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Kinetic, isotherm, and thermodynamic study of Cu(II) ion removal from groundwater using acid-activated carbon based on coconut tree waste (*Cocos nucifera* L.)

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ABSTRACT

This work focuses on determining the potential of activated carbon synthesised from coconut stem biomass (CSAC) as an effective adsorbent activated with hydrochloric acid (HCl) in adsorbing copper ions (Cu^{2+}) from contaminated groundwater. Heavy metal pollution, particularly copper, poses serious environmental threats, and low-cost agricultural waste-derived adsorbents offer a sustainable solution for remediation. CSAC was synthesised via chemical activation with 0.1 M HCl and characterised using SEM, SEM-EDX, FTIR, and BET analysis. The surface area increased significantly from 82.465 to 230.096 m²/g post-activation. To evaluate the adsorption behaviour, batch experiments were performed under varying conditions of initial Cu²⁺ concentrations (25–150 mg/L), adsorbent dosage (2–3.5 g), pH (3–10), contact time (0–180 min), and temperature (298-338 K). Atomic absorption spectroscopy (AAS) was used to analyse the residual content of Cu²⁺ ions after the adsorption process. The kinetic analysis revealed that the adsorption process conformed to the pseudo-firstorder model, with a high correlation coefficient ($R^2 = 0.9782$), indicating that physisorption primarily governed the mechanism. The Freundlich isotherm best describes the equilibrium data ($R^2 = 0.9993$), implying multilayer adsorption on a heterogeneous adsorbent surface. Furthermore, thermodynamic evaluations demonstrated that the process occurred spontaneously ($\Delta G < 0$), was endothermic ($\Delta H = +22.19$ kj/mol), and involved an increase in system disorder, as reflected by a positive entropy change ($\Delta S = +0.0711 \text{ kj/mol} \cdot K$). Although conducted at a laboratory scale, the study shows significant potential for practical application in industrial wastewater treatment. The novelty of this research lies in utilizing HCl-activated coconut stem carbon as a cost-efficient and high-performance material for Cu(II) removal, addressing a gap in the use of underexplored agricultural waste materials. As future research, exploring multi-contaminant scenarios and assessing regeneration and costefficiency will be critical to confirming the viability of CSAC in real-world industrial settings.

Keywords: adsorption, copper (II), activated carbon, coconut waste, kinetics, isotherms, intra-particle diffusion.

INTRODUCTION

Environmental pollution by various chemical elements and highly toxic heavy metals has become an urgent global concern due to its detrimental impacts on groundwater quality. This condition requires a rapid and effective response. Heavy metal contamination in aquatic environments is predominantly attributed to both geogenic processes and anthropogenic activities, including the extensive use of pesticides that significantly exacerbate water pollution (Zaynab et al., 2022).

Copper element pollution in groundwater mainly comes from industrial waste. If this condition is not handled properly, the industrial waste containing copper elements can pollute surface water and groundwater, thus disrupting the ecological balance (Yulia et al., 2024). Although copper is an element that plays a role in enzyme activity, electron transport, and connective tissue formation, excess copper can cause toxic effects in the bodies of living things. High copper levels exceeding 1000 ppb can interfere with the digestive system of living organisms, causing liver and kidney damage and ultimately producing harmful free radicals. In addition, the environment can experience bioaccumulation of copper elements across trophic levels within ecological systems (Liu et al., 2023).

Copper contamination in groundwater can pose serious health risks to living organisms, including gastrointestinal disorders as well as potential liver and kidney toxicity (Qiao et al., 2025; Teschke, 2024). To reduce these risks, WHO and USEPA have set a safe limit of copper ions between 1.3 and 2 mg/L (USEPA, 2021; WHO, 2011). Several treatment methods have been developed, among which adsorption using activated carbon stands out for its effectiveness and environmental sustainability (Chuah et al., 2005; Liu et al., 2023; Lucaki et al., 2020). The biochar derived from biomass, especially from sawdust, rice husk, and wheat residue, has been widely studied for this purpose (Al-Janabi et al., 2023). In this study, the coconut stem (Cocos nucifera L.) based biomass was used to synthesise activated carbon, using HCl activation to improve its surface properties and increase the adsorption efficiency of Cu(II).

In this study, the biomass of coconut stalks (*Cocos nucifera* L.) was selected as a precursor to synthesise activated carbon. This material is chemically activated using an HCl solution to improve its surface characteristics and increase the specific surface area, the abundance of active functional groups, and the adsorption capacity of its Cu^{2+} ions. To study the surface properties of the resulting coconut stem-based activated carbon (CSAC), it was comprehensively characterised through BET surface area analysis, morphological observations via SEM, and determination of element composition by EDX, to identify functional groups using FTIR spectroscopy.

The main hypothesis of this study is that by activating HCl, it can improve the surface properties and the efficiency of Cu²⁺ removal by CSAC through a fission-driven mechanism. To validate this hypothesis, adsorption performance was systematically evaluated under various operational conditions using isotherm models (Langmuir, Freundlich, and Temkin), kinetic models (Pseudo-First-Order and Pseudo-Second-Order), and thermodynamic analysis, also using intra-particle diffusion modelling to elucidate the underlying adsorption mechanism.

MATERIALS AND METHODS

Preparation of adsorbent (CSAC)

Coconut trunk biomass was obtained from local sources, cut into smaller fragments, and washed with demineralised water to remove dirt and adhering particles. The shredded material was dried in the sun for three days, then dried in an oven at 105 °C for two hours to ensure complete removal of water content. The dried biomass was ground and sieved to obtain particles smaller than 1 mm. Carbonisation was carried out in a furnace maintained at 773 K for two hours under oxygenlimited conditions to produce biochar. The resulting char was cooled in a desiccator to prevent atmospheric water absorption.

Biochar activation was carried out by soaking the material in a 0.1 M hydrochloric acid (HCl) solution with a solid-to-liquid ratio of 1:10 (w/v), and continuous stirring at room temperature for 24 hours to ensure that it was distributed uniformly. After activation, the biochar was separated by filtration and thoroughly rinsed with demineralised water until it reached a neutral pH. The adsorbent was then dried at 110 °C for 12 hours and stored in an airtight container; then, further characterisation and adsorption studies were carried out.

Evaluation of adsorption in batch systems

The research flow chart is illustrated in Figure 1. Batch adsorption tests were operated using 250 mL Erlenmeyer flasks, each containing 100 mL of Cu(II) ion solution with initial concentrations of 25, 50, 100, and 150 mg/L. A certain mass of CSAC, varying between 2.0 and 3.5 g, was then loaded into each flask. The pH of the solution was adjusted between 3 and 10 using 0.1 M HCl or NaOH. Subsequently, the flasks were placed on a rotary shaker and agitated at 200 rpm under controlled temperatures of 298, 308, 318, 328, and 338 K for contact times up to 180 minutes. After adsorption, the mixtures were filtered through micro-filter paper (pore size $\sim 2.5 \ \mu$ m) to separate the solid and liquid phases.

The residual Cu²⁺ concentrations in the filtrate were determined using an atomic absorption spectrophotometer (AAS, PerkinElmer Analyst 400). All experiments were performed in triplicate to ensure reproducibility, and the average values were reported. The data obtained from the experimental results were analysed using kinetic



Figure 1. Preparation of adsorbent (CSAC) and research flow chart

models, namely the PFO and PSO equations, and isothermal models including Langmuir, Freundlich, and Temkin. Furthermore, thermodynamic parameters (ΔG° , ΔH° , and ΔS°) were determined to assess the feasibility, spontaneity, and energy transformation that occurs during the adsorption process.

Adsorption mechanism and evaluation models

Adsorption is a phenomenon in which solute molecules adhere to the surface of a solid known as the adsorbent, forming one or more layers until dynamic equilibrium between the phases is achieved (Akhtar et al., 2025; Ali et al., 2023). This process is described through isothermal models to predict the maximum capacity of adsorption and understand surface interactions under various operational conditions (Biswal and Balasubramanian, 2022). The Freundlich model describes the adsorption process occurring in stages with several layers on a heterogeneous surface with variations in adsorption energy. Meanwhile, the Temkin model focuses on the attractive forces between the adsorbate particles and the adsorbent surface, assuming that the heat of adsorption decreases with increasing surface coverage (Topare and Wadgaonkar, 2023).

Evaluation of adsorption kinetics typically employs the PFO and PSO models. The PSO model characterises a chemisorption process involving chemical bonding, valence forces, and electron transfer between the adsorbate and the adsorbent surface (Biswal and Balasubramanian, 2023; Islam et al., 2021). In contrast, the PFO model shows that the adsorption rate is linearly dependent on the gap between the equilibrium adsorption capacity and the capacity at a given time, reflecting a mechanism governed by low-energy interactions between the adsorbate and the adsorbent surface during the adsorption process.

The concentration of Cu^{2+} after the adsorption process was analysed using atomic absorption spectrophotometry (AAS), and the resulting data were used to determine the metal removal efficiency (%R) and equilibrium adsorption capacity (q_e), which represents the amount of Cu^{2+} adsorbed per gram of CSAC (Biswal and Balasubramanian, 2022; Rahman et al., 2025)."

$$(\% R) = \frac{(C_0 - C_t)V}{C_0}$$
(1)

$$q = \frac{(C_o - C_e)V}{m} \tag{2}$$

where: q_e represents the adsorption capacity at equilibrium (mg/g), while C_0 and C_t (mg/L) are the initial concentration of Cu^{2+} ions and the concentration at t, respectively. The symbol m denotes the mass of the adsorbent (g), while V refers to the total volume of the solution (L).

RESULTS AND DISCUSSION

Chemical characterisation and elemental analysis of CSAC

In this study, CSAC was activated using HCl solution. Then, the activated carbon was characterised before and after the activation process. The pore structure, morphology, functional groups, and chemical composition were analysed using several instrumental methods, including SEM, SEM-EDX, FTIR, and BET analysis.

SEM analysis

Changes in surface morphology, pore structure, and particle agglomeration in CSAC, which can affect adsorption efficiency, were studied through SEM analysis. In addition, SEM was used to characterise the modification of the pore structure before and after chemical activation and after the adsorption process. Meanwhile, SEM imaging provided detailed information on the surface morphology and composition of conductive and non-conductive materials.

In Figure 2a, the CSAC adsorbent has not been activated; its surface looks irregular, rough,

and covered by organic material that has not been fully degraded. The inhibition of pore structure development may reduce surface area, which is crucial for facilitating ion adsorption on the adsorbent surface (Figure 2b). After chemical activation with HCl solution, it can be seen that the morphology of CSAC has changed drastically, where the surface becomes cleaner and more structured, whereas the pores are more open and even. This activation has been proven effective in removing impurities and expanding the active surface, allowing the diffusion of metal ions into the pores more efficiently. In Figure 2c, after being used for the Cu(II) absorption process, particles accumulate on the surface of CSAC, which is marked by the appearance of bright spots on the SEM image; this indicates the presence of adsorbed metal ions. Some pores appear closed or blocked due to Cu(II) ion deposition, indicating that the adsorption process has effectively occurred. However, the blockage of some pores can cause a decrease in the interaction capacity between ions and the active surface of the adsorbent. This indicates that metal ions are likely to attach to the active sites through electrostatic forces and diffuse into the pore structure (Lach and Okoniewska, 2024).

EDX analysis on Cu(II) adsorption by CSAC

The elemental composition of the CSAC-activated carbon surface was analysed using EDX. The obtained spectrum (Figure 3) revealed significant changes in the elemental composition after the adsorption process, marked by the appearance of characteristic peaks for Cu and variations in the intensity of other elements. These results confirm the occurrence of the Cu²⁺ ion adsorption on the CSAC surface, which interacts with functional groups containing carbon and oxygen elements.



Figure 2. SEM of CSAC (a) before HCl activation, (b) after HCl activation, (c) after Cu²⁺ ion adsorption



Figure 3. EDX images of three conditions: (a) before, (b) after activation with HCl, and (c) after application of Cu(II) adsorption

The elemental composition of the CSAC surface was identified using EDX analysis. Figure 3 (a–c) illustrates the experimental findings and is summarised in Table 1. The data can reveal significant changes in the elemental composition at three stages, namely: (1) before activation, (2) after chemical activation using HCl solution, and (3) after being used in the Cu²⁺ ion absorption process. This change in composition reflects the modification of the surface structure due to chemical activation.

Table 1 summarises all the results of observations of the elemental composition on the surface of coconut stem activated carbon (CSAC) through EDX analysis, as illustrated in Figure 3(a–c). Figure 3a shows that before the activation process, the CSAC surface is dominated by carbon (C) elements of 81.51% and oxygen (O) of 17.24%, accompanied by the presence of other elements in small amounts with minor elemental constituents including zirconium (Zr), as well as alkali, alkaline earth metals, and halogens such as Na, K, Ca, and Cl. These trace elements may influence the surface properties and potentially enhance or hinder the adsorption performance of the material. As shown in Figure 3b, the HCl activation process led to a substantial rise in carbon percentage to 86.26% and a concurrent reduction in oxygen content to 12.67%. This shows the success of the activation process in removing volatile compounds and inorganic impurities, which directly increases the available active sites and structural cleanliness of the adsorbent. The absence of Na and K after activation indicates the efficiency of HCl treatment in eliminating inorganic components that do not significantly contribute to the adsorption mechanism.

In the final stage (Figure 3c), after the CSAC was used to adsorb Cu^{2+} ions, the carbon and oxygen content were relatively stable at 86.05% and 12.51%, respectively, indicating the stability of the post-adsorption surface structure. The element Cu^{2+} was detected at a level of 0.62%, which confirmed the successful adsorption of metal ions by CSAC. A decrease in Ca levels from 0.14% to 0.08% indicates the possibility of ion exchange interactions occurring during the adsorption process. Meanwhile, the relatively constant presence of elements Cl and Zr suggests that they do not actively contribute to the Cu^{2+} adsorption process but persist as part of a surface matrix or active residue that does not react directly.

Element	CSAC before activation (%)	CSAC after activation HCI (%)	CSAC after adsorption Cu ²⁺ (%)
С	81.51	89.78	89.76
0	17.24	10.05	10.01
Na	0.22		
К	0.63		
Ca	0.08	0.04	0.02
CI	0.32	0.06	0.06
Zr	0.09	0.07	0.08
Cu			0.09
Total	100%	100%	100%

Table 1. CSAC composition before and after HCl activation and adsorption of ion Cu²⁺

Characterisation of functional groups in CSAC using FTIR

Fourier transform infrared (FTIR) spectroscopy was utilised to examine the functional groups and chemical compounds present in CSAC, enabling a non-destructive assessment of its surface chemistry and structural composition. This type of spectroscopy operates in the infrared region of the electromagnetic spectrum, which covers 14000 cm⁻¹ to 10^{-1} or a wavelength range of 2.50–50 µm.

Figure 4 illustrates the FTIR spectrum before the activation process, which shows absorption bands at wave numbers 3400 cm⁻¹ (-OH group), 1700 cm⁻¹ (carbonyl group, C=O), and 1600 cm⁻¹ (aromatic bond C=C), and decreases the intensity of the hydroxyl and carbonyl peaks. To reduce volatile compounds and increase carbon purity. There was an increase in absorption of 1100 cm⁻¹; the enhanced absorption peak around 1050 cm⁻¹ suggests a higher presence of C-O functional groups, which may contribute to improved adsorption performance, which is significant for electrostatic interactions and the complexation of metal ions with CSAC. The hydroxyl (C–OH), carbonyl (C=O), and ether (C–O) functional groups significantly contribute to the development of cationic complexes through surface charge interactions (Long et al., 2021). The dominance of C-O groups after the HCl activation process indicates an increase in affinity for Cu(II) coordination through active sites, which can ultimately increase the adsorption efficiency of CSAC. This condition indicates that chemical activation can increase adsorption efficiency, ion exchange capacity, and specific surface area, as well as accessible active sites.

BET surface area analysis of CSAC

The specific surface area was measured using the BET technique of coconut CSAC to provide an overview of the pore morphology and surface properties. From the test results, the surface area of CSAC before activation was recorded at $82.465 \text{ m}^2/\text{g}$. After the activation process with hydrochloric acid (HCl) solution, the surface area increased to 230.096 m²/g. This increase is related to the loss of impurities and a number of volatile compounds during the activation process. This causes the pore structure of CSAC to open. This activation not only expands the pores but also contributes to the formation of new microand meso-pores and volumetric expansion on the active surface. These changes can directly affect the adsorption capacity of the material, as stated by Ioannidou and Zabaniotou (2007).

Influence of key operating parameters on Cu²⁺ adsorption using CSAC

This study analyses the influence of various operational parameters the removal efficiency of Cu²⁺ ions on CSAC. The amount of ions adsorbed on the CSAC surface was expressed as the q_e, mg/g. The parameters studied included the variation of the initial concentration of Cu²⁺ (25–150 mg/L), the effect of solution pH (3–10), the dosage of CSAC adsorbent range (2–3.5 g), and the contact time (0–180 min). The obtained experimental data were collected, compiled for analysis through the application of Equations 1 and 2. The comprehensive evaluation of each parameter and the obtained experimental results are visually illustrated in Figure 5.



Figure 4. FTIR of CSAC spectrum: (a) before HCl activation, (b) after HCl activation



Figure 5. Effect of parameter variations: (a) Cu²⁺ concentration (25, 50, 100, and 150 mg/L), (b) CSAC dose (2, 2.5, 3, and 3.5 g), (c) pH Variation (3–10), (d) contact time (minutes)

Influence of variation in Cu²⁺ concentration on CSAC adsorption performance

As shown in Figure 5a, increasing the initial concentration of Cu^{2+} from 25 to 150 mg/L can cause an increase in qe from 0.828 mg/g to 4.035 mg/g. This is due to the presence of a greater diffusion driving force, which causes faster mass transfer and migration of metal ions to the CSAC surface. From a thermodynamic perspective, a steeper concentration gradient can increase the efficiency of ion transport to active adsorption sites, thereby accelerating the adsorption rate (Gomravi et al., 2021). This result is in line with the observation of Aydin et al. (2008), who concluded that a higher initial concentration of Cu2+ can obtain greater ion adsorption. However, although there was an increase in the adsorption capacity, the removal efficiency (%R) decreased from 99.84% to 80.69%, this was due to the limited number of active sites available on the adsorbent surface. Thus, at higher adsorbate concentrations, the intense competition between Cu²⁺ ions to occupy active sites becomes limited and accelerates its

saturation, ultimately reducing the overall system performance (Nugraha et al., 2025).

Influence of CSAC dosage on adsorption efficiency and capacity

The changes in CSAC from 2 g to 3.5 g, as shown in Figure 5b, result in a decline in equilibrium adsorption capacity (q_e) from 1.00 mg/g to 0.711 mg/g. This is likely due to excess adsorption sites that lead to inadequate capture of Cu²⁺ ions and underutilised adsorption surface utilisation due to not optimal concentration of Cu²⁺ ions. The result is that the capacity of CSAC to absorb mass unity of Cu²⁺ ions is very poor (Phuengprasop et al., 2011). In another aspect, the removal efficiency (%R) of Cu2+ ions also improved, increasing from 82.16% to 99.64%, correlating with the rise in the adsorbent dose, found out that with the increase in the dosage of the Cane Papyrus-based adsorbent, the efficiency of removal of Cu2+ ions was increased to 95% at a concentration of 50 g/L. After all the active sites have been filled, further increasing the dosage will not enhance the adsorption capacity per gram, but will improve the overall removal efficiency. This happens when the metal ions in solution have restrictions on their capacity to interact with the adsorbent (Chakraborty et al., 2022).

Relationship between pH and Cu(II) adsorption performance

Figure 5c shows that the adsorption capacity (q_e) exhibited a substantial rise from 0.275 mg/g at pH 3 to 0.828 mg/g at pH 7, indicating that the adsorption efficiency of Cu²⁺ by CSAC is highly pH-dependent. The highest removal percentage (%R) of 99.4% was achieved in the pH range of 6–7. Under acidic conditions, H⁺ ions compete with Cu²⁺ ions to occupy the reactive sites on the adsorbent surface, thereby causing the protonation of the functional group and decreasing the electrostatic interaction between the metal ions and the negatively charged surface. This collectively decreases the efficiency and adsorption capacity. In contrast, at alkaline pH, the formation of Cu(OH)2 deposits decreases the concentration of free Cu²⁺ ions in the solution, ultimately inhibiting the adsorption process. The optimum conditions are at pH 6, where Cu²⁺ ions are in a stable ionic form and can interact effectively with the functional groups on the surface of the CSAC.

The pH value at the zero charge point of CSAC (pHpzc) is estimated to be between 6.5 and 7.5. Below pHpzc, the prevalence of positive surface charge causes electrostatic repulsion to Cu^{2+} ions. At the same time, at a pH close to pHpzc, the interaction becomes more neutral and favourable to adsorption (Al-Hazeef et al., 2024). Although the surface charge becomes negative at a higher pH, the efficiency still decreases due to the formation of metal precipitates. Optimisation of pH is essential to maximise the adsorption

capacity of Cu²⁺ while avoiding precipitation and ion competition that can reduce system efficiency (Zhang et al., 2021).

Influence of contact time on the adsorption kinetics of Cu²⁺ onto CSAC

Figure 5d shows the kinetics governing the adsorption of Cu2+ ions onto CSAC, where at 10 minutes, the q was recorded at 0.475 mg/g and the removal efficiency (%R) was 57%. This suggests that Cu²⁺ ions are well-held to the active sites on CSAC surfaces. Moreover, after some time, at 60 minutes, adsorption capacity further increased to 0.678 mg/g with a removal efficiency (%R) of 81.4%. This means a considerable fraction of active sites have been filled (Jiang et al., 2022). At 120 minutes, the adsorption rate is nearing a plateau at 0.783 mg/g, with %R 93.92%, which suggests that the system is near equilibrium. At the 180th minute, \boldsymbol{q}_{max} was 0.828 mg/g and %R 99.4%. This behaviour is similar to activated carbon adsorption, where complete equilibration is typically reached within 120 to 180 minutes.

Analysis of isotherms, kinetics, and thermodynamics of Cu(II) adsorption by CSAC

The adsorption of Cu(II) onto CSAC was evaluated using Langmuir and Freundlich isotherms to determine maximum capacity and surface heterogeneity. Kinetic studies applied PFO, PSO, and IPD models to identify rate-controlling mechanisms. Thermodynamic parameters (ΔG° , ΔH° , ΔS°) were calculated via the Van't Hoff equation to assess spontaneity and thermal effects. A negative ΔG° confirmed spontaneous adsorption, while ΔH° and ΔS° indicated endothermic behaviour and entropy changes. Model validation

Model	Linear Equation	Plot (Y vs X)	
Langmuir	1/qe = 1/qmax + 1/(qmax KL Ce)	1/qe vs. 1/Ce	(3)
Freundlich	log qe = log KF + (1/n) log Ce	log qe vs. log Ce	(4)
Temkin	Qe = B In(Ce) + A A= BIn(KT)	qe vs ln (Ce)	(5)
Pseudo-first-order (PFO)	log(qe - qt) = log qe - (K1/2.303) t	log(qe - qt) vs. t	(6)
Pseudo-second-order (PSO)	t/qt = 1/(K2 qe²) + t/qe	t/qt vs t	(7)
Intra-particle diffusion (IPD)	qt = ki t ^{0.5} + C	qt vs. t^0.5	(8)
Gibbs free energy	ΔG° = -RT ln Kd	Direct calculation	(9)
Van't Hoff	$\ln Kd = (\Lambda S^{\circ}/R) - (\Lambda H^{\circ}/RT)$	In Kd vs 1/T	(10)

Table 2. Linear equations, plot parameters, and equation numbers used in this study

was based on R², slope, and intercept values from linear regression, as summarised in Table 2.

Isothermal adsorption

Experimental data for initial Cu(II) concentration variations (25–150 mg/L) with a CSAC time of 3 g, volume of 100 mL, are presented in Table 4, which includes values C₀, C_e, q_e, log C_e, log q_e, 1/ C_e, $1/q_e$, and ln C_e. Calculation of linear regression and variable transformations on all three isothermal models (Langmuir, Freundlich, and Temkin). The regression parameters obtained are then used to calculate the model constants and validate the fit of each model. The experimental data in Table 3 were then analysed and plotted according to Equations 3, 4, and 5, as illustrated in Figure 6.

The normality test of the logarithmic transform results (ln C_e and log q_e) was carried out using the Shapiro-Wilk method, which yielded a p

value of 0.764. This value indicates that the data is normally distributed, so using linear regression is considered valid, even though the number of data points is relatively small (n = 4). The coefficient of determination (R²) is calculated based on the proportion of total variation that can be explained by the regression model compared to the total variation of the data, using the equation R² = $1 - \Sigma(yi - \hat{y}i)^2 / \Sigma(yi - \bar{y})^2$.

In Figure 6, Linear regression analysis produces the Langmuir model equation y = 1.5219x+ 0.3037 (R² = 0.966), Freundlich model y =0.4948x - 0.2032 (R² = 0.9993), and Temkin model y = 1.0281x - 0.0538 (R² = 0.9454). On the basis of the Langmuir model parameters, the maximum adsorption capacity (q_{max}) was obtained at 3.29 mg/g, while the Langmuir constant (K_L) was 5.01 L/mg. Meanwhile, for the Freundlich model, the adsorption capacity constant (K_F) was 0.626, and the intensity factor (n) was



Figure 6. Absorption isothermal model: (a) Langmuir, (b) Freundlich and (c) Temkin

Table 3. Experimental data for Cu(II) adsorption isotherm model on CSAC

Co (mg/L)	Ce (mg/L)	qe (mg/g)	log Ce	log qe	1/Ce	1/qe	In Ce
25	1.52	0.782	0.181844	-0.10679	0.657895	1.278772	0.41871
50	4.89	1.471	0.689309	0.167613	0.204499	0.67981	1.587192
100	19.27	2.691	1.284882	0.429914	0.051894	0.371609	2.958549
150	31.05	3.778	1.492062	0.577262	0.032206	0.26469	3.435599

2.00, indicating favourable adsorption conditions. For, the Temkin model parameters yield a constant (A) of 0.949 L/g with an adsorption heat constant (B) of 1.028 J/mol.

These findings indicate that the three isotherm models correlate well with the experimental data. However, the Freundlich model shows the highest determination coefficient ($R^2 = 0.9993$), followed by the Langmuir ($R^2 = 0.966$) and Temkin ($R^2 = 0.9454$) models. This indicates that multilayer adsorption occurs on heterogeneous surfaces, as captured by the Freundlich model, while the relatively high R^2 of the Langmuir model also indicates that monolayer adsorption occurs on homogeneous active sites. These findings are consistent with those reported by Zhang et al. (2021).

Furthermore, the dimensionless separation factor (R_L) can be calculated using Equation 11 to determine whether it is in accordance with the adsorption process.

$$R_{L} = \frac{1}{1 + K_{L} \times C_{o}} \tag{11}$$

The separation factor (R_{τ}) values for initial Cu²⁺ concentrations of 25 mg/L and 250 mg/L were obtained as 0.0079 and 0.0008, respectively. Since all R_{I} values are in the range of $0 < R_{I}$ < 1, the adsorption process of Cu²⁺ onto CSAC is categorised as very good, consistent with the observations reported by Jiang et al. (2022). In addition, the adsorption behaviour is associated with the character of the heterogeneous surface, this allows for the progressive development of multilayer adsorption with energy variations influenced by the specific nature of the adsorption site (Chen et al., 2022). These findings further confirm that the adsorption of Cu²⁺ onto CSAC mimics the Freundlich isotherm model, by characterising adsorption on a non-uniform surface

and supporting the formation of multilayers (Foo and Hameed, 2010).

Kinetics study of Cu(II) adsorption kinetics at CSAC

The adsorption experiments used varying initial Cu²⁺ concentrations of 25, 50, 100, and 150 mg/L, with a fixed CSAC dosage of 3 g. Contact time ranged from 0 to 120 minutes. The data obtained from the observations are summarised and displayed in Table 4.

Experimental data were analysed using PFO by plotting $log(q_e - q_t)$ versus contact time. In addition, PSO was evaluated by plotting t/q_t versus time, using Equations 6 and 7, respectively. The kinetic analysis results are illustrated in Figure 7.

The adsorption kinetics of Cu(II) on CSAC was evaluated using the PFO and PSO models to identify the most appropriate model based on key kinetic parameters, including the equilibrium adsorption capacity (q_e), k_1 constant, and k_2 constant.

The transformed $\ln(q_e - q_t)$ data normality test was performed before regression analysis using the Shapiro–Wilk procedure. The testing produced a p-value exceeding 0.05, indicating that the data were normally distributed and met the assumptions to be applied to linear regression, although the amount of data was limited (n = 7). The determination index (R²) was calculated by relating the explained variation to the overall variation, based on the formula R² = $1 - \Sigma(y_i - \hat{y}_i)^2$ / $\Sigma(y_i - \bar{y})^2$. The computational process was conducted using Microsoft Excel and Python.

The PFO model yields the regression equation $\ln(q_e - q_t) = -0.0247t + 1.095$, characterised by an R² value of 0.9944. The findings suggest that the model successfully explains nearly all of the variability observed in the experimental data. From the exponential value of the intercept, the

Times (minutes)	Co (mg/L)	Ce (mg/L)	q _e	q _e -q _t (mg/g)	t/q _t	In(q _e -q _t)
0	100	0	0	2.857	0	1.049772
10	100	21.21	0.707	2.150	4.651	0.765468
30	100	43.16	1.43867	1.418	21.151	0.349482
60	100	63.02	2.100667	0.756	79.330	-0.27927
90	100	74.81	2.493667	0.363	247.71	-0.61243
120	100	80.73	2.493667	0.166	722.89	-1.7957
150	100	83.84	2.794667	0.062	2406.4	-2.7753
180	100	85.71	2.857	-	-	-

Table 4. Cu(II) adsorption kinetics data on CSAC for pseudo-first-order and pseudo-second-order models



Figure 7. Adsorption kinetic model: (a) PFO kinetics, (b) PSO kinetics

equilibrium adsorption capacity (q_e) was obtained as 2.988 mg/g. Meanwhile, the constant value of the adsorption rate k_1 is determined from the slope of the regression line of 0.0247 min⁻¹.

In contrast, the regression results from the PSO model yield the equation $t/q_t = 12.731t - 339.16$, characterised by an R² value of 0.6753. The estimated q_e value of the cut-off point yields a negative number (-0.00295 mg/g), which is physically meaningless and makes the k₂ constant invalidly calculated. In addition, the low value of the determination coefficient indicates that this model cannot accurately represent the kinetic mechanism of the adsorption system being tested.

Thermodynamic study of Cu²⁺ adsorption on CSAC

Thermodynamic analysis is needed to determine and assess the spontaneity and energetic properties of Cu(II) adsorption on CSAC by observing the changes in the equilibrium constant (K = q_e/C_e) at various temperatures. Complete transformed and raw experimental data are summarised in Table 5, including temperature (K), reciprocal temperature (1/T), initial and equilibrium concentrations (C₀ and C_e), equilibrium adsorption capacity (q_e), calculated equilibrium constants (K and ln(K)), and Cu(II) removal efficiency (%R). These parameters provide the basis for determining the thermodynamic properties.

The linear plot of ln K against 1/T serves as the basis for determining the thermodynamic parameters ΔH° and ΔS° , which are derived from the slope and intercept of the fitted line according to Equations 9 and 10. The corresponding results in Table 5 were then plotted to obtain the kinetic evaluation, as illustrated in Figure 8.

Linear regression between ln(K) and 1/T was applied to assess the thermodynamic characteristics associated with Cu(II) uptake onto CSAC, as illustrated in Figure 8. The regression yielded a strong linear relationship with the equation ln(K) = -2669.7(1/T) + 8.5483 and a determination coefficient value of R² of 0.974, indicating that the model can explain almost all variations of the experimental data. Shapiro– Wilk normality test of ln(K) data yielded p = 0.764 (p > 0.05), which confirmed that regression could be applied statistically despite the limited sample count (n = 4).

The thermodynamic parameters ΔH° and ΔS° were obtained from the slope and intercept of the regression line, yielding values of 22.19 kJ/mol and 0.0711 kJ/mol K, respectively. The calculated ΔG° value, with the equation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, was negative at all evaluated temperature ranges, ranging from -1.56 kJ/mol at 298 K to

Table 5. Experimental data for calculation of Cu(II) adsorption thermodynamic parameters in CSAC

Temperature (K)	1/T	CO (mg/L)	Ce	q _e	K=q _e /C _e	Ln(K)	%R
298	0.003356	25	1.15	0.795	0.691304	-0.36918	95.4
308	0.003247	25	0.98	0.800667	0.817007	-0.20211	96.08
318	0.003145	25	0.67	0.811	1.210448	0.19099	97.32
328	0.003049	25	0.54	0.815333	1.509877	0.412028	97.84



Figure 8. Linear relationship between ln K and 1/T based on the van't Hoff equation for Cu(II) adsorption onto CSAC

-3.44 kJ/mol at 328 K. This condition indicates that the adsorption process is spontaneous. Furthermore, the decrease in ΔG° with increasing temperature and the positive ΔH° value reflect its endothermic nature.

Intra-particle diffusion rate

Table 6 offers a comprehensive summary of the measured data employed in evaluating diffusion within particles, including the time square root (\sqrt{t}), equilibrium concentration (C_e), and adsorption capacity (q_t) at the three initial concentrations of Cu(II), namely 25, 50, and 100 mg/L. These values form the basis for the regression analysis and parameter estimation shown in Table 6.

Intraparticle diffusion refers to the mass transport process of species loaded into the solid phase. It is often adopted to examine the transport process of Cu²⁺ ions into the adsorbent matrix. This study was conducted at three concentrations of Cu²⁺, namely 25, 50, and 100 mg/L,

to determine how changes in concentration affect diffusion kinetics. The results were assessed by plotting q_e versus t according to Equation 8, with the corresponding data shown in Table 2. The evaluation results of the IPD model are depicted in Figure 9.

When the concentration was set at 50 mg/L, the linear regression analysis produced an R² value of 0.9910, indicating excellent linearity conformity. The value of R² is calculated based on the smallest squared approach using the formula R² = 1 – $\Sigma(y_i - \hat{y}_i)^2 / \Sigma(y_i - \bar{y})^2$. Normality tests based on the Shapiro-Wilk approach were performed on the qt datasets before regression analysis. The obtained p-values were 0.7157 for 50 mg/L and 0.2671 for 100 mg/L initial concentrations, indicating that normally distributed data and linear regression can be validly applied. In contrast, at a concentration of 25 mg/L, the normality test yielded p = 0.0295, which indicates data abnormalities and limits the application of linear regression statistically.

 Table 6. Experimental data for analysis of intra-particle diffusion models on initial concentration variations of Cu(II)

√t	C _e (25 mg/L)	C _e (50 mg/L)	C _e (100 mg/L)	q _t (25 mg/L)	q _t (50 mg/L)	q _t (100 mg/L)
3.162	13.75	39.33	83.53	3.75	3.557	5.49
5.477	10	30.94	59.77	5	6.353	13.41
7.746	5	24.34	38.27	6.667	8.553	20.58
9.487	2.5	21.14	32.68	7.5	9.620	22.44
10.954	1	12.06	20.66	8	12.647	26.45
12.247	0.75	9.85	13.96	8.08	13.383	28.68
13.416	0.5	6.32	10.37	8.167	14.56	29.88
14.491	0.25	2.89	6.7	8.25	15.703	31.1



Figure 9. Representation of the intraparticle diffusion model

Intra-particle diffusion analysis was conducted to investigate the mass transport mechanism during the adsorption of Cu²⁺ onto CSAC. Linear regression between the transient adsorption capacity (qt) and the square root of time (\sqrt{t}) revealed the intra-particle diffusion constant (ki), which exhibited an increasing trend with rising initial Cu²⁺ concentrations. At 25 mg/L, the ki value was 0.0041 mg/g· \sqrt{t} , with the corresponding regression equation y = 0.0041x +0.030. With the rise in initial concentration to 50 mg/L and 100 mg/L, ki values rose to 0.0107 and 0.0222 mg/g· \sqrt{t} , respectively, following the regression equations y = 0.0107x + 0.0024 and y = 0.0222x + 0.0089. This pattern suggests that higher metal concentrations enhance the mass transfer driving force, promoting faster migration of Cu²⁺ ions into the porous matrix of CSAC. Additionally, the greater number of available Cu²⁺ ions increases the probability of collisions with active surface sites, further accelerating the diffusion process.

In addition, the non-zero interception value (C) at the entire concentration, especially at 25 mg/L (C = 0.030 mg/g), indicates that adsorption kinetics are not solely governed by intraparticle diffusion. The considerable C value indicates the influence regarding the influence of boundary layer resistance on the overall mass transfer mechanism. This shows that at low concentrations, the diffusion resistance of the film is more dominant in determining the adsorption rate of Cu²⁺ ions (Topare and Wadgaonkar, 2023).

Comparison of CSAC with agricultural wastebased activated carbon

An evaluation was performed to compare the adsorption performance of CSAC with that of other activated carbons derived from agricultural residues for Cu(II) ion removal from water (Table 7). This comparison aims to highlight the adsorption capacity, removal efficiency, and sustainability potential of CSAC as an environmentally friendly adsorbent in heavy metal remediation.

Absorbent	BET (m²/g)	q _{max} (mg/g) To Cu(II)	q _e (mg/gram)	Dominant isotherm model	Dominant kinetic model	R²	References
CSAC (coconut stem activated carbon)	230.096	3.29	4.035	Freundlich	Pseudo-first order	0.999	This study
Biochar cecum crossing	172.6	2.57	3.12	Freundlich	Pseudo-second order	0.9	49
Activated carbon sawdust	250.4	4.05	4.50	Langmuir	Pseudo-first order	0.992	34
Banana peel biochar	198.7	2.95	3.35	Freundlich	Pseudo-second order	0.981	33
Bagasse biochar	210.3	3.12	3.75	Langmuir	Pseudo-first order	0.98	50

Table 7. Comparison of various adsorbents by main parameters

The sawdust-derived activated carbon achieved the highest Cu ion adsorption efficiency, characterised by a specific surface area of 250.4 m^2/g and a q_{max} of 4.05 mg/g. CSAC shows comparable efficiency, with a substantial surface area of 230.096 m^2/g with a q_e_max value of 3.29 mg/g. In contrast, the adsorbent of rice husk biochar (cecum crossing biochar) had the lowest adsorption capacity of 2.57 mg/g. These findings confirm the important role of high surface area and well-developed pore structure in facilitating the effective absorption of Cu(II) ions.

From a mechanistic point of view, the CSAC shows excellent adsorption behaviour, according to the first-order pseudo-kinetic model with a very high R² value, i.e., 0.999, which suggests that the rate-limiting step is mainly regulated by physical adsorption combined with chemical interactions at the active site. While most adsorbents are also compatible with the Freundlich isothermal model, this implies multilayer adsorption on heterogeneous surfaces, CSAC that retain competitive adsorption characteristics and support a combination of monolayer adsorption mechanisms and surface location-specific.

The combination of large surface area, highly favourable kinetic behaviour, and fairly high adsorption capacity positions CSAC as a highly effective and sustainable adsorbent material. This makes it worth considering for industrial applications in heavy metal remediation, especially in the wastewater treatment systems that require rapid and efficient removal of Cu(II).

CONCLUSIONS

The findings of this study demonstrated that HCl-activated CSAC is a highly effective adsorbent for Cu²⁺ removal from aqueous solutions. The specific surface area increased from 82.465 m^2/g to 230.096 m^2/g as a result of chemical activation. Significantly improving adsorption performance. SEM-EDX characterisation revealed morphological changes with increased pore development, while FTIR analysis identified the functional groups responsible for Cu²⁺ binding. The kinetics of Cu(II) adsorption by CSAC included a PFO model ($R^2 = 0.9782$), characterised by the dominance of physisorption, while the Freundlich isotherm ($R^2 = 0.9993$) described multilayer adsorption on heterogeneous surfaces, with a maximum capacity (q_{max}) of 3.29 mg/g.

Thermodynamic analysis confirmed that the process was spontaneous ($\Delta G^{\circ} < 0$) and endothermic ($\Delta H^{\circ} = 22.19$ kJ/mol), with higher temperatures increasing the adsorption efficiency. Increasing the initial concentration of Cu²⁺ increased the adsorption capacity to 4.035 mg/g, and the optimal adsorbent dosage of 3 g/L achieved a maximum removal efficiency of 99.64%. The most favourable conditions were observed at pH 6–7, with equilibrium reached within 180 min and a Cu²⁺ adsorption rate of 99.4%. Overall, CSAC demonstrates high efficiency, economic feasibility, and sustainability for industrial wastewater treatment targeting heavy metal removal.

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