of sampling sites were contaminated with Ni, ranking second after Cd [4]. Therefore, these metals...
should be removed from wastewater before discharge into the municipal pipe network or environment.

In recent years, the adsorption technology for heavy metals removal from wastewater has attracted considerable attention because of convenience and low cost [5]. Biochar, which is by-product of biomass pyrolysis, exhibits multiple physicochemical properties to facilitate adsorption and fixation of heavy metals from water used as adsorbent. The micro- and nanopores, aromatic structures, surface adsorption sites and ions of biochar exhibit strong adsorption potentiality for heavy metals [6].

The type of biomass raw materials and pyrolysis temperature can affect the physicochemical properties of biochar, which in turn affect its heavy metal adsorption capacity [7]. Significant differences exist in the properties of livestock manure biochar [8] and wood biochar [9] because of the differences in composition of the two types of feedstock. The properties of biochar are remarkably influenced by the pyrolysis temperature, heating rate, and residence time [10,11]. In addition to the physicochemical properties of the biochar, the adsorption conditions, including coexisting substances, the biochar dosage, adsorption time, adsorption temperature, and initial concentration also strongly affect the adsorption performance. Furthermore, clarifying the adsorption mechanism will help improve adsorption performance by modifying biochars. Indeed, the application of biochars in heavy metal adsorption and the mechanisms have been widely investigated [12–14]. However, our literature review indicates that most studies focus on the morphological and qualitative analysis of before and after adsorption. Thus, the adsorption capacity and mechanisms of biochar from different feedstocks at varied pyrolysis temperatures require systematic and quantitative investigation.

To address the gap, this study aimed to investigate systemically the physical, chemical, and morphological characteristics of biochars derived from livestock manure (cattle manure, CM) and wood biomass (cherry wood, CW) obtained at different pyrolysis temperatures. Further, the adsorption capacities of biochars for mixed and individual heavy metals in wastewater were evaluated. The theoretical models of heavy metal adsorption by the two types of biochars were analyzed to qualitatively compare the absorption mechanisms. Specifically, the contributions of different adsorption mechanisms were also quantitatively evaluated innovatively. This study provides important insight into comprehensive recycling and utilization of biomass waste and wastewater treatment.

2. Materials and methods

2.1 Biochar preparation

CM was collected from a livestock plant in Jinyindao, Beijing, and CW was obtained from a suburb in Beijing, China. The raw materials were dried for 24 hours in an oven at 100°C and pulverized to obtain particles of around 10.0 mm size. The powdered biomass was pyrolyzed in a tubular pyrolyzer under N₂ atmosphere. The pyrolysis temperature was raised to 400°C, 500°C, and 600°C at a rate of 10°C-min⁻¹ and held for 1 h. The obtained biochars were referred to as CMB4, CMB5, and CMB6 (cattle manure biochar under 400°C, 500°C, and 600°C, respectively), and CW84, CWB5, and CWB6 (cherry wood biochar under 400°C, 500°C, and 600°C, respectively). The biochars were transferred to desiccators after cooling below 100°C inside the reactor. The sieved particles were dried at 105°C for 48 h, and then, stored in airtight plastic bags for future experiments.

2.2 Characterization of CMB and CWB obtained at different pyrolysis temperatures

The biochar yield was calculated based on the difference in the mass of raw material and the biochar after completion of the pyrolysis. The suspensions (in triplicate) were prepared by adding 1 g biochar into 20 mL of deionized (Milli-Q pore) water and shaken for 2 h. The pH of suspension was measured. The ash content was determined via combustion of biochar samples in an open ceramic crucible at 700°C for 6 h. The metal ions of biochar (K, Ca, Na, and Mg) were measured with an atomic absorption spectrophotometer (900 T, PerkinElmer, USA). The surface area and porosity of the biochar were determined using Brunauer–Emmett–Teller method with N₂ adsorption at 77 K. Additionally, scanning electron microscopy (SEM) was used to analyze the morphology. The C, N, S, and H of the samples were analyzed using an Elemental Analyzer (Vario El cube), whereas O content was calculated based on mass balance: O = 100–(C + H + N + S + ash). Surface functional groups were determined via Boehm titration [15].

2.3 Heavy metal adsorption experiments

Batch heavy metal adsorption experiments were conducted to evaluate the adsorption potential of CMB and CWB. The artificial industrial wastewater was prepared using deionized water treated with Pb²⁺, Cd²⁺, and Ni²⁺ at 100 mg·L⁻¹, respectively. The adsorption experiments were conducted by adding 0.6 g biochar into 150 mL of artificial industrial wastewater in a 250 mL glass bottle with a blue cover, which was shaken at 150 rpm in a mechanical shaker at room temperature. After 24 hours, the mixed solution was centrifuged to separate the solids from liquids. The residual concentrations of Pb²⁺, Cd²⁺, and Ni²⁺ in the aqueous filtrate were measured via inductively coupled plasma analysis (ICP; Perkin Elmer Optical Emission Spectrometer Optima 8300, USA).
Adsorption kinetic studies were performed via batch experiments under the same conditions and procedures as described above. The samples were taken at different times (10, 20, 40, 60, 120, 180, 300, 600, and 1200 min) to obtain kinetic data.

For adsorption isotherm studies, the different initial individual Pb\(^{2+}\), Cd\(^{2+}\), and Ni\(^{2+}\) concentrations of 0, 10, 20, 30, 50, 100, 200, and 300 mgL\(^{-1}\) were measured to obtain isotherm data.

### 2.4 The contribution of mechanisms of heavy metal adsorption by biochar

The quantitative analysis of the different mechanisms of heavy metal adsorption by biochar are listed in Table 1. The mechanisms including metal ion exchange (Q\(_e\)), precipitation with minerals (Q\(_p\)), functional group complexation (Q\(_f\)) and heavy metal -π coordination (Q\(_t\)) were determined by ignoring other potential mechanisms with negligible contribution [6].

(i) The interaction of heavy metals with minerals (Q\(_{e+p}\)) was attributed to the combination of ion exchange (Q\(_e\)) and mineral precipitation (Q\(_p\)), as shown in Eq (1):

\[
Q_{e+p} = Q_e + Q_p \quad \text{Eq}(1)
\]

(ii) The ion exchange (Q\(_e\)) was calculated as the net amount of exchanged metal cations (K\(^+\), Ca\(^{2+}\), Na\(^+\), and Mg\(^{2+}\)) released from the biochar, which is equal to the difference in cation concentration in solution without and with heavy metal, as shown in Eq (2):

\[
Q_e = Q_K + Q_{Ca} + Q_{Na} + Q_{Mg} \quad \text{Eq}(2)
\]

where Q\(_K\), Q\(_{Ca}\), Q\(_{Na}\), and Q\(_{Mg}\) represent the net amounts of K, Ca, Na, and Mg released from biochar into the solution with heavy metals subtracting from the solution without heavy metals.

(iii) To eliminate the effect of minerals in biochar, the CMB6 and CWB6 were demineralized using 1 molL\(^{-1}\) HCl solution, which were then referred to as dCMB4 and dCWB6, respectively. Almost no minerals were observed in the deionized water containing dCMB4 and dCWB6, while the surface oxygen-containing functional groups were not altered. Hence, the heavy metal adsorption by biochar after demineralization (Q\(_{de}\)) was determined by the sum of the functional group complexes (Q\(_f\)) and heavy metal -π coordination (Q\(_t\)), as shown in Eq (3):

\[
Q_{de} \times Y = Q_t - Q_e + Q_p \quad \text{Eq}(3)
\]

where Q\(_t\) (mg·g\(^{-1}\)) is the total adsorption of heavy metal on biochar; Q\(_{de}\) (mg·g\(^{-1}\)) denotes the adsorption amount of heavy metal by demineralized biochar; and Y stands for the yield of demineralized biochar from original biochar. Thus, mineral precipitation (Q\(_p\)) can be calculated using Eq (4):

\[
Q_p = Q_t - Q_{de} \times Y - Q_e \quad \text{Eq}(4)
\]

(v) The functional group complexation in demineralized biochar (Q\(_{df}\)) was calculated based on the decline in pH due to H\(^+\) release, according to the following reaction mechanisms using Equations (5) and (6):

\[
\text{−COOH} + \text{Pb}^{2+} + \text{H}_2\text{O} \rightarrow \text{−COOPb}^+ + \text{H}_3\text{O}^+ \quad \text{Eq}(5)
\]

\[
\text{−OH} + \text{Pb}^{2+} + \text{H}_2\text{O} \rightarrow \text{−OPb}^+ + \text{H}_3\text{O}^+ \quad \text{Eq}(6)
\]

The adsorption attributed to the complexation of biochar with oxygen-containing functional groups (Q\(_f\)) was calculated using Eq (7):

\[
Q_t = Q_{de} \times Y - Q_f \quad \text{Eq}(7)
\]

The Q\(_{de}/Q_t\), Q\(_{df}/Q_t\), Q\(_f/Q_t\), and Q\(_{de}/Q_t\) ratios were calculated to quantitatively evaluate the contribution of different mechanisms to the heavy metal adsorption by CMB6 and CWB6.

### 2.5 Statistical analysis

The adsorption experiments were performed in triplicate, and the standard deviation was obtained via descriptive statistics. The adsorption kinetics and isotherms were fitted using Origin 8.0, and R\(^2\) values were used to compare the performance of equations.
3. Results and discussion

3.1 The properties of biochars

Biochar yield is dependent on pyrolysis temperature and the type of raw material. As shown in Table 2, the CMB and CWB yields decreased from 71.6% to 41.3% and 62.6% to 33.4%, respectively, when pyrolysis temperature increased from 400°C to 600°C. The biomass was mainly composed of hemicellulose, cellulose, and lignin, which were decomposed according to the order of hemicellulose (250°C–350°C), cellulose (325°C–400°C), and lignin (300°C–550°C) [16]. Therefore, the biomass degradation and more syngas production at increased pyrolysis temperature resulted in reduced biochar yield. Otherwise, the yields of CMB were significantly higher than those of CWB pyrolyzed at similar temperatures. In general, lignin constitutes for 20%–40% of the dry weight of woody materials [17]. Therefore, the higher biochar yield of CMB than that of CWB can be attributed to the low lignin level and high mineral content of CM [18], suggesting that CMB is more economically viable than CWB.

In general, the pH of CMB and CWB increases with the increase in pyrolysis temperature. At pyrolysis temperatures of 400°C to 600°C, the pH of CMB ranged from 9.79 to 11.37, whereas the pH of CWB gradually increased from 7.59 to 10.84, indicating stronger alkalinity of CMB (Table 2). CM and CWB contain several minerals, mainly K, Ca, Na, and Mg. During pyrolysis, these minerals in raw materials are released via decomposition of organic acids and carbonates, and are converted to hydroxides [19], such as KOH, Ca(OH)2, Mg(OH)2, and NaOH. Therefore, the higher pH of CMB than that of CWB is attributed to the high mineral content of CM.

The total mineral contents of CMB and CWB increased from 32.6 mg·g⁻¹ to 52.4 mg·g⁻¹ and from 15.0 mg·g⁻¹ to 36.0 mg·g⁻¹, respectively, due to the effect of concentration caused by the net loss of dry mass during pyrolysis. Overall, inorganic elements promote heavy metal adsorption via ion exchange and precipitation [20]. Correspondingly, the ash content of CMB (34.72–48.64%) was higher than that of CWB (11.35–15.15%). The high ash content of CMB is also attributed to the high levels of mineral constituents in the CM.

The results for the elemental analyses of CMB and CWB are shown in Table 2. Compared with CWB, CMB contained lower levels of C (35.9–48.9 wt%), H (0.14–1.47 wt%), and O (0.43–23.37 wt%). As the pyrolysis temperature increased from 400°C to 600°C, the C content increased and the N content decreased. Pyrolysis temperature affects the S content minimally because it is substantially lower than the other elements. Notably, as pyrolysis temperature increased, the O content of CMB decreased from 23.37% to 0.43%, while that of CWB decreased from 25.17% to 6.32%.

Molar O/C and H/C ratios are the main parameters used to characterize the aromaticity and polarity of biochars [21]. As pyrolysis temperature increased, the O/C and H/C of CMB and CWB decreased, which indicates that CMB6 and CWB6 exhibit higher aromaticity and polarity, whereas CWB4 and CWB4 contain more oxygen-containing functional groups and show better complexation ability than the other biochars [22,23]. In the present study, the bulk [(O + N)/C] ratio of CMB was higher than that of CWB. Thus, CMB has higher bulk polarity than CWB. As shown in Table 2, the concentration of the total surface oxygen-containing groups in CMB4 (7.91 mmol·g⁻¹) and CWB4 (3.65 mmol·g⁻¹) was nearly 10-fold higher than that of CMB6 (1.35 mmol·g⁻¹) and CWB6.
3.2 Comparison of the heavy metal adsorption capacities of CMB and CWB

The target heavy metals were Pb, Cd, and Ni, which were selected because of their toxicity and prevalence in industrial wastewater [25]. The initial pH of the mixed heavy metal wastewater was approximately 6.75 and was increased by the addition of CMB and CWB (Figure 2) except CWB4. The increased pH of wastewater facilitated heavy metals removal via chelation and precipitation.

The adsorption capacity of CMB was significantly higher than that of CWB (Figure 3). The adsorption capacities of CMB and CWB for heavy metals followed the order of Pb$^{2+}$ > Cd$^{2+}$ ≈ Ni$^{2+}$. The adsorption capacity of CMB increased with the increase in pyrolysis temperature. CMB6 exhibited excellent adsorption capacities of 40.8, 24.2, and 25.1 mg·g$^{-1}$ for Pb$^{2+}$, Cd$^{2+}$, and Ni$^{2+}$, respectively. However, interestingly, the heavy metal adsorption capacity of CWB4 and CWB6 was higher than that of CWB5. As mentioned above, CMB6 has high mineral content that promotes precipitation and cation exchange, while CWB4 contains rich oxygen-containing functional groups that promote heavy metal complexation. Therefore, it is speculated that CWB4 has superior adsorption capacity for heavy metals than CWB5 because of the higher number of oxygen-containing functional groups. After further carbonization, the oxygen-containing functional groups are lost to form syngas and the mineral content is enriched in CWB6 with increasing pyrolysis temperature. The released minerals provide cation exchange site resulting in higher adsorption capacity of CWB6 compared to CWB5.

In order to compare the sorption performance of the studied biochars, a review of literature was done about the biochars in other studies used for adsorbing heavy metals [26–32]. In Table 3, it can be seen that the CMB6 showed comparably high adsorption capacity for Pb$^{2+}$, Cd$^{2+}$, and Ni$^{2+}$. Therefore, the CMB6 is a potential adsorbent for further studies.

Figure 1. SEM image of different biochars.

Figure 2. The change of pH of wastewater by adding different biochars.
Adsorption kinetics and isotherm models of CMB and CWB

The heavy metal adsorption kinetics of the biochars were simulated by pseudo-first-order (PFOD) and pseudo-second-order (PSOD) kinetic models, respectively, which can be expressed as reported previously [33]:

\[ Q = Q_t \times \exp(k_1 \times t) \]

\[ Q = (k_2 \times Q_t^2 \times t)/(1 + k_2 \times Q_t \times t) \]

where \( Q \, (\text{mg} \cdot \text{g}^{-1}) \) represents the amount of heavy metal adsorbed at time \( t \); \( Q_t \, (\text{mg} \cdot \text{g}^{-1}) \) denotes the amount of heavy metal adsorbed at equilibrium; and \( k_1 \, (\text{min}^{-1}) \) and \( k_2 \, (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}) \) are the rate constants of PFOD and PSOD reactions.

Mononuclear and binuclear adsorption mechanisms in solid-solution systems are described by the PFOD and PSOD models, respectively. The heavy metal adsorption kinetics of the biochars is shown in Figure 4 and Table 4. The results show that the slow kinetics of heavy-metal adsorption by biochars fitted both the PFOD and PSOD models \((R^2 \geq 0.98)\), assuming that physical adsorption and chemisorption work together contributed to heavy metal adsorption on CMB and CWB, which reached equilibrium within minutes. Owing to the maximum levels of equilibration adsorption, CMB6 emerged as highly promising adsorbent for Pb \((Q_{\text{max}} = 42.07–51.87 \, \text{mg} \cdot \text{g}^{-1})\), Cd \((Q_{\text{max}} = 23.08–26.78 \, \text{mg} \cdot \text{g}^{-1})\) and Ni \((Q_{\text{max}} = 23.18–27.31 \, \text{mg} \cdot \text{g}^{-1})\).

Figure 3. The heavy metals adsorption capacity from wastewater of CMB (a) and CWB (b).
The different initial individual concentrations of $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, and $\text{Ni}^{2+}$ were 0, 10, 20, 30, 50, 100, 200, 300 mg·L$^{-1}$, based on the adsorption isotherm. The equilibrium adsorption mechanisms were described using Langmuir and Freundlich models, based on the following equations [33]:

Langmuir $Q = \frac{Q_{\text{max}} \times K_L \times C_e}{1 + K_L \times C_e}$

Freundlich $Q = K_F \times C_e^n$

where $Q$ (mg·g$^{-1}$) and $C_e$ (mg·L$^{-1}$) are the amounts of adsorbed heavy metal and the concentrations at equilibrium, respectively; $Q_{\text{max}}$ (mg·g$^{-1}$) denotes the maximum adsorption capacity reaching equilibrium; $K_L$ represents the Langmuir constant; and $K_F$ is the Freundlich adsorption equilibrium constant. The symbol $n$ represents Freundlich index.

The simulation results of Langmuir and Freundlich models for heavy metal adsorption by CMB6 and CWB6 are shown in Figure 5 and Table 5. The Langmuir equation describes the adsorption process of $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, and $\text{Ni}^{2+}$ with higher correlation coefficients ($R^2 > 0.90$) than the Freundlich equation, indicating that monolayer surface chemical adsorption was the primary adsorption mechanism [5,13]. Based on the $Q_{\text{max}}$, the adsorption order was as follows: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. The $Q_{\text{max}}$ values of CMB6 were 53.83 mg·g$^{-1}$ for $\text{Pb}^{2+}$, 26.42 mg·g$^{-1}$ for $\text{Cd}^{2+}$, and 20.04 mg·g$^{-1}$ for $\text{Ni}^{2+}$.

![Figure 4. Kinetic model fitting curve for heavy metals adsorption by CMB6 and CWB6.](image)

**Table 3.** Comparision of sorption performance of biochars in different studies.

| Raw materials       | Pyrolysis temperature (°C) | Heavy metals | Initial concentration (mg·L$^{-1}$) | Adsorbed amount $Q_e$ (mg·g$^{-1}$) | Reference |
|---------------------|-----------------------------|--------------|-------------------------------------|-------------------------------------|-----------|
| Tea waste-Sewage sludge | 300                         | Cd           | 10–80 mg·L$^{-1}$                    | 20                                  | [26]      |
| Rape straw          | 500                         | Pb           | 0–5 mmol·L$^{-1}$                    | 46.93                               | [27]      |
| Green waste         | 600                         | Cd           | 5.6 mmol·L$^{-1}$                    | 6.72                                | [28]      |
| Peanut shell        | 400                         | Pb           | 3–30 mg·L$^{-1}$                    | 3.87                                | [29]      |
| wasted kelp and hijikia | 500             | Cd           | 200 mg·L$^{-1}$                     | 23.16                               | [30]      |
| sawdust             | 650                         | Cd           | 50 mg·L$^{-1}$                      | 12.5                                | [31]      |
| apricot stones      | 500                         | Pb           | 100 mg·L$^{-1}$                     | 48.435                              | [32]      |
| Cattle manure       | 600                         | Pb           | 100 mg·L$^{-1}$                     | 45.825                              |           |
| Cherry wood         | 600                         | Pb           | 100 mg·L$^{-1}$                     | 24.5                                |           |

**Table 4.** Kinetic model fitting parameters for heavy metals adsorption by CMB6 and CWB6.

| System | $k_{(1)}$ | $Q_{(1)}$ | $R^2$ | $k_{(2)}$ | $Q_{(2)}$ | $R^2$ |
|--------|-----------|-----------|-------|-----------|-----------|-------|
| Pb CMB6 | 0.00386 ± 3.87171 · 10$^{-4}$ | 42.07135 ± 1.71631 | 0.98494 | 7.49922 · 10$^{-5}$ ± 1.4439 · 10$^{-5}$ | 51.87405 ± 2.87538 | 0.98522 |
| Pb CWB6 | 0.00624 ± 3.39813 · 10$^{-4}$ | 28.99239 ± 0.57263 | 0.99536 | 1.94137 · 10$^{-4}$ ± 2.75033 · 10$^{-5}$ | 34.4675 ± 1.27382 | 0.99058 |
| Cd CMB6 | 0.0076 ± 6.83806 · 10$^{-4}$ | 23.07597 ± 0.71721 | 0.98605 | 3.28116 · 10$^{-4}$ ± 3.30012 · 10$^{-5}$ | 26.7842 ± 0.67429 | 0.99431 |
| Cd CWB6 | 0.0062 ± 3.81621 · 10$^{-4}$ | 21.25593 ± 0.4752 | 0.98619 | 2.60704 · 10$^{-4}$ ± 5.51644 · 10$^{-5}$ | 25.29156 ± 1.39985 | 0.97948 |
| Ni CMB6 | 0.0067 ± 7.1342 · 10$^{-4}$ | 23.18738 ± 0.88514 | 0.98091 | 2.72036 · 10$^{-4}$ ± 2.64761 · 10$^{-5}$ | 27.3050 ± 0.68005 | 0.99512 |
| Ni CWB6 | 0.0053 ± 3.70296 · 10$^{-4}$ | 14.98709 ± 0.39534 | 0.9928 | 2.96166 · 10$^{-4}$ ± 6.95117 · 10$^{-5}$ | 18.16668 ± 1.15753 | 0.97699 |
and 30.41 mg·g⁻¹ for Ni²⁺ corresponding to the maximum metal ion content (52.4 mg·g⁻¹) and the highest BET surface area (22.1 m²·g⁻¹).

3.4 Contribution of heavy metal adsorption mechanisms

As mentioned above, the results of quantitative analysis of the heavy metal adsorption mechanisms based on metal ion exchange (Qₓₑ), mineral precipitation (Qₓₚ), functional group complexation (Qₓₑ) and heavy metal -π coordination (Qₓₑ) of CMB6 and CWB6 are presented in Table 6. For the CMB6, the Qₓₑ/Qₓₑ ration was the higher more than 40% except for Pb, indicating that ion exchange was the dominant mechanisms of Cd and Ni adsorption because of metal ion content in CMB6 (Table 1). The Pb Qₓₑ/Qₓₑ of CMB6 was the highest (79%), indicating that the Pb adsorption was also attributed to the interaction with minerals and metal ions, and mineral precipitation. Conversely, the Qₓₑ/Qₓₑ of CWB6 was substantially lower than CMB6 under 60%, which was in accordance with higher levels of oxygen-containing functional groups and lower minerals content of CWB6. Based on the contribution of different mechanisms to heavy metal adsorption, ion exchange, and mineral precipitation were the two dominant mechanisms of heavy metal adsorption by biochar. In future, the biochar can be modified by impregnating metal ions into biomass or biochar to improve its heavy metal adsorption capacity and removal from industrial wastewater [33,34].
5 Conclusion

In this study, the physicochemical properties and the heavy metal adsorption capacities of biochars derived from CM and CW under different pyrolysis temperatures were systematically evaluated and compared. The results showed that there are significant differences in the physicochemical properties between the two types of biochars. CMB 6 exhibited excellent adsorption of Pb$^{2+}$ (40.8 mg·g$^{-1}$), Cd$^{2+}$ (24.2 mg·g$^{-1}$), and Ni$^{2+}$ (25.1 mg·g$^{-1}$), suggesting potential practical applications. The adsorption kinetics and isotherm models of CMB and CWB indicated that the monolayer surface chemical adsorption was the main adsorption mechanism. CMB6 emerged as a very promising adsorbent for Pb ($Q_{\text{max}} = 42.07–51.87$ mg·g$^{-1}$), Cd ($Q_{\text{max}} = 23.08–26.78$ mg·g$^{-1}$), and Ni ($Q_{\text{max}} = 23.18–27.31$ mg·g$^{-1}$). The quantitative analysis showed that ion exchange and mineral precipitation were the two dominant mechanisms of heavy metal adsorption by biochar, especially accounting for about 70% for CMB6. Overall, this study will provide new opportunities for developing a low-cost and high-efficient adsorbent to remove heavy metals from wastewater.

Acknowledgments

The team would like to appreciate for the supports from the Key Laboratory of Clean Production and Utilization of Renewable Energy, Ministry of Agriculture and Rural Affairs, China Agricultural University; National Center for International Research of BioEnergy Science and Technology, Ministry of Science and Technology, China Agricultural University; and Beijing Municipal Key Discipline of Biomass Engineering.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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