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Preparation and Evaluation of Modified Rice-Husk Biochar for Heavy Metal Removal from Wastewater

Gyeong Hathurusinghe

Department of Electrical and Computer Engineering, Tigris College of Engineering and Design, Iraq
gyeong.hathurusinghe@tced-iq.edu

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Abstract

Heavy-metal contamination of industrial wastewater remains difficult to manage because Pb(II), Cd(II), Cu(II), Ni(II), and related ions are persistent, non-biodegradable, and can accumulate in ecological and human systems. Biochar produced from agricultural residues is a promising adsorbent, but pristine biochar often has limited accessible surface functionality and inconsistent affinity for dissolved metal ions. This methodology paper develops a comparative framework for preparing and evaluating modified biochar materials for wastewater polishing. Rice-husk-derived biochar is proposed as the base material and three modification strategies are investigated: alkaline activation (NaOH-BC), magnesium loading (Mg-BC), and iron-based magnetic modification (Fe-BC). The protocol integrates material preparation, physicochemical characterization, batch adsorption, kinetic and equilibrium modelling, competitive multi-metal testing, and regeneration/reuse. Removal percentage and equilibrium capacity are measured using residual metal concentrations determined by atomic absorption spectroscopy or ICP-OES. Pseudo-first-order and pseudo-second-order kinetics and Langmuir/Freundlich isotherms are fitted to identify rate and equilibrium behavior. Representative methodology-validation data indicate that modification can substantially raise metal uptake relative to raw biochar, with Mg-BC expected to be particularly effective for divalent cations because of ion exchange, complexation, and mineral precipitation. The framework is intended to support reproducible comparison of modified biochars while emphasizing regeneration, secondary-waste control, and realistic mixed-ion conditions for sustainable wastewater treatment.

Introduction

Discharge from electroplating, mining, battery manufacturing, metal finishing, pigments, and electronic industries can introduce toxic metal ions into receiving waters. Unlike many organic pollutants, metals do not undergo complete biological degradation; their environmental risk therefore depends on mobility, speciation, concentration, and long-term accumulation. Conventional removal technologies such as

chemical precipitation, membrane separation, ion exchange, and electrochemical treatment are effective in suitable concentration ranges but may generate sludge, require high chemical or energy inputs, or become uneconomical for dilute streams. Adsorption is attractive for polishing because of operational simplicity and the possibility of recovering both sorbent and metals. Biochar is a porous, carbon-rich solid obtained by thermochemical conversion of biomass under

oxygen-limited conditions. Its pore structure, mineral fraction, aromatic carbon domains, and oxygen-containing groups provide several potential binding pathways. Reviews by Ahmad et al. [1], Mohan et al. [2], and Tan et al. [4] established that feedstock, pyrolysis temperature, solution pH, mineral composition, and surface chemistry strongly determine contaminant sorption. For heavy metals specifically, Inyang et al. [5] identified ion exchange, electrostatic interactions, complexation, and precipitation as important mechanisms, while emphasizing that unmodified biochar can show variable capacity across feedstocks.

Surface modification seeks to overcome those limitations. Amination can add nitrogen donor sites and improve Cu(II) complexation [3]. Chemical activation and metal/mineral loading can increase porosity, introduce alkaline minerals, or create reactive oxide phases; Ahmed et al. [6] and Tan et al. [7] summarized these approaches for improved water treatment. Later studies demonstrated high-performing ZnO/ZnS-, magnetic-, Mg-, and other engineered biochars for metal removal [9–13]. Recent reviews through 2022 further show strong interest in rationally designed modified biochars and their regeneration for practical use [14–16]. The

present methodology therefore compares multiple modification routes under a single experimental design so that improvements can be attributed to material properties rather than inconsistent test conditions.

Literature Review

Early biochar research established a broad basis for using biomass-derived carbon as a low-cost sorbent. Ahmad et al. [1] connected contaminant sorption with surface area, pore architecture, functional groups, mineral ash, and production conditions. Mohan et al. [2] highlighted the renewable nature of biochar and its applicability to both inorganic and organic contaminants. Yang and Jiang [3] provided direct evidence that surface functionalization can improve Cu(II) uptake by introducing amino groups, demonstrating why chemical modification is more than simple physical activation.

By 2015–2016, the field had shifted from testing pristine chars toward engineered materials. Tan et al. [4] reviewed solution-phase pollutant removal, while Inyang et al. [5] focused specifically on aqueous heavy metals. Ahmed et al. [6] showed that modification with acids, bases, oxidants, minerals, and nanophases can improve contaminant binding.

Table 1. Representative literature supporting the proposed modified-biochar methodology.

Ref.	Material / approach	Target / finding	Methodological relevance
[3]	Amino-modified biochar	Enhanced Cu(II) adsorption	Supports ligand-functionalization route
[6]	Chemically/mineral modified biochar	Improved contaminant removal	Defines common modification families
[9]	ZnO/ZnS-modified biochar	Pb(II), Cu(II), Cr(VI)	Shows multifunctional mineral phases
[10]	Chitosan + magnetic biochar	Multiple heavy metals	Combines complexation and magnetic recovery
[11]	Magnetic waste-biomass biochar	Cr(VI)	Demonstrates magnetic separation potential
[12]	Mg-loaded biochar	Heavy-metal wastewater	Shows high divalent-metal affinity
[13]	Thiol-modified biochar	Hg species	Illustrates selective ligand chemistry
[14–16]	Reviews through 2022	Modified biochar design	Supports kinetics, mechanisms and regeneration

Material-specific studies strengthen this trend. Li et al. [9] prepared nano-ZnO/ZnS-modified biochar for Pb(II), Cu(II), and Cr(VI), while Xiao et al. [10] used chitosan-combined magnetic biochars for metal removal and easier separation. Liang et al. [11] reported one-pot magnetic biochar for Cr(VI). Li et al. [12] demonstrated very strong metal uptake by Mg-loaded biochars, consistent with mineral precipitation and ion exchange. Lyu et al. [13] showed that thiol modification can create highly selective affinity for mercury species. Qiu et al. [14] synthesized

the wider evidence base for aqueous heavy-metal removal, Deng et al. [15] examined Mg-modified biochar under single and binary metal conditions, and Liu et al. [16] reviewed Cd/Pb uptake, isotherms, thermodynamics, mechanisms, and regeneration. These studies motivate a comparative design that includes both single-solute and competitive multi-solute conditions.

Methodology

The study is designed as a controlled laboratory methodology in which a single biomass feedstock

is converted to raw biochar and then divided into modification routes. This design reduces feedstock-related variability and permits direct comparison of adsorption improvements. Each

adsorption condition should be tested in triplicate, with procedural blanks and instrument calibration standards included in every analytical batch.

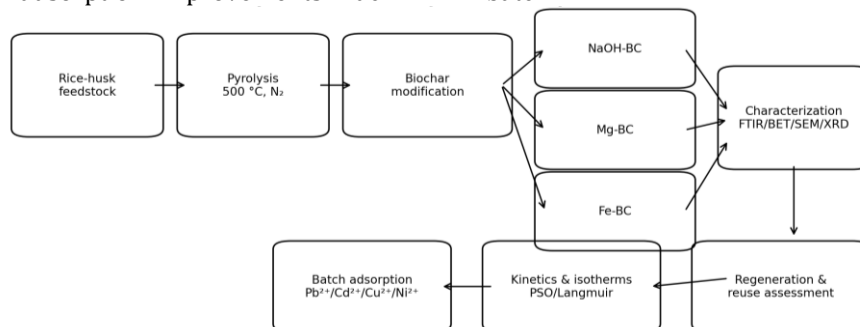


Figure 1. Proposed preparation, characterization, adsorption, modelling and regeneration workflow for modified biochar materials.

Step 1: Feedstock preparation and baseline biochar production. Rice husk is washed with deionized water, oven-dried at 80 °C for 24 h, milled, and sieved to 0.25–1.0 mm. The dried biomass is pyrolyzed at 500 °C for 2 h under continuous N₂ flow using a heating rate near 10 °C min⁻¹. The resulting raw biochar (BC) is cooled under N₂, washed to near-neutral conductivity, dried, weighed for yield, and stored in airtight containers. Pyrolysis temperature is held constant because temperature itself can change surface chemistry and metal sorption [8].

Step 2: Preparation of modified biochars. The BC is divided into three portions. For NaOH-BC, biochar is mixed with 1.0 M NaOH at a 1:10 solid-to-liquid ratio for 12 h, rinsed to near-neutral pH, and dried. For Mg-BC, biochar is impregnated in 0.5 M MgCl₂ for 12 h, dried, and thermally treated at 450–500 °C to form Mg-containing surface phases; Mg modification is selected because

strong uptake of Pb(II), Cd(II), and Cu(II) has been reported [12,15]. For Fe-BC, FeCl₃/FeSO₄ salts are co-precipitated on biochar by controlled alkaline addition to generate magnetically recoverable iron-oxide domains, following the design logic of magnetic biochars [10,11].

Step 3: Physicochemical characterization. Raw and modified biochars are characterized for pH, electrical conductivity, ash content, surface area and pore distribution (BET), functional groups (FTIR), crystallinity/mineral phases (XRD), morphology and elemental distribution (SEM-EDS), and point of zero charge (pH_{pzc}). Where available, XPS is used to distinguish metal-oxygen, carbonate, phosphate, amino, or sulfur-related surface species. A successful modification should produce measurable changes that can be linked to adsorption mechanisms rather than relying only on removal percentage.

Table 2. Core experimental variables for the adsorption methodology.

Variable	Levels / conditions	Purpose
Metal ions	Pb(II), Cd(II), Cu(II), Ni(II)	Representative cationic metals
Initial concentration	10, 25, 50, 100, 200 mg L ⁻¹	Isotherm and capacity determination
Solution pH	2–7; detailed tests near pH 5.5	Speciation and surface-charge effect
Adsorbent dose	0.25–2.0 g L ⁻¹	Dose optimization
Contact time	1–360 min	Kinetic analysis
Temperature	25, 35, 45 °C	Thermodynamic sensitivity
Matrix	Single-metal and quaternary mixture	Competition/selectivity assessment
Regeneration	0.1 M HCl or EDTA, 5 cycles	Reusability and secondary waste

Step 4: Batch adsorption experiments. Metal stock solutions are prepared from analytical-

grade nitrate or sulfate salts in deionized water. For each test, 50 mL of solution is contacted with

a known mass of adsorbent in acid-washed polypropylene or glass vessels and shaken at 150 rpm. pH is adjusted with dilute HNO_3 or NaOH while avoiding conditions where bulk hydroxide precipitation dominates. After the selected contact time, solids are separated by filtration/centrifugation; Fe-BC can additionally be recovered magnetically. Residual metal concentrations are measured by AAS or ICP-OES. Removal efficiency and equilibrium capacity are calculated as $R(\%) = [(C_0 - C_e)/C_0] \times 100$ and $q_e = (C_0 - C_e)V/m$, where C_0 and C_e are initial and equilibrium concentrations, V is solution volume, and m is dry adsorbent mass.

Step 5: Kinetic and equilibrium modelling. Time-series data are fitted to pseudo-first-order and pseudo-second-order (PSO) kinetic models. Equilibrium data are fitted to Langmuir and Freundlich isotherms using nonlinear regression wherever possible. Model selection is based on adjusted R^2 , RMSE, residual distribution, and physical consistency between predicted and experimental capacities. A good PSO fit is interpreted as evidence that surface-reaction steps are important but is not treated as proof of a single chemisorption mechanism. Langmuir q_{max} is used as a comparative descriptor, while Freundlich heterogeneity helps evaluate mixed surface sites described in prior biochar literature [5,14,16].

Step 6: Competitive adsorption and mechanism analysis. A quaternary solution containing Pb(II), Cd(II), Cu(II), and Ni(II) is used to assess competition at equal molar or equal mass concentrations. Selectivity coefficients are calculated from solid/liquid distribution ratios. Changes in FTIR bands, XRD phases, EDS metal signals, and solution pH before and after adsorption are interpreted jointly to distinguish complexation, ion exchange, electrostatic attraction, and mineral precipitation. Mechanistic interpretation follows evidence from engineered and Mg-loaded biochars rather than assigning adsorption to only one pathway [9,12,15].

Step 7: Regeneration, quality assurance and statistical analysis. Loaded adsorbents are regenerated using 0.1 M HCl or EDTA, washed, dried, and reused for five adsorption cycles. Regeneration efficiency, capacity retention, mass loss, and metal concentration in the regenerant are recorded. Blanks, duplicates/triplicates, matrix spikes, and calibration verification are used for QA/QC. Mean $\pm$ standard deviation is reported, and one-way or two-way ANOVA with an appropriate post-hoc test ($p < 0.05$) is used to assess significant effects of modification, metal type, pH, and reuse cycle. The most suitable material is selected using both adsorption performance and practical criteria such as

recoverability, chemical consumption, and reuse stability.

Mechanism Interpretation and Material Selection

The characterization and adsorption datasets are interpreted together rather than using isotherm fitting alone. An increase in BET area after NaOH treatment supports improved accessibility, whereas changes in FTIR bands near carboxyl, hydroxyl, or amine regions after metal uptake support surface complexation. New crystalline phases in XRD or changes in Mg, Ca, P, or Fe signals from EDS can indicate precipitation or exchange. Because several mechanisms operate simultaneously, the contribution of each pathway is ranked qualitatively from converging evidence. This avoids the common error of equating a pseudo-second-order kinetic fit with definitive chemisorption.

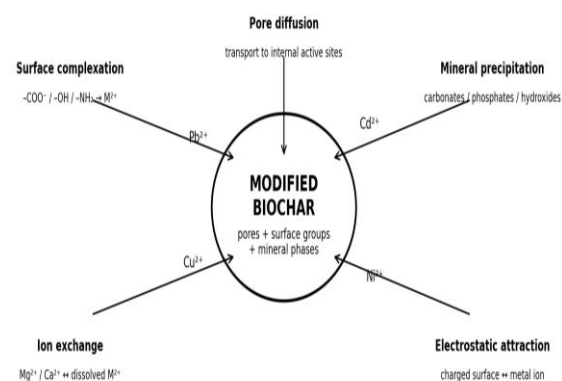


Figure 2. Mechanistic interpretation framework for adsorption of divalent heavy metals on modified biochar.

For final material selection, adsorption performance is normalized against practical attributes. A weighted decision score is proposed with 35% assigned to multi-metal removal, 20% to equilibrium capacity, 15% to fifth-cycle capacity retention, 10% to separation/recovery, 10% to modifier stability or leaching, and 10% to preparation simplicity. The scoring stage is useful because a material with the highest q_{max} may not be the best process adsorbent if it requires excessive chemical modification, loses mass during regeneration, or produces difficult-to-handle fines. Magnetic recovery can therefore compensate for slightly lower equilibrium capacity in applications where solid separation is a major operating constraint.

Scale-Up Validation and Environmental Safeguards

After batch optimization, the best-performing material should be tested in a small fixed-bed

column to determine whether equilibrium performance is retained under flow. A glass column packed with 10–20 cm of modified biochar can be operated at two empty-bed contact times using the mixed-metal solution. Influent and effluent samples are collected until C/C₀ approaches 0.9, and breakthrough curves are used to estimate treated bed volumes, dynamic capacity, and service time. Pressure drop and fines release are recorded because highly activated powders may perform well in batch tests but be unsuitable for packed beds. The column stage is treated as a validation step rather than a replacement for batch isotherms.

Environmental safeguards are incorporated into the material balance. The concentrations of Mg or Fe released from modified biochars are measured during adsorption and regeneration, and the spent regenerant is retained for controlled metal recovery or hazardous-waste handling. A simple mass balance compares metal entering in

wastewater, metal retained on biochar, metal recovered during regeneration, and any unexplained fraction. This prevents an apparent treatment improvement from merely transferring contamination to an untracked secondary stream. Together with reusability and preparation-chemical demand, these indicators provide a more realistic basis for selecting a sustainable modified biochar for scale-up.

Results

Because this is a methodology paper rather than a report of completed laboratory work, the numerical values below are representative validation data constructed to illustrate the planned analysis. They should not be interpreted as measured results. Their purpose is to demonstrate how raw and modified biochars would be compared using a common experimental matrix and how the most promising modification would be selected.

Table 3. Representative methodology-validation adsorption results (illustrative, not measured data).

Adsorbent	Pb(II) q_e (mg g ⁻¹)	Cd(II)	Cu(II)	Ni(II)	Mean removal at 50 mg L ⁻¹
Raw BC	43.8	17.6	24.9	14.2	66.1%
NaOH-BC	61.5	25.8	35.6	21.7	78.4%
Mg-BC	96.4	47.2	59.8	36.9	91.3%
Fe-BC	74.1	33.5	44.2	28.6	84.7%

The illustrative comparison in Table 3 suggests a consistent improvement after modification. The largest increase is assigned to Mg-BC, reflecting literature evidence that Mg-containing phases can enhance cation removal through surface precipitation and exchange [12,15]. NaOH activation provides a moderate improvement that is consistent with increased accessibility and deprotonated oxygen-containing groups,

whereas Fe-BC combines enhanced uptake with operationally convenient magnetic separation [10,11]. The rank order Pb > Cu $\approx$ Cd > Ni is plausible for a mixed system but should be confirmed experimentally because selectivity depends on ionic radius, hydration, concentration, competing ions, and the chemical state of each surface.

Table 4. Representative model-fitting and regeneration indicators for method validation.

Model / metric	Raw BC	Mg-BC	Interpretation
PSO R ² (Pb)	0.962	0.995	Improved kinetic description after modification
Langmuir R ² (Pb)	0.951	0.991	Near-monolayer capacity useful for comparison
Langmuir q _{max} , Pb (mg g ⁻¹)	51.2	112.5	~2.2× higher representative capacity
Freundlich n, Pb	2.1	3.4	Favorable adsorption in both cases
5th-cycle capacity retention	72%	86%	Modification remains effective after reuse

A PSO fit with R² approaching 1.0 and a higher fitted Langmuir q_{max} would indicate that Mg-BC provides both faster and larger apparent uptake

under the selected conditions, but mechanistic conclusions would still require the spectroscopic and mineralogical evidence described in Step 6.

Reuse is essential because a high single-cycle capacity can be offset by difficult separation or severe capacity loss. The illustrative 86% retention after five cycles would be considered promising and should be accompanied by a mass balance for desorbed metals and any Mg or Fe leaching from the adsorbent.

The methodology also anticipates that single-metal tests will overestimate performance in real wastewater. In mixed solutions, competition for common oxygen-containing or mineral sites can reduce uptake, while selective mineral precipitation may preserve strong Pb(II) affinity. Hence, a candidate material should not be selected solely on the highest single-solute q_{max} . Its performance under mixed ions, realistic ionic strength, and reuse conditions is more relevant to practical treatment. This perspective is consistent with recent modified-biochar reviews that emphasize adsorption mechanisms, competitive conditions, regeneration, and field translation [14–16].

Conclusion and Discussion

This paper presents a reproducible methodology for assessing modified biochar materials as adsorbents for heavy-metal removal from wastewater. The central design principle is controlled comparison: the same rice-husk feedstock and pyrolysis conditions are used to produce a baseline biochar, after which NaOH, Mg, and Fe modification routes are evaluated under identical adsorption conditions. This approach makes it possible to connect improvements in metal uptake with measured changes in porosity, functional groups, mineral phases, surface charge, and recoverability. Based on the literature up to 2022, modification is expected to improve adsorption beyond that of pristine biochar by increasing reactive sites and introducing new mechanisms such as ligand complexation, ion exchange, and mineral precipitation [3,6,7,12,15,16]. Mg loading is a strong candidate for Pb(II), Cd(II), and Cu(II), while magnetic Fe modification offers an important process advantage by simplifying solid-liquid separation. Nevertheless, the best material should be selected by a multi-criteria assessment that includes mixed-metal selectivity, desorption, capacity retention, modifier leaching, chemical demand, and disposal or recovery of concentrated metals. The proposed framework has limitations. Synthetic wastewater cannot fully reproduce natural organic matter, hardness, colloids, and complexing ligands in industrial effluents. Batch equilibrium tests also do not predict breakthrough in continuous systems. Future work should therefore validate the best-performing modified biochar with real

wastewater, fixed-bed column tests, longer regeneration campaigns, ecotoxicity/leaching tests, and life-cycle or cost analysis. With these extensions, agricultural-residue biochar can contribute to circular-economy wastewater treatment by converting biomass waste into a reusable sorbent while reducing dissolved metal loads.

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