A Comparative Study on the Adsorption Performance and Mechanisms of Different Biochar Materials for Heavy Metal Ions in Water

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Abstract. The escalating issue of heavy metal contamination in aqueous environments poses a significant threat to ecological balance and human health. Biochar, a carbon-rich material derived from biomass pyrolysis, has emerged as a cost-effective and environmentally benign adsorbent for water remediation. However, the adsorption efficacy of biochar is profoundly dependent on its original feedstock. This study provides a comprehensive comparison of the adsorption performance and underlying mechanisms of three distinct biochars, derived from rice husk (RHB), pine wood (PWB), and chicken manure (CMB), for the removal of lead (Pb (II)) and cadmium (Cd (II)) from water. The materials were prepared via slow pyrolysis at 500°C and systematically characterized by means of BET, SEM, FTIR, and XRD. Batch adsorption experiments were conducted to evaluate the effects of pH, contact time, and initial ion concentration. The results indicated significant differences in both performance and mechanisms. CMB, rich in minerals and exhibiting a high pH in aqueous solution, exhibited the highest adsorption capacity for Pb (II) (148.5 mg/g) primarily through precipitation and ion exchange. Conversely, RHB, with its high specific surface area (289.4 m²/g) and siliceous structure, showed a superior performance for Cd (II) (89.2 mg/g), which was driven by surface complexation and physical adsorption. PWB demonstrated moderate, non-specific adsorption. Kinetic studies revealed that the pseudo-second-order model best described the adsorption process for all materials, which indicates chemisorption is a key rate-limiting step. The isotherm data of RHB and PWB fitted well with the Langmuir model, while that of CMB was more suitable for the Freundlich model due to its heterogeneous surface. This research underscores the critical importance of feedstock selection in designing biochar adsorbents tailored to remove specific heavy metal pollutants.

1 Introduction

Due to industrial, urban, and agricultural activities, toxic heavy metal ions have been continuously discharged into water bodies, posing an enduring environmental issue. Pb (II), Cd (II) are heavy metals which are quite a worry as they are non-biodegradable, toxic, and capable of bio-accumulating, leading to major health issues such as neurological disorders and kidney damage. Therefore, it is necessary to have efficient, low-cost and sustainable removal methods [1]. Traditional methods such as chemical precipitation, ion exchange, and membrane filtration have obvious drawbacks, including high cost, inability to remove completely, and generation of secondary sludge. This has prompted the search for alternative methods, among which adsorption is a hopeful approach due to its simple operation, high efficiency, and low cost. Thus, there is a demand for a novel, efficient, available and sustainable adsorbent.

In this context, biomass pyrolysis-produced biochar, a kind of solid matter, is drawing substantial notice. Biochar absorbs a large amount of low-value natural waste, converts it into useful products, and also aids in carbon sequestration. It has a large specific surface area (SSA), high porosity, and numerous functional groups, (e.g., oxygen-containing groups including carboxyl groups and hydroxyl groups) as well as minerals. Heavy metals can be removed via the surface precipitation, ionic exchange, electrostatic attraction, and surface complexation of biochar. However, the physical and chemical properties and adsorption performance of biochar are highly dependent on its feedstock and pyrolysis conditions. Because feedstocks differ in their contents of cellulose, lignin, and minerals, their chemical properties are also different. Recent research on biochar (2023-2024) has advanced our understanding of heavy metal adsorption. Wei et al. (2024) adopted machine learning to predict and interpret biochar-metal interactions, identifying complex multi-mechanism pathways. Bayar et al. (2024) pointed out that biochar is a low-cost and environmentally friendly option for heavy metal removal, clarifying the selection of

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feedstocks and modification of pyrolysis techniques. Wang et al. (2024) prepared chitosan-modified magnetic biochar, which shows excellent performance in removal of Cr (VI), As (III) and Pb (II) through synergistic effects. Moreover, recent studies on nanobiochar and characterizations (XPS, EXAFS) provide a better understanding of metal-biochar molecular interactions, focusing on the roles of surface functional groups, minerals and π-π electron systems in adsorption. Although some studies have been conducted, a systematic comparison of biochars derived from different feedstocks such as high-silica agricultural residues, high-lignin woody biomass and high-ash/mineral animal waste under the same pyrolysis conditions is still lacking [2]. Therefore, the present work investigates the comparative adsorption of aqueous Pb (II) and Cd (II) onto biochars prepared from rice husk biochar (RHB), pine wood biochar (PWB), and cow manure biochar (CMB) to clarify the predominant adsorption mechanisms for the two heavy metals and correlate the biochars' characteristics with their absorption capacity.

2 Materials and methods

2.1 Biochar Preparation

Three feedstocks were selected: rice husk (RHB), pine wood (PWB), and chicken manure (CMB). Feedstocks were washed with deionized (DI) water, dried (80 °C, 24 h), and ground (< 2 mm). The samples were then subjected to a slow pyrolysis process. Batches (~100 g) were placed in a muffle furnace crucible and purged with N_2 (200 mL/min, 30 min) to establish an oxygen-limited environment. The temperature was raised at a heating rate of 10°C/min to 500°C and maintained for 2 hours. The furnace cooled naturally under N_2. The resulting biochar products (RH-BC, PW-BC, CM-BC) were collected, ground, and sieved (100-mesh, < 150 μm) for subsequent experiments. The biochars were stored in sealed glass desiccators. The biochar yield was calculated as the ratio of the dry biochar weight to the initial dry biomass weight.

2.2 Biochar Characterization

The properties of the biochar were correlated with its adsorption capacity via the characterization of biochar. pH and EC (1:10 w/v suspension) were determined. Ash content was determined by heating at 250° for 6h. Elementary composition: C, H, N was analyzed using a Vario EL cube elemental analyzer. BET specific surface area and pore characteristics were determined using a Micromeritics ASAP 2020 analyzer from nitrogen adsorption-desorption isotherms (77 K) after degassing [3]. Surface morphology was examined by SEM (Hitachi SU8010). Surface functional groups were determined using FTIR (Bruker Tensor 27, 4000 - 400 cm-1). Crystalline mineral phases were analyzed using X-ray diffraction (XRD, Bruker D8 Advance, Cu-Kα). Zeta potential was measured (Malvern Nano ZS) to determine surface charge as a function of pH.

2.3 Batch Adsorption Experiments

Batch experiments were conducted to evaluate the Pb (II) and Cd (II) removal efficiencies. Stock solutions (1000 mg/l) of Pb $(NO_3)_2$ and Cd $(NO_3)_2$ were prepared using analytical grade reagents. Batch experiments were conducted with 25 mL metal solution in 50 mL polyethylene tubes at a biochar dosage of 1.0 g/L, and the mixtures was agitated using a rotary shaker (150 rpm, 25±1 °C). The effect of solution pH was investigated over the range of 2.0-8.0, with pH adjusted using 0.1M HCl or 0.1 M NaOH. pH Adjustment Protocol: The initial pH of the metal solutions was adjusted to the desired values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0) by dropwise addition of 0.1 M HCl or 0.1M NaOH, with continuous stirring using a magnetic stirrer, prior to biochar addition. For the first 2 h after biochar addition, the pH was monitored every 30 min and readjusted if it deviated from the target value by more than ±0.2. The final pH was measured and recorded after adsorption equilibrium was achieved. Equilibrium Determination: preliminary kinetic experiments were carried out to determine the equilibrium time. Samples were collected at different time points (5, 10, 20, 30, 60, 120, 240, 360, 480, 720, 1440 min) and analyzed for residual metal concentrations. Equilibrium was defined as the point where the change in metal removal efficiency for three consecutive readings was less than 2% over a 2-hour period. Based on these results, 24 h was selected as the equilibrium time for isotherm experiments to ensure full equilibration of all biochar-metal systems. Adsorption kinetics was investigated by collecting samples over a time range of 5 min- 24 h at the optimal pH (5.5, determined in the preliminary experiment). Adsorption isotherms were constructed with initial metal concentrations ranging from 10 to 200 mg/L, and the experiments were maintained for 24 h [4]. After adsorption, the suspensions were filtered through 0.45-μm membrane filters, and the residual metal concentrations in the filtrates were determined using an atomic absorption spectrophotometer (AAS, PerkinElmer PinAAcle 900T). All experiments were replicated three times. The equilibrium adsorption capacity qe (mg/g) and metal removal efficiency R (%) were calculated based on the initial and remaining metal concentrations [5].

3 Results and discussion

3.1 Biochar Physicochemical Characteristics

Table 1 presents the properties of the biochars. Feedstock type determines the final properties regardless of identical pyrolysis conditions: 289.4m^2/g is the highest S_BET value for RHB, which results from the abundant silica content that acts as a template. In contrast, CMB presented the lowest specific surface area of BET (35.1 m^2/g), but the highest ash content with 48.2%, and a strongly basic pH (10.4). The high ash content corresponds to a high proportion of inorganic minerals (e.g., phosphates, carbonates), which were confirmed by XRD analysis. Regarding pine wood biochar (PWB) derived from lignocellulosic biomass, it showed intermediate properties: relatively lower S_BET (165.7 m^2/g), very low ash (2.1%), and the highest carbon content (84.5%). The zeta potential of all biochars was net negative and higher than their respective point of zero charge (pHpzc), indicating an attraction between the biochars and cationic bioavailable metals. However, the surface charge and pHpzc values of the biochars varied significantly. CMB maintained a negative charge even at low pH, PWB and RHB had pHpzc values of about 3.5 and 4.2, respectively. These significant differences in surface area, mineral composition, pH, and surface functional groups are thought to result in the different adsorption behaviors of the biochars toward metals.

Table 1. Physicochemical characteristics of the prepared biochars.

Property	Rice Husk Biochar (RHB)	Pine Wood Biochar (PWB)	Chicken Manure Biochar (CMB)
Pyrolysis Temp. (°C)	500	500	500
Yield (%)	38.5	31.2	52.8
Ash Content (%)	34.6	2.1	48.2
pH (1:10 w/v)	7.8	6.9	10.4
Carbon (C, %)	56.2	84.5	35.1
S_BET (m^2/g)	289.4	165.7	35.1
Total Pore Vol. (cm^3/g)	0.21	0.14	0.05
pH_pzc	4.2	3.5	~6.8
Ca (mg/g)	12.5	4.3	85.6
Mg (mg/g)	5.8	1.9	20.4
P (mg/g)	3.1	0.8	62.7

3.2 Effect of Solution pH on Adsorption

Solution pH is a master variable for all heavy metal adsorption, controlling adsorbent surface charge and metal ion speciation. Within the pH range from 2.0 to 8.0, there was an overarching trend with all biochar: very little adsorption at extremely low pH (pH 2.0), followed by a gradual increase as pH rose, reaching a plateau around pH 5.0-6.0. At low pH conditions, high H^+ concentrations protonate the biochar surface, resulting in strong electrostatic repulsion between the positively charged metal cations (Pb^{2+}, Cd^{2+}) and the protonated surface, as well as competition between H+ and metal cations for active adsorption sites. As pH increases, the biochar surface becomes more deprotonated and exhibits a higher density of negatively charged functional groups, leading to stronger electrostatic attraction between the biochar and metal cations and reduced H^+ competition. For RHB and PWB, the sharp increase in adsorption between pH 3-5 matches up with the measured point of zero charge (pHpzc) values of 4.2 & 3.5, respectively. In contrast, CMB exhibited distinct absorption behavior, with significantly higher metal removal efficiency even at lower pH, attributed to its strong buffering capacity. This is attributed to its high alkalinity and the presence of dissolved carbonates and phosphates, which induce metal precipitation independent of surface complexation. When pH exceeds 6.0 (for Cd) or 7.0 (for Pb), metal hydroxide precipitate, making it difficult to distinguish the contributions of adsorption and precipitation to metal removal. Based on these results, a pH of 5.5 which gave the maximum adsorption and no precipitations in all of following experiments.

3.3 Adsorption Kinetics

Adsorption kinetics studies were conducted to determine the adsorption rate and rate-limiting steps. Adsorption of Pb (II) and Cd (II) for 24 hours, following a two-phase kinetic behavior. Adsorption was fast in the initial stage (2-4 hours), followed by a gradual slowdown until equilibrium was approached. The first quick uptake is because there are easily reachable active sites on the external surface of biochars, slowing happens when the process limits come from inside the particles or complexing reactions. To describe this two-phase behavior, fitted data was obtained to the pseudo-first-order (PFO) and pseudo second order (PSO) kinetic models. The corresponding kinetic parameters are presented in Table 2 below. The results showed that the PSO model provided a good fit for the absorption of both metal ions onto all biochars, with correlation coefficients (R^2) greater than 0.99. Additionally, the equilibrium capacities (qe, cal) calculated in the PSO model matched perfectly well with the experimental values (qe, exp). Since the PSO model is fitting so well, it can be inferred that the rate-limiting step of the adsorption process is chemisorption with valence forces between the adsorbent and adsorbate, rather than being solely limited by a mass transfer mechanism.

Table 2. Kinetic parameters for Pb (II) and Cd (II) adsorption by the biochars (Initial Conc. = 50 mg/L, pH = 5.5).

Metal	Biochar	qe,exp (mg/g)	Pseudo-First-Order		Pseudo-Second-Order		
			k_1 (1/min)	R^2	qe,cal (mg/g)	k_2 (g/mg·min)	R^2
Pb (II)	RHB	38.6	0.045	0.941	39.8	0.0031	0.998
	PWB	22.1	0.051	0.955	22.9	0.0045	0.999
	CMB	47.9	0.068	0.962	48.5	0.0052	0.999
Cd (II)	RHB	31.5	0.039	0.933	32.4	0.0028	0.997
	PWB	16.8	0.042	0.940	17.3	0.0039	0.998
	CMB	28.4	0.055	0.951	29.0	0.0041	0.999

3.4 Adsorption Isotherms

Adsorption isotherms refers to the equilibrium relation between the concentration of adsorbate in the solution and the amount of adsorbate adsorbed onto the solid adsorbent, providing insights into the adsorption capacity, affinity, and mechanism. The experimental equilibrium data were fitted to the two isotherm models of Langmuir and Freundlich. The obtained parameters of both models are presented in Table 3. Langmuir model assumes that adsorption is a monolayer process on a homogeneous surface, while Freundlich model describes the adsorption process on heterogeneous surfaces. By looking at the correlation coefficient (R^2) values, the Langmuir model fitted the data for RHB ($R^2 > 0.99$) and PWB ($R^2 > 0.98$) well, meaning that adsorption occurred as a monolayer on relatively uniform surfaces. In contrast, the Freundlich model gave a higher R^2 value for CMB ($R^2 > 0.97$), which has a more heterogeneous surface due to its complex mineral composition. The Freundlich parameter n> 1 for CMB confirmed favorable adsorption. The maximum adsorption capacity (qmax) derived from the Langmuir model facilitates the comparison of adsorption performance for Pb (II), with the order of qmax being: CMB (148.5mg/g)>RHB (95. 4 mg/g)>PWB (51. 2 mg/g). The high Pb (II) adsorption capacity of CMB strongly suggests that precipitation is a key removal mechanism. Notably, the order of qmax for Cd (II) adsorption was reversed: RHB (89.2 mg/g)> CMB (70.1 mg/g)> PWB (38.8 mg/g). These reverse points out an important aspect: the most effective biochar feedstock varies depending on the target pollutant. RHB has a larger surface area and a silica-based functional group that preferentially bind to Cd (II). Pb (II) is primarily removed from aqueous solutions through precipitation caused by CMB.

Table 3. Langmuir and Freundlich isotherm model parameters for Pb (II) and Cd (II) adsorption.

Metal	Biochar	Langmuir Model			Freundlich Model		
		qmax (mg/g)	b (L/mg)	R^2	KF (mg/g(L/mg) $^{1/n}$)	n	R^2
Pb (II)	RHB	95.4	0.21	0.992	20.3	2.85	0.945
	PWB	51.2	0.15	0.988	9.8	2.41	0.931
	CMB	148.5	0.35	0.954	45.1	3.12	0.986
Cd (II)	RHB	89.2	0.18	0.995	15.6	2.90	0.950
	PWB	38.8	0.11	0.981	5.7	2.25	0.922
	CMB	70.1	0.24	0.948	18.2	2.77	0.974

3.5 Adsorption Mechanisms

To find out main adsorption mechanism(s), the biochar characterization data, batch experiment results, and post-adsorption information must be integrated. Table 4 presents the key FTIR and XRD results after Pb (II) and Cd (II) saturation of the biochars. For RHB, the large specific surface area (S BET, Table 1) means that physical adsorption and pore filling play important roles. However, FTIR analysis after adsorption (Table 4) had clear shift peaks for - OH, C=O, Si-O-Si, which indicates that surface complexation between metal ions and these oxygen-containing functional groups is mainly responsible for surface complexation, and it is prominent especially for Cd (II) on the siliceous structure. For PWB (little ash content and limited surface functional groups), adsorption is likely dominated by weak physical adsorption on its porous carbon matrix, accompanied by minor surface complexation. The overall poor performance for both metals is attributed to the lack of effective adsorption sites.

CMB exhibits distinctly different adsorption behavior. The low S_BET (Table1) means that physical adsorption is a minor contributor to metal removal. Instead, chemical precipitation which favored by its high ash content, alkalinity, and high contents of P and Ca (Table 1) is the major pathway, at least for Pb (II). Post-adsorption XRD results (Table 4) showed the appearance of new crystalline structures, which were identified as lead phosphate [$Pb_5(PO_4)_3(OH)$] and also lead carbonates ($PbCO_3$). This directly confirms the occurrence of precipitation via XRD analysis. Additionally, the huge release of Ca^{2+}/Mg^{2+} ions showed that exchange with native cations is another important pathway. And the FTIR analysis further supported this finding, as it showed prominent shifts in the P-O vibration bands, which showed that the phosphate group were involved in the precipitation reaction. Thus, while RHB relies on high surface area and surface complexation for metal removal, CMB acts mainly as a chemical reactant, with metals being taken out through the process of precipitation and ion exchange.

Table 4. Summary of key FTIR and XRD results before and after adsorption.

Biochar	Analysis	Observation Before Adsorption	Key Observation After Pb (II) Adsorption	Key Observation After Cd (II) Adsorption
RHB	FTIR	Strong -OH (3410 cm^{-1}), C=O (1705 cm^{-1}), Si-O-Si (1090 cm^{-1})	Peak shift of -OH to 3390 cm^{-1}, C=O to 1690 cm^{-1}. Si-O-Si band broadened.	Peak shift of -OH to 3395 cm^{-1}, C=O to 1692 cm^{-1}. Significant shift in Si-O-Si.
	XRD	Broad peak for amorphous silica (2θ ≈ 22°)	No new major crystalline peaks.	No new major crystalline peaks.
PWB	FTIR	Broad -OH (3430 cm^{-1}), C=O (1700 cm^{-1}), C=C (1620 cm^{-1})	Minor shifts in -OH and C=O peaks.	Minor shifts in -OH and C=O peaks.
	XRD	Broad peak for amorphous carbon (2θ ≈ 24°)	No new crystalline peaks.	No new crystalline peaks.

CMB	FTIR	-OH (3400 cm^{-1}), CO_3^{2-} (1430 cm^{-1}), P-O (1040 cm^{-1})	Significant shift in CO_3^{2-} to 1410 cm^{-1} and P-O to 1025 cm^{-1}.	Shift in CO_3^{2-} to 1420 cm^{-1} and P-O to 1030 cm^{-1}.
	XRD	Calcite ($CaCO_3$), Hydroxyapatite [$Ca_5(PO_4)_3(OH)$]	New peaks: Cerussite ($PbCO_3$), Hydroxy pyromorphite [$Pb_5(PO_4)_3(OH)$]	New peaks: Otavite ($CdCO_3$), weak Cd-phosphate phases.

4 Conclusions

The adsorption performance and mechanisms of three biochars derived from rice husk (RHB), pine wood (PWB), and chicken manure (CMB) were systematically studied for the removal of aqueous Pb (II) and Cd (II). These results clearly indicate that the feedstock biomass determines the physical and chemical properties of the resulting biochar, which in turn governs its adsorption affinity toward specific heavy metal contaminants.

Chicken manure biochar (CMB) containing high ash and having many mineral assemblages of phosphates and carbonates and strong alkalinity has the highest adsorption capacity for Pb (II) (148.5 mg/g). Pb (II) was removed by CMB through chemical precipitation, which forms stable lead phosphate and lead carbonate minerals. Ion exchange between Pb (II) and the inherent Ca^{2+}/ Mg^{2+} in CMB also plays an important supplementary role.

In contrast, rice husk biochar (RHB)–possessing a large specific surface area (289.4 m^2g^{-1}) and a siliceous skeleton–showed the highest adsorption capacity for Cd (II) (89.2 mg/g). This adsorption mainly occurred via surface complexation with numerous hydroxyl and carboxyl groups, as well as physical adsorption. Pine wood biochar (PWB) served as a baseline; it showed moderate and non-specific adsorption for both metals, which was limited by its low surface functional groups and intermediate specific surface areas.

Furthermore, the pseudo-second-order kinetic model and isotherm fitting results were consistent with these mechanistic differences: the Langmuir model (for RHB, PWB) corresponds to chemisorption on homogeneous sites, while the Freundlich model (for CMB) corresponds to heterogeneous chemisorption and precipitation. The study indicates that it is not effective to use the same biochar for all forms of pollution; the use of intelligent biochar adsorbent design requires selecting suitable materials to target specific contaminants.

Future studies will attempt to optimize the pyrolysis conditions for these feedstock-pollutant pairs and verify their performance in realistic multi-metal real-world wastewater.

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