



Research Article

Sustainable Approach for The Removal of Cu(II) from Aqueous Solutions Using Lotus Seedpod-alginate Composite Biosorbents

Van-Tai Nguyen^{1,a}, Hue Tran Nguyen-Le^{2,a}, Hong Thi Anh Nguyen³, Nguyen-Phuong-Dung Tran⁴, Kim-Phung Ly⁵, Quoc-Khanh Huynh¹, Minh-Nhut Nguyen², Phuong Lan Tran-Nguyen^{1,*}

¹ Faculty of Mechanical Engineering, Can Tho University, Can Tho City, Vietnam

² Faculty of Chemical Engineering, Can Tho University, Can Tho City, Vietnam

³ Department of Chemistry, Can Tho University, Can Tho City, Viet Nam

⁴ Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

⁵ Stem Cell Laboratory, Department of Molecular Biology, Institute of Biotechnology and Food, Can Tho University, Can Tho City, Vietnam

^a the first two authors equally contributed to this study

*Corresponding Email: tnplan@ctu.edu.vn

Abstract

Turning waste or agricultural byproducts into valuable products has recently become a concern of scientists. In this study, the facile and cost-effective synthesis of a biocomposite derived from lotus seedpod (LS) and alginate (AG) was further applied for Cu²⁺ ion uptake from aqueous solutions. SEM images revealed the layered structures of the composites, which were thin and irregularly stacked sheets of a complex 3D network. The abundant functional groups on the surface of the LS-based material and its negative zeta potential value of -37.50 mV also facilitated efficient Cu²⁺ removal. Adsorption results revealed a Cu²⁺ adsorption efficiency (AE) and experimental capacity of 68.99% and 17.38 mg g⁻¹, respectively, after 30 min. The coefficient values of the Sips isotherm ($R^2 = 0.952$) and pseudo-second-order kinetic models ($R^2 = 0.995$) suggest that the monolayer adsorption mechanism on a heterogeneous surface is governed primarily by physicochemical interactions. Although the AEs decreased from 68.99% to 44.81% after four cycles, LSA showed strong adsorption potential, highlighting LS as a sustainable and inexpensive material for the development of low-cost and high-efficiency biocomposites for wastewater treatment. This approach supported environmental treatment and agricultural waste valorization, while the chemical and mechanical stability of the composite further confirmed its practical applicability.

ARTICLE HISTORY

Received: 23 Dec. 2025

Revised: 21 Apr. 2025

Accepted: 1 Jun. 2026

Published: 22 Aug. 2026

KEYWORDS

3D network;
Biocomposite adsorbents;
Cu²⁺ ions;
Lotus seedpod

Introduction

Water pollutants containing heavy metals, toxic dyes and organic substances, primarily resulting from the discharge of industrial and domestic effluents, are nondegradable and highly toxic even at trace concentrations, causing significant threats to both ecosystems and human health (Bayuo et al., 2022; Fotsing et al., 2020). Among them, copper (Cu) is known as a hazardous metal and causes dangerous damage to human organs

at concentrations above 0.2 mg L⁻¹ (Bayuo et al., 2022). Consequently, finding an appropriate method

for the removal of Cu²⁺ from aquatic environments is crucial. Despite the various treatment techniques, adsorption has attracted increased attention because of its cost-effectiveness, operational simplicity, and flexibility (Fotsing et al., 2020). Thus, numerous adsorbents, especially biomass-derived materials from

agricultural waste peels, have been developed on the basis of cost efficiency and environmental compatibility (Bayuo et al., 2022). Although lotus seedpod (LS) is considered an agricultural waste that causes environmental pollution, LS and its functionalized-based materials have been applied for removal processes and have shown high regeneration potential (Li et al., 2025; Liu et al., 2019). On the basis of these observations, a bioadsorbent incorporated between LS and alginate (AG) extracted from brown algae was introduced in this work. AG, a natural polysaccharide composed of α -L-guluronic and β -D-mannuronic acid units, can form water-insoluble hydrogels via ionic cross-linking with multivalent cations or acid-induced gelation, particularly the coordination of Ca^{2+} ions with oxygen atoms, leading to a stable three-dimensional network (Gao et al., 2020). AG has the potential for metal ion uptake because of its abundant hydroxyl and carboxyl functional groups; thus, AG has been extensively demonstrated to effectively recover valuable metals and remove toxic contaminants from aqueous environments (Gao et al., 2020; Mohammed et al., 2024). With respect to Cu^{2+} adsorption, the synthesized hydrogel microspheres composed of carboxymethyl cellulose, AG and graphene oxide could remove 64 mg of Cu^{2+} ions per gram of adsorbent because of the synergistic interaction between graphene oxide and the hydrogel (Allouss et al., 2020). Within 60 minutes, an eco-friendly composite of olive waste and AG also achieved maximum adsorption capacity (AC) and adsorption efficiency (AE) values of 47.20 mg g⁻¹ and 94.54%, respectively (Elboughdiri et al., 2024). However, the presence of multiple ions in solution might interfere with the removal performance of materials, resulting in low ACs. In particular, a mesoporous HNT-BC@Alg biopolymer derived from halloysite nanotubes, biochar and AG presented maximum ACs of 2.85 mg g⁻¹, 6.96 mg g⁻¹, 16.87 mg g⁻¹, and 26.49 mg g⁻¹ for nickel (Ni), cadmium (Cd), Cu, and lead (Pb), respectively (Hassan et al., 2021). Additionally, LS pretreatment was necessary before composite synthesis because of the release of functional groups in complex lignocellulose structures, including cellulose, hemicellulose and lignin, leading to improved removal performance of heavy metal ions (Li et al., 2025; Mohammed et al., 2024). LS-derived biochar and LS-treated with citric acid resulted in ACs of 20 mg g⁻¹ (carbamate pesticides) and 90.89 mg g⁻¹ (dye), confirming the efficacy of LS-based materials for the removal of diverse pollutants (Barik et al., 2025). Furthermore, LS functionalized with carboxyl groups resulted in a high AC for Pb^{2+} removal, which was 111.1 mg g⁻¹ in 10 min (Liu et al., 2019).

As previously noted, the feasibility of using LS to produce effective bioadsorbents was investigated

without the need for multiple chemical pretreatment steps of the feedstock, which reduced time and energy consumption, improved cost-effectiveness, and promoted a sustainable approach. Furthermore, spherical bioadsorbent beads (LSA), formed by integrating LS with AG, were successfully developed, facilitating easy recovery after adsorption and enhancing practical applicability. LSA exhibited synergistic effects derived from its constituent materials, improved the adsorption performance, and enabled reusability for Cu^{2+} removal. The composites were synthesized in a straightforward manner with various parameters, including the AG concentration, CaCl_2 concentration, cross-linking time, and mass ratio of LS to AG (g g⁻¹). Moreover, the Cu^{2+} adsorption performance was evaluated under different parameters, including the Cu^{2+} concentration, composite dose, contact time, competing ions, and type of water source. The LSA adsorption mechanism was further elucidated through kinetics, isotherm models and thermodynamic studies, whereas the regeneration cycle was implemented to assess LSA sustainability. In addition, the chemical and mechanical stability and the risk of Cu^{2+} leaching of LSA composites after adsorption were determined.

Materials and methods

All the chemicals used in this work are described in detail in Supplementary Text S1. The preparation of the treated LS and LSA biocomposites is described in Supplementary Text S2 and Supplementary Table S1, whereas the fabrication of LSA followed previous methods with some modifications (Figure 1 and Supplementary Table S2) (Elboughdiri et al., 2024; Fotsing et al., 2020). The physicochemical properties of the materials were characterized through analytical techniques, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), atomic absorption spectrometry (AAS), the Brunauer–Emmett–Teller (BET) method, the isoelectric pH (pH_i) and the zeta potential (Supplementary Text S3). The pH_i of LSA was also determined according to a previous method (Nguyen et al., 2020). Additionally, the mechanical stability, adsorption, and regeneration of LSA are described in Supplementary Texts S4, S5 and S6, respectively. Isotherm (Langmuir, Freundlich and Sips) and kinetic (pseudofirst-order (PFO) and pseudosecond-order (PSO)) models were employed to elucidate the mechanism underlying the interaction between LSA and Cu^{2+} ions (Table 1) (Maryanti et al., 2020; Wang et al., 2018). In addition, the thermodynamic properties of LSA, including the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), were explored (Saha and Chowdhury, 2011).

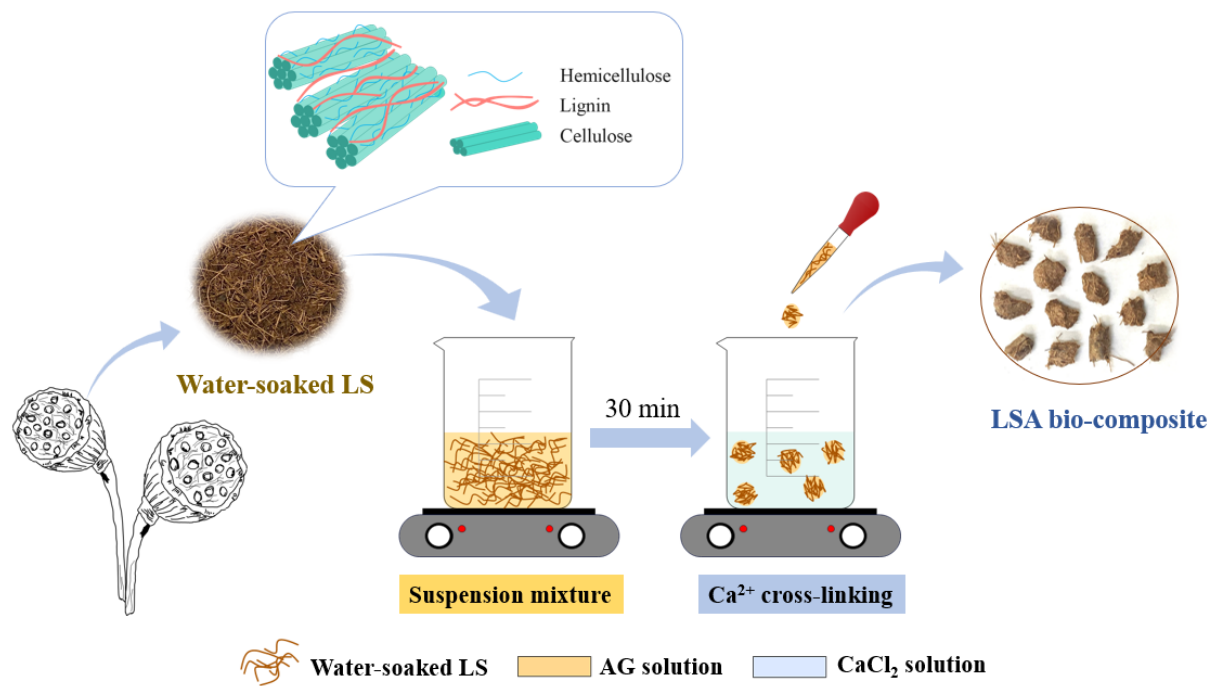


Figure 1 Synthesis procedure of LSA bio-composite.

Table 1 Adsorption isotherm and kinetic models of LSA12

Adsorption models	Nonlinear equation	Value	Meaning
Isotherm			
Langmuir	$AC = \frac{AC_{max} \times K_L \times C_e}{1 + K_L \times C_e}$ (Eq.1)	$R^2 = 0.942$	AC and AC_{max} ($mg\ g^{-1}$): equilibrium and maximum adsorption capacity K_L ($L\ mg^{-1}$): Langmuir empirical constant R_L : Langmuir parameter
	$R_L = \frac{1}{1 + K_L \times C_e}$ (Eq.2)	$K_L = 0.100\ (L\ mg^{-1})$	
		$AC_{max} = 36.680\ (mg\ g^{-1})$ $0.803 \leq R_L \leq 0.289$	
Freundlich	$AC = K_F C_e^{\frac{1}{n}}$ (Eq.3)	$R^2 = 0.921$ $n_F = 3.150$ $K_F = 7.88\ (L\ g^{-1})$	K_F ($L\ g^{-1}$): Freundlich constant n : the adsorption intensity
Sips	$AC = \frac{AC_s \times a_s \times C_e^n}{1 + a_s \times C_e^n}$ (Eq.4)	$R^2 = 0.952$ $AC_s = 32.290\ (mg\ g^{-1})$ $a_s = 0.134$ $n = 0.975$	AC_s ($mg\ g^{-1}$): maximum adsorption capacity of Sips model a_s : Sips isotherm model constant n : adsorption intensity
Kinetics			
PFO	$AC_e = AC \times (1 - e^{(-k_1 \times t)})$ (Eq.5)	$R^2 = 0.982$ $k_1 = 0.151\ (1\ min^{-1})$ $AC_e = 18.26\ (mg\ g^{-1})$	AC_e and AC ($mg\ g^{-1}$): equilibrium adsorption capacity and adsorption capacity at t time k_1 ($1\ min^{-1}$): PFO rate constant t (min): adsorption time
PSO	$AC_e = \frac{AC^2 \times k_2 \times t}{1 + AC^2 \times k_2 \times t}$ (Eq.6)	$R^2 = 0.995$ $k_2 = 0.032\ (g\ mg^{-1}\ min^{-1})$ $AC_e = 18.28\ (mg\ g^{-1})$	k_2 ($g\ mg^{-1}\ min^{-1}$): PSO rate constant t (min): adsorption time

Results and discussion

1) Effects of treatment methods on Cu²⁺ removal efficiency

Before composite synthesis, the various LS treatment methods were initially evaluated because of their significant influence on removal performance. The efficiency of the conventional and subcritical methods on Cu²⁺ removal using treated LS indicated that in the presence of deionized water, differences in AE were observed, indicating the effectiveness of the conven-

tional method (Figure 2). The highest AE of 59.54% was achieved under conventional treatment conditions: 90 °C, 30 min and a ratio of LS to water = 1:15 g mL⁻¹, whereas no difference in adsorption performance for all treated samples under subcritical conditions was detected (Figure 2a). Compared with the conventional method, the subcritical condition did not increase the AE because Cu²⁺ ions were primarily captured via functional groups in the LS through electrostatic interactions (Figure 2b) (Liu et al., 2019).

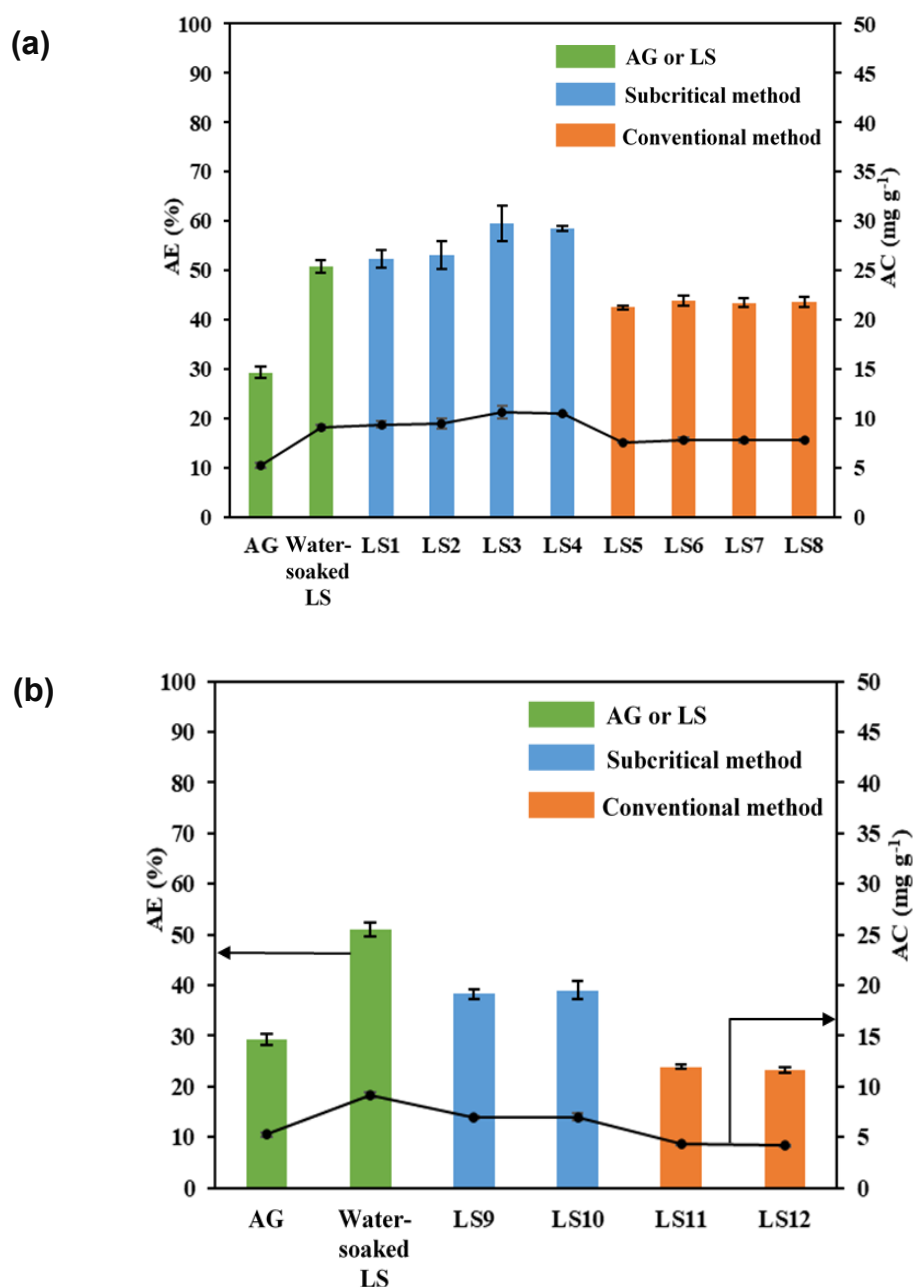


Figure 2 The effect of subcritical and conventional treatment methods of LS on the Cu²⁺ removal using H₂O (a) and H₂SO₄ (b) at the fixed adsorption conditions: pH 5.5, dose of 1.0 g L⁻¹, Cu²⁺ concentration of 20 mg L⁻¹ and 30 min.

Under these treatment conditions, the loss of functional groups and adsorption sites might have occurred, resulting in the lower AEs of the treated samples for the conventional method. Similar reasons have been reported for the changes in various chemical transformations in plants under subcritical water conditions (Mikucka et al., 2022). During severe operations (high pressure and temperature), water could hydrolyze and oxidize LS into new water-soluble phenolic compounds that were unable to capture Cu²⁺. Compared with that of the treated LS, the AE of the water-soaked LS reached 50.87%. Thus, further chemical and subcritical treatments were not necessary before LSA synthesis in this work.

The bands at 3,439–3,427 cm⁻¹ and 2,929–2,924 cm⁻¹ corresponded to the stretching vibrations of the O–

H bond and C–H group, respectively (Figure 3a) (Liu et al., 2019). In the AG spectrum, the characteristic peaks at 1,620 cm⁻¹, 1,426 cm⁻¹, 1,030 cm⁻¹, and 776 cm⁻¹ corresponded to undissociated carboxylic groups, symmetric stretching of free carboxylate groups, asymmetric C–O–C stretching, and C–O stretching of mannuronic acid units, respectively (Adzmi et al., 2012; Liu et al., 2019). Peaks at 1,729 cm⁻¹ and 1,522 cm⁻¹ in the LS spectrum were attributed to the C=O bond of esters (hemicellulose) and the C=C stretching in aromatic rings, whereas the C=O or C=C stretching of polyphenols and flavonoids appeared at 1,617 cm⁻¹ (Li et al., 2025; Liu et al., 2019). The presence of tannins, flavonoids and glycosides was also indicated at 1,380 cm⁻¹. The C–O bond of esters in hemicellulose was attributed to 1,247 cm⁻¹, as the C–O in crystalline

cellulose and flavonoids ranged from 1,160–1,068 cm^{-1} (Li et al., 2025; Liu et al., 2019). The surface morphology exhibited a rough surface with few gaps and a dense and relatively homogeneous structure of AG, causing a reduction in the surface area of AG and interference from the Cu^{2+} adsorption process (Lei et al., 2008; Mohammed et al., 2024). However, LS had a layered morphology with multiple stacked sheets, abundant gaps, and pores, characteristic of the lignocellulose structure (Figure 3b–c) (Li et al., 2025; Liu et al., 2019).

2) Effects of parameters on LSA synthesis

2.1) Effects of AG concentration

An important factor influencing Cu^{2+} removal performance and composite properties was the AG concentration. An increase in AG loading caused dramatic decreases in AE (15.30%) and AC (2.82 mg g^{-1}) (Figure 4a). High AG concentrations (2.0%–5.0%) were unfavorable for Cu^{2+} uptake because of the

compact structure of AG and the encapsulation of internal pores and functional groups of LS by AG, causing a reduction in the surface area and number of adsorption sites (Gao et al., 2020; Mohammed et al., 2024). The moisture loss of LSA2 was approximately 15.16% greater because LSA2 contained hydrophilic Ca^{2+} -alginate, which retained water in the polymer matrix during the first stage (Figure 4b–c) (Fajardo et al., 2012). At 200 $^{\circ}\text{C}$ –400 $^{\circ}\text{C}$, the decomposition of LS occurred, corresponding to a weight loss of 38.98%, whereas the loss of LS and breakage of some typical bonds in AG (LSA2) accounted for 48.11% (Hornung et al., 2024; Liu et al., 2015). Furthermore, the lignin in both materials was degraded at 400 $^{\circ}\text{C}$ –500 $^{\circ}\text{C}$ (Cagnon et al., 2009). [21]. After 500 $^{\circ}\text{C}$, the residual matter was obtained at 48.81% (LS) and 33.81% (LSA2), which were partially undecomposed lignin and ash content after the complete combustion of organic matter (Mukherjee et al., 2022).

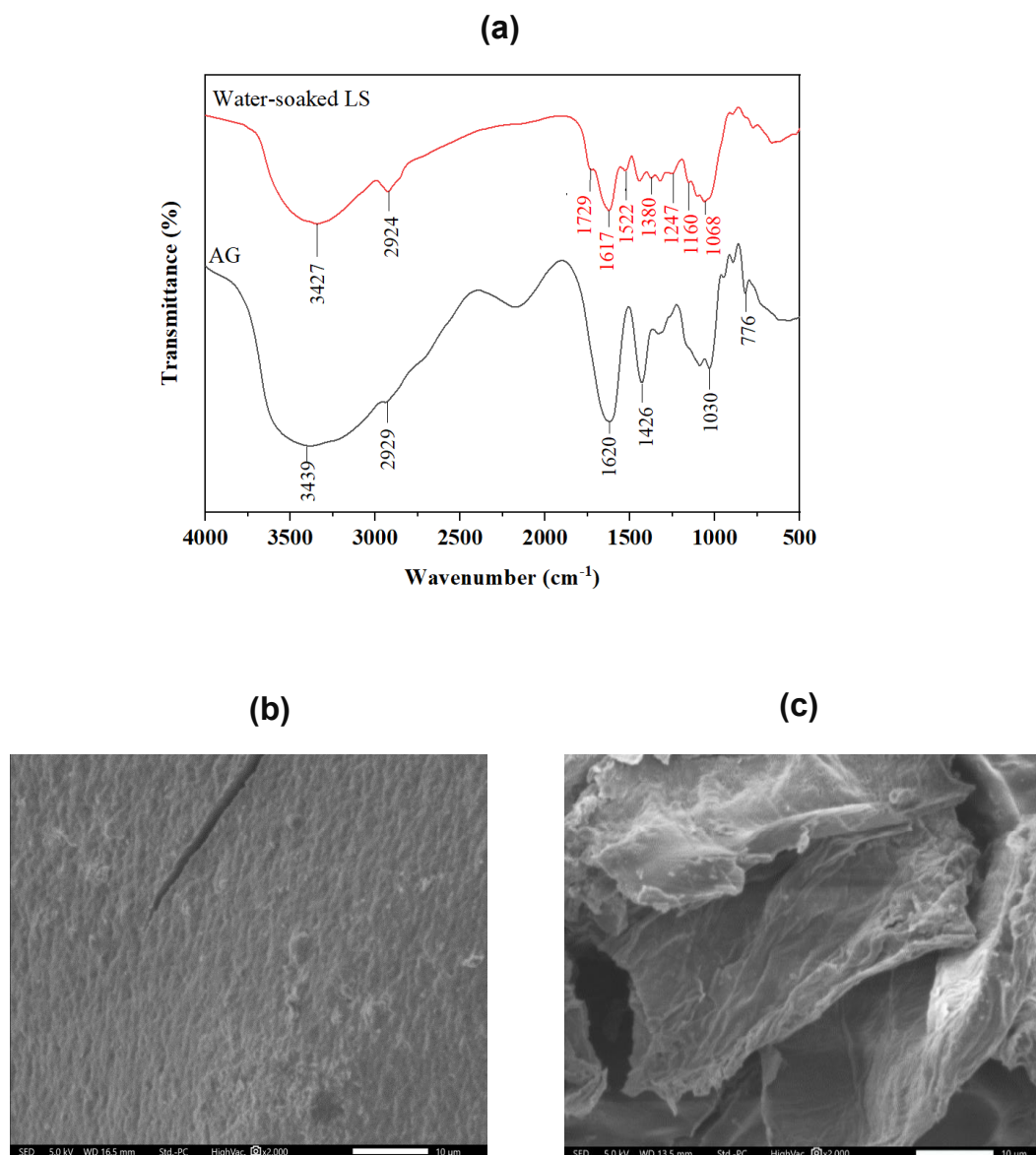


Figure 3 FTIR spectra of AG and LS (a); SEM images of AG (b) and LS (c).

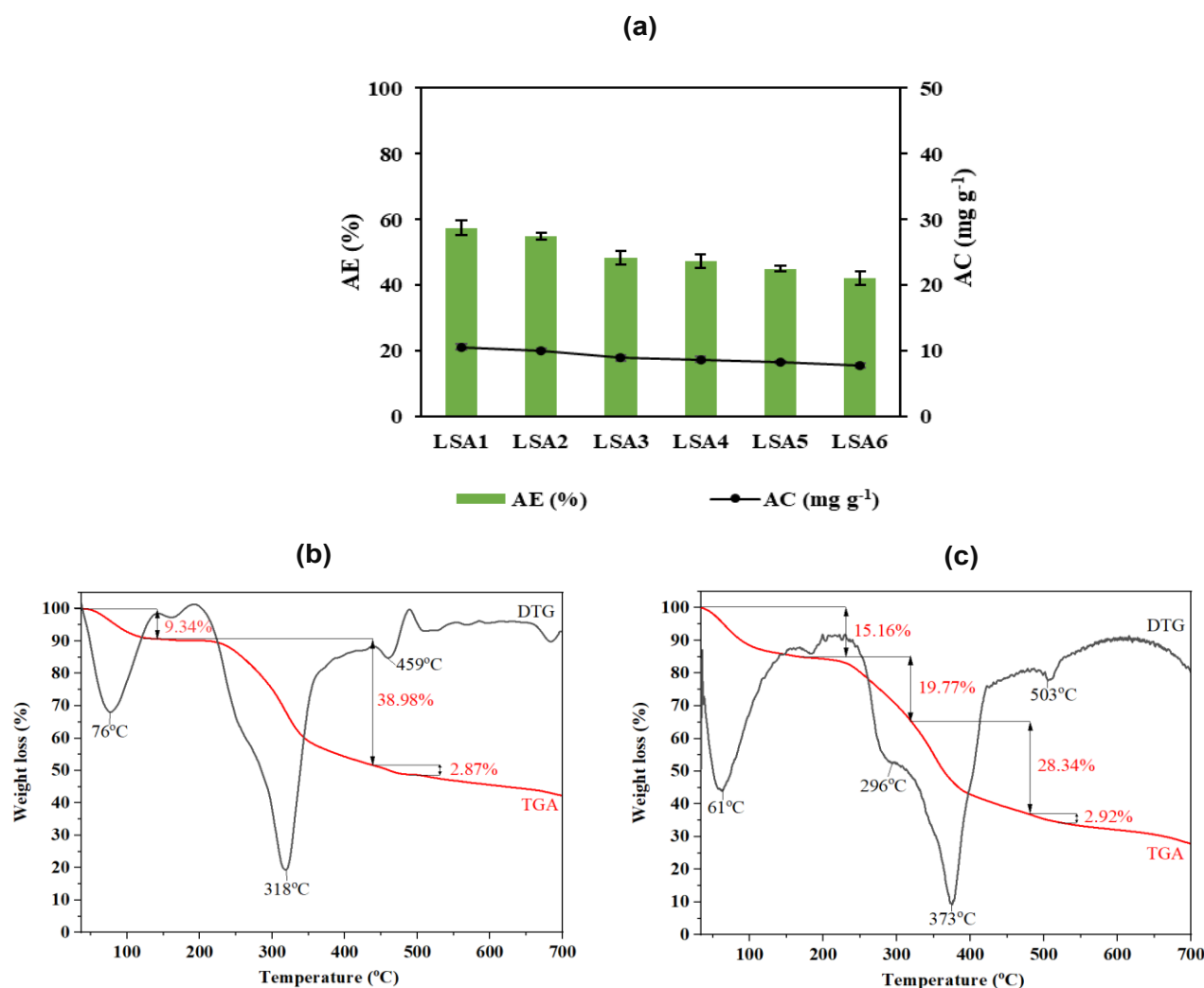


Figure 4 Effect of AG concentration (1.0%–5.0%) on the removal of Cu^{2+} at the synthesis conditions: CaCl_2 concentration of 2.0%, cross-linking time of 120 min and mass ratio of LS:AG = 2.0 : 1.0 (g g^{-1}) and the fixed adsorption conditions: pH 5.5, dose of 1.0 g L^{-1} , Cu^{2+} concentration of 20 mg L^{-1} and 30 min (a); TGA results of LS (b) and LSA2 (c).

To further clarify the components in the LSA, an increase in the AG loading led to more AG losses of 16.77% (LSA1) and 24.01% (LSA4) (Supplementary Figure S1a–b). Moreover, the mass loss of cellulose and hemicellulose (30.04% and 21.66%, respectively) and lignin (4.36% and 3.51%, respectively) in LSA1 and LSA4 was similar to that in LSA2 (Cagnon et al., 2009; Hornung et al., 2024; Liu et al., 2015). In addition, the characteristic functional groups in LSA exhibited increased vibrations at $1,640\text{--}1,619 \text{ cm}^{-1}$, $1,419\text{--}1,416 \text{ cm}^{-1}$ and $1,032\text{--}1,022 \text{ cm}^{-1}$, which are typical groups of AGs (Supplementary Figure S1c) (Adzmi et al., 2012; Liu et al., 2019). There was less change in the functional groups in all of the composites. The dramatic effect of the AG concentration on the LSA composition was determined by the increase in Ca^{2+} content ($191.5 \text{ mg g}^{-1}\text{--}353.46 \text{ mg g}^{-1}$), which indicated cross-linking between the Ca^{2+} and -COO^- groups in AG (Supplementary Table S3) (Gao et al., 2020; Merakchi et al., 2019). A relatively high AG concentration reduced the porosity of LSA and hindered Cu^{2+}

diffusion into the composites (Gao et al., 2020; Mohammed et al., 2024). To improve the structural porosity and enhance the Cu^{2+} uptake of LSA, a 1.5% AG concentration (LSA2) was selected for further experiments.

2.2) CaCl_2 concentration

The presence of Ca^{2+} in LSA promoted cross-linking, enhancing structural stability and removal performance. A slight increase in the AC and AE by 5.06% and 0.93 mg g^{-1} , respectively, was observed for LSA8 (Figure 5a). However, higher CaCl_2 concentrations caused a slight decrease in AE (10.04%) and AC (1.85 mg g^{-1}), which was attributed to a denser structure that limited the accessibility of active adsorption sites for Cu^{2+} (Gao et al., 2020; Mohammed et al., 2024). These tendencies were linked to the incorporation of LS and Ca^{2+} , where LSA7 at a 0.1% CaCl_2 concentration formed an unstable gel network, whereas LSA8 exhibited a more uniform, stable and porous structure with a greater surface area (Gao et al.,

2020). The actual Ca^{2+} concentration increased between 18.73 mg g^{-1} (LSA7) and 35.43 mg g^{-1} (LSA8) (Supplementary Table S3) and further increased to 65.24 mg g^{-1} – 230.58 mg g^{-1} , corresponding to increasing CaCl_2 concentration (0.4% – 2.0%). Excess Ca^{2+} ultimately reduced the adsorption performance by competing with Cu^{2+} for available functional groups of LSA (Abasalizadeh et al., 2020; Macena et al., 2025). The characteristic functional groups of LSA revealed that a higher CaCl_2 concentration led to a sharper and more intense band at 1030 cm^{-1} , which reflected a change in the polysaccharide structure and an increase in the C–O–C stretching band (Supplementary Figure S2a) (Musumba et al., 2020). Smaller changes in the wavenumbers at $1,640 \text{ cm}^{-1}$ and $1,530 \text{ cm}^{-1}$, which are attributed to the crosslinking between the Ca^{2+} and $-\text{COO}^-$ groups of AG, were detected at LSA2, indicating Ca^{2+} saturation on the composite surface (Li et al., 2016). Owing to the strong effect of Ca^{2+} on the properties of the LSA structure, a 0.2% Ca^{2+} concentration (LSA8) was chosen for further experiments.

3) Cross-linking time

A small change in the adsorption performance during the cross-linking time (15 min – 360 min) was shown at fixed CaCl_2 and AG concentrations (Figure 5b) (Gao et al., 2020; Mohammed et al., 2024), indicating that a prolonged cross-linking time was unfavorable for additional cross-linking formation. The amount of Ca^{2+} incorporated into the composites (LSA12–LSA15) at various cross-linking times also confirmed the insignificant change in Ca^{2+} content (30.60 mg g^{-1} – 37.93 mg g^{-1}) (Supplementary Table S3). Thus, the cross-linking network in LSA reached saturation after 15 min (LSA12) because of the rapid interaction between the Ca^{2+} and $-\text{COO}^-$ groups of AG (Gao et al., 2020).

4) Mass ratio of LS to AG

The factor that most influenced the adsorbent composition and removal ability was the mass ratio of LS to AG. Because of the electrostatic interactions between Cu^{2+} and the functional groups in LS, the AE and AC dramatically increased by approximately twofold (32.80% – 69.67%) and 8.44 mg g^{-1} (7.51 mg g^{-1} – 15.95 mg g^{-1}), respectively (Figure 5c) (Liu et al., 2019). Moreover, an increase in the LS loading improved the porosity and structural openness of LSA, facilitating better diffusion and interaction between Cu^{2+} and the adsorption sites (Li et al., 2025; Mohammed et al., 2024). However, a further increase in the weight ratio of 5.0:1.0 (g g^{-1}) (LSA19) did not improve the removal performance owing to saturation of the adsorption sites. The zeta potential values of AG, LS, LSA16 and LSA12 were -44.77 mV , -23.40 mV , -34.60 mV and -37.50 mV , respectively, facilitating uptake through electrostatic interactions and aligning with previous works (Alallam et al., 2025; Gao et al., 2020;

Li et al., 2016; Liu et al., 2019). Moreover, an increase in the cellulose and hemi-cellulose content from 22.93% (LSA16) to 28.34% (LSA12) indicated that more functional groups were present in LSA12 (Supplementary Figure S2b and Figure 4). Hence, LSA12 was selected as the optimal composite for further studies.

a) Characterization of LSA12

The surface morphology of LSA12 featured thin, irregularly stacked sheets forming a complex 3D network with grooves, gaps, and voids (Figure 6a–c) (Li et al., 2025; Liu et al., 2019), which were coated with a smooth chelation-derived layer that enhanced mechanical stability and durability (Gao et al., 2020; Mohammed et al., 2024). The N_2 adsorption–desorption isotherm showed a hysteresis loop starting at $P/P_0 = 0.8$, characteristic of an IUPAC type IV isotherm and indicative of N_2 condensation in narrow mesopores (Figure 6d). The composite exhibited micro/mesoporous properties, with an average pore size of 1.08 nm (Sing, 1985). Additionally, the low surface area ($0.28 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.002 \text{ cm}^3 \text{ g}^{-1}$) were attributed to structural shrinkage and densification (Mohammed et al., 2024), suggesting that Cu^{2+} removal was governed primarily by functional group adsorption rather than pore filling. The formation of LSA was proposed on the basis of hydrogen bonding and chelation (Figure 6e). Initially, the composite was generated via hydrogen bonding between the functional group in AG and $-\text{OH}$ in LS (Hart et al., 2023). Subsequently, an “egg-box” structure was established through chelation between the polyguluronate units in AG and Ca^{2+} (Abasalizadeh et al., 2020; Merakchi et al., 2019). Overall, LSA exhibited a flexible and durable structure with abundant functional groups, enabling the effective removal of Cu^{2+} from contaminated wastewater.

Under acidic conditions, the protonation of $-\text{COO}^-$ groups reduced electrostatic repulsion, causing a retractive network and a lower swelling ratio of approximately 800% (Supplementary Figure S3a–b). At pH 5–7, deprotonation increased chain repulsion, leading to network expansion and a maximum swelling ratio of 1261% (Shi et al., 2014). Under alkaline conditions, high OH^- concentrations further enhanced repulsion with $-\text{COO}^-$ groups and facilitated ion exchange between Ca^{2+} and Na^+ , disrupting the cross-linked structure and causing excessive swelling with partial structural weakening (Fajardo et al., 2012; Shi et al., 2014). These phenomena agreed with the observed visual changes in LSA12 across pH conditions relative to the initial LSA12. Bead sizes noticeably increased from acidic to neutral pH, whereas structural deformation occurred under alkaline conditions, indicating partial breakdown of the cross-linked network. Agitation tests over 1440 min indicated

only slight weight loss (1.65% - 5.52%), confirming the good mechanical stability of LSA12 (Supplementary Figure S3c–d). The bead morphology remained significantly unchanged, with no evident disintegration.

Overall, LSA12 demonstrated robust stability under agitation, supporting its potential for wastewater treatment applications.

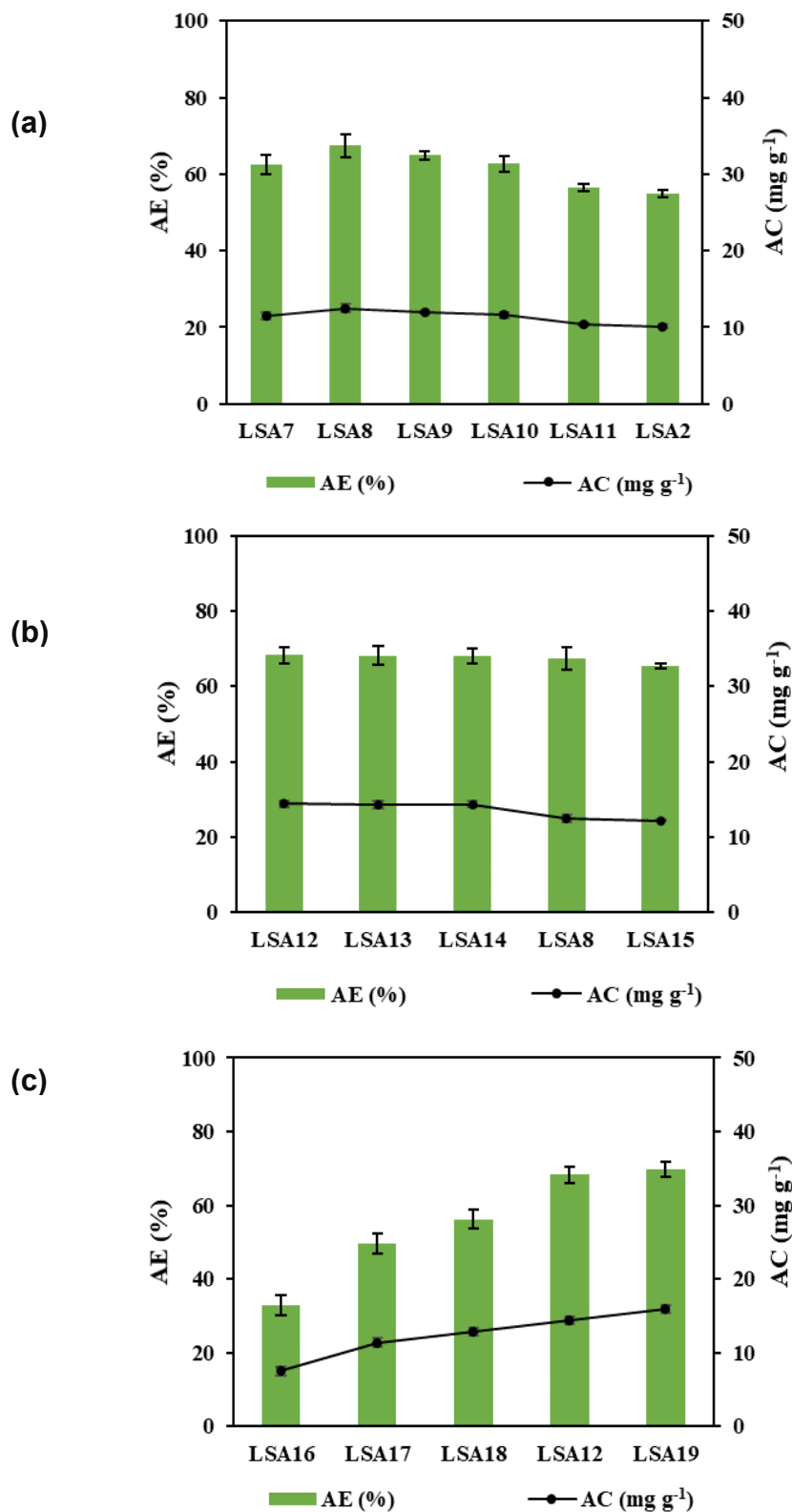


Figure 5 Effect of CaCl_2 (0.1%–2.0%) at the synthesis conditions: AG concentration of 1.5% and a ratio of LS:AG = 2.0:1.0 (w/w) in 120 min (a); effect of cross-linking time (15 min–360 min) at the synthesis conditions: a weight ratio of LS:AG = 2.0 : 1.0 (w/w), the AG concentration of 1.5% and CaCl_2 concentrations of 0.2% (b); effect of weight ratio of LS:AG (0.2:1.0–5.0:1.0, g g⁻¹) at the synthesis conditions: AG concentration of 1.5% and CaCl_2 concentration of 0.2% for 15 min (c) on the removal of Cu^{2+} at the adsorption conditions: pH 5.5, dose of 1.0 g L⁻¹, Cu^{2+} concentration of 20 mg L⁻¹ and 30 min.

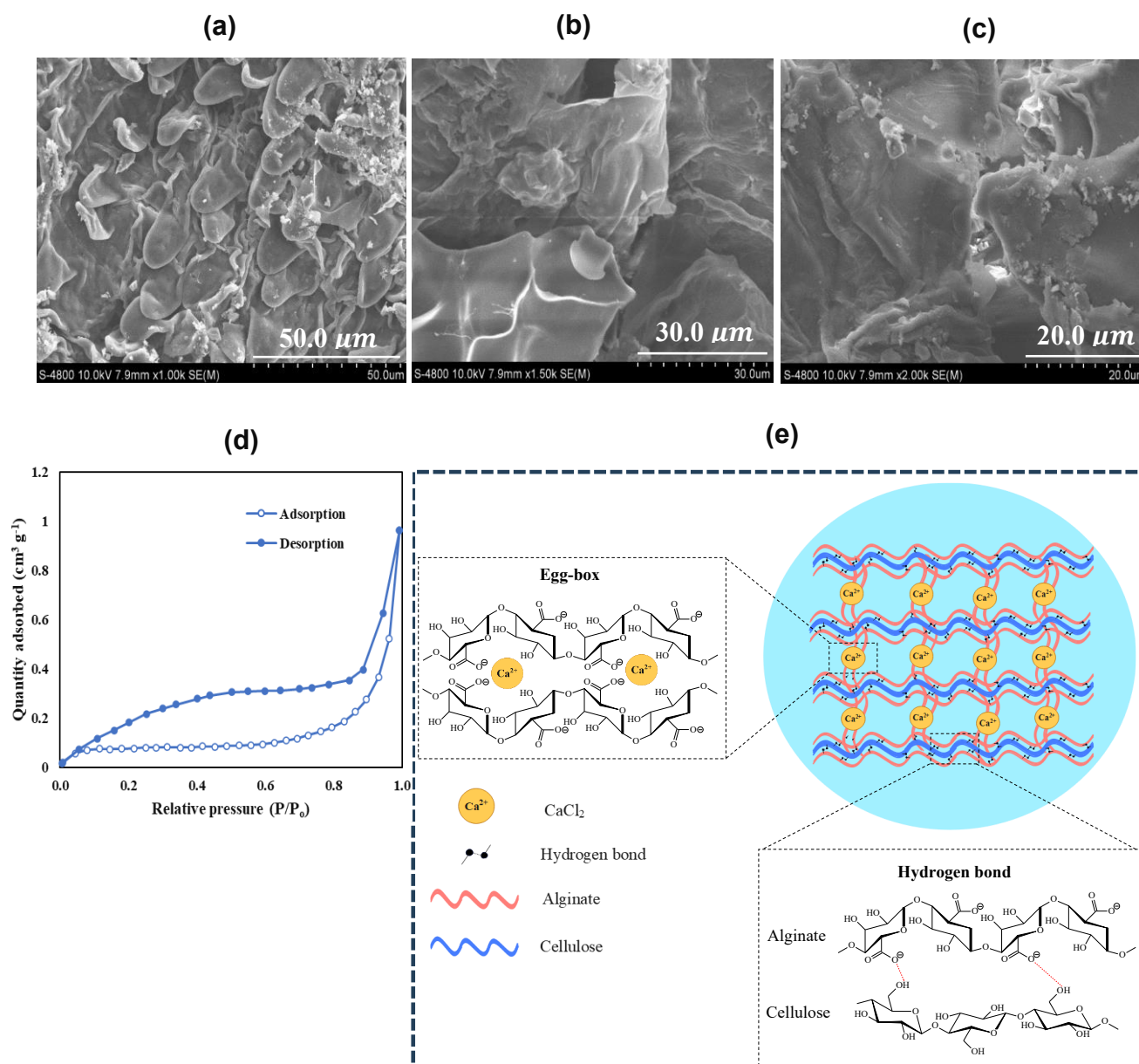


Figure 6 SEM images of LSA12 bio-composite at different magnifications: 1.00k (a), 1.50k (b) and 2.00k (c); BET results of LSA12 bio-composite (d); The proposed synthesis mechanism of LSA bio-composite.

b) Evaluation of Cu²⁺ removal using LSA

1) Adsorption process conditions

The pHi of LSA12 was 6.22, which was characterized by a positively charged surface at a pH < 6.22 and vice versa (Supplementary Figure S4). Theoretically, Cu²⁺ removal was more favorable at pH > 6.22 because of reduced electrostatic repulsion and decreased competition from H⁺ ions. In this work, the working condition at pH 5.5 was selected for further investigations because of the formation of Cu(OH)₂ in media with a pH above 5.5 (Elboughdiri et al., 2024; Wang et al., 2022).

The initial metal concentration significantly influenced the adsorption process; in particular, the AE values decreased by 2.6 times (78.67% - 29.86%) at higher metal concentrations (10 mg L⁻¹ - 100 mg L⁻¹). At low concentrations, Cu²⁺ ions easily reach available adsorption sites and functional groups in the composite

(Figure 7a) (Salam et al., 2011). In addition, the high amount of Cu²⁺ loaded at a specific adsorbent dose resulted in a lack of adsorption site vacancies. Conversely, the AC concentration noticeably increased from 10.09 mg g⁻¹ to 30.63 mg g⁻¹. Thus, a 50 mg L⁻¹ Cu²⁺ concentration was chosen for further investigations.

With respect to the composite dosage, a high amount of adsorbent caused an increase in the AE concentration (35.36% - 80.73%), whereas the AC concentration gradually decreased (37.96 mg g⁻¹ - 8.14 mg g⁻¹) (Figure 7b). At low dosages, the adsorption rapidly occurred owing to the easy diffusion of Cu²⁺ to the composite surface. The Cu²⁺ concentration in the solution was constant, whereas an increase in the LSA dosage was applied, causing a decrease in the amount of Cu²⁺ adsorbed per unit mass of LSA (Sheraz et al., 2024). Thus, a 2.0 g L⁻¹ dosage was selected for

subsequent experiments to achieve effective Cu^{2+} removal and economic use.

The contact time for Cu^{2+} adsorption was determined at equilibrium. Slight increases in AEs (61.87% – 68.99%) and ACs (16.28 mg g^{-1} - 17.38 mg g^{-1}) were obtained from 15 min to 30 min (Figure 7c). The initial rapid adsorption was attributed to physical mass transfer between the solid and liquid phases [1], followed by a plateau after 30 min, indicating saturation of the adsorption sites. Compared with the longer equilibrium times reported elsewhere (180 min–360 min) (Elboughdiri et al., 2024; Fotsing et al., 2020; Hassan et al., 2021), 30 min was selected as the optimal contact time for highly efficient and time-saving adsorption.

To extend the applicability of LSA to real wastewater, the effects of interfering metal ions and different water sources were evaluated. The presence of Ca^{2+} and Mg^{2+} resulted in the most pronounced reductions in AEs, by 23% and 13%, respectively, because of the high charge density of divalent ions and their stronger interaction with negatively charged functional groups on LSA12 (Figure 7d) (Abasalizadeh et al., 2020; Macena et al., 2025). Ca^{2+} exhibited the strongest competitive effect, forming chelates with $-\text{COOH}$ groups in AG and occupying available adsorption sites on LSA (Gao et al., 2020; Merakchi et al., 2019). This trend was consistent with the results of previous works, which revealed the lower competitive ability of monovalent ions (Na^+ and K^+) than that of divalent ions (Ca^{2+} and Mg^{2+}) (Wang et al., 2018). Furthermore, the Cu^{2+} removal efficiency decreased in both tap water and river water relative to that in deionized water (Figure 7e), reaching approximately 58.75% and 53.75%, respectively. This reduction was due to the presence of coexistent ions and dissolved organic matter, which hindered Cu^{2+} access to the adsorption sites (Abasalizadeh et al., 2020; Macena et al., 2025; Wang et al., 2018). Nevertheless, the limited decrease in AEs reflected the stable performance of LSA and its potential for Cu^{2+} removal from real wastewater.

2) Adsorption isotherm and kinetic models

The mechanism underlying the interaction between LSA12 and Cu^{2+} was elucidated via isotherm and kinetic models. The calculated R_L values indicated that Cu^{2+} adsorption was favorable within the investigated concentration range (Table 1) (Maryanti et al., 2020). The n_F value of 3.15 indicated good adsorption characteristics (Humpola et al., 2013). Moreover, the coefficient values (R^2) were in the following order: Sips (0.952) > Langmuir (0.942) > Freundlich (0.921), indicating that Cu^{2+} was adsorbed onto LSA12 through heterogeneous, monolayer, and independent adsorption processes (Fotsing et al., 2020; Maryanti et al., 2020). Nevertheless, the AC_{max} (36.680 mg g^{-1}) and AC_s (32.290 mg g^{-1})

indicated the favorable ability of the composite to adsorb Cu^{2+} . The similar values between the AC_s and experimental AC (30.627 mg g^{-1}) at a Cu^{2+} concentration of 100 mg L^{-1} confirmed the good fit of the Sips model. In addition, the adsorption mechanism was investigated by fitting the data to the PFO and PSO kinetic models. Owing to the higher R^2 (0.995), the PSO model better described the adsorption process. Cu^{2+} adsorption onto LSA12 is governed primarily by a chemisorption mechanism and the formation of strong interactions between LSA12 and metal ions (Bullen et al., 2021). Moreover, the AC_e value of PSO (18.280 mg g^{-1}) was consistent with the experimental AC value at 1440 min (17.380 mg g^{-1}), indicating that the adsorption rate is highly controlled by the availability of active sites on the adsorbent (Bullen et al., 2021).

2.1) Adsorption thermodynamics

These negative ΔG values between $-1.14 \text{ kJ mol}^{-1}$ and $-4.83 \text{ kJ mol}^{-1}$ demonstrated the spontaneous adsorption process from 303 K to 323 K (Table 2). Moreover, the ΔH value ($-54.67 \text{ kJ mol}^{-1}$) indicated an exothermic adsorption process, whereas the negative value of ΔS ($-0.165 \text{ kJ mol}^{-1} \text{ K}^{-1}$) revealed a reduction in randomness during the adsorption process and a significant decrease in the number of ions in the solution after removal (Nguyen et al., 2020). The Cu^{2+} ions retained on the LSA12 surface evinced the ordered system because of the oriented structure of ions fixed at specific adsorption sites (Cano-Salazar et al., 2022; Saha and Chowdhury, 2011). The physico-chemical adsorption process was more predominant than the physical or chemical adsorption processes were in this work (Saha and Chowdhury, 2011). Thermodynamic analysis of Cu^{2+} adsorption revealed a spontaneous process, as evidenced by negative ΔG values, with ΔH and ΔS varying across the investigated temperatures (Elboughdiri et al., 2024; Nguyen et al., 2020; Marrane et al., 2022; Santos et al., 2024). Adsorbents, including thiosemicarbazide-modified cellulose and modified plant stem bark, had negative ΔH values ($-50.93 \text{ kJ mol}^{-1}$ and $-48.10 \text{ kJ mol}^{-1}$, respectively) and negative ΔS values ($-143.507 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and $-0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively), indicating strongly exothermic adsorption with a physico-chemical mechanism (Nguyen et al., 2020; Santos et al., 2024). In contrast, the high ΔH value ($-11.06 \text{ kJ mol}^{-1}$) indicated predominantly physical adsorption using cellulose-g-hydroxyapatite (Marrane et al., 2022). Moreover, an olive waste powder/AG composite exhibited a favorable endothermic process, with positive values of ΔH ($15.73 \text{ kJ mol}^{-1}$) and ΔS ($0.058 \text{ kJ mol}^{-1} \text{ K}^{-1}$) (Elboughdiri et al., 2024).

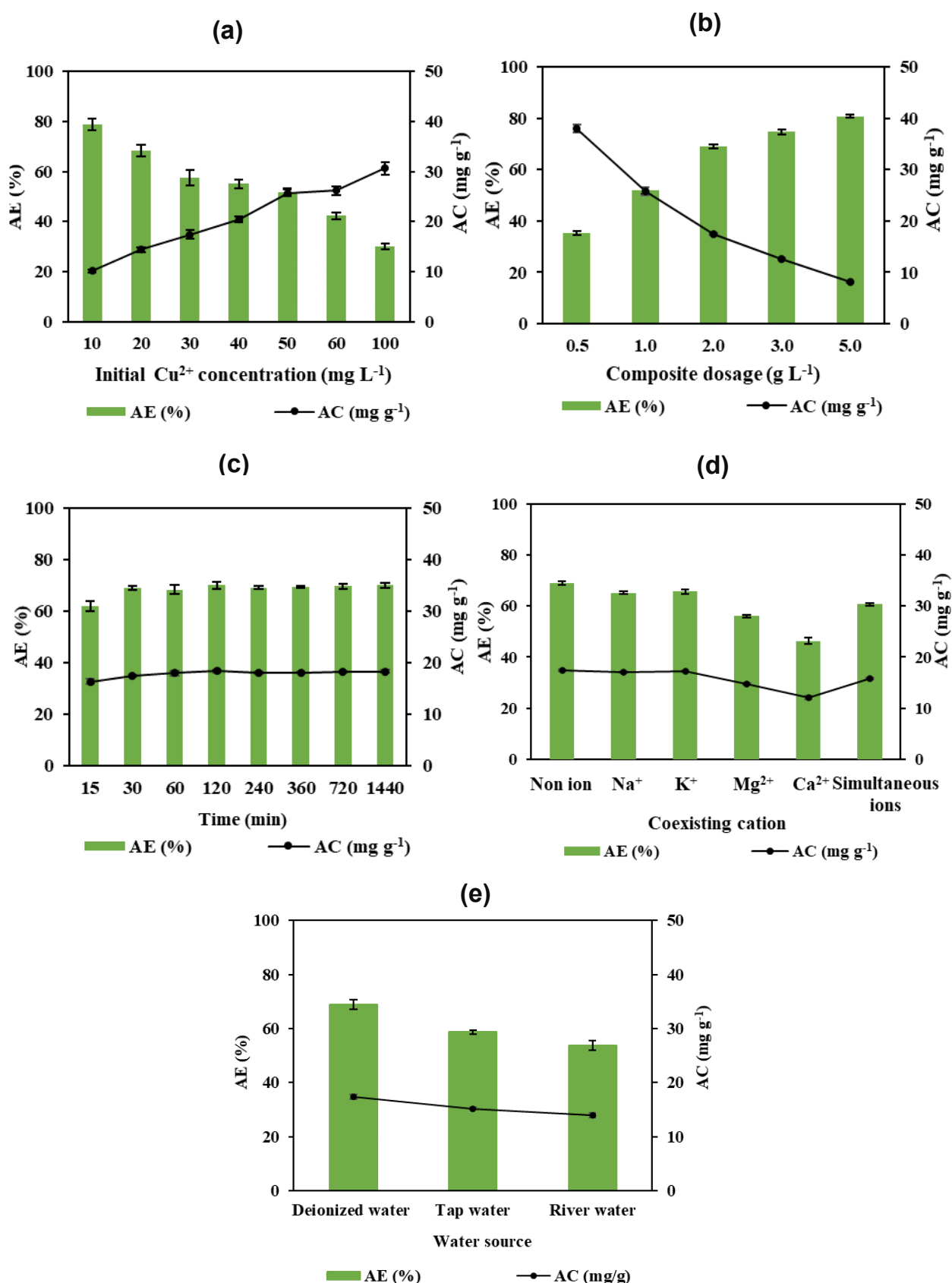


Figure 7 The Cu^{2+} removal parameters using LSA12: effect of initial Cu^{2+} concentration at the adsorption conditions: pH 5.5, dose of 1 g L^{-1} in 30 min (a); effect of composite dose at the adsorption conditions: pH 5.5, 50 mg L^{-1} Cu^{2+} concentration within 30 min (b); effect of contact time at the adsorption conditions: pH 5.5, 50 mg L^{-1} Cu^{2+} concentration and dose of 2.0 g L^{-1} (c); effect of coexisting cations at the adsorption conditions: 50 mg L^{-1} Cu^{2+} concentration, dose of 2.0 g L^{-1} , cation concentration of 0.01 M for 30 min (d); effect of different water source on the removal of Cu^{2+} under conditions: pH 5.5, initial Cu^{2+} concentration of 50 mg L^{-1} , Cu^{2+} concentration, dose of 2.0 g L^{-1} for 30 min (e).

Table 2 Thermodynamic parameters for Cu²⁺ ion adsorption process between LSA12 and the previous adsorbents

Absorbent	T (K)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	Reference
Olive waste powder/AG composite	293.00	-12.704	15.73	0.058	Elboughdiri et al. (2024)
	303.00	-16.869			
	313.00	-24.343			
Thiosemicarbazide-modified cellulose	302.00	-7.586	-50.93	-143.507	Nguyen et al. (2020)
	304.00	-7.299			
	306.00	-7.012			
	308.00	-6.725			
	310.00	-6.438			
Modified plant stem bark	288.15	-25.550	-48.10	-0.078	Santos et al. (2024)
	298.15	-24.770			
	308.15	-23.980			
	318.15	-23.200			
Cellulose-g-hydroxyapatite	298.17	-25.170	-11.06	0.047	Marrane et al. (2022)
	308.15	-25.450			
	318.33	-26.120			
	328.25	-26.530			
	338.24	-27.060			
LSA bio-composite	303.00	-1.140	-54.67	-0.165	This study
	313.00	-3.480			
	323.00	-4.830			

2.2) Proposed Cu²⁺ adsorption mechanisms

The Cu²⁺ adsorption mechanism followed physical adsorption, ion exchange, electrostatic interactions and chelation (Figure 8). First, the large difference between the hydrated ionic radius of Cu²⁺ (~0.42 nm) and the average pore diameter of LSA12 (~1.08 nm) could drive partial physical adsorption through diffusion into the surface and micropores of the adsorbent, mainly van der Waals forces and electrostatic interactions (Hart et al., 2023; Musumba et al., 2020; Suppruek et al., 2021). The negative zeta potential value of LSA (-37.50 mV) supported the electrostatic interactions between LSA and positively charged Cu²⁺ (Gao et al., 2020; Liu et al., 2019). Chelation between Cu²⁺ and the oxygen atoms in OH- groups (cellulose or AG) occurred, as determined by FTIR spectroscopy (Supplementary Figure S5). Changes in the shift and intensity of the -OH and -COO⁻ bands were observed after adsorption (3,446 and 1,634 cm⁻¹, respectively), along with the appearance of metal-carboxylate complexes in AG (1,399 cm⁻¹) (Gao et al., 2020; Júnior et al., 2019; Lessa et al., 2020; Papageorgiou et al., 2010). Furthermore, the BET results of LSA-Cu²⁺ revealed a significant increase in the specific surface area (1.375 m² g⁻¹) and pore size (3.753 nm).

The improvement in porosity because of the restructuring of LSA during the adsorption process, likely the interaction between Cu²⁺ and -COO⁻ groups on AG, is shown in Supplementary Figure S6 (Hari et al., 2022; Ručigaj et al., 2024). Another reason was the ion exchange process between Cu²⁺ and Ca²⁺ in LSA, as evidenced by a reduction in Ca²⁺ concentration (28.67 mg g⁻¹–11.61 mg g⁻¹) after 8 regeneration cycles (Supplementary Table S4) (Urbanova et al., 2019). The

Ca²⁺ concentration after desorption decreased by 2.27 times (25.63 mg g⁻¹–11.28 mg g⁻¹).

2.3) Resuability

The effects of different desorbing agents indicated the superior DE of EDTA, with an AE of 52.27% at the 2nd cycle (Supplementary Figure S7). This was attributed to its strong complexation ability, which resulted in the formation of stable six-membered rings chelated with Cu²⁺ (Liu et al., 2019; Shen et al., 2017). In comparison, HCl, HNO₃ and CH₃COOH yielded lower AEs of 44.06%, 41.78%, and 38.46%, respectively, because of weaker dissociation and reduced H⁺ competition with Cu²⁺ (Chen et al., 2024; Fang et al., 2016; Suratman et al., 2016). In addition, the difference in the AEs of NaCl (44%) and NH₄Cl (28.67%) was explained by the stronger competitive adsorption and ion exchange ability of Na⁺ with Ca²⁺ (in the alginate cross-linking network) and adsorbed Cu²⁺ on LSA, whereas NH₄⁺ displayed weaker exchange capacity (Chen et al., 2024; Mahata et al., 2021; Suratman et al., 2016). A low AE (6.99%) when H₂O₂ was used indicated that Cu²⁺ binding to LSA was not purely physical but involved strong interactions (Chen et al., 2024; Suratman et al., 2016). Overall, EDTA was identified as the most effective regeneration agent for LSA.

To evaluate long-term usability, the regeneration performance of LSA12 was investigated. A noticeable decline in the AE (68.99%–31.49%) was observed after eight consecutive cycles, although good reusability was maintained throughout the three cycles (Supplementary Figure S8). The decrease after the 4th cycle was ascribed to incomplete desorption, leading to

progressive saturation of active sites. Visual observations of LSA under different desorbing agents and repeated adsorption–desorption cycles revealed minimal morphological changes over five cycles, indicating good structural stability (Supplementary Figure S9). However, after the 5th cycle, the LSA surface became rougher with partial structural degradation.

The FTIR spectra of fresh LSA12, LSA12-Cu²⁺ and regenerated LSA12 revealed that after Cu²⁺ adsorption, the increased diffraction intensity and the shift at 3,446 cm⁻¹ were related to different bending vibrations of C–H bonds to the metal cations (Supplementary Figure S5) (Júnior et al., 2019). The increased intensity of the band at 1634 cm⁻¹ was due to the coordination between the Cu²⁺ and -COO⁻ groups of AG and the carbonyl/phenolic groups of LS (Lessa et al., 2020). The peak at 1,399 cm⁻¹ was assigned to the carboxylate symmetric vibration for metal-carboxylate complexes in AG (Lessa et al., 2020; Papageorgiou et al., 2010). Furthermore, the changes in the peak at 1,163 cm⁻¹–1,034 cm⁻¹ indicated the interaction between the Cu²⁺ and -OH

groups of the saccharide structure and AG. The sharp peak at 1,163 cm⁻¹ was also assigned to the metal–oxygen vibration of bound hydroxylated or hydrated metal ions (Lessa et al., 2020). In addition, the appearance of peaks at 1,520 cm⁻¹ and 1,446 cm⁻¹ (spectrum III) indicated that the aromatic rings and free carboxylate groups were partially restored and that the desorption process did not cause major structural changes (Adzmi et al., 2012; Li et al., 2025). Another experiment on the evaluation of LSA stability during the adsorption process involved observing Cu²⁺ leaching. The Cu²⁺ leaching percentage noticeably increased (3.19%–13.35%) during the first 120 min and almost reached equilibrium (18.59%) after 360 min (Supplementary Figure S10). Partial Cu²⁺ desorption from the LSA surface occurred, likely due to electrostatic attraction and physical adsorption. However, the overall leaching percentage remained relatively low (<20%), suggesting that Cu²⁺ is stable in the LSA structure (Yusop et al., 2026).

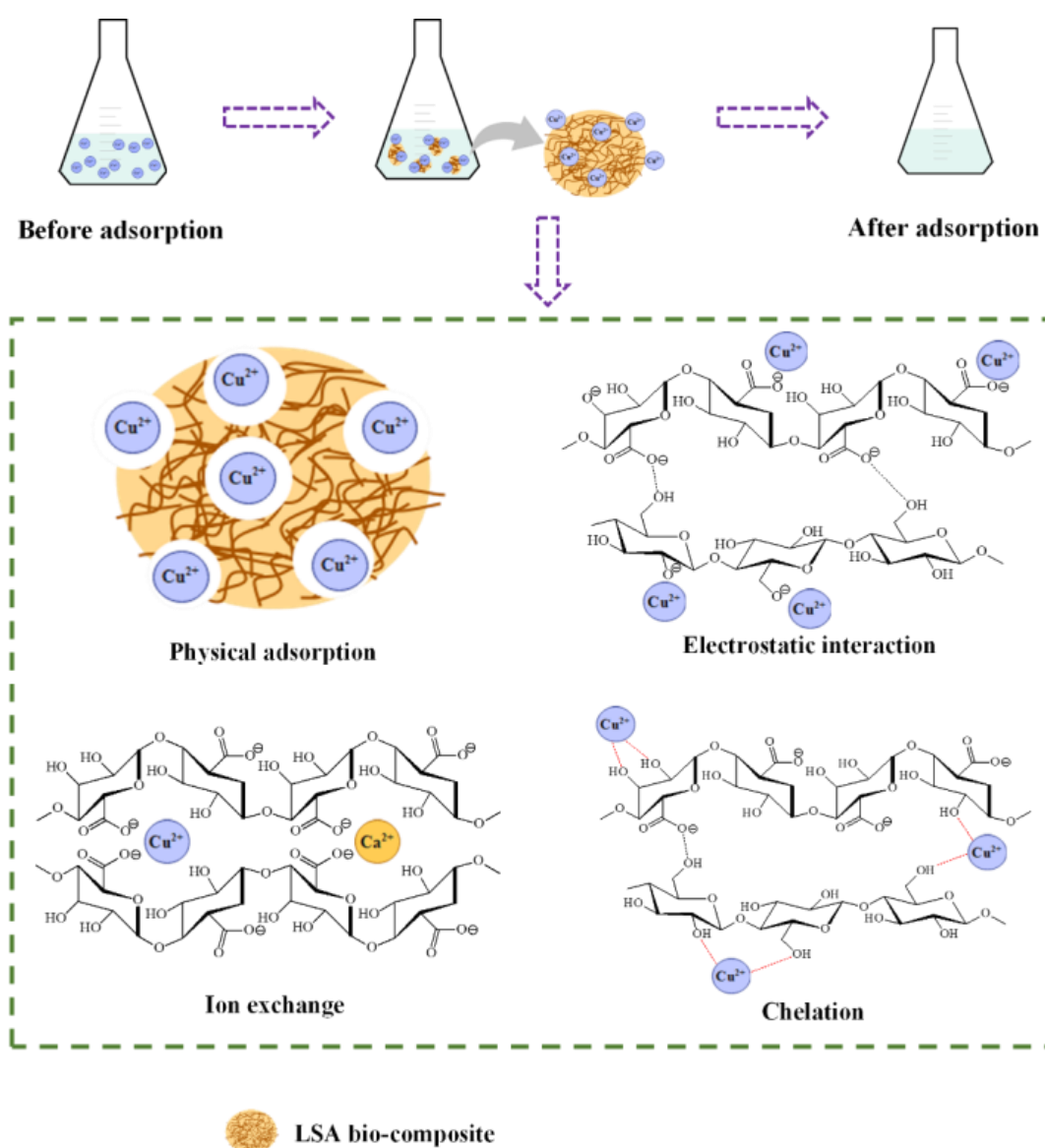


Figure 8 The Cu²⁺ adsorption mechanism of LSA bio-composite.

2.4) Comparison of removal capacity between LSA and some previous materials

The AC_{max} of LSA (43.77 mg g^{-1}) within 30 min benefited from its cost-effectiveness and rapid adsorption kinetics (Table 3).

Some studies on olive waste powder/AG (139.76 mg g^{-1}), cocoa cortex/AG (76.92 mg g^{-1}), graphene oxide-encapsulated carboxymethyl cellulose-AG (73.27 mg g^{-1}), and pectin-cellulose microfiber composite beads (88.50 mg g^{-1}) reported higher AC_{max} values than those of LSA, but a longer adsorption time (90 min–600 min) was required (Allouss et al., 2020; Elboughdiri et al., 2024; Fotsing et al., 2020; Lessa et al., 2020). In contrast, other adsorbents (cellulose hydrogels, hyacinth roots, coconut shells and carboxymethyl cellulose sponges) exhibited lower concentrations (28.40 mg g^{-1} , 21.79 mg g^{-1} , 19.89 mg g^{-1} , and 6.8 mg g^{-1} , respectively) at long contact times (150–1,440 min), limiting their practical applicability (Lin et al.,

2021; Singha and Das, 2013; Teow et al., 2018). Moreover, complex and costly chemical treatment of cellulose was needed to increase Cu^{2+} adsorption. Although a high AC_{max} was achieved by using olive waste powder/AG, a longer equilibrium time (600 min) was reported (Elboughdiri et al., 2024). In this work, LSA was treated by a simple physical method, resulting in a moderate AC, a short contact time (30 min), and easy recovery after adsorption, highlighting that it is a cost-effective and environmentally friendly material for Cu^{2+} removal. The degradation of LSA after regeneration was also due to the partial disruption of cross-links by Ca^{2+} and the loss of active sites during desorption. Thus, further research is needed to improve LSA12 reusability for practical applications and explore more stable cross-linking strategies, including covalent cross-linkers or alternative multivalent ions, to enhance structural integrity and reusability.

Table 3 Comparison of Cu^{2+} adsorption of LSA and other adsorbents

Absorbent	Cellulose treatment methods	Adsorption conditions	AC_{max} ($mg\ g^{-1}$)	Reference
Olive waste powder/AG composite	Physical treatment (washing, boiling, drying and grinding)	pH 5.50, dosage of 1.000 g L^{-1} , initial concentration of 50 mg L^{-1} , and 600 min	139.760	Elboughdiri et al. (2024)
Cocoa cortex/AG	Chemical treatment (1 M HCl and 1 M NaOH at $70\text{ }^{\circ}\text{C}$)	pH 4.17, dosage of 0.005 g L^{-1} , initial concentration of 100 mg L^{-1} , and 220 min	76.920	Fotsing et al. (2020)
Graphene oxide encapsulated carboxymethyl cellulose/AG	No treatment (commercial carboxymethyl cellulose)	pH 5.00, dosage of 2.000 g L^{-1} , initial concentration of 150 mg L^{-1} , and 90 min	73.270	Allouss et al. (2020)
Pectin/cellulose microfibers composite beads	Chemical treatment (3% NaOH at $70\text{ }^{\circ}\text{C}$, H_2O_2 bleaching at $50\text{ }^{\circ}\text{C}$, and HCl hydrolysis at $70\text{ }^{\circ}\text{C}$)	pH 4.00, dosage of 1.500 g L^{-1} , initial concentration of 100 mg L^{-1} , and 120 min	88.500	Lessa et al. (2020)
Cellulose hydrogel	No treatment (commercial cellulose)	pH 4.70, dosage of 0.400g L^{-1} , initial concentration of 300 mg L^{-1} , and 480 min	28.400	Teow et al. (2018)
Hyacinth roots	Physical treatment (boiling, washing, and drying)	pH 6.00, dosage of 7.000 g L^{-1} , initial concentration of 25 mg L^{-1} , and 150 min	21.790	Singha and Das (2013)
Coconut shell	Physical (washing, and drying and grinding) and chemical treatment (0.1 N NaOH and 0.1 N H_2SO_4)	pH 6.00, dosage of 6.000 g L^{-1} , initial concentration of 25 mg L^{-1} , and 180 min	19.890	Singha and Das (2013)
Carboxymethyl cellulose sponges	Chemical treatment (commercial CMC, 1.0 M H_2SO_4)	pH 5.50, dosage of 12.500 g L^{-1} , initial concentration of 100 mg L^{-1} , and 1440 min	6.800	Lin et al. (2021)
LSA composite	Physical treatment (washing, boiling, drying and grinding)	pH 5.50, dosage of 2.000 g L^{-1} , initial concentration of 50 mg L^{-1} , and 30 min	36.680	This study

Conclusions

In this study, the biocomposites were successfully synthesized and their structural stability was enhanced under facile processing at optimal concentrations—AG and CaCl_2 concentrations of 1.5% and 0.2%, respectively—at an LS:AG ratio of 2.0:1.0 (g g^{-1}) for 15 min. The obtained LSA could remove approximately 70% of the Cu^{2+} at a pH of 5.5 and at dosages of 2.0 g L^{-1} and 50 mg L^{-1} for 30 min. The Cu^{2+} adsorption mechanism included ion exchange, electrostatic interactions and chelation complexes. Furthermore, the adsorption data were best fit to the Sips isotherm and PSO kinetics models, indicating that the adsorption process occurred on a heterogeneous surface, monolayer and physicochemical adsorption mechanism. The composite underwent 8 cycles and maintained its structural stability, indicating potential applications in wastewater treatment processes.

Acknowledgements

This study was funded by Can Tho University, Code: CTCS2024-12-05.

Data availability statement

Information and data used in the study will be disclosed upon request.

Author ORCID

Van-Tai Nguyen: 0000-0003-4760-6870

Hue Tran Nguyen-Le: 0009-0008-2411-608X

Hong Thi Anh Nguyen: 0000-0001-8200-3798

Nguyen-Phuong-Dung Tran: 0000-0002-3611-3803

Kim-Phung Ly: 0000-0003-3064-9014

Quoc-Khanh Huynh: 0000-0002-5668-534X

Minh-Nhut Nguyen: 0000-0002-4569-4945

Phuong Lan Tran-Nguyen: 0000-0001-8703-5465

Author contributions

Van-Tai Nguyen: Investigation, Writing – Review & editing, Funding acquisition

Hue Tran Nguyen-Le: Writing – Original draft

Hong Thi Anh Nguyen: Writing – Review & editing

Nguyen-Phuong-Dung Tran: Writing – Review & editing

Kim-Phung Ly: Methodology, Writing – Review & editing

Quoc-Khanh Huynh: Writing – Review & editing

Minh-Nhut Nguyen: Writing – Review & editing

Phuong Lan Tran-Nguyen: Resources, Writing – Original draft, Supervision

Conflicts of interest

The authors declare that there are no conflicts of interest in competing financial or personal relationships that could have appeared to influence the work reported in this work.

References

- Abasalizadeh, F., Moghaddam, S. V., Alizadeh, E., Akbari, E., Kashani, E., Fazljou, S. M. B., Torbati, M., & Akbarzadeh, A. (2020). Alginate-based hydrogels as drug delivery vehicles in cancer treatment and their applications in wound dressing and 3D bioprinting. *Journal of Biological Engineering*, 14(1), 8.
- Adzmi, F., Meon, S., Musa, M. H., & Yusuf, N. A. (2012). Preparation, characterisation and viability of encapsulated *Trichoderma harzianum* UPM40 in alginate-montmorillonite clay. *Journal of Microencapsulation*, 29(3), 205–210.
- Alallam, B., Kadir, E. A., Dewi, F. R. P., Yong, Y. K., & Lim, V. (2025). Extraction and characterization of sodium alginate from native Malaysian brown seaweed *Sargassum polycystum*. *International Journal of Biological Macromolecules*, 287, 138552.
- Allouss, D., Essamlali, Y., Chakir, A., Khadhar, S., Zahouily, M. (2020). Effective removal of Cu (II) from aqueous solution over graphene oxide encapsulated carboxymethylcellulose-alginate hydrogel microspheres: Towards real wastewater treatment plants. *Environmental Science and Pollution Research*, 27(7), 7476–7492.
- Barik, H., Qaiyum, M. A., Samal, P. P., Dey, B., & Dey, S. (2025). Highly efficient removal of crystal violet dye using citric acid-modified Lotus (*Nelumbo nucifera*) seed pod. *Biomass Conversion and Biorefinery*, 15(8), 11835–11849.
- Bayuo, J., Rwiza, M., & Mtei, K. (2022). A comprehensive review on the decontamination of lead(II) from water and wastewater by low-cost biosorbents. *RSC Advances*, 12(18), 11233–11254.
- Bullen, J. C., Saleesongsom, S., Gallagher, K., & Weiss, D. J. (2021). A revised pseudo-second-order kinetic model for adsorption, sensitive to changes in adsorbate and adsorbent concentrations. *Langmuir*, 37(10), 3189–3201.
- Cagnon, B., Py, X., Guillot, A., Stoeckli, F., & Chambat, G. (2009). Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors. *Bioresource Technology*, 100(1), 292–298.
- Cano-Salazar, L. F., Martinez-Luevanos, A., Claudio-Rizo, J. A., Carrillo-Pedroza, F. R., Montemayor, S. M., & Rangel-Mendez, J. R. (2022). Synthesis, structural characterization and Cu(II) adsorption behavior of manganite (g-MnOOH) nanorods. *ACS Omega*, 7(32), 28076–28092.
- Chen, H., Pan, Y., Zhang, W., Long, A., Chen, M., Xiao, X., Wang, Z., Tang, M., Peng, Y., Sun, S., Zhang, H., & He, Q. (2024). Adsorption-desorption of copper (II) by temperature-sensitive nano-

- biochar@ PNIPAM/alginate double-network composite hydrogel: Enhanced mechanisms and application potentials. *Chemical Engineering Journal*, 495, 153356.
- Elboughdiri, N., Ferkous, H., Rouibah, K., Boubli A., Delimi, A., Yadav, K. K., Erto, A., Ghernaout, D., Salih, A. A. M., Benaissa, M., & Benaissa, M. (2024). Comprehensive investigation of Cu^{2+} adsorption from wastewater using olive-waste-derived adsorbents: Experimental and molecular insights. *International Journal of Molecular Sciences*, 25(2), 1028.
- Fajardo, A. R., Silva, M. B., Lopes, L. C., Piaí, J. F., Rubira, A. F., & Muniz, E. C. (2012). Hydrogel based on an alginate- Ca^{2+} /chondroitin sulfate matrix as a potential colon-specific drug delivery system. *RSC Advances*, 2(29), 11095–11103.
- Fang, Y., Tang, M., & Grassian, V. H. (2016). Competition between displacement and dissociation of a strong acid compared to a weak acid adsorbed on silica particle surfaces: The role of adsorbed water. *The Journal of Physical Chemistry A*, 120 (23), 4016–4024.
- Fotsing, P. N., Woumfo, E. D., Măicăneanu, S. A., Vieillard, J., Tcheka, C., Ngueagni, P. T., & Siéwé, J. M. (2020). Removal of Cu (II) from aqueous solution using a composite made from cocoa cortex and sodium alginate. *Environmental Science and Pollution Research*, 27(8), 8451–8466.
- Gao, X., Guo, C., Hao, J., Zhao, Z., Long, H., & Li, M. (2020). Adsorption of heavy metal ions by sodium alginate based adsorbent - A review and new perspectives. *International Journal of Biological Macromolecules*, 164, 4423–4434.
- Hari, D., & Kannan, A. (2022). A DFT study on Ca-alginate interactions with divalent transition metals. *Materials Today: Proceedings*, 62, 1532–1543.
- Hart, A., Porbeni, D.W., Omonmhenle, S., & Peretomode, E. (2023). Waste bone char-derived adsorbents: Characteristics, adsorption mechanism and model approach. *Environmental Technology Reviews*, 12(1), 175–204.
- Hassan, M., Liu, Y., Naidu, R., Du, J., Qi, F., Donne, S. W., & Islam, M. M. (2021). Mesoporous biopolymer architecture enhanced the adsorption and selectivity of aqueous heavy-metal ions. *ACS Omega*, 6(23), 15316–15331.
- Hornung, A., Stenzel, F., & Grunwald, J. (2024). Biochar-just a black matter is not enough. *Biomass Conversion and Biorefinery*, 14(5), 5889–5900.
- Humpola, P. D., Odetti, H. S., Fertitta, A. E., & Vicente, J. L. (2013). Thermodynamic analysis of adsorption models of phenol in liquid phase on different activated carbons. *Journal of the Chilean Chemical Society*, 58(1), 1541–1544.
- Júnior, W. J. N., Silva, M. G. C., & Vieira, M. G. A. (2019). Competitive biosorption of Cu^{2+} and Ag^{+} ions on brown macro-algae waste: Kinetic and ion-exchange studies. *Environmental Science and Pollution Research*, 26(23), 23416–23428.
- Lei, J., Kim, J. H., & Jeon, Y. S. (2008). Preparation and properties of alginate/polyaspartate composite hydrogels. *Macromolecular Research*, 16(1), 45–50.
- Lessa, E. F., Medina, A. L., Ribeiro, A. S., & Fajardo, A. R. (2020). Removal of multi-metals from water using reusable pectin/cellulose microfibers composite beads. *Arabian Journal of Chemistry*, 13(1), 709–720.
- Li, J., Wu, Y., He, J., & Huang, Y. (2016). A new insight to the effect of calcium concentration on gelation process and physical properties of alginate films. *Journal of Materials Science*, 51(12), 5791–5801.
- Li, X., Wang, Y., Chen, C., Tian, C., Yu, X., Liu, J., Li, Q., & Wang, S. (2025). Sustainable biochar derived from waste lotus seedpod for efficient adsorption of residual carbamate pesticides. *Heliyon*, 11(5), e42741.
- Lin, X., Jin, J., Guo, X., & Jia, X. (2021). All-carboxymethyl cellulose sponges for removal of heavy metal ions. *Cellulose*, 28(5), 3113–3122.
- Liu, Y., Zhao, Y. C., Zhang, C. Y., Guo, Y., Cui, L., Zhu, P., & Wang, D. Y. (2015). Bio-based nickel alginate and copper alginate films with excellent flame retardancy: Preparation, flammability and thermal degradation behavior. *RSC Advances*, 5(79), 64125–64137.
- Liu, Y., Gao, Q., Pu, S., Wang, H., Xia, K., Han, B., & Zhou, C. (2019). Carboxyl-functionalized lotus seedpod: A highly efficient and reusable agricultural waste-based adsorbent for removal of toxic Pb^{2+} ions from aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 568, 391–401.
- Macena, M., Pereira, H., Cruz-Lopes, L., Grosche, L., & Esteves, B. (2025). Competitive adsorption of metal ions by lignocellulosic materials: A review of applications, mechanisms and influencing factors. *Separations*, 12(3), 70.
- Mahata, B. K., Chung, K. L., & Chang, S. (2021). Removal of ammonium nitrogen ($\text{NH}_4^{+}\text{-N}$) by Cu-loaded amino-functionalized adsorbents. *Chemical Engineering Journal*, 411, 128589.
- Marrane, S. E., Dänoun, K., Allouss, D., Sair, S., Channab, B. E., Rihhil, A., & Zahouily, M. (2022). A novel approach to prepare cellulose-g-hydroxyapatite originated from natural sources as an efficient adsorbent for heavy metals: Batch adsorption

- optimization via response surface methodology. *ACS Omega*, 7(32), 28076–28092.
- Maryanti, R., Nandiyanto, A. B. D., Manullang, T. I. B., Hufad, A., & Sunardi, S. (2020). Adsorption of dye on carbon microparticles: Physicochemical properties during adsorption, adsorption isotherm and education for students with special needs. *Sains Malaysiana*, 49(12), 2949–2960.
- Merakchi, A., Bettayeb, S., Drouiche, N., Adour, L., & Lounici, H. (2019). Cross-linking and modification of sodium alginate biopolymer for dye removal in aqueous solution. *Polymer Bulletin*, 76(7), 3535–3554.
- Mikucka, W., Zielinska, M., Bulkowska, K., & Witonska, I. (2022). Subcritical water extraction of bioactive phenolic compounds from distillery stillage. *Journal of Environmental Management*, 318, 115548.
- Mohammed, A., Mohammed, C., Mautner, A., Kistow, M., Chaitram, P., Bismarck, A., & Ward, K. (2024). On the performance of Sargassum-derived calcium alginate ion exchange resins for Pb²⁺ adsorption: Batch and packed bed applications. *Environmental Science and Pollution Research*, 31(21), 31224–31239.
- Mukherjee, A., Patra, B. R., Podder, J., & Dalai, A. K. (2022). Synthesis of biochar from lignocellulosic biomass for diverse industrial applications and energy harvesting: Effects of pyrolysis conditions on the physicochemical properties of biochar. *Frontiers in Materials*, 9, 870184.
- Musumba, G., Nakiguli, C., Lubanga, C., Mukasa, P., & Ntambi, E. (2020). Adsorption of lead (II) and copper (II) ions from mono synthetic aqueous solutions using bio-char from ficus natalensis fruits. *Journal of Encapsulation and Adsorption Sciences*, 10(4), 71–84.
- Nguyen, T. A., Tran, D. B., Le, H. D. C., Nguyen, Q. L., & Pham, V. (2020). Thiosemicarbazone-modified cellulose: Synthesis, characterization, and adsorption studies on Cu (II) removal. *ACS Omega*, 5(24), 14481–14493.
- Papageorgiou, S. K., Kouvelos, E. P., Favvas, E. P., Sapalidis, A. A., Romanos, G. E., & Katsaros, F. K. (2010). Metal–carboxylate interactions in metal–alginate complexes studied with FTIR spectroscopy. *Carbohydrate Research*, 345(4), 469–473.
- Ručigaj, A., Golobič, J., & Kopač, T. (2024). The role of multivalent cations in determining the cross-linking affinity of alginate hydrogels: A combined experimental and modeling study. *Chemical Engineering Journal Advances*, 20, 100678.
- Saha, P., & Chowdhury, S. (2011). Insight into adsorption thermodynamics. *Thermodynamics*, 16, 349–364.
- Salam, O. E. A., Reiad, N. A., & ElShafei, M. M. (2011). A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, 2(4), 297–303.
- Santos, Y. T. C., Salvestrini, S., Vieira, C. B. G., Menezes, J. M. C., Ribeiro, A. J. A., Nunes, J. V. S., Coutinho, H. D. M., Junior, D. M. S., Filho, F. J. P., & Teixeira, R. N. P. (2024). Sorption thermodynamic and kinetic study of Cu(II) onto modified plant stem bark. *Environmental Science and Pollution Research*, 31(52), 61740–61762.
- Shen, X., Qiu, G., Yue, C., Guo, M., & Zhang, M. (2017). Multiple copper adsorption and regeneration by zeolite 4A synthesized from bauxite tailings. *Environmental Science and Pollution Research*, 24(27), 21829–21835.
- Sheraz, N., Shah, A., Haleem, A., & Iftikhar, F. J. (2024). Comprehensive assessment of carbon-, biomaterial- and inorganic-based adsorbents for the removal of the most hazardous heavy metal ions from wastewater. *RSC Advances*, 14(16), 11284–11310.
- Shi, X., Zheng, Y., Wang, G., Lin, Q., & Fan, J. (2014). pH- and electro-responsive characteristics of bacterial cellulose nanofiber/sodium alginate hybrid hydrogels for dual controlled drug delivery. *RSC Advances*, 4(87), 47056–47065.
- Sing, K. S. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure and Applied Chemistry*, 57(4), 603–619.
- Singha, B., & Das, S. K. (2013). Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes. *Colloids and Surfaces B: Biointerfaces*, 107, 97–106.
- Suppapruet, M., Threepopnatkul, P., Sittattrakul, A., & Lerdwijitjarud, W. (2021). Effect of chelating agents on removal of heavy metal cations of cellulose-based ion exchange resins from water hyacinth. *E3S Web of Conferences*, 302, 02020.
- Suratman, A., Kamalia, N. Z., & Kusumawati, W. A. (2016). Adsorption and desorption of Zn(II) and Cu(II) on Ca-alginate immobilized activated rice bran. In The 10th Joint Conference on Chemistry, Yogyakarta, Indonesia. *IOP Conference Series: Materials Science and Engineering*, 107, 012017.
- Teow, Y. H., Kam, L. M., & Mohammad, A. W. (2018). Synthesis of cellulose hydrogel for copper (II) ions adsorption. *Journal of Environmental Chemical Engineering*, 6(4), 4588–4597.
- Urbanova, M., Pavelkova, M., Czernek, J., Kubova, K., Vyslouzil, J., Pechova, A., Molinkova, J., Vetchy, D., & Brus, J. (2019). Interaction pathways and structure–chemical transformations of alginate gels in physiological environments. *Biomacromolecules*, 20(11), 4158–4170.

- Wang, Y. Y., Liu, Y. X., Lu, H. H., Yang, R. Q., & Yang, S. M. (2018). Competitive adsorption of Pb (II), Cu (II), and Zn (II) ions onto hydroxyapatite-biochar nanocomposite in aqueous solutions. *Journal of Solid State Chemistry*, 261, 53–61.
- Wang, Y., Zheng, K., Jiao, Z., Zhan, W., Ge, S., Ning, S., Fang, S., & Ruan, X. (2022). Simultaneous removal of Cu²⁺, Cd²⁺ and Pb²⁺ by modified wheat straw biochar from aqueous solution: Preparation, characterization and adsorption mechanism. *Toxics*, 10(6) 316.
- Yusop, M. F. M., Rashid, M. M., Alam, M. M., & Ahmad, M. A. (2026). Cu²⁺-surface-modified activated carbon from nutshells for enhanced metformin removal: Mass transfer simulation, attraction mechanism and F-test studies. *Water, Air, & Soil Pollution*, 237(9), 518.
-