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Iron-modified calcinated coconut fiber biochar for simultaneous removal of copper and zinc: optimization, production cost assessment, and machine Learning modeling

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Abstract

This study developed and evaluated an iron modified biochar (AcBC) from coconut fiber in Ben Tre, Vietnam, for the adsorption of Cu²⁺ and Zn²⁺. Characterization (SEM-EDS, BET, XRD, FTIR) showed that mineral rich coconut fiber pyrolyzed without inert gas undergoes strong surface mineralization, forming crystalline silicates that block pores and functional groups, resulting in raw biochar (RBC) with low surface area, limited porosity, and few active sites. After iron salt co precipitation with NaOH, AcBC exhibited major improvements, including a nearly twenty fold increase in surface area from 5 to 100 m²/g, well developed mesopores, and the return of functional groups. Silicate minerals also contributed to adsorption by providing active sites and supporting iron oxide and iron silicate formation. AcBC achieved about twenty percent higher removal efficiency and maximum capacities of 34.75 mg/g for Cu²⁺ and 29.69 mg/g for Zn²⁺, more than double those of RBC. To systematically describe the adsorption mechanisms, four kinetic models (pseudo-first-order, pseudo-second-order, Weber-Morris intraparticle diffusion, and Boyd) and four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich) were utilized. Crucially, tree-based machine learning interpreted via SHAP analysis successfully quantified the mechanisms; Extreme Gradient Boosting accurately predicted adsorption capacity $R^2 > 92\%$, identifying specific surface area, % Si, and % O as the most important material properties, while that of cation descriptors relative atomic mass, effective ionic radius and first order hydrolysis constants. With low cost production, simple synthesis, and strong performance, AcBC represents a practical and scalable option for treating heavy metal contaminated wastewater in developing regions.

Keywords Adsorption·Heavy metals·Coconut biochar·Iron salt modification·Wastewater treatment

1. INTRODUCTION

Industrial effluents containing heavy metals pose long-term risks because these persistent and non-biodegradable pollutants can damage the liver, kidneys, cardiovascular system, and nervous system [1–3]. Wastewater often contains lead, copper, zinc, nickel, cadmium, and chromium [2], and copper and zinc frequently coexist due to similar physicochemical properties and shared industrial uses [3]. Although essential trace elements [4–6], both have narrow safe ranges: excess copper can cause hepatic and neurological disorders, while excess zinc decreases copper and iron absorption, leading to secondary copper deficiency associated with anemia, immune suppression, and reduced high density lipoproteins [4].

In ecosystems, copper and zinc contamination affects the environment mainly in two ways. First, these metals are toxic to aquatic organisms [7, 8]. In mining and metallurgical regions,

zinc often bioaccumulates in fish, causing physiological disorders, reduced reproduction, inhibited growth, and weakened immunity [7]. Second, they interact with other pollution processes. In eutrophic waters, copper can intensify toxicity during algal bloom events, though the effect is generally additive rather than strongly synergistic [8]. When present in irrigation water, copper and zinc accumulate in soil and plants, cause phytotoxicity, and enter the food chain. Although zinc can support crop productivity, irrigation water containing more than 2 mg per liter may become toxic to plants [9].

Adsorption by biochar derived from abundant agricultural by-products has gained significant attention as a low-cost, efficient, and environmentally friendly approach for pollution remediation [10, 11]. Biochar can be produced from various residues, including rice husk [12], coffee grounds [13–15], wood [16], corn straw [17–19], nut shells [20], coconut residues [21], and aloe vera peels [22, 23]. Among these feedstocks, coconut fiber is notable for its high lignocellulosic composition, with a cellulose content of up to 65 percent, which enhances biochar yield, porosity, and mechanical strength [21]. Coconut fiber and other coconut residues also contain significant inorganic minerals such as potassium, calcium, magnesium [21], and silicon, a common component of plant biomass [24, 25]. Silicon in biomass has gained increasing interest not only for natural silicon extraction [24] but also as a modification or doping agent to improve material properties [25–27]. In biochar, silicon can enhance structural stability and chemical durability [25, 28] and create additional adsorption sites for heavy metal removal [28].

Biochar is generally produced by pyrolysis, in which biomass is decomposed under oxygen-limited conditions at 300 to 700 °C to remove volatiles, enrich carbon, and form pores while limiting carbon loss and mineral formation [10, 11]. To reduce production constraints, this study aims to utilize a simple and cost-effective calcination technique as an alternative to conventional pyrolysis. However, under these non-inert fabricating conditions, the high concentration of silicates in the biomass tends to recrystallize into SiO₂ or crystalline mineral phases on the biochar surface [28]. This phenomenon severely diminishes the material quality by reducing the specific surface area, blocking active pores, and lowering the overall metal ion adsorption efficiency [28]. To address these critical limitations of calcinated biochar, this study proposes a targeted modification method via the co-precipitation of iron salts in an alkaline medium. Furthermore, the optimization of the modification process was systematically evaluated, and the underlying adsorption mechanisms were thoroughly elucidated through characterization of the exhausted biochar. Additionally, six machine learning models were deployed to assess the significance of various contributing factors, thereby precisely predicting the material's adsorption mechanisms.

2. MATERIALS AND METHOD

2.2 Material preparation

Coconut fiber obtained from Ben Tre Province, Vietnam, was calcinated according to the protocol of N. V. Thanh [29], and subsequently subjected to pre-treatment and iron modification based on previous studies [30, 31]. For clarity, the raw biochar and its iron-modified counterpart are designated as RBC and AcBC, respectively. Comprehensive details regarding the fabrication procedures, optimized preparation conditions, and specific chemicals and apparatus utilized are provided in the Supplementary Material.

2.3 Material characterization

The isoelectric point (pH_{pzc}) was determined by the pH drift method using NaCl solution

following Islam I.u. et al. [32]. Morphology was examined with SEM-EDS (S-4800, Hitachi, Japan). The surface functional groups were characterized by Fourier transform infrared spectroscopy (FTIR, Frontier model, PerkinElmer, USA) in the wavenumber range of 4000–400 cm^{-1} , with 16 scans at a resolution of 4 cm^{-1} . X ray diffraction was performed using Cu $K\alpha$ radiation (40 kV, 40 mA, 2θ range 0° to 90°) on a Rigaku SmartLab diffractometer at a scan rate of two degrees per minute. Porous structure and surface characteristics of RBC and AcBC were evaluated by nitrogen adsorption desorption isotherms at 77 K using a BET analyzer (Micromeritics Instruments, USA) after degassing at 150 $^\circ\text{C}$ for 15 hours.

2.4 Adsorption experiments

Batch adsorption experiments were performed in duplicate for both RBC and AcBC, and average values were used for analysis. Adsorption of Cu^{2+} and Zn^{2+} was examined in single metal solutions and in binary systems containing both ions. For each test, 50 mL of metal solution and a measured mass of adsorbent were added to a 250 mL glass flask, then shaken at 25 $^\circ\text{C}$ and 100 rpm for the required contact time. When necessary, the initial pH was adjusted with NaOH or HNO_3 .

After adsorption, solid and liquid phases were separated using a 25 mm nylon syringe filter with a 0.22 μm pore size (Labfil, ALWSCI Corporation, China). Residual Cu^{2+} and Zn^{2+} concentrations in the filtrate were measured by atomic absorption spectrometry using a novAA 800 instrument (Analytik Jena, Germany). The adsorption capacity q_e (mg per g) was calculated according to Equation [33].:

$$Q_e = \frac{(C - C_e) \cdot V}{m} \quad \text{Eq. 2}$$

Whereas: C: initial concentration of the metal ion (mg/L); C_e : equilibrium concentration after adsorption (mg/L); Q_e : equilibrium adsorption capacity (mg/g); V: volume of the solution (L); m: mass of adsorbent used (g).

The adsorption efficiency (E) of the materials was calculated using Equation [33]:

$$E = \frac{(C - C_e)}{C} \cdot 100 \quad \text{Eq. 3}$$

Whereas: C: initial concentration of the metal ion (mg/L); C_e : equilibrium concentration after adsorption (mg/L); E: Adsorption efficiency (%).

The environmental factors investigated in this study included contact time, initial contaminant concentration, initial pH, and adsorbent dosage. To systematically elucidate the adsorption mechanisms, the experimental data were fitted using four kinetic models (pseudo-first-order, pseudo-second-order, Weber–Morris intraparticle diffusion, and Boyd) and four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich). Comprehensive details regarding these environmental parameter experiments, along with the equations for kinetic and isotherm modeling, are provided in the Supplementary Document.

2.5 Machine learning based prediction

To comprehensively analyze and predict the adsorption capacity and underlying mechanisms, a dataset comprising 134 experimental data points (provided in Supplementary Material 2) was

compiled. The input features were categorized into three distinct groups: biochar descriptors, cation descriptors, and experimental conditions, while the adsorption capacity (Q_e) served as the target output. Six advanced tree-based machine learning algorithms, namely Random Forest (R), Extra Trees (E), Gradient Boosting Decision Tree (G), Extreme Gradient Boosting (X), Light Gradient Boosting Machine (LGB), and CatBoost (CAT) were deployed for modeling.

To eliminate potential statistical bias arising from the continuous fluctuations of operational experimental conditions, a targeted feature selection strategy was implemented, following the methodology proposed by S. Zhao et al. [34]. Initially, the average SHAP values across all six models were computed exclusively for the biochar and cation descriptors to evaluate their intrinsic baseline importance. From this preliminary assessment, the top three most influential parameters from each of these two structural groups were selected. Finally, these six prominent descriptors were integrated with the experimental condition parameters to reconstruct the final, optimized SHAP feature importance profile.

Finally, the optimized configuration of descriptors selected via SHAP was utilized as the final input feature set to reconstruct and train the six tree-based machine learning models, employing an 75:25 train/test split. This targeted modeling approach aims to evaluate whether the simplified feature profile can maintain the prediction accuracy of adsorption capacity (Q_e).

3. RESULTS AND DISCUSSION

3.1 Physical and chemical properties of materials

Figure 1, mineral ash particles were widely distributed at 5000 $\times$, while higher magnifications (50,000 $\times$ and 100,000 $\times$) revealed smooth planes, layered porous regions, stacked angular structures, and visible cracks and voids that may enhance adsorption. In contrast, AcBC showed a more homogeneous morphology than RBC, with SEM images (50,000 $\times$ –100,000 $\times$) revealing uniformly distributed fine particles likely iron particle formation. These observations are consistent with the BET and EDS results (Table 1). EDS indicated reduced Al, Ca, K and the appearance of Fe, Na, Cl, and S, with Na. BET results showed strong structural changes: surface area increased from 5.05 to 100.92 m²/g, external area from 3.25 to 107.77 m²/g, and pore diameter decreased from 53.05 to 7.53 nm, while micropores nearly disappeared might due to iron oxide deposition [29] or NaOH-induced corrosion.

XRD analysis (Figure 2) confirmed the highly crystalline nature of RBC. The strongest peak at around 26.8° and a smaller peak at 36.6° showed SiO₂ as the dominant and well crystallized component [35], while peak at $2\theta \approx 21.3^\circ$ corresponded to silicate mineral [35, 36]. Several peaks, including 39.5°, overlapped with CaCO₃ [37], and the 50.26° peak suggested calcium silicate [26]. In AcBC, reduced peak intensities and a broadened baseline suggested the removal of amorphous or weakly bound minerals. The persistent 26.8° reflection confirmed that SiO₂ remained largely unchanged [26].

The FTIR spectrum (Figure 3) supported the physicochemical characterization of RBC. Bands at 774 and 793 cm⁻¹ were indicative of Si–C or Si–O stretching [26], while asymmetric Si–O–Si stretching vibrations appeared at 1001 and 1035.5 cm⁻¹ [38]. Additionally, carbonate signals associated with CaCO₃ were present in the 1408.6 and 688.6 cm⁻¹ regions [37]. Following iron modification, these silicon- and carbonate-related peaks either disappeared or exhibited a significant reduction in intensity. Conversely, a new broad –OH band emerged at 3384.1 cm⁻¹, indicating surface hydroxyl formation [39], while the appearance of Fe–O vibrations at 464.8 and 530 cm⁻¹ successfully confirmed the presence of crystalline iron oxides [38]. Furthermore,

the minor peaks observed at 1643.6, 1358, and 1512.7 cm^{-1} were attributed to the formation of Fe–carboxyl complexes [40, 41].

3.2 The effects of iron salt concentrations

As shown in Figure 4, AcBC prepared at an iron salt concentration of 0.2:0.1 M achieved the highest adsorption efficiencies, removing over 80% of Cu^{2+} and 60% of Zn^{2+} , which were significantly higher than those of RBC (~60% for Cu and 40% for Zn). While increasing the iron concentration from 0.1:0.05 to 0.2:0.1 M enhanced performance, higher concentrations (0.3:0.15 M) led to a decline. At a fixed biochar-to-iron-salt mass ratio of ~0.5 g/g, a low concentration (0.1:0.05 M) likely provided insufficient active sites due to incomplete coating. At the optimal 0.2:0.1 M ratio, iron particles were uniformly distributed on the surface. Conversely, excessive concentration (0.3:0.15 M) induced particle agglomeration, which blocked the active pores and masked functional groups, thereby reducing the adsorption efficiency.

3.3 The effect of the biochar-to-iron salt mass ratio (R/R)

As illustrated in Figure 5, the highest adsorption efficiency was achieved at an R/R ratio of 0.5 g/g. The efficiency increased as the ratio rose from 0.25 to 0.5 g/g, but subsequently declined at higher ratios (1, 1.5, 2, and 3 g/g). This trend indicates that an optimal balance between the biochar matrix and the iron precursor is required. At a low ratio (~0.25 g/g), the excess iron precursor likely led to particle agglomeration and pore blockage rather than effective surface adherence. Conversely, at high ratios (>1 g/g), the insufficient iron amount failed to form a continuous coating on the larger biochar mass, thereby reducing the active site density. Similar behaviors have been documented by Yang et al. [42] and Zeng et al. [43], who reported that excessive iron loading caused particle agglomeration and pore blockage, ultimately decreasing the adsorption capacity. Consequently, based on both optimization experiments, the optimal preparation conditions (an iron salt concentration of 0.2:0.1 M and an R/R ratio of 0.5 g/g) were selected to synthesize the AcBC for subsequent tests.

3.4 Adsorption kinetic

3.4.1 Adsorption kinetic of monometallic system

The adsorption kinetic profiles for Cu^{2+} and Zn^{2+} in the monometallic system onto RBC and AcBC were evaluated using pseudo-first-order (PFO), pseudo-second-order (PSO), Weber-Morris (WM) intraparticle diffusion, and Boyd models. The experimental fitting curves for Cu^{2+} and Zn^{2+} are illustrated in Figure 6a and Figure 6b, respectively, with all corresponding parameters summarized in Table 2. The kinetic curves in Figure 6 explicitly demonstrate that both adsorbents reached a practical plateau and neared equilibrium within the first 240 minutes. Consequently, a contact time of 240 minutes was verified as optimal and selected for all subsequent equilibrium experiments.

Regarding fitting pseudo kinetic models, the experimental data of both raw and modified biochars was well described by the reaction-based kinetic models, with the PSO model consistently achieving higher correlation coefficients than the PFO model. Specifically, for RBC, the R^2 values reached 0.9334 for Cu and 0.9479 for Zn. More importantly, the calculated equilibrium adsorption capacities $Q_{e,cal}$ from the PSO model (13.01 mg/g for Cu and 8.35 mg/g for Zn) matched the experimental values Q_e of 13.16 mg/g and 8.74 mg/g, respectively) much closer than those predicted by the PFO model. A similar dominant trend was observed for AcBC in this monometallic system, where the PSO model yielded high R^2 values of 0.9403 for

Cu and 0.9380 for Zn. The substantial increase in the PSO rate constant (k_2) from RBC to AcBC, rising from 0.0021 to 0.0239 g/(mg·min) for Cu and from 0.0033 to 0.0294 g/(mg·min) for Zn, clearly underscores that the modification dramatically accelerated the initial adsorption rate. These results, combined with the chemical properties of the materials, strongly demonstrate that chemisorption is the primary rate-controlling mechanism.

To further illuminate the diffusion resistance control, the Weber-Morris and Boyd models were implemented. Interestingly, the Weber-Morris model provided excellent nonlinear fits for both materials, showing remarkably high correlation coefficients ($R^2 > 0.96$ for all cases in Table 2, reaching 0.9989 for Zn adsorption on AcBC). The intraparticle diffusion rate constant k_{id} exhibited a massive surge after modification, jumping from 3.47 to 9.52 mg/(g·min^{0.5}) for Cu and from 2.09 to 6.14 mg/(g·min^{0.5}) for Zn. This confirms that the expanded surface area and improved mesoporosity of AcBC significantly facilitated internal mass transfer. However, because the boundary layer thickness parameter (C) remained extremely close to zero for most runs except 0.0005 for Zn-AcBC, it suggests that intraparticle diffusion heavily impacts the overall rate control, though it is not the sole rate-limiting step. This is further validated by the Boyd model plot behavior and its fitting parameters in Table 2, where the negative or low R^2 values for AcBC suggest that film diffusion plays a minimal role, thereby cementing the coupled control of intraparticle transport and surface chemisorption.

3.4.2 Adsorption kinetic of simultaneous two-metal system

To evaluate competitive behavior, the kinetic profiles for the simultaneous binary-metal system were simulated, with fitting curves shown in Figure 7a (Cu) and Figure 7b (Zn), and parameters summarized in Table 3. Due to competition for the same active sites, a mutual suppression effect occurred, causing a noticeable drop in the equilibrium adsorption capacities for both metals compared to the monometallic system. Under binary conditions, the experimental capacities Q_e decreased to 9.64 mg/g (Cu) and 4.75 mg/g (Zn) for raw RBC, and to 12.14 mg/g (Cu) and 7.61 mg/g (Zn) for modified AcBC. Nevertheless, AcBC retained higher multi-metal capacities than RBC, confirming that the iron-salt modification successfully provided more robust active sites to buffer competitive constraints.

Consistent with the monometallic system, the PSO model and Weber-Morris model remained the best mathematical description for both biochars even under competitive stress. Consequently, the kinetic rates under competitive conditions continue to be governed by the coupled-control mechanism of pore intraparticle transport and surface chemisorption.

3.5 Adsorption isotherm

3.5.1 Adsorption isotherm of monometallic system

From the adsorption isotherm curves presented in Figure 8 (Figure 8a for Cu²⁺ and Figure 8b for Zn²⁺), the mathematical parameters of the four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich) were calculated and summarized in Table 4 (Isotherm parameters in the monometallic system). Raw biochar (RBC) exhibited a rapid saturation tendency, performing effectively only at low initial metal concentrations (< 5 mg/L) while the iron-modified biochar (AcBC) maintained a good performance over a broader concentration range.

For the raw biochar (RBC), the mathematical evaluation indicated that the experimental data for both metals were best described by the Langmuir model, yielding determination coefficients R^2 of 0.9461 for Cu²⁺ and 0.9022 for Zn²⁺. The Temkin model also showed a reasonable fit (R^2

= 0.9141 for Cu^{2+} and 0.8932 for Zn^{2+} , which suggests that the heat of adsorption decreases linearly with coverage due to adsorbate-adsorbent interactions. However, the superior fit of the Langmuir model implies that the adsorption on RBC predominantly occurs on a homogenous surface, resulting in calculated maximum monolayer capacities ($Q_{e,\text{cal}}$) of 16.77 mg/g for Cu^{2+} and 15.18 mg/g for Zn^{2+} . This uniform but limited binding capability is further evidenced by low Temkin equilibrium binding constant ($A = 3.35 \text{ L/g}$ for Cu^{2+}).

For the iron-modified biochar (AcBC), a clear mechanistic shift was observed as the Freundlich model provided the highest correlation, with R^2 values reaching 0.9445 for Cu^{2+} and an excellent 0.9739 for Zn^{2+} , noticeably outperforming the Langmuir model ($R^2 = 0.8119$ for Cu^{2+} ; 0.8805 for Zn^{2+}). This transition strongly indicates that the iron-salt modification successfully altered the biochar surface from a relatively homogenous state to a highly heterogeneous structure. This enhanced affinity and multi-site capability are robustly supported by the Freundlich heterogeneity factors ($n > 1$, ranging from 2.54 to 3.93), a massive surge in the Temkin binding constant A to 77.41 L/g for Cu^{2+} . Furthermore, the Temkin model also has a good correlation fit for AcBC ($R^2 = 0.8507$ for Cu^{2+} and 0.8293 for Zn^{2+}), reinforcing the concept of a heterogeneous adsorption surface where the heat of adsorption decreases linearly with surface coverage. Interestingly, while the prior kinetic studies adhered to the PSO model, implying a chemisorption controlled process, the Temkin adsorption energy-related constants obtained here ($B = 3.56$ for Cu^{2+} and 3.44 for Zn^{2+}) heavily indicate the dominance of physical adsorption at equilibrium.

3.5.2 Adsorption isotherm simultaneous two-metal system

From the competitive curves in Figure 9 and parameters in Table 5, the introduction of a co-existing ion induced a noticeable decline in equilibrium adsorption capacities for both biochars, highlighting active site competition.

For RBC, a distinct divergence emerged: Cu^{2+} data remained best described by the Langmuir model ($R^2 = 0.9022$, $Q_{e,\text{cal}} = 15.18 \text{ mg/g}$), whereas Zn^{2+} shifted favorably toward the Freundlich model ($R^2 = 0.7983$) over Langmuir ($R^2 = 0.5940$). This indicates that competition with copper severely disrupted the uniform monolayer distribution of zinc on RBC, further supported by a severely lowered Langmuir affinity constant ($K_L = 0.0533 \text{ L/mg}$).

For AcBC, although the Freundlich model remained the superior good fit for both metals ($R^2 = 0.9739$ for Cu^{2+} and 0.72 for Zn^{2+}). In addition, the highest heterogeneity factor ($n = 6.91$) was registered for Zn^{2+} . This indicates that Cu^{2+} occupied most of the high-affinity sites, leaving only a limited number of positions accessible for Zn^{2+} .

3.6 The effect of adsorbent dosage

Figure 10 shows that adsorption efficiency strongly depended on adsorbent dosage. At an initial concentration of 20 mg/L, efficiency increased rapidly with rising solid-to-liquid ratios, from 1 to 5 g/L for RBC and up to 2 g/L for AcBC, after which further dosage increases produced little improvement. For AcBC, an optimal dosage of 2 g/L achieved over 97% Cu^{2+} removal and nearly 85% Zn^{2+} removal, yielding equilibrium concentrations of 0.5 mg/L (Cu) and 2.8 mg/L (Zn). Although dosages $\geq 5 \text{ g/L}$ produced $\sim 99\%$ removal for both ions, such levels are impractical due to excessive material use and sludge generation. Thus, 2 g/L was selected as the optimal dosage at 20 mg/L initial concentration. RBC followed a similar trend but performed substantially worse, with efficiencies 20–30% lower than AcBC in the 1–2 g/L

range. Moreover, RBC required dosages above 10 g/L to approach 99% removal, underscoring the superior adsorption efficiency and cost-effectiveness of the iron-modified AcBC material.

3.7 The effect of initial pH

The effect of initial pH showed a clear positive correlation between pH and adsorption efficiency. As pH increased from 2 to 6 for Cu^{2+} and from 2 to 6.5 for Zn^{2+} , both materials exhibited progressively higher efficiency. This trend is governed first by the pH_{pzc} of the materials. Because both RBC and AcBC had pH_{pzc} values above 7, their surfaces were positively charged in the studied pH range, causing electrostatic repulsion with cationic Cu^{2+} and Zn^{2+} . Increasing pH reduced this positive charge, strengthened electrostatic attraction, and improved adsorption. The second factor relates to metal hydroxide precipitation: although the pH limits ($\text{pH} < 6$ for Cu and < 6.5 for Zn) were set to avoid precipitation, small amounts of hydroxide formation may still occur near these limits, lowering free metal-ion concentration and producing an apparent but not entirely adsorption-driven increase in removal efficiency.

3.8 Characterization of exhausted adsorbent and proposed adsorption mechanism

3.8.1 Characterization of exhausted adsorbent

For the RBC material, SEM-EDS images (Figure 12) revealed relatively large precipitated aggregates composed mainly of Cu and Zn. Among these, the Cu-containing aggregates exhibited a large cluster size, whereas those of Zn showed significantly smaller particles distributed across the adsorbent surface. Combined with the EDS results, this accumulation demonstrated that the precipitation occurred predominantly on the surface of the mineral ash particles. On the other hand, the FTIR spectra (Figure 3) showed that the peaks associated with carbonate (688.6 cm^{-1}) and Si–C/Si–O (793 cm^{-1}) stretching were markedly weakened. These results suggest that the adsorption process was accompanied by surface precipitation involving both carbonate groups and silicate mineral phases. Additionally, the post-adsorption XRD patterns (Figure 2) of the material showed no significant alterations, with the primary variation manifested as a higher background noise compared to the fresh adsorbent.

Regarding AcBC, another interesting trend was observed, wherein the iron species were preferentially distributed on the surface of the mineral ash particles; meanwhile, although the iron phases still formed on the carbon surface, their density was significantly lower and more scattered. Mirroring the behavior of RBC, the contents of adsorbed Cu and Zn also exhibited a higher presence on the mineral ash phases. This indicates that these silicate mineral ash particles not only directly serve as adsorption sites but also suggests their role as structural templates (supports) for the formation of the iron phases. The FTIR results showed that after adsorption, the peaks at 1643.6 , 1358 , and 1512.7 cm^{-1} associated with $-\text{COOH}/\text{Fe-carboxyl}$ and those at 530 and 464.8 cm^{-1} corresponding to Fe–O disappeared or were significantly reduced in intensity. This clearly demonstrates the intensive involvement of these chelation-capable active sites in the adsorption process of the modified material. In addition, the XRD patterns (Figure 2) showed a general decrease in peak intensity, but the peak at 36.6° increased considerably after Zn adsorption on AcBC. This trend may be attributed to the interaction between Zn and the silicate mineral, as this peak has been reported as a characteristic fingerprint of certain natural silicate minerals present in biochar [25].

3.8.2 Machine learning-based prediction

Figure 13 presents the SHAP importance matrix and the corresponding feature ranking for the cation groups, biochar properties, and overall optimal configuration. Specifically, the SHAP

distribution analysis for biochar properties reveals that three parameters exert the most decisive influence on the model: specific surface area (SSA), %Si, and %O content. Among these, SSA exhibits the strongest impact on the material's adsorption capacity. This quantitative result clearly demonstrates the efficacy of the modification strategy, as AcBC achieved a structural breakthrough in porosity, with its surface area increasing more than 20-fold (from 5 m²/g in RBC to over 100 m²/g). This trend aligns with previous studies [44], where the SHAP value of the surface area also played a pivotal role in controlling adsorption performance, ranking second only to N/C. The subsequent parameters, %Si and %O, reinforce the findings in Section 3.8.1; specifically, silicate mineral phases may exert negative effects on adsorption efficiency, yet they can also serve as adsorption sites and iron carriers. On the other hand, %O is directly linked to the presence of functional groups or chemical adsorption sites on the material's surface, such as -OH, -OOH, and Fe-O.

Regarding the cation descriptors, the three most critical factors identified are relative atomic mass (RAM), first-order hydrolysis constant (log K), and the effective ionic radius (R), respectively. Among these, RAM and R are related to physical adsorption and the diffusion capacity into pores, which further reinforces the finding that physical adsorption dominates based on the adsorption isotherm model results. On the other hand, log K represents the degree of hydrolysis of the metal ions; as log K increases, the hydrolysis capacity enhances, which is directly linked to surface complexation adsorption mechanisms [34]. The study [34] also noted that log K possessed the second-highest SHAP value among the cation descriptors.

Based on the above results, three biochar properties (SSA, %Si, %O), three cation descriptors (RAM, R, log K), and the environmental condition parameters were integrated into a global SHAP calculation. The results presented in Figure 13c indicate that environmental conditions exert the greatest influence on the adsorption outcomes. Specifically, the two most critical factors are initial concentration and adsorbent dosage, followed by SSA a parameter belonging to the biochar properties. Through this approach, novel guidelines and strategies for material modification and improvement can be effectively proposed.

To further evaluate the predictive capability and accuracy of the models, the aforementioned factors were utilized as input variables to predict the adsorption capacity using six tree-based algorithms. The prediction results are presented in Table 6. The outcomes demonstrate that Extreme Gradient Boosting (XGBoost) achieved the highest accuracy, exceeding 99% for the training set and 92% for the testing set. Given this high level of accuracy, Figure 14 visually illustrates the regression lines for both the training and testing datasets based on the Extreme Gradient Boosting algorithm.

3.9 Estimation of AcBC Production Cost and Market Potential

According to the FAO, global coconut production is about 61.9 million tons per year, largely concentrated in tropical regions [41]. Coconut fiber biochar is already used in water treatment at 3.5–4.6 USD/kg [33] and can be a cheaper alternative to activated carbon. Table 7 summarizes the laboratory scale production cost in this study. The cost of RBC fell within the global biochar price range (0.09–8.85 USD/kg, mean 2.65 USD/kg) [33], while AcBC cost 7.54 USD/kg, about three times higher. Despite this increase, the modified biochar remains within reported global cost ranges and is economically feasible given its improved adsorption performance. Moreover, AcBC shows clearly superior performance, allowing treated wastewater to meet Vietnam's National Technical Regulation on Industrial Wastewater-QCVN

40:2025/BTNMT (Column A) and offering cost advantages at higher pollutant concentrations (Table 8).

Utilizing calcination instead of conventional pyrolysis offers a pragmatic approach to reducing both the operational complexity and production costs of material synthesis. However, calcination often triggers the recrystallization of silicate mineral phases on the material surface, a phenomenon previously reported to detrimental effect on the adsorption capacity of biochar [28]. This structural limitation is particularly pronounced in silicate-rich biomass feedstocks, such as coconut fiber and rice husk [12]. In this study, the modified biochar (AcBC) successfully overcame this critical drawback. Although AcBC did not achieve the maximum theoretical adsorption capacities documented in previous literature (Table 9), it still exhibited moderate-to-high removal efficiencies, particularly within low-to-medium concentration ranges (<40 mg/L). This improvement is highly remarkable when contrasted with the limited initial performance of the pristine RBC.

4. CONCLUSION

This study successfully developed the AcBC adsorbent tailored for heavy metal removal, offering competitive production costs and straightforward fabrication conditions feasible for large-scale applications in developing countries. Along with confirming its techno-economic viability, the experimental results underscore the pivotal role of silicate-dominated mineral ash particles. These mineral phases not only function as inherent adsorption sites but also serve as structural templates for iron oxide deposition, as evidenced by EDS mapping showing a denser, more uniform iron distribution on mineral surfaces than on carbon matrices. The iron salt coprecipitation modification significantly enhanced the material's performance boosting the calculated adsorption capacity ($Q_{e,cal}$) from 16.77 mg/g to 34.75 mg/g for Cu^{2+} and from 15.18 mg/g to 29.69 mg/g for Zn^{2+} . This improvement is well-supported by BET analysis, which revealed a structural breakthrough in porosity, with the specific surface area expanding from 5.05 to 100.92 m^2/g . Crucially, the integration of tree-based machine learning models and SHAP interpretability analysis successfully quantified and validated the core driving forces behind the adsorption process. Among the tested algorithms, Extreme Gradient Boosting demonstrated exceptional predictive accuracy, exceeding 99% for the training set and 92% for the testing set.

Despite these insights, a comprehensive life cycle assessment (LCA) of the material remains an open avenue for future research. Additionally, navigating the dual nature of %Si, where dominant SiO_2 formations may induce minor spatial hindrance yet concurrently act as essential active site supports, presents an ongoing optimization challenge.

Declaration of Competing Interest

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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Credit author statement

Xuan Thanh Bui: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft, Writing – review & editing. Khuat Thuy Trang: Investigation, Writing original draft. Phacharapol Induvesa: Methodology, Resources, Supervision, Funding acquisition, Writing – review & editing. Nguyen Thuy Chung: Conceptualization, Methodology, Resources, Supervision, Funding acquisition, Writing – review & editing.

5. FIGURES AND TABLES

5.1 Figures

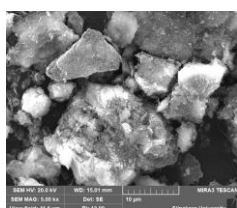


Figure. 1a The 5000x SEM image of the RBC

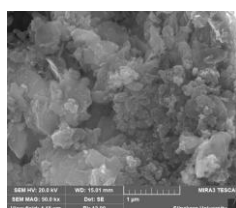


Figure. 1b The 50,000x SEM image of the RBC

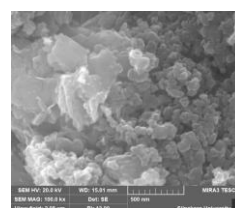


Figure. 1c The 100,000x SEM image of the RBC

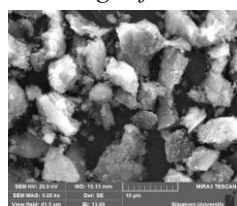


Figure. 1d The 5000x SEM image of the AcBC

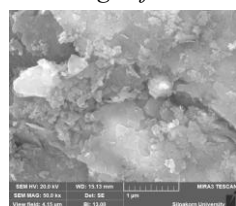


Figure. 1e The 50,000x SEM image of the AcBC

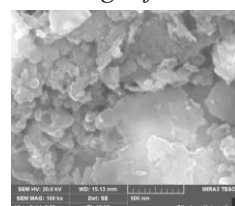


Figure. 1f The 100,000x SEM image of the AcBC

Figure. 1 The SEM images of the materials are presented at different magnifications

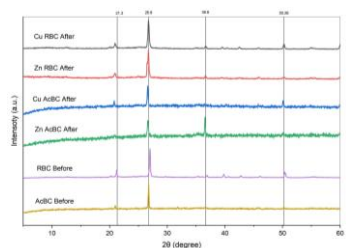


Figure. 2 X-ray diffraction (XRD) patterns of RBC and AcBC before and after adsorption

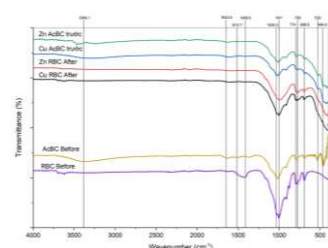


Figure. 3 FTIR spectra of RBC and AcBC before and after adsorption

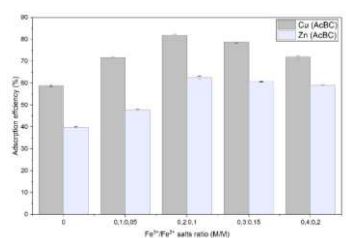


Figure. 4 The effects of iron salt concentrations

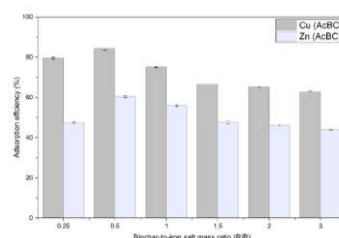


Figure. 5 The effect of the biochar-to-iron salt mass ratio (R/R)

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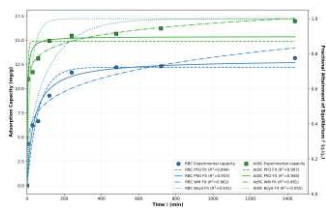


Figure. 6a Kinetic plot of monometallic system for the adsorption of Cu

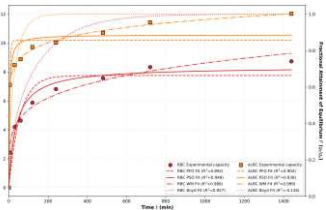


Figure. 6b Kinetic plot of monometallic system for the adsorption of Zn

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Figure. 6 Kinetic plots of monometallic system for the adsorption processes

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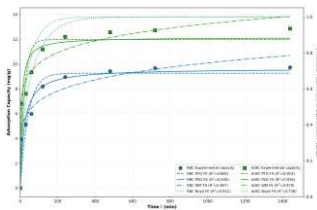


Figure. 7a Kinetic plot of simultaneous two-metal system for the adsorption of Cu

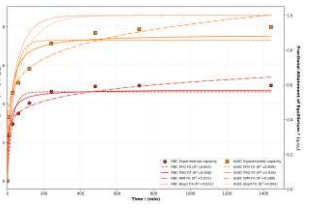


Figure. 7b Kinetic plot of simultaneous two-metal for the adsorption of Zn

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Figure. 7 Kinetic plots of simultaneous two-metal system for the adsorption processes

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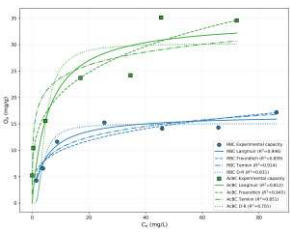


Figure. 8a Isotherm plot of monometallic two-metal system for the adsorption of Cu

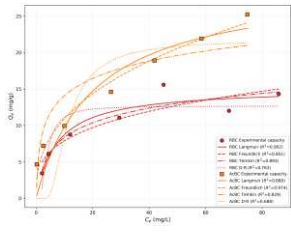


Figure. 8b Isotherm plot of monometallic two-metal system for the adsorption of Zn

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Figure. 8 Isotherm plots of monometallic system for the adsorption processes

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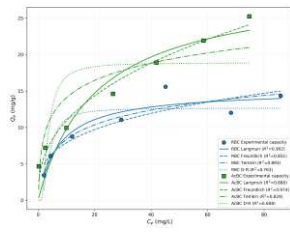


Figure. 9a Isotherm plot of simultaneous two-metal system for the adsorption of Cu

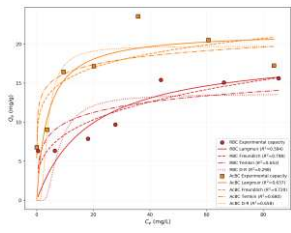


Figure. 9b Isotherm plot of simultaneous two-metal system for the adsorption of Zn

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Figure. 9 Isotherm plots of simultaneous two-metal system for the adsorption processes

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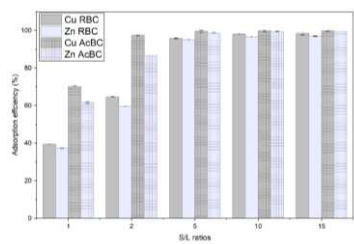


Figure. 10 The effect of solid-to-liquid ratio (S/L)

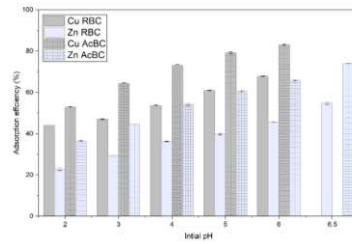


Figure. 11 The effect of initial pH

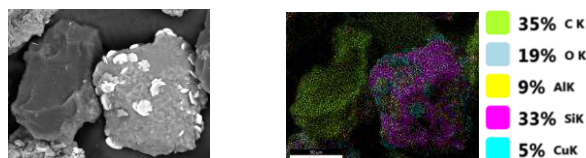


Figure. 12a The EDS images of RBC adsorbed Cu

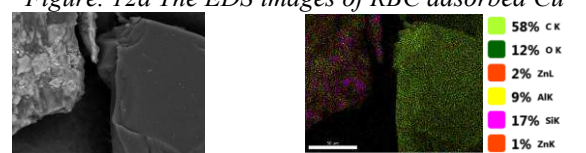


Figure. 12b The EDS images of RBC adsorbed Zn

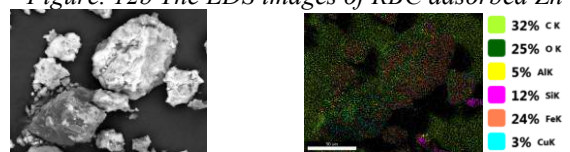


Figure. 12c The EDS images of AcBC adsorbed Cu



Figure. 12d The EDS images of AcBC adsorbed Zn

Figure. 12 The EDS images of exhausted RBC and AcBC

	R	E	G	X	LGB	CAT	Average importance value
Relative Atomic Mass (RAM)	0.11	0.11	0.13	1.00	1.00	0.21	
First order hydrolysis constant (log K)	0.10	0.14	0.24	0.00	0.00	0.04	
Effective Ionic Radius (Å) R	0.10	0.19	0.15	0.00	0.00	0.00	
Higher hydrolysis constant (HHC)	0.09	0.11	0.19	0.00	0.00	0.15	
Nuclear Charge Number (NC)	0.13	0.13	0.01	0.00	0.00	0.11	
Electronegativity of solution ion (ENR)	0.09	0.11	0.05	0.00	0.00	0.20	
Free energy of hydration (kJ/mol) (FER)	0.11	0.13	0.05	0.00	0.00	0.09	
Solubility product constant (SPC)	0.09	0.07	0.11	0.00	0.00	0.05	

Figure. 13a Biochar properties

	R	E	G	X	LGB	CAT	Average importance value
Specific surface area (m ² /g)	0.27	0.00	0.40	1.00	1.00	0.36	
%Si	0.61	1.00	0.90	0.00	0.00	0.44	
%O	0.24	0.00	0.38	0.00	0.00	0.34	
Point of zero charge (PZC)	0.25	0.00	0.00	0.00	0.00	0.38	
%C	0.18	0.00	0.03	0.00	0.00	0.34	
%Fe	0.29	0.00	0.11	0.00	0.00	0.01	

Figure. 13b Cation descriptors

	R	E	G	X	LGB	CAT	Average importance value
Concentration	1.00	1.00	1.00	1.00	1.00	1.00	
Adsorbent dosage	1.13	1.17	1.30	1.17	0.80	1.24	
Specific surface area (m ² /g)	0.41	0.48	0.44	1.41	1.10	0.72	
Time	0.42	0.59	0.71	0.63	0.40	0.79	
pH	0.49	0.30	0.36	0.36	1.20	0.41	
Relative Atomic Mass (RAM)	0.20	0.33	0.14	0.70	1.21	0.27	
%Si	0.31	0.73	0.75	0.00	0.00	0.65	
%O	0.29	0.16	0.28	0.00	0.00	0.32	
Effective Ionic Radius (Å) R	0.31	0.37	0.31	0.00	0.00	0.42	
First order hydrolysis constant (log K)	0.22	0.43	0.38	0.00	0.00	0.34	

Figure. 13c Overall configuration

Figure. 13 SHAP feature importance matrices and corresponding average importance rankings

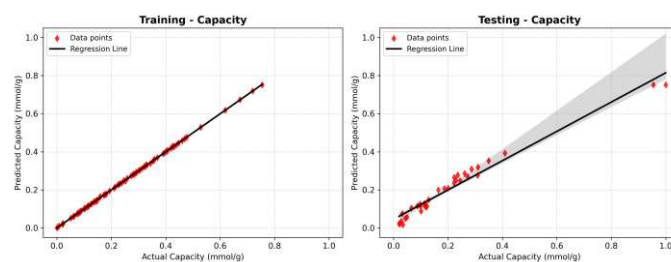


Figure. 14 Prediction adsorption capacities across training and testing datasets

5.2 Tables

Table 1 Physicochemical characteristic of RBC and AcBC

Material	S_{BET}^* (m ² /g)	S_{mic}^{**} (m ² /g)	S_{mic}/S_{BET}	S_{ext}^{***} (m ² /g)	Pore Diameter ^{****} (nm)	pH _{pzc}	Elemental contents (%)									
							C	O	Si	Al	Ca	K	Fe	Na	Cl	S
RBC	5.06	1.82	0.36	3.22	53.05	7.10	40.22	37.00	10.09	8.09	3.92	0.67	-	-	-	-
AcBC	100.92	-	-	107.77	7.53	7.60	40.77	38.64	5.22	2.42	2.01	0.57	6.11	1.89	1.76	0.67

*BET experiments were conducted out gas temperature at 150 °C and measured using N₂ adsorption with the Brunauer-Emmett-Teller (BET) method.

**Pore surface area calculated using the t plot method.

***External surface area calculated using the t plot method.

****Pore diameter calculated using D-H method.

Table 2 Characteristic parameters of monometallic system adsorption kinetic models

Model	Parameter	Unit	RBC		AcBC	
			Cu	Zn	Cu	Zn
Experiment result	Q _e	mg/g	13.16	8.73	16.96	12.02
	Q _{e,cal}	mg/g	12.21	7.75	14.87	10.18
	K ₁	min ⁻¹	0.02	0.02	0.27	0.24
	R ²	-	0.8938	0.8922	0.9069	0.9036
PFO	Q _{e,cal}	mg/g	13.01	8.35	15.38	10.56
	K ₂	g·mg ⁻¹ ·min ⁻¹	0.002	0.003	0.02	0.03
	R ²	-	0.9334	0.9479	0.9403	0.9380
	k _d	mg·g ⁻¹ ·min ^{-0.5}	3.46	2.09	9.52	6.14
WM	n	-	0.19	0.20	0.08	0.09
	C	mg/g	0.0000	0.0000	0.0000	0.0005
	R ²	-	0.9623	0.9861	0.9911	0.9989
	K ^B	min ⁻¹	0.0068	0.0056	0.0308	0.0236
Boyd	R ²	-	0.9312	0.9273	-0.0553	-0.1363

Table 3 Characteristic parameters of simultaneous two-metal system adsorption kinetic models

Model	Parameter	Unit	RBC		AcBC	
			Cu	Zn	Cu	Zn
Experiment result	Q _e	mg/g	9.72	4.96	12.84	7.99
	Q _{e,cal}	mg/g	9.25	4.63	11.96	7.31
PFO	K ₁	min ⁻¹	0.02	0.04	0.04	0.03
	R ²	-	0.8814	0.8406	0.8145	0.8387
	Q _{e,cal}	mg/g	9.64	4.74	12.14	7.61
PSO	K ₂	g·mg ⁻¹ ·min ⁻¹	0.005	0.011	0.020	0.008
	R ²	-	0.9303	0.9156	0.9264	0.9185
	k _d	mg·g ⁻¹ ·min ^{-0.5}	3.39	2.05	5.78	2.79
WM	n	-	0.16	0.13	0.12	0.15
	C	mg/g	0.0000	0.0000	0.0000	0.0000
	R ²	-	0.9574	0.9747	0.9689	0.9805
Boyd	K ^B	min ⁻¹	0.0112	0.0150	0.0175	0.0103
	R ²	-	0.9112	0.7377	0.8206	0.8416

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Table 4 Characteristic parameters of monometallic system adsorption isotherm models

Model	Parameter	Unit	RBC		AcBC	
			Cu	Zn	Cu	Zn
Langmuir	$Q_{c,cal}$	mg/g	16.77	15.18	34.75	29.69
	K_L	L/mg	0.21	0.14	0.17	0.05
	R^2	-	0.9461	0.9022	0.8119	0.8805
	$R_L(C = 5 \text{ mg/L})$	-	0.45	0.57	0.67	0.90
	$R_L(C = 100 \text{ mg/L})$	-	0.04	0.07	0.09	0.32
Freundlich	K_f	$(\text{mg/g})(\text{L/mg})^{\frac{1}{n}}$	5.51	3.95	11.29	4.40
	n	-	3.93	3.34	3.81	2.54
	R^2	-	0.8592	0.8507	0.9445	0.9739
Temkin	A	l/g	3.35	1.76	77.41	5.99
	B	-	2.97	2.91	3.56	3.44
	R^2	-	0.9141	0.8932	0.8507	0.8932
D-R	Q_s	mg/g	15.04	12.65	30.24	21.71
	K_{dr}	mol^2/Kj^2	0.0000	0.0000	0.0000	0.0000
	R^2	-	0.8313	0.7631	0.7012	0.6884

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Table 5 Characteristic parameters of simultaneous two-metal system adsorption isotherm models

Model	Parameter	Unit	RBC		AcBC	
			Cu	Zn	Cu	Zn
Langmuir	$Q_{c,cal}$	mg/g	15.18	19.22	29.69	21.59
	K_L	L/mg	0.13	0.05	0.05	0.26
	R^2	-	0.9022	0.5940	0.8805	0.6371
	$R_L(C = 5 \text{ mg/L})$	-	0.088	0.80	0.41	0.72
	$R_L(C = 100 \text{ mg/L})$	-	0.01	0.19	0.05	0.13
Freundlich	K_f	$(\text{mg/g})(\text{L/mg})^{\frac{1}{n}}$	3.95	4.32	4.40	11.00
	n	-	3.34	3.45	2.54	6.91
	R^2	-	0.8507	0.7983	0.9739	0.7200
Temkin	A	l/g	1.76	16.03	5.99	2171.73
	B	-	2.91	1.95	3.44	1.63
	R^2	-	0.8932	0.6520	0.8293	0.6801
D-R	Q_s	mg/g	12.65	13.62	18.88	19.75
	K_{dr}	mol^2/Kj^2	0.0000	0.0000	0.0000	0.0000
	R^2	-	0.7631	0.2978	0.6084	0.6578

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Table 6 Performance metrics of machine learning models for predicting adsorption capacity

Model	R^2 train	Root mean squared error (train)	Mean squared error (train)	R^2 test	Root mean squared error (test)	Mean Squared Error (test)
X	0.9998	0.0016	0	0.9263	0.059	0.0034
E	1	0	0	0.9176	0.0624	0.0038
G	0.993	0.0137	0.0001	0.9165	0.0628	0.0039
R	0.9884	0.0177	0.0003	0.8951	0.0704	0.0049
CAT	0.9959	0.0053	0	0.8726	0.0776	0.006
LGB	0.6596	0.0963	0.0092	0.5635	0.1436	0.0206

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Table 7 Estimation of AcBC Production Cost

Process stage	Operation step	Cost estimation method	Cost (USD/Kg)
Raw material preparation	Collection of raw material	Free collection of coconut fiber from local farms	0
	Natural drying	Air drying	0
	Labor cost for material preparation (sieving, preliminary washing, and drying)	Labor rate (USD/h) × time (h): 0.5 × 1.0	0.5
RBC production	Pyrolysis of coconut fiber	Furnace power (kW) × operation time (h) × electricity cost (USD/kWh): 2.0 × 1.0 × 0.08	0.16
	Washing	Laboratory water and electricity cost for producing distilled water: 5.0 L DI water/kg biochar	0.8
	Drying	Oven power (kW) × operation time (h) × electricity cost (USD/kWh): 1.2 × 4.0 × 0.08	0.38
	Labor cost	Labor rate (USD/h) × time (h): 0.5 × 1.0	0.5
Modification (AcBC production)	FeCl ₃ ·6H ₂ O	0,164 g × 10 USD/kg	1.64
	FeSO ₄ ·7H ₂ O	0,336 g × 4 USD/kg	1.34
	Magnetic stirring (24h)	Stirrer power (kW) × operation time (h) × electricity cost (USD/kWh): 0.06 × 24 × 0.08	1.15
	Drying	Oven power (kW) × operation time (h) × electricity cost (USD/kWh): 1.2 × 4.0 × 0.08	0.38
Subtotal (RBC production)			2.34
Subtotal (AcBC production)			6.85
Overhead cost		10% of base cost	0.83
Total estimated cost			7.54

Table 8 Comparison of Treatment Efficiency and Production Cost between RBC and AcBC

Material	C ₀ (mg/L)	S/L ratio (g/L)	Efficiency Cu/Zn	C _e (mg/L, Cu/Zn)	Time (mins)	Column A QCVN 40	Cost (USD/m ³)
AcBC	5	1	90% / 89%	0.5 / 0.6	5 (Cu)-30 (Zn)	approved	7.5
RBC		1	89% / not approved	0.3	480	approved (Cu)	3.2
AcBC	20	2 (Cu) – 2.5 (Zn)	96% / 95%	0.5 / 0.5	120	approved	15 – 18.75
RBC		5 (Cu) – 5.5 (Zn)	96% / 95%	0.7 / 0.5	240	approved	16 – 17.6

Table 9 Comparison of the Q_e with other magnetic biochar

Reference	Biomass origin	Modification precursor	Contaminant	Q _e (mg/g)
[36]	Straw	FeSO ₄ ·7H ₂ O, FeCl ₃ ·6H ₂ O, NaOH	Cu ²⁺	149.2
[62]	Commercial biochar	FeSO ₄ ·7H ₂ O, NaBH ₄		66.16
[63]	Kelp	FeCl ₃		55.86
	Hijikia			47.75
[34]	Pinecone	FeSO ₄ ·7H ₂ O, MnSO ₄ , NaOH		13.4
	White popinac			10.4
	Sugarcane bagasse			19.8
RBC	Coconut fiber	FeSO ₄ ·7H ₂ O, FeCl ₃ ·6H ₂ O, NaOH		16.77
AcBC				34.75
[63]	Kelp	FeCl ₃	Zn ²	22.22
	Hijikia			19.13
[64]	Empty fruit branch			1.18
RBC	Coconut fiber	FeSO ₄ ·7H ₂ O, FeCl ₃ ·6H ₂ O, NaOH		15.18
AcBC				29.69

5.3 References

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