



Enhanced Removal of Copper from Synthetic Wastewater Using a Water Hyacinth-Based Activated Carbon and Chitosan Composite Adsorbent

Rosita Dwi Chrisnandari*, May Kurnia Pratiwi, Ria Lusiyan

Department of Chemical Engineering, Politeknik Negeri Malang, Jl. Soekarno Hatta No. 9, Malang 65141, Indonesia

ABSTRACT

Copper (Cu) contamination of rivers or groundwater is a worldwide problem caused by anthropogenic activities, commonly from the industrial sector. Cu accumulation in the body could have detrimental effects on human health as well as pose a major threat to the aquatic environment. We report the rate of Cu removal by a composite made from activated carbon of water hyacinth and chitosan in an artificial aqueous Cu solution which is likely to be encountered in terrestrial environments. In this investigation, water hyacinth has been processed by carbonization in a batch reactor at 350°C for 90 minutes. The chars were also chemically modified with HCl 6 N for 24 hours to investigate the potential for sorption enhancement. The properties of the resulting chars including their water content, ash content, volatile matter, fixed carbon, and iodine absorption capacity properties have been determined and compared to Indonesia's standard (SNI 06-3730-1995). Composites have been produced by mixing the activated carbon with chitosan (1% w/v; 2% w/v; 3% w/v) from crab shells in an STTP-Ethanol solution. The composite was characterised using Fourier transform infrared spectroscopy (FT-IR). The effects of contact time parameters on batch system adsorption were investigated. Adsorption isotherm models including Langmuir and Freundlich were applied to interpret the equilibrium data in aqueous solutions. For a kinetic model consistent with experimental data, pseudo-first-order and pseudo-second-order models were examined. The maximum adsorption capacity was calculated as 0,006510 mg/g. Meanwhile, the most suitable isotherm and kinetic models were Langmuir and pseudo-second-order kinetic models, respectively. Adsorption has optimum results at room temperature, with an initial metal concentration of 0.135 mg/L, contact time of 60 min, and 1 g dosage for the adsorbent. The highest removal rate for Cu was observed for the composite with typical rates ranging from 95.74 – 96.41%. The removal rate for activated carbon from water hyacinth is lower and ranges from 94.12 – 95.07%. Meanwhile, the removal rate using chitosan alone is 95.33%. This study confirms that the addition of chitosan improves the efficiency of activated carbon to remove Cu compared to the original state.

Keywords: adsorption, chitosan, composite, Cu removal, water hyacinth.

1. INTRODUCTION

In industrial wastewater, heavy metals ranging from Cu, Cr, Ni, Fe, Mn, Zn, Cs, Ag, and Pb, are frequently detected [1,2]. Among those, Copper (Cu) is the most commonly found. Copper exposure resulting in symptoms including diarrhea, vomiting, and even hypotension and at excessive doses can be harmful and causing detrimental effects such as anemia, interfere with the production of red blood cells, and result in poisoning that damages the kidneys, liver, intestines, lungs, and ultimately causes death [3]. Concentrations of Cu surpassing 1 ppm in

drinking water can be harmful to human health [4]; concentrations between 2.5 and 3.0 ppm in aquatic environments can be fatal to fish and toxic to other aquatic species [5]; and concentrations above 20 ppm can be dangerous to sheep and other livestock [6,7]. According to Republic of Indonesia Government Regulation Number 82 of 2001 [8], the maximum amount of Cu that can be present in industrial effluent is 0.02 mg/L. Therefore, it is essential to implement effective measures to reduce copper concentrations in industrial liquid waste prior to its release into the environment.

*Corresponding author:

E-mail: rositadwi86@polinema.ac.id (Rosita Dwi Chrisnandari)

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Numerous techniques devised for the removal of heavy metals include chemical precipitation methods, ion exchange processes, membrane technologies, electrochemical methods, and adsorption. Adsorption is widely employed because to its simplicity and comparatively inexpensive cost. This approach may be used to a variety of adsorbents, such as zeolites, clays, and mesoporous materials [9]. Finding inexpensive, plentiful adsorbents with adsorption capabilities equivalent to those of traditional alternatives has drawn more attention in recent years. Since natural materials like biomass are more readily available and ecologically benign, various adsorbent materials based on them have been created recently.

Eichhornia crassipes, sometimes known as water hyacinth (WH), is a cheap, sustainable, and quickly expanding source of biomass that could potentially converted into carbonaceous material. WH is an aquatic plant that thrives in all freshwater habitats and belongs to the *Pontederiaceae* family. Given the substantial amount of cellulose (35%) and hemicellulose (30%) content and low lignin (10%) quantity, WH biomass has been applied as an efficient adsorbent for removal of heavy metals and other nanoparticles [10].

The excessive WH growth on surface of the water can obstruct sunlight, hindering aquatic plant development and lowering the water's total photosynthesis. They also impede hydroelectric systems, streams, irrigation, and river transportation. The selective elimination of these aquatic weeds costs enormous amounts of money every year all throughout the world. Therefore, turning WH into carbonaceous material for the treatment of heavy metals contaminated wastewater may be a viable strategy for controlling this problematic organism and eliminating heavy metals ions from wastewater [9].

Carbon material derived from WH can be coupled with other substances like chitosan to forming composite and enhance adsorption effectiveness. Chitosan is the second most common polymer found in nature following

cellulose. Since chitosan contains hydroxyl and amino groups that may create coordination bonds with metal ions, it can be employed as a natural adsorbent for metal ions. As an adsorbent, chitosan has been used extensively to remove hazardous contaminants from water.

Particle size, crystalline structure, and degree of deacetylation all have a significant impact on chitosan's adsorption effectiveness. Higher levels of deacetylation reduced the polysaccharide chain partially, enhance the quantity of amino groups, and promote crystallinity by conducting a more constant polymeric chain packing. The amount of active sites, on the other hand, is determined by particle size and surface area; larger particles generally result in lower adsorption efficiency because of their lesser particular surface area. As a result, the degree of deacetylation remains crucial since it significantly impacts the quantity of amino groups involved in the adsorption process [11].

Previous studies have demonstrated the potential of chitosan [12–14], biochar and activated carbon produced from water hyacinth [15–17] as separate adsorbents for the removal of heavy metals. Water hyacinth-derived activated carbon has exhibited strong adsorption performance because of its porous structure and the presence of oxygen-containing functional groups [18], while chitosan contains hydroxyl and amino groups that can facilitate the complexation of metal ions [10]. However, most previous studies have focused on the adsorption performance of these materials individually, providing limited information on the potential synergistic effects that may arise from their combination in a composite adsorbent. In particular, the utilization of chitosan and water hyacinth-derived activated carbon as a composite adsorbent for Cu^{2+} removal remains insufficiently explored. Furthermore, the adsorption behavior of such a composite, including its equilibrium isotherms, adsorption kinetics, and the roles of functional groups in composite formation and Cu^{2+} adsorption, has not been

comprehensively investigated. Therefore, this study aimed to synthesize and evaluate a water hyacinth-derived activated carbon–chitosan composite for the removal of Cu^{2+} from synthetic wastewater and to examine its adsorption behavior through isotherm and kinetic analyses.

2. RESEARCH METHODS

2.1. Preparation of Water Hyacinth-Based Activated Carbon

Water hyacinth was obtained from river in Malang district. Water hyacinth thoroughly washed with distilled water and subsequently dried under direct sunlight until completely dry. Carbonization was then carried out at 350 °C for 1 hour and 30 minutes to produce carbon derived from the water hyacinth. The resulting carbon was ground and sieved to obtain a powder with a particle size of 60 mesh. Chemical activation was performed using a 6 N HCl (Smartlab 37%) solution for 24 hours [19]. The activated carbon was rinsed with distilled water until a neutral pH was reached. Finally, the material was dried in an oven at 105°C for 5 hours and stored in a desiccator until it cooled to room temperature.

2.2. Preparation of Chitosan-Based Composite

A mixture of 3% (w/v) Sodium Tripolyphosphate (STPP) solution (technical grade) and 99% ethanol (Merck Pro Analys) was prepared at a ratio of 4:1 (v/v). Crab shell chitosan powder (commercial) was weighed according to the designated mass variables, dissolved in 100 mL of acetic acid solution (Merck), followed by continuous stirring for 2 hours. Subsequently, 1 g of water hyacinth-derived activated carbon was added and the mixture was stirred for an additional 1 hour. The chitosan-activated carbon mixture was then added dropwise into the STPP–ethanol solution while continuously stirring for 2 hours. The resulting composite was washed using distilled water until a neutral pH was achieved, then dried in an oven at 50°C for 30 minutes. The characterization of its surface area, pore diameter, and pore volume was not

conducted due to the limited quantity of the synthesized composite.

2.3. Preparation of Standard Cu Solution and Artificial Cu Waste

The standard copper solution was prepared by dissolving 3.2297 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck Pro Analys) and 5 mL of concentrated H_2SO_4 (Merck 98%) in distilled water to a final volume of 1000 mL, yielding a concentration of 167.97 mg/L. From this solution, a series of standard solutions with concentrations ranging from 0.0033 to 0.0503 mg/L were prepared, each supplemented with 2.5 mL of concentrated ammonia (Merck 25%) and diluted to 50 mL. Absorbance measurements were carried out using a UV-Vis spectrophotometer (VIS-7200A) at a wavelength of 615 nm. In addition, artificial Cu waste with a concentration of 0.135 mg/L was prepared by dissolving 0.53 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and adjusting the volume to 1000 mL.

2.4. Adsorption Process

Each type of adsorbent was weighed (1 g) and placed into an erlenmeyer flask. Batch adsorption was then performed using 50 mL of artificial Cu wastewater, stirred using a magnetic stirrer at 150 rpm with varying contact times (30, 45, 60, and 75 minutes). Upon completion of each experiment, the filtrate and residue were separated using filter paper. The filtrate absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 615 nm, and the Cu concentration in the solution was subsequently determined.

The amount of metal ions absorbed onto the adsorbent at equilibrium, q_e , was calculated using equation (1):

$$q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

where V is the volume of the solution (L), C_o is the initial Cu concentration ($\text{mg} \cdot \text{L}^{-1}$), C_e is the concentration of Cu remaining in the solution after adsorption ($\text{mg} \cdot \text{L}^{-1}$), and m is the mass of the adsorbent (g) [20].

2.5. Moisture Content Analysis

Moisture content analysis was conducted by heating 1 g of activated carbon sample at 105°C for 1 hour. The sample was then cooled in a desiccator for 15 minutes, after which the mass of the crucible containing the sample was measured [19].

$$\text{Moisture Content (\%)} = \frac{m_2 - m_3}{m_2 - m_1} \times 100\% \quad (2)$$

Description :

m_1 = mass of empty crucible (g)

m_2 = mass of crucible + sample before oven-drying (g)

m_3 = mass of crucible + sample after oven-drying (g)

2.6. Ash Content Analysis

Ash content analysis was carried by placing 1 g of activated carbon sample in a furnace and heating it at 815°C for 1 hour. The sample was then cooled in a desiccator for 15 minutes, after which the mass of the crucible containing the sample was measured.

$$\text{Ash Content (\%)} = \frac{m_2}{m_1} \times 100\% \quad (3)$$

Description :

m_1 = mass of initial sample (g)

m_2 = mass of the ash produced (g)

2.7. Volatile Matter Analysis

Volatile matter analysis was performed by placing 1 g of activated carbon sample in a furnace and heating it at 950°C for 7 minutes. The sample was then cooled in a desiccator for 15 minutes, after which the mass of the crucible containing the sample was measured [19].

$$\text{Volatile Matter Content (\%)} = \frac{m_2 - m_3}{m_2 - m_1} \times 100\% \quad (4)$$

Description :

m_1 = mass of empty crucible (g)

m_2 = mass of crucible + sample before furnace treatment (g)

m_3 = mass of crucible + sample after furnace treatment (g)

2.8. Fixed Carbon Content Calculation

Fixed carbon is the fraction of carbon remaining in the material after subtracting moisture, volatile matter, and ash. The fixed carbon content is determined using the following formula [19].

$$\%FC = 100\% - (\text{moisture} + \text{ash} + \text{volatile matter}) \quad (5)$$

Where FC is fixed carbon of the sample.

2.9. Iodine Adsorption Capacity Test

The iodine adsorption test was carried out by preparing 0.1 N iodine solution (Merck), 0.1 N sodium thiosulfate solution (Merck), and 1% starch indicator (technical grade). A total of 0.5 g of water hyacinth-based activated carbon was placed into an erlenmeyer flask, followed by the addition of 25 mL of 0.1 N iodine solution, and the mixture was stirred for 15 minutes. The mixture was then allowed to stand for 2 hours and subsequently filtered. A 10 mL portion of the filtrate was titrated with 0.1 N sodium thiosulfate until a light yellow color appeared, after which 3–4 drops of starch indicator were added, until producing a blue color. Titration was continued until the solution became colorless. As a reference, the iodine solution was, previously, also titrated without the addition of adsorbent and used as a blank.

$$\text{Iodine Absorption Capacity} = \frac{(A - \frac{B \times N}{n}) \times 126.93 \times fp}{a} \quad (6)$$

Description :

A = volume of iodine solution (mL)

B = volume of $\text{Na}_2\text{S}_2\text{O}_3$ used (mL)

fp = dilution factor

N = concentration of $\text{Na}_2\text{S}_2\text{O}_3$

n = concentration of Iodine

a = mass of activated carbon (g)

126,93 = amount of Iodine according to 1 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution

2.10. FTIR Analysis

FTIR analysis was performed using an IR Prestige 21 instrument. The sample was finely ground, mixed with KBr (2:98), and pressed into a pellet under a pressure of 8 tons. Measurements were conducted using the IR

Solution software, and the results were analyzed using the peak table.

2.11. Determination of Adsorption Isotherms

Adsorption isotherms present the relationship between the amount of substance adsorbed and the concentration of the adsorbate under equilibrium conditions. Generally, there are two isotherm models that are commonly used to characterize this behavior: the Langmuir model and the Freundlich model.

2.11.1. Langmuir Isotherm

The Langmuir model assumes that adsorption occurs on a homogeneous surface, where each adsorption site can accommodate only a single adsorbate molecule. The Langmuir equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{C_e}{Q} \quad (7)$$

Description :

C_e = equilibrium concentration of the solution (mg/L)

q_e = adsorption amount at equilibrium (mg/g)

Q = Langmuir constant related to adsorption capacity

b = Langmuir constant

In practice, the value of Q and b be obtained by plotting C_e/q_e (y-axis) againsts C_e (x-axis). The intercept value of the plot corresponds to $1/(Qb)$, the slope represents $1/Q$. If the R^2 value approaches 1, it can be concluded that the adsorption process follows the Langmuir isotherm model [20]

2.11.2. Freundlich Isotherm

The Freundlich model describes adsorption process occurring on a heterogeneous surface, where the active sites of the adsorbent possess different affinities toward the adsorbate molecules. The Freundlich isotherm can be expressed as follows:

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (8)$$

q_e = amount of adsorbate adsorbed at equilibrium (mg/g)

C_e = equilibrium concentration of the solution (mg/L)

K = constant representing adsorption capacity

n = constant representing adsorption affinity

Experimentally, the values of K and n can be obtained by plotting $\log q_e$ (y-axis) against $\log C_e$ (x-axis). The intercept value of the plot corresponds to $\log K$, while the slope represents $1/n$. If the R^2 value approaches 1, this indicates that the adsorption process follows the Freundlich isotherm model [20].

2.12. Determination of Adsorption Kinetics

Adsorption kinetics examines the rate of the adsorption process and the interaction mechanisms between the adsorbent and the adsorbate. To understand these phenomena, several kinetic models can be applied, one of which is the pseudo-first-order model.

2.12.1. Pseudo-First-Order Model

This model states that the rate of change in adsorbate concentration depends on the amount of adsorbate remaining available for adsorption on the adsorbent surface. The pseudo-first-order kinetic equation is expressed as follows

$$\log (q_e - q_t) = \log q_e - \frac{K}{2.303} t \quad (9)$$

Description :

q_e = amount of ions adsorbed at equilibrium (mg/g)

q_t = amount of ions adsorbed at time t (mg/g)

K = adsorption rate constant (minute⁻¹)

The values of constant K and the adsorption capacity q_e can be determined by plotting $\log(q_e - q_t)$ (y-axis) against time (t) (x-axis). The slope of the resulting linear line corresponds to $-K$, while the intercept represents $\log(q_e)$. If the R^2 value approaches 1, the adsorption process is considered to

follow the pseudo-first-order kinetic model [20].

2.12.2. Pseudo-Second-Order Model

The pseudo-second-order model assumes that the rate of the adsorption reaction depends on the square of the amount of adsorbate being adsorbed. The equation for this model can be expressed as follows

$$\frac{t}{qt} = \frac{1}{Kqe^2} + \frac{1}{qe} t \quad (10)$$

Description:

qe = amount of ions adsorbed at equilibrium (mg/g)

qt = amount of ions adsorbed at time t (mg/g)

K = adsorption rate constant ($\text{g/mg} \cdot \text{min}^{-1}$)

The values of the constant K and the adsorption capacity qe can be determined by plotting t/qt (y-axis) against time, t (x-axis). The slope of the resulting linear plot corresponds to $1/qe$, while the intercept provides the value of $1/(Kqe^2)$. When the R^2 value approaches 1, the adsorption process is considered to follow the pseudo-second-order kinetic model.

This kinetic analysis is performed by monitoring the change in adsorbate concentration as a function of time at predetermined intervals, which enables the determination of the reaction rate constant and the activation energy associated with the adsorption process [20].

3. RESULTS AND DISCUSSION

3.1. Chemical Properties Analysis of Water Hyacinth-Based Activated Carbon

The characterization of water hyacinth-based activated carbon shows that it possesses a relatively low moisture content, which contributes to the stability of the material during the adsorption process as shown in Table 1. A low moisture level also indicates good storage stability, as the activated carbon is less prone to degradation during storage [21]. In addition, the activated carbon exhibits a relatively low ash content, indicating a minimal presence of inert inorganic minerals, thereby ensuring that the

adsorption performance of the material is not adversely affected [22].

Table 1. Chemical properties of water hyacinth-based activated carbon.

Parameter	SNI 06-3730-1995	Experimental result
Moisture Content (%)	max. 15	13.42
Ash Content (%)	max. 10	5.85
Volatile matter content (%)	max. 25	25.15
fixed carbon content (%)	min. 65	55.55
Iodine absorption (mg/g)	min. 750	967.84

A certain amount of volatile matter is still present; however, it remains within an acceptable range for adsorption applications, as most volatile compounds have decomposed during the carbonization process [23]. Meanwhile, the relatively high fixed-carbon content reflects the abundance of effective carbon within the pore structure of the activated carbon, which becomes an important parameter in determining its quality and adsorption capability [24,25]. The prepared activated carbon exhibited a fixed carbon content of 55.55%, which is below the minimum requirement of 65% established by the Indonesian National Standard (SNI 06-3730-1995). This finding indicates that the carbonization and activation processes were not sufficient to produce a highly carbonized material comparable to commercial activated carbon. The relatively low carbonization temperature of 350 °C may have contributed to this result, as it might not have completely decomposed cellulose, hemicellulose, and lignin into a stable carbon matrix [26]. Consequently, a greater proportion of volatile matter and oxygen-containing compounds may have

remained in the material, leading to a lower fixed carbon content.

In general, a low fixed carbon content may indicate a less developed carbon structure, potentially limiting specific surface area, pore development, and overall adsorption capacity [27]. However, adsorption performance is determined not only by fixed carbon content but also by other factors, including the availability of surface functional groups and the pore accessibility [28,29].

Therefore, increasing the carbonization temperature, residence time, and activation procedure may increase the fixed carbon content, promote pore development, and enhance adsorption capacity. Future studies should further investigate these parameters to produce activated carbon that meets the SNI requirement while maintaining the beneficial surface functional groups provided by chitosan.

The iodine adsorption value is also considerably high, indicating that the water-hyacinth-based activated carbon possesses a sufficient surface area and pore structure [30] to serve effectively as an adsorbent for the removal of heavy metal ions such as Cu^{2+} . The addition of an activator influences the pore structure of activated carbon. Carbon treated with HCl develops deeper pores compared to the non-activated material. The activation process increases pore size and generates new pores, thereby enhancing the material's ability to adsorb molecules larger than those accommodated by macropores [31].

The adsorption performance of activated carbon is strongly determined by its specific surface area, pore volume, and pore size distribution, as these structural properties influence the accessibility of adsorption sites and facilitate mass transfer of metal ions. Meanwhile, chitosan provides abundant amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functional groups that can promote chemical interactions with Cu^{2+} ions through coordination and surface complexation. The incorporation of chitosan may increase the number of chemically active functional

groups and provide additional binding sites for heavy metal ions. Therefore, the overall adsorption performance is likely determined by the balance between improved surface functionality and possible reduction in pore accessibility. One limitation of this study is that BET analysis was not performed to determine the surface area and pore structure. Consequently, the effects of chitosan incorporation on the surface area and pore structure of activated carbon could not be quantitatively assessed.

3.2. Results of FT-IR Analysis

FTIR analysis, as shown in Figure 1 revealed that chitosan and water hyacinth-based activated carbon contains functional groups, including OH, C=O, and NH at specific wavenumbers, as summarized in Table 2. The presence of these functional groups provides potential active sites for the adsorption of metal ions [32,33]. After compositing, the FTIR spectrum shows OH, C=O, and NH groups with noticeable shifts in wavenumber, suggesting interactions between activated carbon and chitosan. The broad absorption band observed at approximately $3200\text{--}3500\text{ cm}^{-1}$ corresponds to the overlapping O–H and N–H stretching vibrations, indicating the presence of hydroxyl and amino groups contributed by both activated carbon and chitosan. The characteristic absorption bands associated with C=O (carbonyl), N–H, and C–O stretching vibrations further confirm the successful incorporation of chitosan into the composite. The absence of distinguishable C–H stretching and bending bands in the composite spectrum may be attributed to their overlap with the broad O–H and N–H absorption bands. In addition, interactions between chitosan and activated carbon during composite preparation may have reduced the strength of aliphatic C–H vibrations.

In conclusion, composite material is successfully formed, characterized by key functional groups that enhance its performance as a heavy-metal adsorbent. Among these groups, NH_2 group in chitosan

play a significant role in metal binding due to their polycationic characteristic [34]. The lone-pair electrons of nitrogen atoms can interact with Cu^{2+} ions by forming coordination bonds. Hydroxyl ($-\text{OH}$) groups also contribute to Cu^{2+} adsorption through surface complexation and electrostatic

interactions, whereas carbonyl ($\text{C}=\text{O}$) and $\text{C}-\text{O}$ groups may be involved in ion exchange and metal complex formation. Therefore, the adsorption mechanism, as depicted in Figure 2, is likely governed by the combined effects of coordination, surface complexation, and electrostatic attraction.

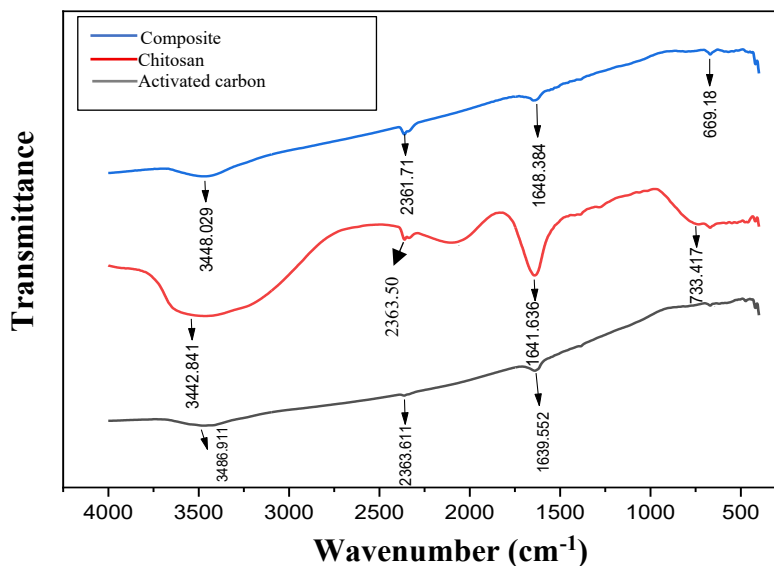


Figure 1. Comparison of FT-IR profiles of activated carbon, composites, and chitosan.

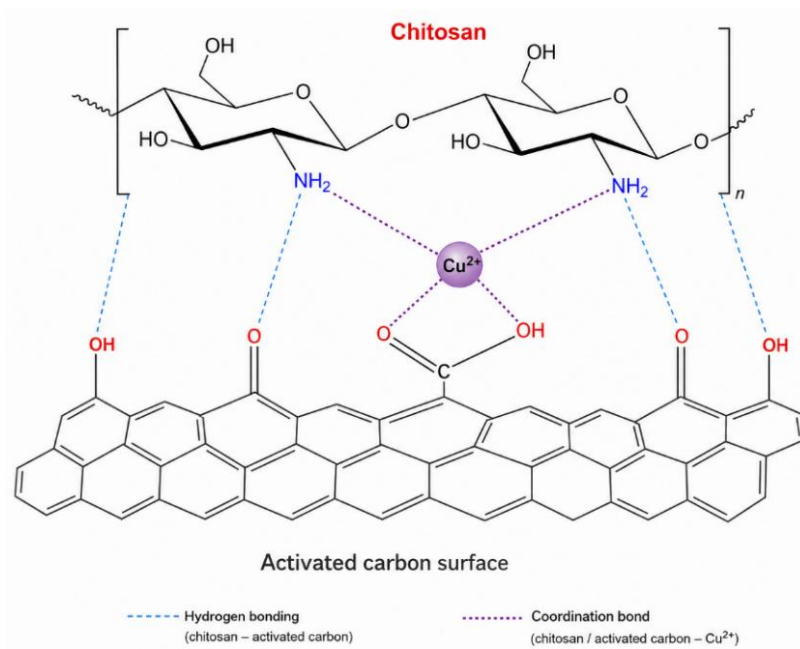
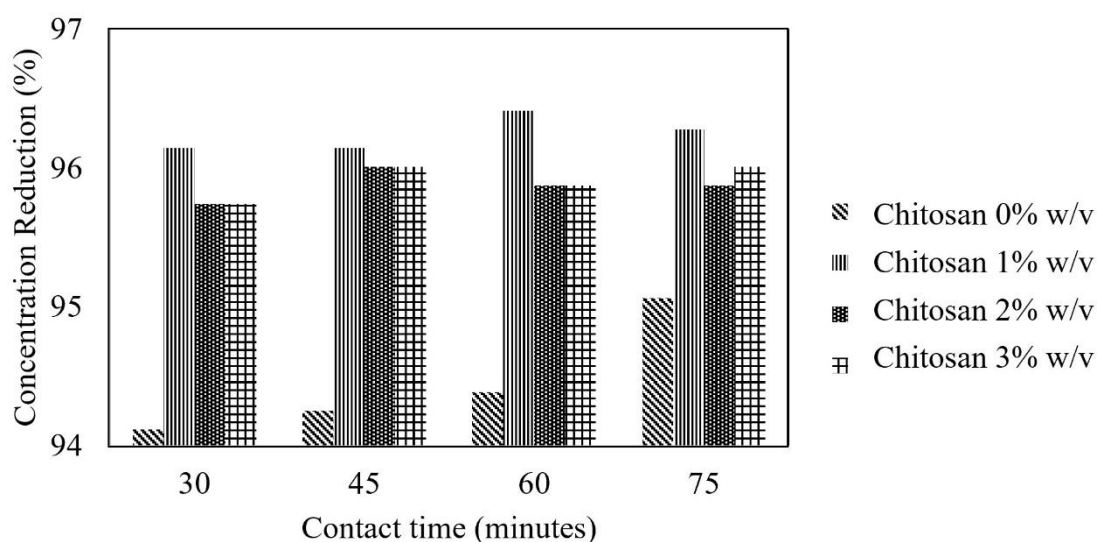


Figure 2. Interaction between chitosan, activated carbon and ion Cu^{2+} .

Table 2. Differences in functional groups of activated carbon, composite, and chitosan.

Functional Group	Wavenumber (cm ⁻¹)		
	Activated Carbon	Composite	Chitosan
-OH	3486.9110	3448.0290	
-N-H	-	-	3442.8410
N-H/C-O stretch	2363.6110	2361.7100	2102.2200
C=O	1639.5520	1648.3840	
C-N bend	-	-	1641.6360
N-H bend	-	669.1800	733.4170

**Figure 3.** Correlation between contact time and copper (Cu²⁺) reduction.

3.3. Analysis of Copper (Cu²⁺) Concentration After Adsorption and Calculation of Reduction Efficiency

The values of $C_t = 0.006$ mg/L, $q_e = 6.45 \times 10^{-3}$ mg/g, and Cu²⁺ reduction efficiency = 95.333% correspond to the optimum adsorption condition obtained using chitosan as a single adsorbent at 1% (w/v) dosage and 60-minute contact time.

In this study, the adsorption performance of water hyacinth-based activated carbon, chitosan, and their composite was compared for Cu artificial wastewater to provide a controlled system for evaluating the intrinsic adsorption performance of the activated carbon-chitosan composite. This approach facilitates a clearer evaluation of the adsorption mechanism and equilibrium behavior by reducing interference from other dissolved species.

Nevertheless, natural and industrial wastewaters are substantially more complex than synthetic solutions because they contain various coexisting constituents, including competing cations (e.g., Ca²⁺, Mg²⁺, Na⁺, Zn²⁺, Pb²⁺, and Fe³⁺), dissolved anions (e.g., SO₄²⁻, NO₃⁻, and Cl⁻), natural organic matter, suspended solids [35], and fluctuating pH conditions. These constituents may affect adsorption through several mechanisms. Competing metal ions may occupy the same active adsorption sites as Cu²⁺, potentially reducing adsorption selectivity and removal efficiency. Natural organic matter may accumulate on the composite surface, partially blocking active sites, or form soluble complexes with Cu²⁺, thereby decreasing the concentration of Cu²⁺ available for adsorption. Furthermore, pH strongly influences both Cu²⁺ speciation and the protonation state of the amino (-NH₂) and

hydroxyl (–OH) functional groups on chitosan, which may subsequently affect the adsorption affinity of the composite [36].

Accordingly, the adsorption performance observed in this study should be interpreted as the intrinsic performance of the composite under controlled laboratory conditions. Further studies should assess the composite using real wastewater to evaluate its adsorption selectivity, operational robustness, and potential applicability under environmentally relevant conditions.

Based on the Table 3, adsorption using activated carbon alone reached its optimal performance at a contact time of 75 minutes, achieving a copper removal efficiency of 95.06%. The adsorption process using the activated carbon-chitosan composite with chitosan masses of 1%, 2%, and 3% (w/v)

showed that the best performance was obtained with the 1% (w/v) chitosan composite at a contact time of 60 minutes, achieving a copper reduction efficiency of 96.41% as shown in Figure 3. For the other chitosan mass variations, the reduction efficiency ranged from 95%-96%, which was still higher than that obtained using water hyacinth-based activated carbon alone. This indicates that the activated carbon-chitosan composite is more effective in removing Cu from artificial wastewater compared to activated carbon alone. When compared with chitosan used as a single adsorbent under its optimal conditions (1% w/v and 60 minutes), the composite also exhibited superior performance, as chitosan alone achieved a removal efficiency of only 95.33%.

Table 3. Analysis result of Cu^{2+} concentration after adsorption and its reduction efficiency.

Mass of Chitosan in Composite (%w/v)	Contact Time (minutes)	C_0 (mg/L)	C_t (mg/L)	qt 1×10^{-3} (mg/g)	qe 1×10^{-3} (mg/g)	Reduction Efficiency of Copper (Cu^{2+})
0	30	0.1350	0.0079	6.3550	6.4500	94.1160
	45		0.0077	6.3650		94.2510
	60		0.0075	6.3750		94.3860
	75		0.0060	6.4500		95.0630
1	30	0.1350	0.0052	6.4900	6.5100	96.1450
	45		0.0052	6.4900		96.1450
	60		0.0048	6.5100		96.4150
	75		0.0050	6.5000		96.2800
2	30	0.1350	0.0057	6.4650	6.4850	95.7390
	45		0.0053	6.4850		96.0090
	60		0.0055	6.4750		95.8740
	75		0.0055	6.4750		95.8740
3	30	0.1350	0.0057	6.4650	6.4850	95.7390
	45		0.0053	6.4850		96.0090
	60		0.0055	6.4750		95.8740
	75		0.0053	6.4850		96.0090
1 (optimal mass)	(optimal contact time)	0.1350	0.0060	6.4500		95.3330

The water hyacinth–chitosan composite developed in this study integrates two abundant and renewable biomass resources into a single adsorbent material. Water hyacinth-derived activated carbon provides a porous carbon matrix that allows adsorption through improving its pore structure, whereas chitosan supplies amino ($-NH_2$) and hydroxyl ($-OH$) functional groups that can interact with Cu^{2+} ions. This synergistic combination of these complementary properties may enhance the accessibility of active adsorption sites while maintaining a relatively simple preparation process.

From a scalability perspective, the composite preparation process uses commercially available chemicals and does not require high-pressure reactors or advanced fabrication equipment. Moreover, the use of water water hyacinth, an invasive aquatic plant that causes ecological and operational challenges in freshwater ecosystems, together with chitosan derived from crustacean shell waste, promotes biomass valorization. By converting these underutilized biomass resources into value-added adsorbents for wastewater treatment, the proposed approach also supports the principles of a circular economy.

Compared with previously reported water hyacinth-derived adsorbents, composite developed in this study exhibited slightly higher Cu^{2+} removal efficiency, due to the incorporation of chitosan. The amino groups in chitosan may provide additional binding sites and form coordination complexes with Cu^{2+} ions. Although the improvement was small, possibly because of the low initial Cu^{2+} concentration (0.135 mg L^{-1}), the composite offers advantages such as renewable raw materials, environmentally friendly preparation, and simple fabrication.

The maximum adsorption capacity obtained in this study ($0.00651 \text{ mg g}^{-1}$) was lower than those reported for many biomass-derived activated carbons and chitosan-based composites tested at higher metal concentrations. The low adsorption capacity observed in this study was primarily attributed to the low initial Cu^{2+}

concentration (0.135 mg L^{-1}). Consequently, the low Cu^{2+} concentration in the solution resulted in a lower equilibrium adsorption capacity, even though the removal efficiency was high.

Besides the low initial metal concentration, several factors may have contributed to the relatively low adsorption capacity. The carbonization temperature of 350°C may have limited pore development and reduced the available surface area because it is relatively low for producing highly porous activated carbon. In addition, chemical activation using only hydrochloric acid (HCl) may have limited the formation of new micropores. Although HCl can remove inorganic impurities, it is generally less effective in developing microporosity than activating agents such as KOH or H_3PO_4 . Furthermore, incorporating chitosan into the activated carbon matrix may have reduced pore accessibility and surface area. At the same time, chitosan introduced additional functional groups that may promote Cu^{2+} complexation.

Despite its relatively low adsorption capacity, the composite achieved a Cu^{2+} removal efficiency of 96.41%, indicating its potential effectiveness in treating wastewater containing low concentrations of Cu^{2+} . This finding suggests that the composite may be more suitable for polishing wastewater containing trace levels of Cu^{2+} than for treating highly concentrated industrial effluents.

Modest improvement in adsorption performance suggests that the main advantage of the composite lies in its sustainable material utilization and multifunctional adsorption mechanism rather than in a substantial increase in Cu^{2+} removal efficiency. Therefore, the study can be considered as a proof of concept demonstrating the feasibility of converting two biomass waste resources into a functional adsorbent for wastewater treatment. Although the use of inexpensive biomass feedstocks and a straightforward preparation method suggests potential economic feasibility, a comprehensive

analysis and regeneration study are still required to evaluate its practical viability for large-scale applications

3.4. Determination of Adsorption Isotherms

The adsorption isotherm characteristics of the water hyacinth-based activated carbon–chitosan composite were evaluated using both the Langmuir and Freundlich models.

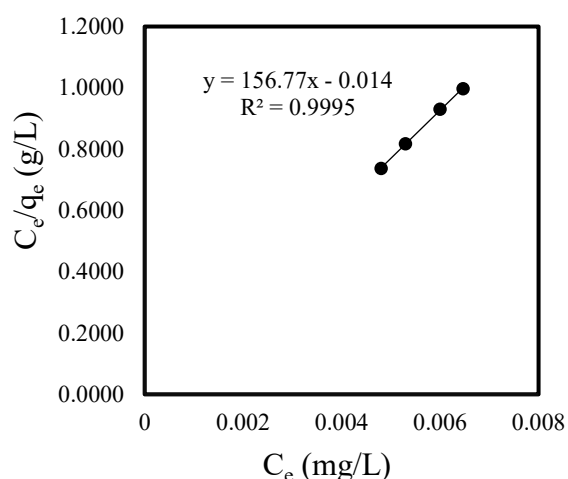


Figure 4. Langmuir adsorption isotherm plot.

As shown in Figure 4, the linear relationship between C_e and C_e/q_e follows the Langmuir model. The resulting linear equation, $y = 156.77x - 0.014$, exhibits a high coefficient of determination ($R^2 = 0.9995$), indicating an excellent fit of the experimental data to the Langmuir isotherm. The Langmuir model suggests that Cu^{2+} adsorption was mainly governed by active sites with similar adsorption energies within the investigated concentration range. Although the Langmuir model is commonly associated with monolayer adsorption on a homogeneous surface, the composite used in this study is structurally heterogeneous because it consists of activated carbon and chitosan, which have different physicochemical properties. Therefore, the good fit of the Langmuir model should not be interpreted as evidence that the entire adsorbent surface is perfectly homogeneous. Instead, it suggests that, within the investigated concentration range, adsorption was dominated by a relatively

uniform group of active sites with similar adsorption energies.

Moreover, the low initial Cu^{2+} concentration (0.135 mg L^{-1}) used in this study may have limited adsorption primarily to the highest-energy surface sites. At higher metal concentrations, adsorption may involve lower-energy or less accessible sites, making multilayer adsorption and surface heterogeneity more important. Although the Langmuir model provided the best fit under the investigated conditions, it does not demonstrate that the adsorbent surface is completely homogeneous.

In contrast, the Freundlich isotherm plot shown in Figure 5 presents the relationship between $\log C_e$ and $\log q_e$. The plot yields a linear equation, $y = -0.0185x - 2.2299$, with an R^2 value of 0.4106, indicating that the experimental data do not fit the Freundlich model.

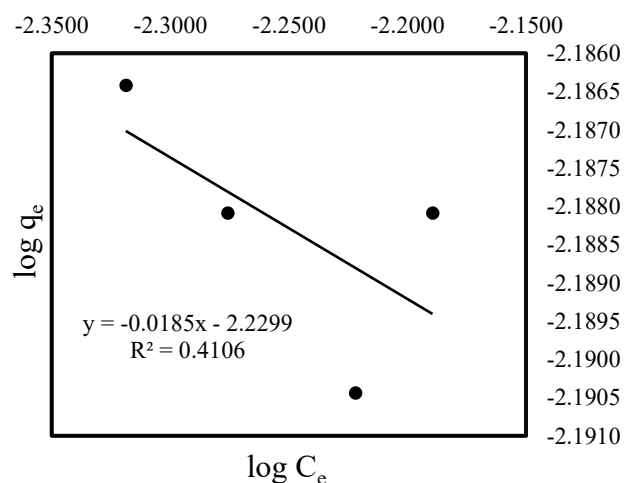


Figure 5. Freundlich adsorption isotherm plot.

The Freundlich model describes adsorption on energetically heterogeneous surfaces and is commonly associated with multilayer adsorption. The lower correlation coefficient obtained for this model suggests that surface heterogeneity had a less dominant influence on adsorption than the specific adsorption sites represented by the Langmuir model under the investigated conditions. However, the composite is structurally heterogeneous because it consists of activated carbon and

chitosan. Therefore, the isotherm results should be interpreted as an empirical description of the adsorption equilibrium rather than definitive evidence of the microscopic adsorption mechanism.

However, the adsorption performance observed in this study should not be directly extrapolated to wastewater with higher Cu^{2+} concentrations. An increase in the initial Cu^{2+} concentration results in more ions competing for a limited number of active adsorption sites. Consequently, the adsorption capacity (mg g^{-1}) may increase because more Cu^{2+} ions are available for adsorption. In contrast, the percentage removal may decrease once the available adsorption sites approach saturation. Therefore, adsorption performance depends on both the initial metal concentration and the adsorption capacity of the material.

The functional groups in the activated carbon–chitosan composite provide active binding sites for Cu^{2+} through coordination and surface complexation. Although, these functional groups are expected to remain effective at higher Cu^{2+} concentrations, however, the number of available binding sites is limited. Once these sites become saturated, additional Cu^{2+} ions remain in the solution, resulting in lower removal efficiency. Thus, treating wastewater with high Cu^{2+} concentrations may require optimization of operational parameters, such as increasing the adsorbent dosage, or extending the contact time.

The adsorption behavior at higher contamination levels could not be experimentally verified because only one initial Cu^{2+} concentration was investigated in this study. Future studies should examine the adsorption performance over a wider concentration range. Such investigations would provide a more comprehensive evaluation of the developed composite potentials for real wastewater treatment.

3.5. Determination of Adsorption Kinetics

To examine the kinetics mechanism of Cu^{2+} absorption by the water hyacinth-based activated carbon–chitosan composite, two

kinetic models were applied: the pseudo-first-order and pseudo-second-order models.

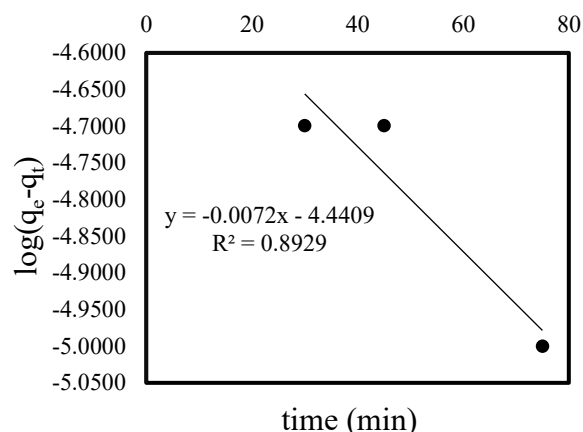


Figure 6. Pseudo-first-order kinetic plot.

Figure 6 presents the pseudo-first-order kinetic plot obtained from the relationship between $\log(q_e - q_t)$ and contact time (t). The plot generates a linear equation of $y = -0.0072x - 4.4409$ with a determination coefficient of $R^2 = 0.8929$. This R^2 value indicates that the fit between the experimental data and the pseudo-first-order model is not sufficiently strong, suggesting that this model does not accurately describe the adsorption mechanism.

The pseudo-first-order model commonly describes adsorption systems dominated by physisorption. However, the relatively low determination coefficient indicates that this model does not adequately represent the adsorption process. Since the R^2 value does not approach 1, it can be concluded that the adsorption of Cu^{2+} ions onto the water hyacinth-based activated carbon–chitosan composite does not fully follow pseudo-first-order kinetic behavior.

In contrast, Figure 7 shows the pseudo-second-order kinetic plot obtained from the relationship between t/q_t and contact time (t). The resulting linear equation, $y = 153.54x + 17.063$, has an R^2 value of 1, indicating an excellent fit between the experimental data and the pseudo-second-order model. This model suggests that the adsorption rate depends on the square of the number of active sites remaining and the concentration of the

adsorbate, which generally reflects a chemisorption mechanism [20].

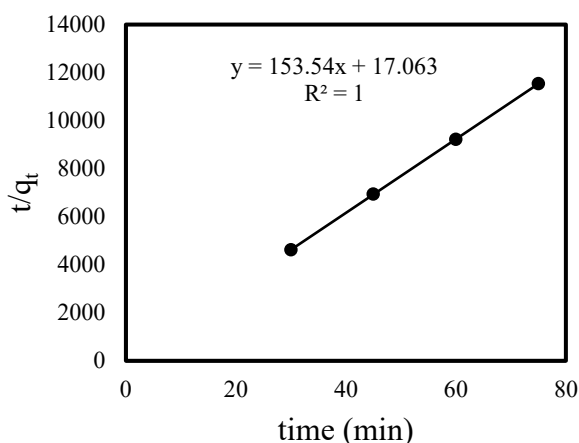


Figure 7. Pseudo-second-order kinetic plot.

Based on the comparison of the two kinetic models, the pseudo-second-order model was found to be more representative in describing the adsorption behavior of Cu^{2+} ions onto the water hyacinth-chitosan composite, as indicated by its higher R^2 value compared to the pseudo-first-order model. This result suggests that the dominant adsorption mechanism is chemical in nature (chemisorption), involving the formation of bonds between Cu^{2+} ions and the active functional groups on the adsorbent surface. Such a mechanism likely occurs through coordination bonding, in which a shared electron pair is used by the metal ion and donor atoms on the adsorbent surface.

The amino and hydroxyl groups identified by FTIR provide chemically active sites that can interact with Cu^{2+} ions through coordination, supporting the possibility of a chemisorption-dominated mechanism. Although the pseudo-second-order (PSO) model is often associated with chemisorption, it is an empirical kinetic model and cannot independently confirm the formation of chemical bonds.

The excellent fit of the PSO model, combined with the FTIR evidence of amino, hydroxyl, carbonyl, and C–O functional groups, suggests that Cu^{2+} adsorption is mainly governed by surface complexation and coordination interactions.

Regeneration and reusability of the activated carbon–chitosan composite were not evaluated. Consequently, the stability and adsorption performance over multiple adsorption–desorption cycles remain unknown. This study primarily focused on the feasibility of synthesizing the composite and evaluating its initial adsorption performance for Cu^{2+} removal.

Regeneration is an important factor in practical wastewater treatment because it affects the operational cost, environmental sustainability, and long-term applicability of an adsorbent. Chitosan-based adsorbents can be regenerated using dilute mineral acids, such as HCl or HNO_3 , or chelating agents, such as EDTA. These agents can desorb metal ions and restore a substantial portion of the adsorption capacity. However, repeated regeneration cycles may gradually reduce adsorption performance through the loss or protonation of amino ($-\text{NH}_2$) groups, chitosan leaching, or changes in the composite structure [36]. Repeated adsorption–desorption may also alter the pore structure of activated carbon and reduce the accessibility of its adsorption sites.

4. CONCLUSION

This study demonstrates that the water-hyacinth-chitosan activated carbon composite is effective as an adsorbent for reducing Cu^{2+} ions in artificial wastewater. FTIR characterization confirms the successful formation of the composite through the appearance of active functional groups such as $-\text{NH}_2$ and Si–O–Si. The optimal performance was achieved with the composite containing 1% (w/v) chitosan and a contact time of 60 minutes, yielding a Cu^{2+} reduction efficiency of 96.41%, higher than that obtained using activated carbon or chitosan alone. The Langmuir isotherm model and the pseudo-second-order kinetic model best describe the experimental data, indicating monolayer adsorption on a homogeneous surface through a chemisorption mechanism. Overall, this composite shows potential as an economical and environmentally friendly adsorbent for

the treatment of copper-containing wastewater.

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AUTHOR CONTRIBUTIONS

R.D.C: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **M.K.P:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **R.L:** Writing – review & editing, Writing – original draft, language refinement.

CONFLICTS OF INTEREST

The authors declare no competing financial interests.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES

The authors acknowledge the use of ChatGPT 5 to assist in the linguistic domain for clarity, conciseness and readability during preparation of the original manuscript. Authors confirm that AI tool was used as supportive instruments, not as substitutes for original thought or academic responsibility. Furthermore, all content has been reviewed and validated to ensure accuracy, originality, and compliance with ethical standards.

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