Fabrication of Dimensionally Stable Rice Husk Biochar Composites and Their Mechanistic Insights into Cu^{2+} Adsorption

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Abstract: To address the challenges of dust emission and poor recoverability associated with conventional powdered biochar, a dimensionally stable and recyclable biochar composite (PCL–CMC@RHB) was fabricated using rice husk biochar (RHB) as the carbon matrix, polycaprolactone (PCL) as a binding polymer, and sodium carboxymethyl cellulose (CMC) as a pore-forming and co-binding agent. The structural morphology and adsorption mechanisms were systematically examined through scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The PCL–CMC coating significantly improved the mechanical integrity and interfacial compactness of RHB while preserving its intrinsic porosity and reactive surface chemistry. Kinetic analysis revealed that the Cu^{2+} adsorption process followed a pseudo-second-order model ($R^2 \approx 0.999$), indicating chemisorption as the dominant mechanism. The optimized composite achieved a maximum Cu^{2+} adsorption capacity of 34.4 mg g^{-1} and a removal efficiency exceeding 96 %, comparable to that of pristine RHB (35.8 mg g^{-1}, ≈ 97 %). These results confirm that polymer incorporation enhanced structural stability without compromising adsorption performance. Moderate PCL–CMC loadings optimized both accessible surface area and reactive site density, maximizing Cu^{2+} uptake and recyclability. FTIR spectra further demonstrated the formation of stable Cu–O coordination complexes through surface complexation and ion-exchange reactions. This study establishes a scalable strategy for engineering dimensionally stable biochar composites that combine high adsorption efficiency, mechanical durability, and environmental reusability—offering a sustainable platform for heavy-metal remediation in water and soil systems..

1. Introduction

Rapid urbanization and industrialization have led to severe ecological degradation, particularly through heavy metal (HM) contamination derived from mining tailings and industrial effluents [1]. Accelerated economic development has exacerbated the accumulation of heavy metals and organic pollutants in soils—persistent contaminants that pose serious threats to ecosystem integrity and human health due to their long-term stability, non-biodegradability, and bioaccumulative potential [2]. Major anthropogenic sources of heavy metals include industrial discharge, atmospheric deposition, sewage sludge, animal manure, and synthetic fertilizers [3]. Globally, more than 20 million hectares of land are contaminated with heavy metals such as Zn, Pb, Ni, As, Hg, Cu, Cd, and Cr, with concentrations exceeding geochemical background or regulatory thresholds [4]. These elements can migrate through terrestrial and aquatic food webs, causing ecological imbalance and potential health risks to humans and wildlife [5–6]. Once introduced into soils, heavy metals are difficult to remove because of their strong persistence and low mobility, leading to long-term accumulation if not effectively extracted or immobilized [7].In recent decades, extensive research has focused on developing remediation technologies to reduce the total concentrations and bioavailability of heavy metals in soils, aiming to mitigate their transfer through the food chain and minimize environmental damage [8]. However, most conventional in situ or ex situ remediation methods—such as chemical leaching, stabilization, or electrokinetic treatment—suffer from long operation times, high chemical costs, secondary pollution, and soil structure deterioration [9].Biochar, a carbon-rich solid derived from the pyrolysis of biomass under limited oxygen, has attracted great attention as an effective and sustainable adsorbent for heavy-metal remediation [10]. Its high specific surface area and porous structure enhance pollutant adsorption, while abundant surface functional groups (e.g., –COOH, –OH, –C=O) provide active sites for cation exchange and complexation [11]. Biochar not only immobilizes heavy metals by surface sorption and precipitation but also improves soil physical properties by decreasing bulk density, increasing porosity, and enhancing water retention [12]. Nevertheless, the field application of powdered biochar still faces several challenges, including difficulties in recovery and reuse, dust generation during handling, and

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the potential for desorption or release of toxic compounds .

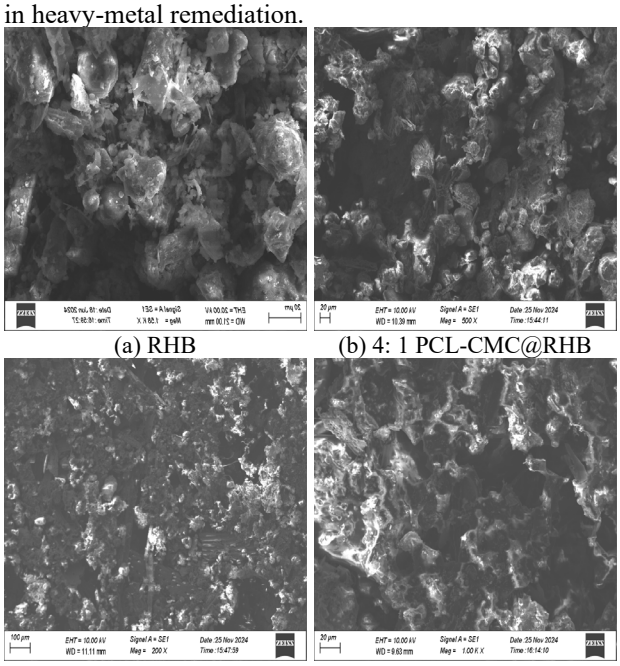
In recent years, biochar composites have evolved rapidly toward enhanced adsorption efficiency, recyclability, and mechanical stability. Integrating biochar with metal oxides, nanoparticles, or polymers introduces new active sites and improves selectivity for heavy metals and organics. Polymer–biochar systems, particularly those using biodegradable binders such as PCL, chitosan, and CMC, effectively transform powdered biochar into dimensionally stable and reusable structures without sacrificing adsorption capacity. Nano- and metal oxide modifications (ZnO, Fe_3O_4, MnOx) further accelerate adsorption and enable magnetic recovery. Recent studies also emphasize morphology control, regeneration, and scalability, underscoring the balance between structural robustness and surface reactivity. These advancements provide strong motivation for developing the PCL–CMC@RHB composite, which couples mechanical durability with efficient Cu^{2+} immobilization.

To address these limitations, it is essential to develop recyclable, structurally stable, and environmentally safe biochar materials. In particular, dimensionally stable (size-controlled or granular) biochar composites offer new opportunities for practical field application, as they combine the adsorption performance of traditional biochar with enhanced mechanical strength and reusability. However, research on the preparation, regeneration, and re-adsorption behavior of such materials remains limited.In this study, a novel dimensionally stable PCL-CMC@RHB composite biochar was fabricated using rice husk biochar (RHB) as the substrate, polycaprolactone (PCL) as a biodegradable binder, and sodium carboxymethyl cellulose (CMC) as a pore-forming agent. The study systematically investigated its adsorption kinetics, mechanisms, its distinction from conventional powdered biochar, and its potential environmental benefits for plant growth and human health protection. Finally, the feasibility of using dimensionally stable biochar for sustainable sediment remediation is discussed, with recommendations for future research on its reusability, regeneration, and long-term ecological safety.

2. Materials

2.1. Materials Preparation

To address the issues of dust formation and irrecoverability in conventional powdered biochar, rice husk biochar (RHB) was used as the core matrix, while PCL served as a binding polymer and CMC as a porogenic additive and secondary binder. CMC possesses excellent rheological and binding properties and promotes pore formation during composite solidification. The synergistic integration of CMC and PCL not only enhances the interfacial compatibility between organic and inorganic phases but also modulates the porosity, creating hierarchical structures with improved transport pathways for ions.The composites were fabricated through a melt-molding process at predefined RHB:PCL ratios of 4:1, 6:1, and 8:1 with a small amount of CMC. This technique produced mechanically strong, water-insoluble biochar composites suitable for aqueous applications.The melt-molding route ensured uniform polymer dispersion and strong adhesion to the biochar surface, forming a continuous yet porous network that resists structural collapse in water. By optimizing the polymer loading, the resulting composites maintained high surface accessibility while exhibiting enhanced structural integrity, providing an ideal balance between mechanical strength, stability, and reactivity for repeated adsorption–desorption cycles.Moreover, the controlled melt-molding strategy enables precise tuning of microstructural features such as pore interconnectivity and surface roughness, which directly govern ion diffusion and adsorption kinetics. The resulting composite exhibits a hierarchically organized architecture that couples macroporous transport channels with microporous reactive domains, ensuring both rapid mass transfer and strong metal–ligand interactions. This rational structural engineering approach represents a significant advancement toward the scalable production of recyclable biochar-based materials with superior physicochemical robustness and sustainable performance in heavy-metal remediation.



(a) RHB (b) 4: 1 PCL-CMC@RHB

(c) 6: 1 PCL-CMC@RHB (d) 8: 1 PCL-CMC@RHB

Figure 1. SEM images of RHB (a), 4:1 PCL - CMC @ BC composite (b), 6:1 PCL - CMC @ BC composite (c), and 8:1 PCL - CMC @ BC composite (d).

SEM Figure 1 micrographs revealed that pristine RHB exhibited irregular lamellar and flaky morphologies with heterogeneous pore sizes, characteristic of highly porous biochar structures. Such features provide abundant active sites and facilitate Cu^{2+} diffusion. With increasing PCL–CMC ratios, surface morphology transformed significantly: partial coating at low ratios maintained open pores, whereas higher ratios resulted in dense, continuous polymer films that reduced

surface roughness. This morphological evolution signifies the progressive encapsulation of biochar particles by the polymer network, yielding enhanced interfacial cohesion and structural integrity. The transition from an open, porous framework to a semi-coated and finally compact morphology reflects a delicate interplay between structural reinforcement and surface accessibility. The PCL component contributes to the formation of a flexible yet mechanically robust matrix that bridges adjacent carbon particles, effectively mitigating fragmentation and improving dimensional stability under aqueous conditions. Simultaneously, CMC introduces hydrophilic functional groups and regulates the pore architecture by inducing localized phase separation during solidification, thereby generating interconnected micro- and mesopores that promote ion transport.An optimal coating ratio preserved porosity while enriching the surface with hydrophilic –OH and –COOH groups from CMC, which are crucial for metal coordination. This hierarchical structure enhances the diffusion of Cu^{2+} into interior sites while maintaining sufficient reactive oxygenated groups for complexation, enabling rapid and stable adsorption. However, excessive polymer coverage diminished the accessible surface area and hindered the exposure of active binding sites, leading to slower adsorption kinetics. These observations highlight that controlled polymer incorporation enables precise tuning of physicochemical properties, providing a strategic pathway to engineer biochar-based composites with co-optimized mechanical integrity, interfacial functionality, and adsorption performance suitable for sustainable water purification and environmental remediation.

2.2. FTIR Analysis and Adsorption Mechanism

FTIR Figure 2 spectroscopy was employed to identify the functional groups responsible for Cu^{2+} binding and to elucidate the molecular-level adsorption mechanism. Characteristic peaks of RHB were preserved in the composites, confirming that the introduction of PCL and CMC occurred primarily through physical encapsulation without altering the inherent carbon matrix or inducing new chemical bonds between the polymer and biochar framework. This preservation of structural integrity ensures that the intrinsic adsorption capacity of the biochar is maintained while its mechanical robustness and hydrophilicity are simultaneously improved through polymer modification.

Before Cu^{2+} adsorption, the broad absorption band centered at 3443 cm^{-1} corresponds to the O–H stretching vibration, indicative of abundant surface hydroxyl and phenolic groups that serve as active metal-binding sites. The peak near 1626 cm^{-1} is assigned to C=O and aromatic C=C stretching vibrations originating from carboxyl and carbonyl groups on the biochar surface, reflecting its partial oxidation during pyrolysis. Meanwhile, the absorption band at approximately 1092 cm^{-1} arises from C–O stretching of ether and ester bonds, mainly derived from CMC, suggesting the presence of polar oxygenated linkages that can participate in coordination reactions.

After Cu^{2+} exposure, the spectra revealed significant shifts and intensity reductions at 3443 and 1092 cm^{-1}, evidencing strong coordination interactions between Cu^{2+} and the oxygen atoms of hydroxyl, carbonyl, and ether groups. The emergence of new absorption features in the low-frequency region (600–700 cm^{-1}) corresponds to metal–oxygen (M–O) vibrations, confirming the formation of Cu–O coordination bonds and possible surface precipitates of $Cu(OH)_2$ or CuO. These spectral transformations collectively indicate that oxygen-containing functional groups act as primary electron donors, transferring charge to Cu^{2+} ions and forming stable inner-sphere complexes through chemisorption. The coexistence of complexation and precipitation pathways suggests a multi-mechanistic adsorption process, where initial Cu^{2+} coordination is followed by nucleation of hydroxide phases on reactive sites. Such dual binding behavior contributes to the high thermodynamic stability and low mobility of immobilized Cu species, underscoring the effectiveness of the PCL–CMC@RHB composite as a recyclable and durable adsorbent for heavy-metal remediation.

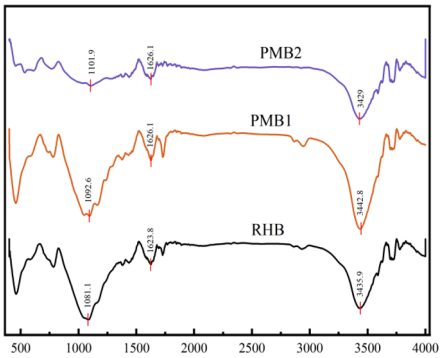


Figure 2. FTIR spectra of RHB and size-type PCL - CMC @ RHB composites

2.3. Stability and Regeneration Performance of Dimensionally Stable Biochar

The composite's mechanical and dimensional stability was evaluated via repeated handling, immersion, and drying cycles, with structural integrity and mass loss recorded. Recyclability was assessed through multiple adsorption–desorption cycles, recovering the biochar by filtration and measuring residual adsorption capacity. Regeneration was performed using 0.1–0.5 M HCl under stirring, followed by washing and drying, and the regenerated composite was reused to determine adsorption retention and functional group preservation.

3. Conclusion

A dimensionally stable and recyclable biochar composite (PCL–CMC@RHB) was successfully fabricated via melt molding, effectively overcoming the inherent limitations associated with powdered biochar, such as poor recoverability and dust-related environmental concerns. The synergistic integration of polycaprolactone (PCL)

and carboxymethyl cellulose (CMC) not only imparted exceptional mechanical integrity and structural robustness but also enabled precise regulation of porosity and enrichment of oxygen-containing functional groups, thereby optimizing the availability of reactive adsorption sites. This dual-function polymeric strategy ensures that the composite maintains its macroscopic morphology while simultaneously enhancing surface chemical activity, a critical requirement for practical environmental applications.

Comprehensive Fourier transform infrared (FTIR) spectroscopy analyses confirmed that Cu^{2+} ions exhibited strong affinity toward hydroxyl and carboxyl moieties, leading to the formation of stable Cu–O coordination complexes through a combination of surface complexation and ion-exchange mechanisms. These findings elucidate the molecular-level interactions governing metal sequestration, highlighting the importance of tailored surface chemistry in enhancing selective adsorption. The optimized composite demonstrated an exceptional balance between mechanical durability and high reactive-site accessibility, thereby achieving superior adsorption efficiency without compromising structural integrity. Such a balance represents a significant advancement in the design of carbonaceous adsorbents, addressing the persistent trade-off between stability and reactivity.

Beyond Cu^{2+}, this design paradigm provides a versatile platform for the selective removal of multi-contaminant systems and supports scalable deployment in sustainable environmental remediation initiatives. The present study thus establishes a robust framework for the rational design of polymer-modified biochar systems, offering fundamental insights into structure–function relationships and informing the development of next-generation carbonaceous materials for global heavy-metal mitigation.

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