Study on the Adsorption Performance of Hydroxyapatite-Loaded Biochar for Cu^{2+}

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Abstract: Hydroxyapatite-loaded biochar (HAP–biochar) composites were synthesized using corn straw biochar (CSB) and chicken manure biochar (CMB) to improve Cu^{2+} removal from aqueous solutions. Composites with varying biochar:HAP ratios were prepared and characterized by SEM, which confirmed uniform HAP dispersion and enhanced porosity. Systematic testing identified the composition corresponding to biochar:HAP = 3:1 (designated CSB-1.5 and CMB-1.5; HAP ≈ 25 wt%) as optimal. Under pH 5.0 and an adsorbent dose of 0.05 g, CSB-1.5 and CMB-1.5 achieved maximum Cu^{2+} capacities of 82.06 and 98.09 $mg \cdot g^{-1}$, respectively. Kinetic and isotherm analyses indicated that adsorption followed a pseudo-second-order model ($R^2 \approx 0.99$) and was dominated by chemisorption via ion exchange and surface complexation; Elovich fitting supported heterogeneous surface behavior. Compared to single-component HAP or pristine biochar, the optimized composites combine improved HAP dispersion, abundant functional groups, and robust pore networks, delivering high removal efficiency and material stability. These features make the optimized HAP–biochar composites promising, low-cost adsorbents for practical heavy-metal remediation.

1. Introduction

Copper (Cu) is an essential trace element for living organisms but becomes toxic at elevated concentrations. Excessive copper released from mining, electroplating, and industrial wastewater can accumulate in the environment, causing soil and water pollution and posing risks to plants, animals, and human health[1]. Therefore, developing efficient and sustainable technologies for Cu^{2+} removal from contaminated environments is of great importance for ecological safety and environmental protection. Traditional single remediation methods are often ineffective for strongly acidified soils because of persistent heavy metal accumulation and low pH. Among available strategies, stabilization using chemical amendments has gained attention[2]. This approach introduces passivating agents to convert heavy metals into less mobile and bioavailable forms, effectively reducing their ecological risk. It is considered practical and economical, with high efficiency and minimal secondary pollution.

Biochar, a carbon-rich porous material produced via pyrolysis of biomass under oxygen-limited conditions, possesses a large surface area, rich pore structure, and abundant functional groups, making it promising for environmental remediation[3]. Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is an environmentally friendly mineral known for its strong affinity toward heavy metal ions through ion exchange and surface complexation[4]. However, due to its high surface energy, HAP particles tend to aggregate, limiting active site exposure and reducing adsorption capacity[5]. Combining biochar with HAP can overcome these drawbacks. Biochar provides a stable support that disperses HAP particles, while HAP adds active sites for metal binding. This synergistic combination enhances both adsorption efficiency and material stability.

In this study, hydroxyapatite-loaded biochar (HAP–biochar) composites were synthesized using corn straw biochar (CSB) and chicken manure biochar (CMB) as carriers. The objectives were to:

(1) prepare composites with different mass ratios of biochar to HAP;

(2) characterize their morphology and structure; and

(3) evaluate their Cu^{2+} adsorption capacity and reveal the underlying adsorption mechanisms.

This study provides a scientific basis for the development of efficient, low-cost, and environmentally friendly adsorbents for heavy metal removal..

2. Materials and Methods

The biochar used in this study was purchased from a commercial environmental technology company. Analytical-grade reagents, including $CuSO_4 \cdot 5H_2O$, $CaCl_2$, $(NH_4)_2HPO_4$, H_2SO_4, NaOH, and $NH_3 \cdot H_2O$, were obtained from the National Pharmaceutical Chemical Reagent Co., Ltd. All aqueous solutions were prepared using ultrapure water..

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2.1. Synthesis of HAP–biochar composites

Hydroxyapatite–biochar composites were prepared using corn-straw (CSB) and chicken-manure biochar (CMB). Different amounts of biochar (0.5–2.0 g) were added to 50 mL of 1.0 mol·L^{-1} $CaCl_2$ solution, followed by 0.5 g of HAP and stirring for 30 min. Then, 50 mL of 0.6 mol·L^{-1} $(NH_4)_2HPO_4$ was added dropwise, and the pH was adjusted to 10.5 with NaOH. After stirring for 120 min, the mixture was aged at 25 °C for 12 h, filtered, dried at 80 °C, ground, and labeled as CSB-0.5–CSB-2 and CMB-0.5–CMB-2.

2.2. Material Characterization and Adsorption Kinetics Experiments

The surface morphology of the composites was characterized using a scanning electron microscope (SEM). The adsorption kinetics of Cu^{2+} on CSB-1.5 and CMB-1.5 were investigated at an adsorbent dosage of 1 g·L^{-1} and an initial Cu^{2+} concentration of 0.1 g·L^{-1} under conditions of 298.15 K and pH 5.0 ± 0.2. The mixtures were shaken at 120 rpm, and samples were collected at intervals from 1 to 1440 min, filtered through a 0.22 μm membrane, and analyzed for Cu^{2+} concentration. All experiments were performed in triplicate to ensure accuracy..

3. Results and Analysis

3.1. SEM Analysis

Figure 1 presents the SEM images of CSB-0.5, CSB-1, CMB-0.5, and CMB-1 composites, clearly demonstrating the significant differences in surface morphology that arise from variations in both the type of biochar and the hydroxyapatite (HAP) loading ratio. The CSB-based composites exhibit a relatively loose and well-developed porous structure characterized by tubular and channel-like pores, which greatly enhance the specific surface area and create more active sites for ion diffusion and exchange. This structural feature allows for improved accessibility of Cu^{2+} ions to the adsorptive sites, thereby promoting stronger interactions between the functional groups of biochar and the metal ions[6]. In contrast, the CMB-based composites show a denser, honeycomb-like morphology with smaller and less interconnected pores, resulting in lower porosity and limited availability of reactive sites for metal binding. Numerous HAP particles are evenly distributed across the surfaces of both CSB and CMB, though minor aggregation is observed in certain regions, particularly at higher loading ratios. The uniform dispersion of HAP enhances the distribution of active phosphate sites, facilitating ion exchange and surface complexation processes[7]. Moreover, the well-developed pore network of CSB composites not only accelerates the diffusion of Cu^{2+} ions but also provides a stable structural framework for sustained adsorption. Consequently, the CSB-based materials exhibit superior Cu^{2+} adsorption capacity compared with CMB-based composites, indicating that the physicochemical structure of the biochar matrix plays a decisive role in determining the overall adsorption performance and efficiency of the HAP–biochar composites..

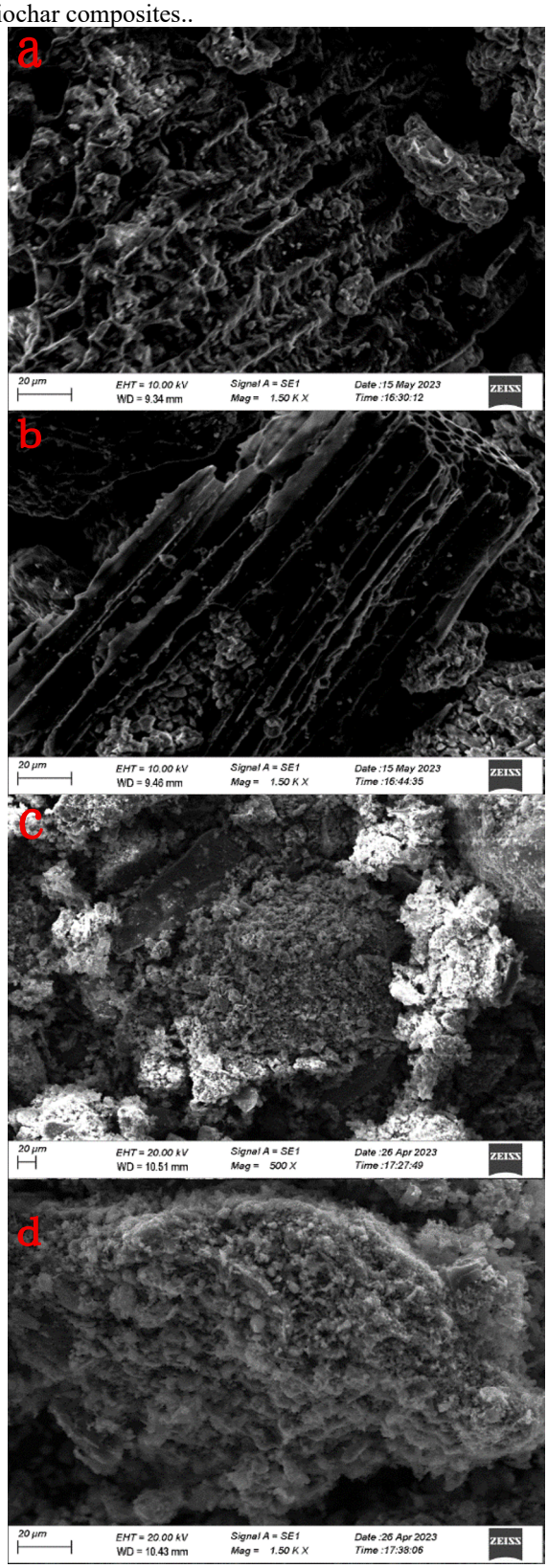

Figure 1. SEM micrographs of the hydroxyapatite-loaded biochar composites: (a) CSB-0.5, (b) CSB-1, (c) CMB-0.5, and (d) CMB-1

3.2. Effect of adsorbent dosage on Cu^{2+} adsorption

The effect of adsorbent dosage on Cu^{2+} removal by CSB-1.5 and CMB-1.5 is presented in Figure 2. As the adsorbent dosage increased from 0.025 g to 0.1 g, the unit adsorption capacities of CSB-1.5 and CMB-1.5 showed a significant downward trend, decreasing from 85.62 and 106.54 $mg \cdot g^{-1}$ to 32.94 and 50.17 $mg \cdot g^{-1}$, respectively. When the dosage was set at 0.05 g, the adsorption capacities reached 81.32 $mg \cdot g^{-1}$ for CSB-1.5 and 98.09 $mg \cdot g^{-1}$ for CMB-1.5. However, a further increase in dosage to 0.075 g caused the capacities to drop to 65.31 $mg \cdot g^{-1}$ and 81.74 $mg \cdot g^{-1}$, respectively. These results clearly indicate that, under fixed Cu^{2+} concentration conditions, the unit adsorption capacity of both materials decreases with increasing adsorbent dosage.

This inverse relationship can be explained by the fact that the total number of Cu^{2+} ions in the system remains constant, while the total number of available adsorption sites increases with higher adsorbent mass. As a result, fewer Cu^{2+} ions are available per unit mass of adsorbent, leading to incomplete occupation of adsorption sites and a decrease in adsorption capacity per gram. Moreover, excessive adsorbent can cause particle aggregation and overlap of active sites, which reduces the exposed surface area and restricts Cu^{2+} diffusion to interior pores, further lowering adsorption efficiency[8].

Although increasing the adsorbent dosage enhances the overall Cu^{2+} removal percentage due to the greater total surface area and more available binding sites, too high a dosage results in underutilization of the adsorbent material and reduced cost-effectiveness. Therefore, balancing removal efficiency and material economy is crucial for practical applications. Based on the experimental data, a dosage of 0.05 g was determined to be the optimal condition for Cu^{2+} adsorption, achieving high removal efficiency while maintaining effective utilization of the HAP–biochar composite adsorbent.

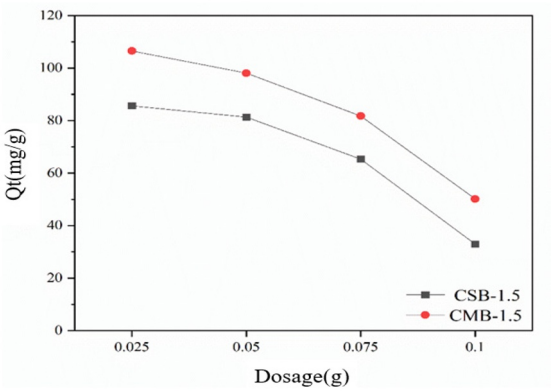

Figure 2 Effect of different dosages on the adsorption of Cu^{2+} by the composite material

3.3. Adsorption Kinetics Experiments

The adsorption kinetics of Cu^{2+} on CSB-1.5 and CMB-1.5 were analyzed using pseudo-first-order, pseudo-second-order, and Elovich models (Fig. 3) to clarify the adsorption mechanism and rate-controlling steps. Both composites showed a rapid Cu^{2+} uptake at the initial stage, followed by a gradual decrease in rate until equilibrium was reached at about 1440 min. The equilibrium adsorption capacities were 82.06 $mg \cdot g^{-1}$ for CSB-1.5 and 98.73 $mg \cdot g^{-1}$ for CMB-1.5, indicating strong Cu^{2+} affinity, with slightly better performance for the CMB-based composite.

The rapid initial adsorption was attributed to abundant surface-active sites and functional groups (–OH, –COOH, PO_4^{3-}) on biochar and hydroxyapatite, which promoted electrostatic attraction, ion exchange, and surface complexation, forming stable Cu complexes or precipitates[9]. As adsorption proceeded, the available active sites were gradually occupied, and Cu^{2+} diffusion into inner pores became restricted, leading to a slower adsorption rate.

This transition from rapid surface adsorption to slower intraparticle diffusion indicates a chemisorption-dominated multi-stage process. Overall, the kinetic results suggest that chemical interactions, along with surface functional groups and pore structure, play key roles in determining the adsorption efficiency and capacity of CSB-1.5 and CMB-1.5..

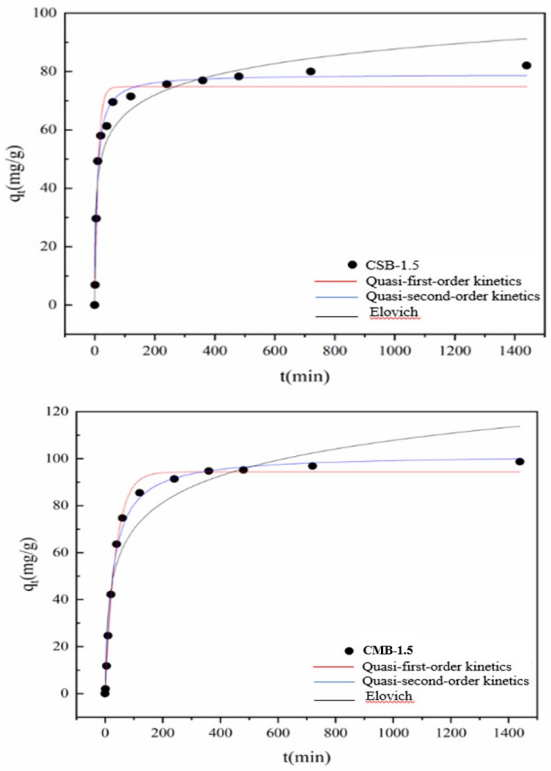

Figure 3 Adsorption kinetic curves of Cu^{2+} by CSB-1.5 and CMB-1.5

According to the fitting results presented in Table 1, the pseudo-second-order kinetic model provided the best correlation with the experimental data, yielding high correlation coefficients (R^2 = 0.99 for both CSB-1.5 and CMB-1.5). This suggests that the adsorption process was dominated by chemisorption involving valence forces through the sharing or exchange of electrons between Cu^{2+} ions and the functional groups on the adsorbent surface[10]. The Elovich model (R^2 = 0.92 for CSB-1.5

and 0.94 for CMB-1.5) further supported the occurrence of a chemically controlled process on heterogeneous surface sites, reflecting the complexity and diversity of adsorption energies on the composite materials. Overall, the kinetic analysis confirmed that Cu^{2+} adsorption on CSB-1.5 and CMB-1.5 primarily occurred through chemical adsorption mechanisms, including ion exchange and surface complexation, rather than through simple physical interactions such as van der Waals forces[11]. These findings emphasize that the surface chemistry, functional group composition, and active site distribution of the HAP–biochar composites play decisive roles in governing their adsorption behavior and overall removal efficiency toward Cu^{2+} ions..

Table 1 Fitted parameters of pseudo-first-order, pseudo-second-order, and Elovich kinetic models

Material	capacity	Pseudo-first-order kinetic		
	mg/g	Qe	K_1	R^2
CSB-1.5	82.06	74.78	0.08	0.96
CMB-1.5	98.73	94.41	0.02	0.95
Material	Pseudo-second-order kinetics			Elovich		
	Qe	K_2	R^2	a	b	R^2
CSB-1.5	78.63	1.27	0.99	76.63	0.10	0.92
CMB-1.5	99.93	0.41	0.99	11.33	0.06	0.94

4. Conclusion

Hydroxyapatite-loaded biochar (HAP–biochar) composites were successfully synthesized using corn straw biochar (CSB) and chicken manure biochar (CMB) to enhance Cu^{2+} removal. SEM, EDS, and XRD confirmed uniform HAP dispersion on the biochar surface, improving porosity and providing more active adsorption sites.

All composites exhibited higher Cu^{2+} adsorption than pure biochar or HAP. CMB-1.5 showed the best performance, with a maximum capacity of 98.09 $mg \cdot g^{-1}$, followed by CSB-1.5 (82.06 $mg \cdot g^{-1}$). The optimal adsorption conditions were pH 5.0 and an adsorbent dosage of 0.05 g, ensuring high efficiency and material utilization.

Kinetic analysis showed that Cu^{2+} adsorption followed a pseudo-second-order model ($R^2 \approx 0.99$), indicating chemisorption dominated through ion exchange and surface complexation. The Elovich model also confirmed heterogeneous surface adsorption.

Overall, HAP–biochar composites, especially CMB-1.5, exhibited excellent Cu^{2+} removal efficiency and stability, demonstrating strong potential as low-cost, eco-friendly materials for heavy metal pollution control and environmental remediation.

Acknowledgements

The authors express their sincere gratitude to the Jiangxi University of Science and Technology for providing experimental facilities and technical assistance.

Declaration of Interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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