Suistainable removal of divalent copper ions from aqueous solution using fly ash and rice husk (*Oryza sativa* L.) biochar-based geopolymer

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ABSTRACT

Contamination of water by heavy metals, especially Cu(II), presents considerable environmental and health hazards owing to their toxicity and endurance. This research examines the eco-friendly extraction of divalent copper ions from water using a biochar-based geopolymer produced from rice husks and fly ash. Rice husks were converted into biochar via pyrolysis at 300 °C for 1 hours, while fly ash served as the precursor for geopolymerization using 12 M NaOH as an alkaline activator. Biochar was partially substituted into the geopolymer matrix at ratios of 50–90% to produce adsorbents labeled BCG50–BCG90. The structural, functional, morphological, and textural properties of the materials were assessed using FTIR, SEM-EDS, BET, and atomic absorption spectroscopy. The effects of pH (4–9), contact time (10–60 min), and initial Cu(II) concentration (10–1000 mg/L) were investigated through adsorption experiments. The results indicated that BCG80 possessed the most favorable characteristics, including a high surface area (744.30 m²/g), sufficient hydroxyl groups, and robust silicate structures. The equilibrium was achieved within 10 minutes at pH 6, where the maximal adsorption efficiency was observed. The Langmuir model was followed by Cu(II) adsorption, as indicated by isotherm analysis, with a maximum adsorption capacity (q_max) of 68.97 mg/g (R^2 = 0.9647). This confirms monolayer adsorption on a comparatively homogeneous surface. The results indicate that the incorporation of rice husk biochar into a fly ash-based geopolymer matrix results in an environmentally benign, sustainable, and effective adsorbent for the removal of copper ions from contaminated water.

Keywords: biochar, geopolymer, fly ash, rice husk, copper adsorption, sustainable water treatment.

INTRODUCTION

Water pollution by heavy metals has become an increasingly alarming environmental issue across many countries (Laoye et al., 2025; Mitra et al., 2024). Industrial activities, mining, and domestic and agricultural waste disposal are the main factors contributing to increased heavy metal levels in water sources. (Afzal et al., 2024; Mishra and De, 2024). Heavy metals like copper Cu(II) are recognized as hazardous substances that pose serious risks to both human well-being and aquatic environments (Almashhadany et al., 2024; Laoye et al., 2025; Tandel et al., 2024). Because they are non-biodegradable and tend to bioaccumulate in organisms, these contaminants

remain among the most challenging pollutants to manage (Bargah, 2024). Prolonged exposure through drinking water contaminated with heavy metals can lead to a wide range of health disorders, including neurological damage, kidney dysfunction, growth impairments in children, and even cancer-related outcomes (Khatoon et al., 2024; Adeeko et al., 2024; Tiwari et al., 2024). Copper was selected as the focus of this study because it is one of the most prevalent heavy metals in industrial effluents, particularly from mining, electroplating, and textile industries (Liu et al., 2023). While copper is an essential micronutrient at trace levels, excess concentrations are highly toxic, causing liver and kidney damage, neurological disorders, and ecological risks due to bioaccumulation in aquatic organisms (Ali et al., 2023). Furthermore, Cu(II) is listed as a priority pollutant by the United States Environmental Protection Agency (EPA), making it a relevant representative contaminant for adsorption studies. Therefore, effective and environmentally friendly water management methods are needed to reduce heavy metal concentrations safely. This research aims to develop new adsorbent materials that can sustainably improve the efficiency of contaminated water management.

Various techniques have been developed to manage contaminated water, including chemical precipitation (Wahba et al., 2024), ion exchange (Al Amri and Sivamani, 2024), electrochemistry (Manikandan et al., 2024), membrane filtration (Pawar, 2024), then adsorption (Taher and Rianjanu, 2024). The adsorption method is one of the most promising because it has high efficiency, lower operating costs, and does not produce secondary waste (Ani et al., 2024; Jamilah et al., 2024; Nayak et al., 2024). Adsorption using porous materials such as activated carbon and zeolite has been widely used, but limitations in terms of production costs and adsorbent regeneration have led to increased research into alternative materials (Choma et al., 2024).

Recent research shows that biochar and geopolymers are materials that are attracting attention in the field of adsorption (Sun and Wang, 2024). Rice husks, a widely available agricultural waste product, can be converted into biochar through a pyrolysis process (Aryal et al., 2024; Faizul Che Pa et al., 2024), produces porous carbon material with a high surface area and active functional groups that enable interaction with heavy metal ions (Sandberg et al., 2023). Fly ash, a waste product from coal combustion (Baláž, 2021), can be used as a base material for geopolymers produced through alkali activation (Yadav et al., 2024). Fly ash-based geopolymers have a porous structure with high chemical stability (Wen et al., 2025), making it a potential material for heavy metal adsorption applications (Angelova et al., 2025). The use of rice husk biochar and fly ash as raw materials not only helps reduce waste but also creates sustainable solutions for managing polluted water.

The effectiveness of biochar and geopolymers as heavy metal adsorbents has been extensively studied, both separately and in combination with other materials. Amen et al (2020) studying biochar derived from rice husks, wheat straw, and corn cobs for the adsorption of Pb(II) and Cr^{6+}, with removal efficiencies of 96.41% and 94.73%, respectively. Wiśniewska et al. (2022) testing biochar derived from mugwort plants and comparing it with activated carbon for the removal of organic pollutants in water. Although this study shows promising results, biochar still has limitations, such as low mechanical strength, unstable pore structure in extreme pH environments, and adsorption efficiency that can decrease due to ion competition in contaminated water.

Geopolymers have emerged as promising materials for addressing water contamination issues. Peres et al. (2022) demonstrated that geopolymers synthesized from fly ash and bottom ash possess strong adsorption capacities for metal ions including Ag$^+$, Co^{2+}, Cu(II), and Pb(II). Similarly, López et al. (2014) reported that metakaolin-derived geopolymers effectively capture Pb(II) and Cs$^+$ through a mechanism not governed by electrostatic interactions. Geopolymer materials have major limitations, namely a smaller surface area compared to activated carbon or biochar, as well as adsorption efficiency that can still be improved. Yan et al (2023) attempting to improve the performance of geopolymers by combining them with graphene, which increases the surface area to 68.85 m²/g. Research specifically combining fly ash geopolymers with rice husk biochar as adsorbent materials is still very limited. There have been few studies that test the effectiveness of this combined adsorbent against Cu(II) ions. The approach in this study combines the advantages of biochar (high surface area) with the chemical stability of geopolymers, with the hope of increasing adsorption efficiency and material durability. This combination will be developed in powder form to

facilitate application as an adsorbent, making it more efficient and environmentally friendly.

Based on the aforementioned points, the main focus of this research is to develop a biochar-based geopolymer adsorbent for reducing Cu(II) ions. This research includes the production of biochar from rice husks and the integration of fly ash and biochar rice husk into a high-pore-structure composite material. The evaluation of adsorption effectiveness was carried out in contaminated water media.

EXPERIMENTAL

Material and methods

For this research, the materials employed were included fly ash obtained from PT. Bosowa Beton Indonesia, South Sulawesi, and rice husks collected from Bone Regency, Indonesia. The rice husks were converted into biochar by pyrolysis at 300 °C for 1 hours, followed by grinding. Both fly ash and biochar were sieved through a 100-mesh standard sieve. Sodium hydroxide (NaOH, 12 M) was used as an alkaline activator for geopolymer synthesis, and demineralised water was used in preparing the geopolymer paste. For the adsorption experiments, copper(II) nitrate pentahydrate ($Cu(NO_3)_2 \cdot 5H_2O$), sodium hydroxide (NaOH, 0.1 M) and hydrochloric acid (HCl, 0.1 M) were employed.

Preparation of geopolymer-modified biochar composite

Biochar-based geopolymer adsorbents were prepared by partially substituting fly ash with biochar at ratios of 50%, 60%, 70%, 80%, and 90% to promote geopolymerization and enhance adsorption properties. The alkaline activator solution (12 M NaOH) was incorporated into the precursor powders at a liquid-to-solid ratio of 1.0, and the resultant paste was permitted to rest for 30 minutes prior to moulding. Samples were mechanically compacted for one minute, oven-dried at 60 °C for 24 hours, then cured at ambient temperature (±27 °C) for four days. To terminate the geopolymerization reaction, the biochar-based geopolymers – designated BCG50, BCG60, BCG70, BCG80, and BCG90 – were crushed, washed to neutral pH, and subjected to a final oven-drying process for 6 hours.

Characterization of geopolymer-modified biochar composite

The biochar-based geopolymer was examined using several characterization techniques. FTIR identified the surface functional groups, while SEM (HITACHI FLEXSEM 1000) revealed morphological features, complemented by EDS for elemental analysis. The specific surface area, closely related to adsorption efficiency, was determined through BET measurements. Residual metal concentrations were quantified with a ZA3000 Atomic Absorption Spectrophotometer, and adsorption experiments were conducted under continuous agitation using a Barnstead MaxQ 2000 digital shaker.

Adsorption experiments

A batch of 20 mg adsorbent was introduced into 50 mL Cu(II) solutions with pH values between 4 and 9 and maintained for 60 minutes. For adsorption isotherm evaluation, 200 mg of adsorbent was contacted with 50 mL of Cu(II) solutions at varying initial concentrations (10, 30, 70, 120, 200, 400, 800, and 1000 mg/L) under the optimum pH condition. The suspensions were agitated at 150 rpm for 10 minutes before being filtered, after which the residual Cu(II) concentration was quantified using Flame Atomic Absorption Spectroscopy (Flame-AAS). In the contact time study, adsorption was monitored at time intervals of 10, 20, 30, 40, 50, and 60 minutes. Each mixture was shaken at 150 rpm for the designated period, filtered, and analyzed for Cu(II) concentration via Flame-AAS.

The adsorption capacity was calculated using the following equation:

$$ q_e = \frac{(C_o - C_e)}{W} \times V \qquad (1) $$

where: q_e denotes the adsorption capacity expressed in mg/g, while C_o and C_e correspond to the initial and equilibrium concentrations of Cu(II) in the solution (mg/L). The variable m refers to the adsorbent mass (g), and V represents the solution volume (L) (Foo and Hameed, 2010; Ho and McKay, 1999).

The Langmuir adsorption isotherm was ascertained by graphing C_e/q_e versus C_e, whereas the Freundlich isotherm was assessed by plotting log

qe against log C_e. The isotherm model exhibiting the highest linear regression coefficient (R^2) was identified as the optimal model to characterize the adsorption behavior (Kumar et al., 2019).

The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \quad (2)$$

The following equation describes the Freundlich model:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where: C_e represents the equilibrium concentration of the adsorbate in the solution (mg/L), $qmax$ signifies the maximum adsorption capacity (mg/g), b denotes the Langmuir constant, Kf is the Freundlich constant, n expresses the adsorption intensity, and q_e refers to the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).

RESULTS AND DISCUSSION

Characterization of adsorbent

Brunauer-Emmett-Teller (BET)

The findings in Table 1 indicate a significant enhancement in surface area with increased biochar input. The surface area rose from 213.948 m²/g in BCG50 to 744.296 m²/g in BCG80. This notable improvement suggests that augmenting the biochar ratio fosters the formation of a more porous structure, hence enhancing the material's adsorption capacity. A notable decrease in surface area was recorded in BCG90 (690.723 m²/g), indicating that high biochar content may lead to partial pore obstruction or structural compaction. BCG80 demonstrates the most advantageous surface area, indicating enhanced capacity for adsorption and pollutant removal applications.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of BCG50–BCG90 showed dominant Si–O–Si/Si–O–Al vibrations in the 450–1100 cm⁻¹ region (Smith, 2024), indicating aluminosilicate structures important for heavy metal binding. The asymmetric Si–O stretching peaks were observed at 1012.66 cm⁻¹ for BCG50

Table 1. Main results of BET analysis

Sample	Surface area (m²/g)
BCG50	213.948
BCG60	619.3870
BCG70	633.752
BCG80	744.296
BCG90	690.723

and 1006.88 cm⁻¹ for BCG80, representing a high degree of geopolymerization. The O–H stretching peaks (3400 cm⁻¹) (Dai et al., 2023) appeared at 3421.83 cm⁻¹ (BCG50), 3433.41 cm⁻¹ (BCG60), 3419.90 cm⁻¹ (BCG70), 3196.15 cm⁻¹ (BCG80), and 3419.90 cm⁻¹ (BCG90), with BCG70 showing the highest intensity. BCG80 also exhibited a distinct CO_2 adsorption peak at 2355 cm⁻¹, indicating the presence of accessible micropores (Kishibayev et al., 2021). Overall, BCG80 demonstrated the most balanced characteristics – strong silicate structure, sufficient hydroxyl groups, and high porosity – making it the optimal formulation for heavy metal adsorption among all tested samples.

Scanning electron microscopy (SEM)

The SEM micrograph, as shown in Figure 2, reveals that the biochar exhibits an irregular and porous surface morphology with visible cavities and channels, indicating potential adsorption sites formed during the pyrolysis process. These pores contribute to the high surface heterogeneity and enhance the capacity of biochar to interact with heavy metal ions in aqueous solutions. In contrast, the biochar-based geopolymer (BCG) composite shows a denser and more compact structure with partially filled pores, suggesting that the geopolymer matrix successfully coated and integrated with the biochar surface. This morphological modification indicates the formation of a stable composite material, which may enhance structural integrity while still maintaining sufficient porosity for adsorption. The comparison between biochar and the composite demonstrates that incorporating geopolymer alters the surface texture and pore distribution, playing an important role in the adsorption behaviour of the material.

EDS analysis

As shown in Table 2, the elemental composition of rice husk biochar is dominated by carbon (49.96% mass; 60.08% atom), followed by
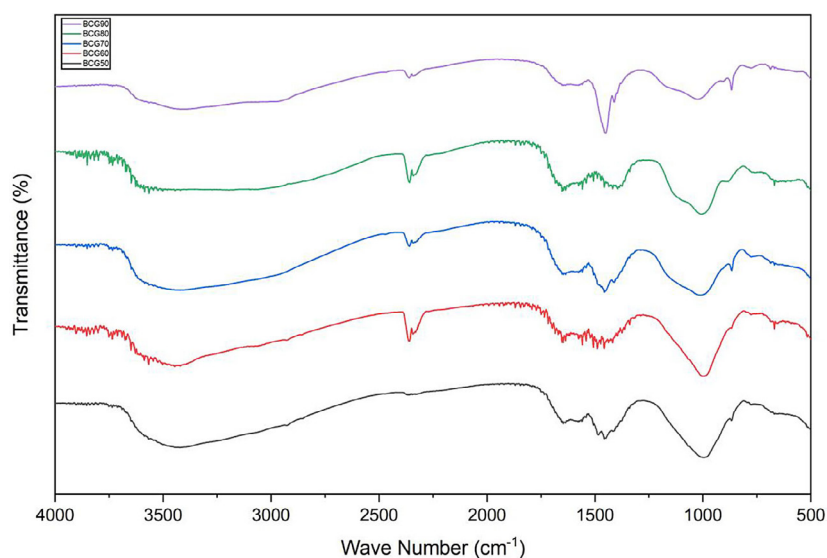
Figure 1. FTIR spectra of (a) BCG50, (b) BCG60, (c) BCG70, (d) BCG80 and (e) BCG90
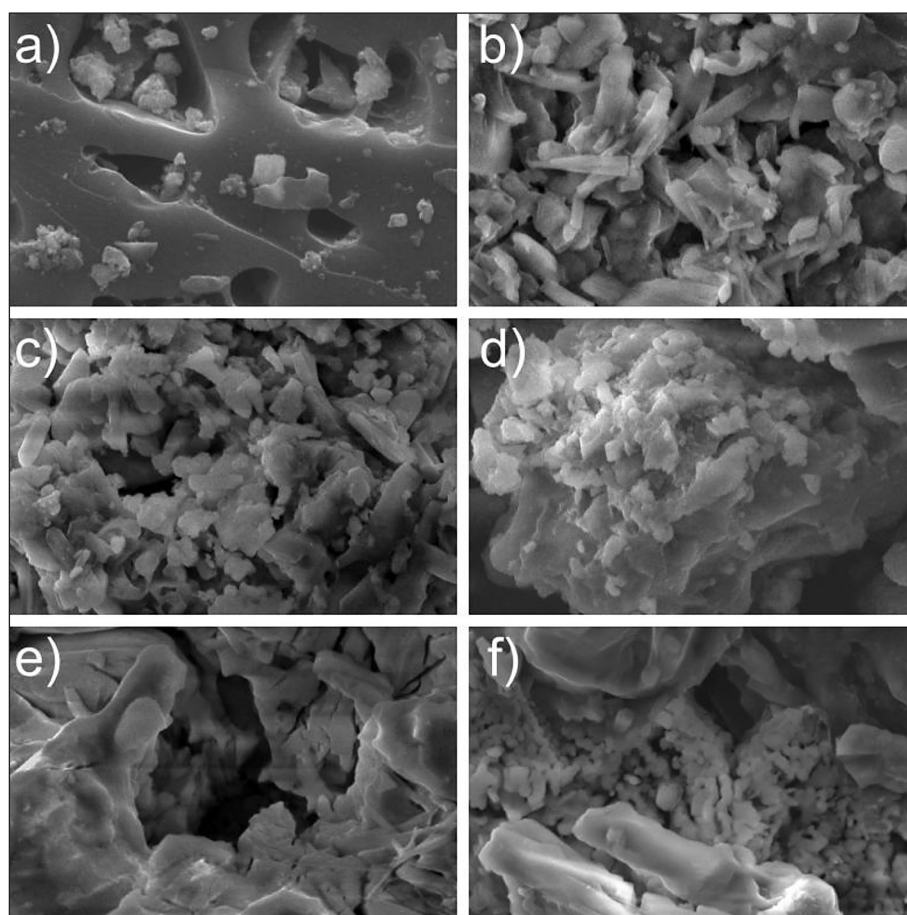

Figure 2. SEM analysis of (a) rice husk biochar (b) BCG50 (c) BCG60 (d) BCG70 (e) BCG80 and (f) BCG90

oxygen (34.02% mass; 30.71% atom) and silica (11.19% mass; 5.76% atom), while aluminium is only present in trace amounts. In contrast, the biochar-geopolymer composite (GBC80) exhibits a significant decrease in carbon (12.78% mass; 19.57% atom) and an increase in oxygen (44.22% mass; 50.83% atom) and aluminium (1.81% mass; 1.23% atom), with silica remaining relatively comparable (9.80% mass; 6.42% atom). These modifications confirm that biochar has

Table 2. EDS result of rice husk biiochar and biochar-based geopolymer

Adsorbent	Element % mass				Element % atom			
	C	O	Al	Si	C	O	Al	Si
Rice husk biochar	49.96	34.02	0.33	11.19	60.08	30.71	0.18	5.76
Biochar-based geopolymer (BCG80)	12.78	44.22	1.81	9.80	19.57	50.83	1.23	6.42

been effectively embedded within the geopolymer framework, as evidenced by the predominance of Si–O–Si and Al–O–Si linkages, which reflect the composite's hybrid structural nature.

Effect of pH

The pH level is pivotal in biosorption, as it directly affects sorption capacity, metal ion speciation, and interactions at the solid–solution interface (Han et al., 2025). This study examined the effect of pH in the range of 4.0–9.0 on Cu(II) adsorption, as illustrated in Figure 3. At acidic conditions (pH < 5), the removal efficiency decreased due to the competition of H^+ ions for active sites and the protonation of functional groups, which reduces the affinity toward metal ions (Kumar and Chang, 2024). The highest adsorption performance was achieved at pH 6, aligning with findings from earlier research (Dada et al., 2024; Muhamad Amin et al., 2024). Under this condition, the lower abundance of H^+ ions enhances electrostatic attraction between Cu(II) ions and the available binding sites (Eduah et al., 2023). Consequently, pH 6 was chosen as the optimum parameter for the following adsorption trials.

Effect of time

The influence of contact duration on the adsorption of metal ions utilizing the biochar-based geopolymer adsorbent was investigated over 10 to 60 minutes, as shown in Figure 4. The removal efficiency fluctuated slightly with increasing contact time, ranging from 75.49% to 76.91%. Specifically, the adsorption efficiency reached 76.91% at 10 minutes, decreased to 75.49% at 20 minutes, and then varied around 76% for the remaining time intervals, with 75.98% observed at 60 minutes. The findings reveal that adsorption equilibrium was reached quickly, within just 10 minutes, and prolonging the contact time further produced no substantial improvement in removal efficiency. This behaviour suggests that the adsorption sites on the biochar-based geopolymer were quickly occupied, and the system reached a near-steady state, consistent with previously reported studies on fast-adsorbing adsorbents (Khan et al., 2025; Kucmanová et al., 2024).

Adsorption isoterm studies

The initial concentration of Cu(II) ions is a key factor influencing adsorption, as it generates
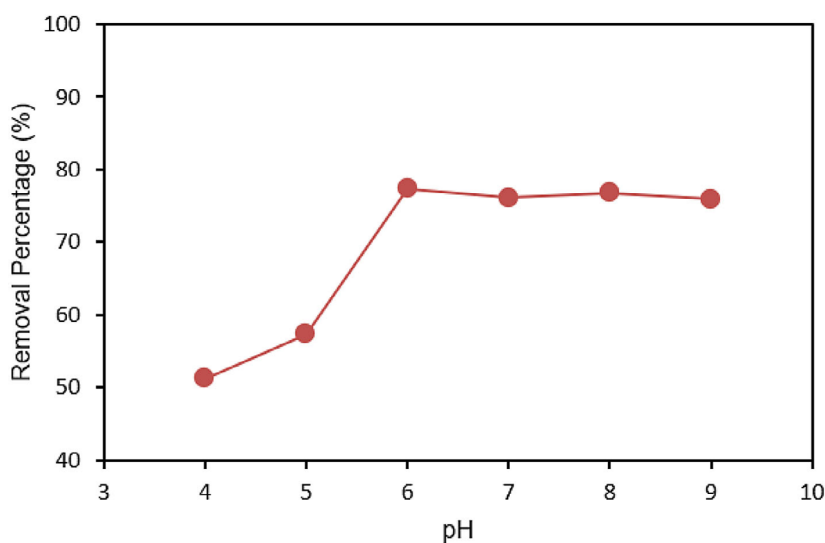
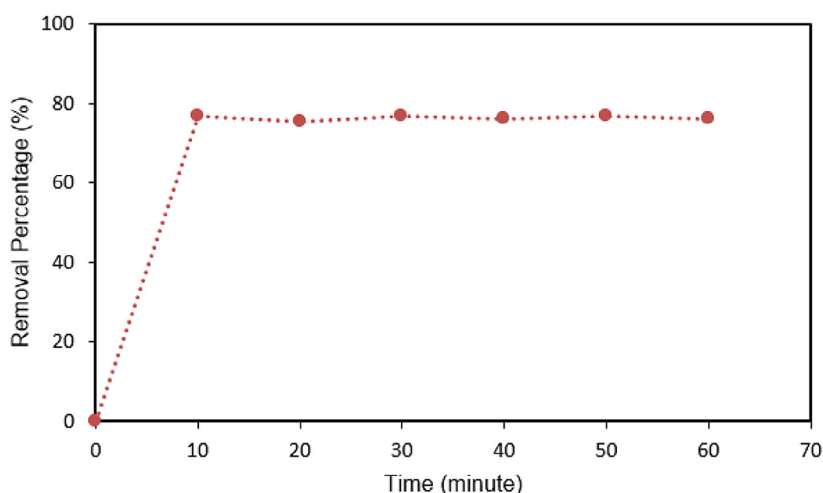**Figure 3.** Impact of pH on Cu(II) elimination

Figure 4. Impact of contact duration on Cu(II) elimination

the driving force required for mass transfer from the liquid phase onto the adsorbent surface (Limsuwan et al., 2024; Mve Mfoumou et al., 2024), the concentration is relatively low (10–120 mg/L), the biochar-based geopolymer achieved very high removal efficiencies (>98%), indicating that abundant adsorption sites were available to capture Cu(II) ions. At low concentrations, the pronounced adsorption affinity is generally linked to strong electrostatic forces and complexation between Cu(II) ions and active surface groups like hydroxyl and carboxyl (Beleño Cabarcas et al., 2024). However, when the initial Cu(II) concentration exceeded 200 mg/L, the removal efficiency declined sharply to ~61% at 200–400 mg/L and ~29% at 800–1000 mg/L. The progressive saturation of adsorption sites explains this phenomenon: once most of the surface active

sites are occupied, further increases in concentration cannot be effectively adsorbed (Guo and Wang, 2024; Jakubov and Jakubov, 2025). At this stage, competition among metal ions for the limited adsorption sites becomes significant, resulting in a lower removal percentage even though the absolute adsorption capacity (q_e) increases (Liu et al., 2024; Y. Zhao et al., 2024).

The isotherm analysis further supports this explanation. The Langmuir model provided a maximum adsorption capacity (qmax) of 68.97 mg/g, with a high correlation coefficient (R^2 = 0.9647). This strong fit indicates that Cu(II) adsorption onto the biochar-based geopolymer followed a monolayer adsorption mechanism on a relatively homogeneous surface (Li et al., 2025; Mohan et al., 2024). In contrast, the Freundlich model gave a lower correlation coefficient (R^2 = 0.8381),
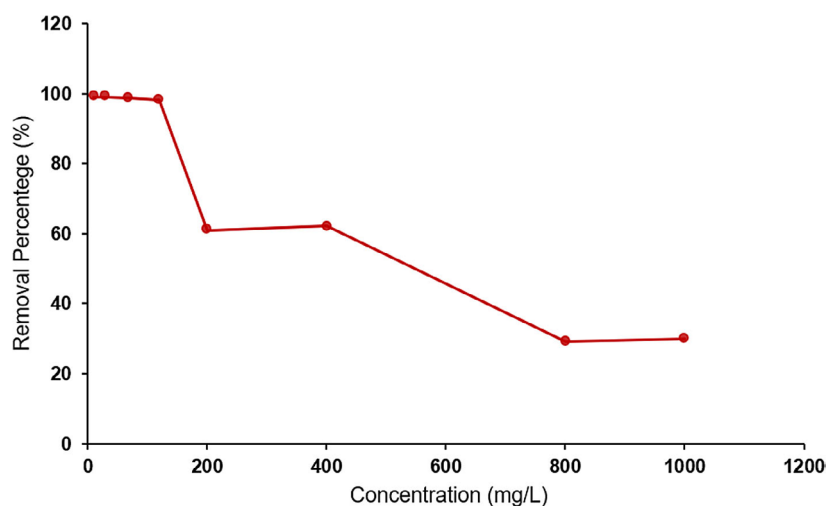

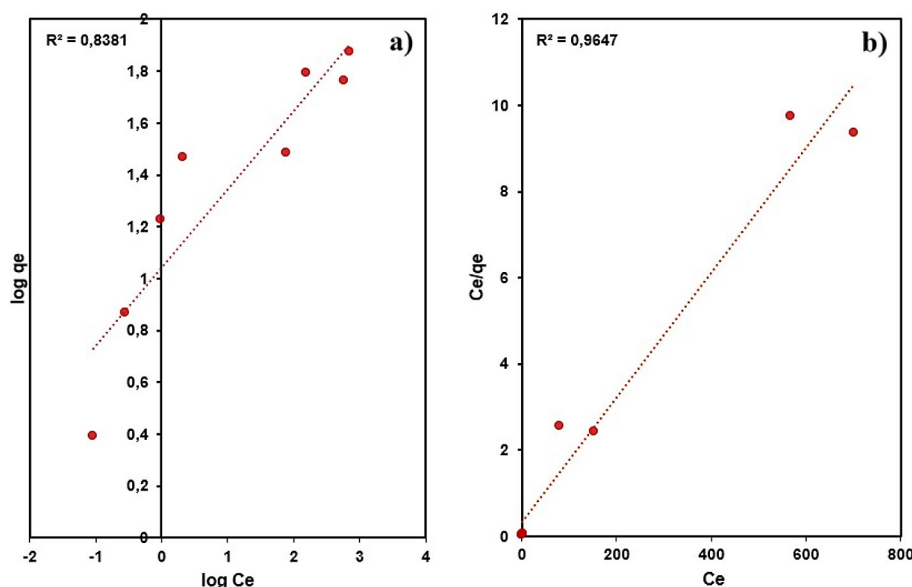**Figure 5.** Impact of initial metal concentration on Cu(II) elimination

Figure 6. Linear plots of (a) Freundlich and (b) Langmuir for Cu(II) removal by biochar-based geopolymer

suggesting multilayer adsorption on heterogeneous sites was less dominant. The Freundlich intensity parameter (n = 3.30) was greater than 1, which indicates favourable adsorption, but the better fitting of the Langmuir model confirms that surface saturation governed the equilibrium adsorption behaviour (Fodeke, 2024; Hammud, 2023)

A comparison of the maximum adsorption capacities of different biochar-based adsorbents reported in the literature is presented in Table 4. As shown, the qmax value obtained in this study (68.97 mg/g) for rice husk biochar-based geopolymer is considerably higher than those reported for pine sawdust biochar (2.5 mg/g), apple tree biochar (11.41 mg/g), orange peels biochar (28.06 mg/g), pineapple pulp biochar (41.9 mg/g), and oak fruit shells biochar (41.97 mg/g). This demonstrates that the incorporation of rice husk biochar into a geopolymer matrix significantly enhances adsorption performance compared to conventional biochar adsorbents.

In comparison, fly ash-derived geopolymers reported by Gupta (2023) achieved adsorption capacities of 28.51 mg/g respectively, which are lower than the 68.97 mg/g obtained in this work. This highlights the synergistic role of rice husk

biochar in enhancing the adsorption efficiency beyond fly ash geopolymers alone.

Nevertheless, several limitations of the tested biochar–geopolymers must be acknowledged. The increase of biochar content beyond an optimal level (e.g., BCG90) reduced the surface area due to partial pore blockage and compaction. Moreover, geopolymers typically exhibit lower porosity compared to activated carbons, and their adsorption capacity can be affected by the presence of competing ions in complex wastewater systems. Mechanical strength and stability may also decline after repeated adsorption–desorption cycles, potentially restricting large-scale applications unless further optimized.

In general, the theoretical and comparative analysis indicate that the adsorption of Cu(II) onto biochar-based geopolymer is governed by the availability of active sites and equilibrium limitations, where higher efficiency is achieved at lower concentrations, while saturation of adsorption sites restricts removal at higher concentrations. The superior qmax of the rice husk biochar-based geopolymer highlights its potential as a highly effective material for heavy metal remediation in aqueous systems.

Table 3. Adsorption isotherm parameters of Cu(II) based on Langmuir and Freundlich models

Parameter	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L	R^2	n	K_F	R^2
Value	68.9665	0.4436	0.9647	3.3033	10.5754	0.8381

Table 4. Comparison of maximum adsorption capacity (q_{max}) of various biochar-based adsorbents for Cu(II) removal

Adsorbent	q_{max} (mg/g)	References
Pine sawdust biochar	2.5	(Lou et al., 2016)
Apple tree biochar	11.41	(Zhao et al., 2020)
Orange peels biochar	28.06	(Afolabi and Musonge, 2023)
Pineaple pulp biochar	41.9	(Charnkeitkong and Sripiboon, 2024)
Oak fruit shells biochar	41.97	(Soudani et al., 2022)
Rice Husk Biochar-based geopolymer	68.97	This study

CONCLUSIONS

This study demonstrates that rice husk biochar incorporated into a fly ash-based geopolymer matrix is an effective and sustainable adsorbent for Cu(II) removal from aqueous solutions. BCG80 exhibited the optimal characteristics of the tested formulations, including a strong silicate framework, sufficient hydroxyl functional groups, and high porosity, contributing to its superior adsorption performance. The adsorption process was highly pH-dependent, with maximum efficiency achieved at pH 6, and equilibrium was reached rapidly within 10 minutes. Isotherm analysis confirmed that Cu(II) adsorption followed the Langmuir model, indicating monolayer adsorption on a relatively homogeneous surface, with a maximum adsorption capacity of 68,97 mg/g. These findings suggest that biochar-based geopolymer composites provide high adsorption efficiency and offer a durable and environmentally friendly solution for heavy metal remediation in contaminated water. Another important consideration for practical application is the regeneration and reusability of the adsorbent. Although regeneration experiments were not conducted in this study, previous works have shown that geopolymers can be regenerated using mild acid or chelating agents, usually with only a slight reduction in adsorption performance after several cycles. However, repeated regeneration may weaken the pore structure and cause leaching of alkali ions. Therefore, future studies should investigate the regeneration potential of rice husk biochar-based geopolymers to evaluate their long-term stability and cost-effectiveness in continuous water treatment systems. Future studies may focus on scaling up the material synthesis, evaluating regeneration and reuse potential, and testing its performance in complex wastewater matrices.

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