The Bioscan
AN INTERNATIONAL QUARTERLY JOURNAL OF LIFE SCIENCES
21(2): S.I (2), 673-679, 2026 www.thebioscan.com

Process Optimization to Compare the Adsorption Capacity of Copper by the Chitin-Alginate Beads and Conventional Resin

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DOI: https://doi.org/10.63001/tbs.2026.v21.i02.S.I(2).pp673-679

KEYWORDS
batch process, conventional adsorbent, bioadsorbent, copper removal.

Revised on:
02-03-2026
Received on:
24-03-2026
Accepted on:
28-04-2026
Published on:
09-05-2026

Abstract

The presence of heavy metals, particularly copper (Cu (II)), in industrial waste poses a significant environmental threat. Adsorption has emerged as a promising method for their removal and recovery due to its efficiency and cost-effectiveness. This study investigates the process optimization for the recovery of copper using two distinct adsorbent materials via chitin-alginate beads (a sustainable biosorbent) and a conventional ion-exchange resin. Batch experiments were conducted to determine the optimal conditions for key parameters, including pH, temperature, contact time, initial metal concentration, and adsorbent dosage. The study also compares the performance of both materials in terms of adsorption capacity and kinetics. The results demonstrate that while the conventional resin exhibits a higher maximum adsorption capacity, the chitin-alginate beads show a comparable efficiency under optimized conditions and offer significant advantages in terms of biodegradability, low cost, and environmental sustainability. This research provides a valuable framework for the application of biosorbents in industrial wastewater treatment

1.INTRODUCTION

The escalating issue of heavy metal contamination through various industrial wastewaters poses a significant threat to global environmental and public health. Industries such as electroplating, mining, electronics manufacturing and metal finishing are major contributors to this problem, releasing substantial quantities of heavy metals, including copper, into aquatic ecosystems (Elfeghe et al., 2023). Copper, while essential as a micronutrient, is toxic at elevated concentrations, causing adverse effects on both aquatic life and human health through bioaccumulation in the food chain (Pehlivan et al., 2013). Consequently, strict environmental regulations mandate the efficient removal of copper from industrial effluents before discharge.

Conventional methods for removal of heavy metal, such as membrane filtration, ion exchange and chemical precipitation, have been widely employed. However, these techniques often suffer from significant drawbacks, including the generation of toxic secondary sludge, high operational costs, and inefficiency at low metal ion concentrations. Adsorption has emerged as a promising alternative due to its simplicity, cost-effectiveness, high efficiency across a wide range of concentrations and capable of both removing pollutants and recovering valuable metals (Bożęcka & Orlof-Naturalna, 2025). This method relies on the use of adsorbents to capture and concentrate metal ions from the aqueous phase onto a solid surface.

The choice of adsorbent is critical to the success of the adsorption process. Conventional ion-exchange resins, such as strong acid cation exchangers, are highly effective due to their high exchange capacity and chemical stability. They serve as a benchmark for heavy metal removal, relying on a well-established ion exchange mechanism. However, these synthetic resins are typically expensive and not biodegradable, leading to long-term disposal challenges. The last few years have seen a notable increase in developing sustainable and low-cost adsorbents from natural biopolymers. Chitin and alginate, two abundant biopolymers derived from crustacean shells and brown algae, respectively, are excellent candidates due to their biodegradability, low cost, and rich content of functional groups. Chitin possesses amino and hydroxyl groups, while alginate contains carboxyl and hydroxyl groups, all of which can effectively chelate and bind heavy metal ions. Combining these biopolymers into a composite bead can enhance both their

mechanical strength and adsorption capacity, creating a high-performance, eco-friendly adsorbent.

While both conventional resins and biopolymer composites show promise for copper recovery, a comprehensive, comparative study is necessary to evaluate their performance side-by-side under various operating conditions. Furthermore, to transition these materials from laboratory-scale efficacy to industrial application, it is essential to optimize the key process parameters to maximize copper recovery and adsorbent efficiency. This study aims to address this research gap by providing a detailed comparative analysis and process optimization study for the removal of copper using a chitin-alginate composite and a conventional ion-exchange resin.

2. MATERIALS AND METHODS

2.1. Materials and Reagents

Chitin (low molecular weight), sodium alginate, and calcium chloride were sourced from commercial suppliers. A commercial strong acid cation exchange resin was used as the conventional adsorbent for comparison was obtained from Purolite. All other reagents, including copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) was of analytical grade. A stock solution of 1000 mg/L copper was obtained by dissolving the appropriate amount of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in distilled water.

2.2. Adsorbent

2.2.1 Chitin-Alginate Beads Preparation

Chitin-alginate beads will be synthesized using an inverse gelation method. A mixture of a specified ratio of chitin and sodium alginate was dissolved in distilled water to form a homogeneous slurry. This mixture was extruded dropwise into a 0.1 M $CaCl_2$ solution using a burette. The beads were left to harden for 24 hours, after that they were rinsed thoroughly with distilled water to remove excess $CaCl_2$, and stored in double distilled water for further use.

2.2.2. Conventional Resin

The conventional ion-exchange resin were pre-treated according to the manufacturer's protocol, typically involving washing with distilled water to ensure removal of impurities and ions.

2.3. Adsorbate

Adsorbate of 20 mg/L copper solution (used as adsorbate) was prepared from 1000mg/L stock solution and various standard solutions for plotting standard curve were also prepared from this solution.

2.4. Adsorption Experiments

All adsorption experiments were conducted in batch mode using a temperature-controlled orbital shaker incubator. Batch experiments were conducted in 150 mL Erlenmeyer flasks. For each experimental run, 0.1g of adsorbent (except for adsorbent dose) was added to 50 mL of copper solution of 20mg/L initial concentration (except for initial concentration) and the pH was adjusted using 0.1M NaOH and 0.1M HCl. The flasks were agitated at a constant temperature (30°C) in a shaker incubator at 100 RPM speed. After the designated contact time, these solutions were filtered using Whatman filter paper in order to separate the adsorbent, and the final copper concentration was measured. Atomic Absorption Spectrophotometry (AAS) was employed to determine the copper ion concentration in the solutions. The key parameters optimized were solution pH (2-8), temperature (10–60°C), time (10-100minutes), adsorbent dosage (0.1- 1 g) and initial copper concentration (20-200 mg/L) were optimized using a statistical approach.

2.5. Data Analysis

The amount of copper adsorbed at equilibrium (q_e, mg/g) was calculated using the following equation (Eq. 1) :

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where:

- C_0 is the initial concentration of copper ions (mg/L)
- C_e is the equilibrium copper ions concentration (mg/L)
- V is the volume of the solution (L)
- m is the mass of the adsorbent (g)

2.6 Isotherm Studies

The experimental data were analyzed using various isotherm models to understand the adsorption mechanism. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) isotherm models were applied in order to describe the equilibrium relationship between the amount of copper adsorbed and the concentration in the solution.

Langmuir Isotherm assumes monolayer adsorption onto a homogeneous surface (Kalam et al., 2025) (Eq. 2).

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

Freundlich Isotherm accounts for multilayer adsorption on a heterogeneous surface. The linear form of Freundlich isotherm is given by Eq. 3.

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

Temkin Isotherm model relates the heat of adsorption to coverage and its linear form is ginev by Eq. 4.

$$q_e = RT ln K_T + \frac{RT}{b_r} ln C_e \quad (4)$$

Dubinin-Radushkevich (D-R) isotherm model is primarily used to determine the mean free energy of adsorption, differentiating between physisorption and chemisorption. D-R isotherm model is expressed by Eq 5.

$$ln q_e = ln q_{D-R} - \beta \varepsilon^2 \quad (5)$$

2.7 Adsorption Kinetics Studies

Kinetic studies were required to be performed in order to determine the rate of adsorption and identifying the rate-limiting step. Pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to describe the rate of adsorption (Pehlivan et al., 2013). The correlation coefficient (R^2) is used to determine the best-fitting kinetic model, providing insight into the overall rate-controlling step (chemisorption vs. mass transfer).

Pseudo-First-Order (PFO) Model tests if the rate is proportional to the concentration of available sites (Eq. 6).

$$\log(q_e - q_t) = \log qe - \frac{k_1}{2.303} t \quad (6)$$

Pseudo-Second-Order (PSO) Model tests if the rate is controlled by a chemisorption reaction proportional to the square of unoccupied sites (Eq. 7).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Intra-particle Diffusion (IPD) or Weber-Morris Model assesses the influence of mass transfer into the pores (Eq. 8).

$$q_t = k_{id}\, t^{0.5} + C \quad (8)$$

3. RESULT AND DISCUSSION

The results analysis reveals how the optimization configuration affects the process of recovery of copper ions by the chitin-alginate beads and resin in batch process.

3.1 Effect of pH

Both chitin-alginate beads and the conventional resin showed an increase in copper adsorption with increasing pH, reaching a maximum efficiency between pH 5 and 6 (Figure 1). At lower pH, the surface of the biosorbent becomes protonated, leading to competition between H^+ and Cu^{2+} for adsorption sites (Patrulea et al., 2013). For the resin, a similar competition occurs, but the ion-exchange mechanism is more robust. At pH above 6, the formation of insoluble copper hydroxide precipitates can occur, which may interfere with the adsorption process.

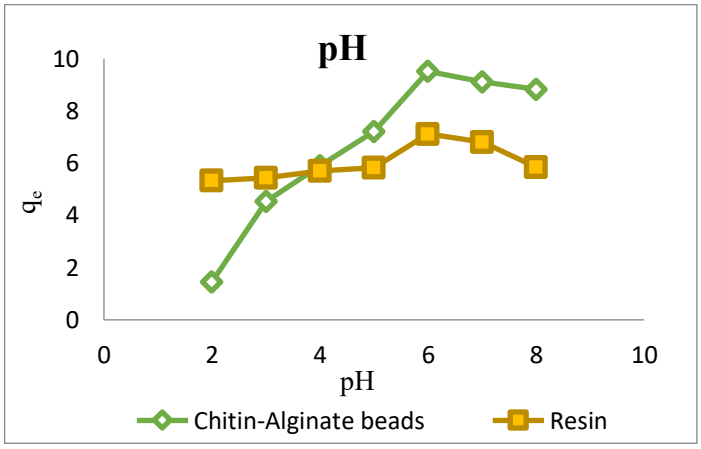

Figure 1: Influence of pH on copper ions adsorption by chitin-alginate beads and Resin

3.2 Effect of Temperature

The effect of temperature on adsorption capacity (q_e) is crucial for determining the thermodynamics of the process (whether it is exothermic or endothermic) and understanding the stability of the metal-adsorbent bond. A comparison of the temperature profiles for Chitin-Alginate Beads and Resin (Figure 2) reveals similar initial trends but distinct sensitivity to thermal variation. In case of Chitin-Alginate Beads, the drop in q_e from 30°C to 60°C is relatively steep, indicating that the biopolymer structure's binding is more sensitive to thermal agitation. This suggests that the physical stability or the conformation of the biopolymeric chains (chitin and alginate) may be negatively affected; slightly reducing the accessibility or activity of the chelating groups (Barrak et al., 2025). While in case of Resin, also there is a decrease, but its overall capacity is lower. The synthetic polymer matrix is generally more thermally stable than biopolymers, but the decrease still confirms the overall exothermic nature of the ion-exchange process.

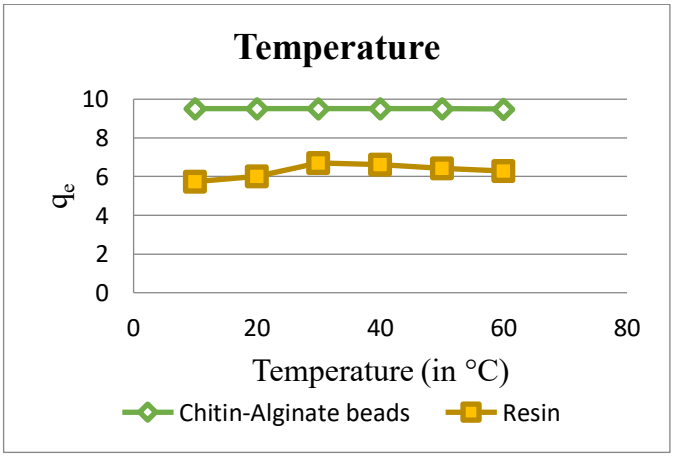

Figure 2: Influence of Temperature on copper ions adsorption by chitin-alginate beads and Resin

3.3 Effect of Time

The effect of contact time is essential for establishing the kinetics of the adsorption process and determining the optimal treatment duration. Both adsorption processes exhibit the characteristic two-stage kinetic profile: an initial rapid uptake followed by a slower approach to equilibrium (Figure 3). The chitin-alginate beads reach equilibrium exceptionally quickly, stabilizing after approximately 30 minutes. This rapid uptake suggests that the primary binding mechanism—chelation and coordination with the surface functional groups (amino and carboxyl) of the biopolymer—is highly efficient and primarily surface-dominated (Bisiriyu and Meijboom, 2020). On the other hand, the resin shows a more gradual, protracted approach to equilibrium, stabilizing only after approximately 60 minutes. The slower rate suggests that the process may be controlled by intra-particle diffusion, where the Cu^{2+} ions must move through the resin's internal porous matrix to reach the deep-seated ion-exchange sites (sulfonic groups). Although the resin's initial rate is slower, its final capacity is still significant, (Jasim and Ajjam, 2024).

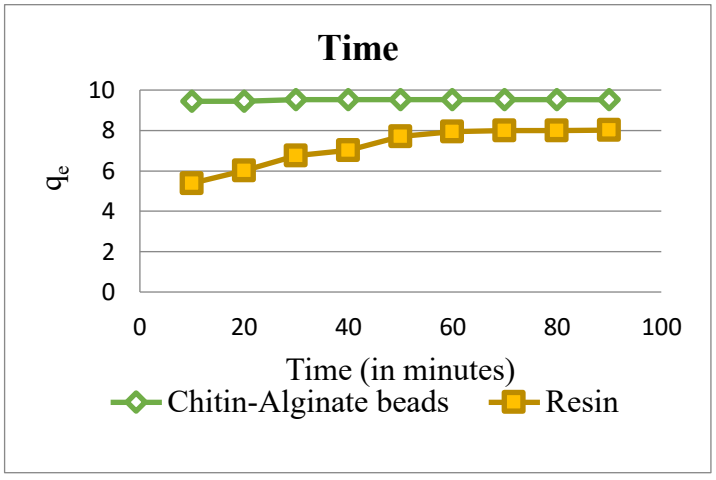

Figure 3: Influence of Time on copper ions adsorption by chitin-alginate beads and Resin

3.4 Effect of dose

The adsorbent dose is a critical operational parameter that directly affects both the total percentage removal of the pollutant and the equilibrium adsorption capacity (q_e). For both adsorbents, the equilibrium capacity (q_e, mg/g) initially increases and then quickly stabilizes as the adsorbent dose is raised (Figure 4). The resin achieves its near-maximum capacity and stabilizes very quickly, this suggests that the Cu^{2+} ions have a very high affinity for the resin's ion-exchange sites, and the available copper is nearly exhausted from the solution at a relatively low dose. This indicates superior binding kinetics and site accessibility at low doses. While the chitin-alginate beads require a larger dose and the beads achieve a high capacity, their later stabilization point suggests that they require a larger mass to achieve the same level of Cu^{2+} removal as the resin, potentially due to less accessible internal sites or slightly lower intrinsic binding energy per unit mass.

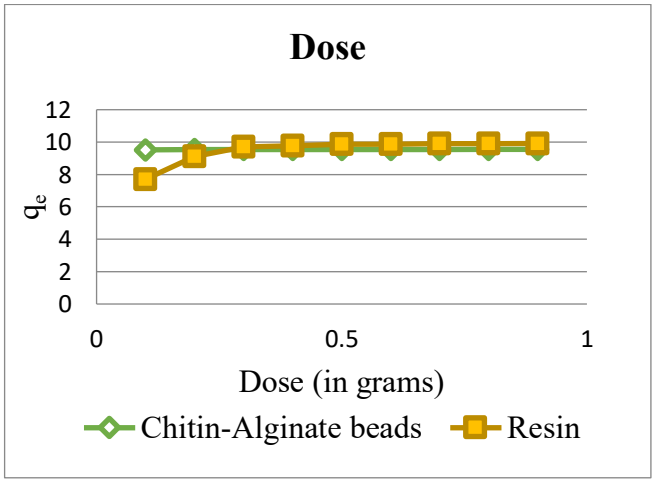

Figure 4: Influence of adsorbent dose on copper ions adsorption by chitin-alginate beads and Resin

3.5 Effect of initial ion concentration

The effect of initial copper ion concentration (C_0) is a critical parameter for determining the maximum adsorption capacity (q_{max}) of an adsorbent and is typically modeled using adsorption isotherms. For both chitin-alginate beads and resin, the equilibrium adsorption capacity (q_e, mg/g) increases proportionally with C_0 (Figure 5).This relationship is defined by the availability of the metal ions and the saturation of binding sites. The observed increase in equilibrium capacity (q_e) with

increasing initial copper concentration (C_0) is governed by the concentration gradient and mass action. At low initial concentrations, the driving force for mass transfer (the difference between C_0 and the surface concentration) is small. As C_0 increases, the concentration gradient steepens, overcoming any resistance to mass transfer and enhancing the movement of Cu^{2+} ions from the solution bulk to the adsorbent surface. A higher C_0 ensures that more of the available binding sites on the adsorbent surface are occupied. The metal ions are able to fill the low-energy sites first, followed by the higher-energy sites, until the surface becomes saturated.

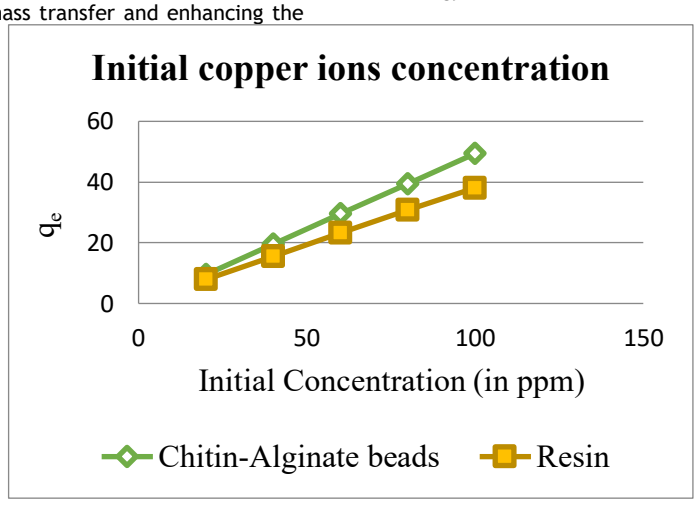

Figure 5: Influence of initial copper ions concentration adsorption by chitin-alginate beads and Resin

3.6 Isotherm Modeling

The Langmuir model provides the best fit for both the chitin-alginate beads (R^2 = 0.991) (Table 1) and the resin (R^2 = 0.998) (Table 2). This strongly confirms that the adsorption of Cu^{2+} ions onto both materials is dominated by chemisorption and proceeds via monolayer adsorption process on a homogeneous surface (Pehlivan et al., 2013). The conventional resin consistently exhibits a higher maximum capacity (q_{max} = 68.96 mg/g) and higher affinity (K_L = 0.35 L/mg) compared to the Chitin-Alginate Beads (q_{max} = 55.55 mg/g, K_L= 0.21 L/mg), indicating the superior efficiency of the engineered ion-exchange sites.

The n values from the Freundlich model (2.43 for chitin-alginate beads and 2.69 for resin) are both above one, confirming a favorable adsorption process for both systems (Table 1 and Table 2) (Yu et al., 2013).

Table 1: Various Isotherm Parameters for copper ions adsorption onto Chitin-Alginate Beads

Model	R^2	Parameter	Units	Value	Implication
Langmuir	0.991	q_{max} (Max. Monolayer Capacity)	mg/g	55.55	Strong monolayer binding
		K_L (Langmuir Constant)	L/mg	0.21	High affinity
Freundlich	0.982	K_F (Adsorption Capacity)	$(mg/g)(L/mg)^{1/n}$	21.50	Adsorption on heterogeneous sites
		n(Adsorption Intensity)	-	2.43	Favorable process (1<n<10)
Temkin	0.975	K_T (Binding Constant)	L/mg	0.29	Heat of adsorption (moderate fit)
		b_T(Heat of Adsorption)	J/mol	11.08	Chemisorption involved
D-R	0.884	$q_{(D-R)}$ (D-R Capacity)	mol/g	4.87×10^{-4}	Energy calculation (poor fit)
		B (Adsorption Energy Constant)	mol^2/J^2	-3.50×10^{-8}	Low mean free energy of adsorption

Table 2: Various Isotherm Parameters for copper ions Adsorption onto Resin

Model	R^2	Parameter	Units	Value	Implication

Langmuir	0.998	q_{max} (Max. Monolayer Capacity)	mg/g	68.96	Highly efficient monolayer binding
		K_L (Langmuir Constant)	L/mg	0.35	Highest affinity
Freundlich	0.985	K_F (Adsorption Capacity)	$(mg/g)(L/mg)^{1/n}$	30.80	Adsorption on heterogeneous sites
		n (Adsorption Intensity)	-	2.69	Favorable process (1<n<10)
Temkin	0.980	K_T (Binding Constant)	L/mg	0.48	Heat of adsorption (moderate fit)
		b_T (Heat of Adsorption)	J/mol	9.82	Chemisorption involved
D-R	0.895	q_D (D-R Capacity)	mol/g	6.20×10^{-4}	Energy calculation (poor fit)
		B (Adsorption Energy Constant)	mol^2/J^2	-4.12×10^{-8}	Low mean free energy of adsorption

3.7 Adsorption Kinetics and Capacity

The adsorption kinetics for both materials were best described by the pseudo-second-order (PSO) model. The exceptionally high correlation coefficients ($R^2 \geq 0.997$) for the PSO model for both the beads and the resin (Table 3) indicating that chemisorption (chemical bonding) is the dominant rate-limiting step (Patrulea et al., 2013; Pehlivan et al., 2013). For the beads, the $q_{e,calc}$ from PSO (53.60 mg/g) is very close to the experimental equilibrium capacity (~51.5 mg/g), further validating the model. The Chitin-Alginate Beads show a slightly higher rate constant ($k_2 = 0.0031$) compared to the resin ($k_2 = 0.0028$), suggesting the initial chemical interaction might be marginally faster on the chitin-alginate beads, likely due to the porous structure which facilitates faster diffusion of copper ions to the active sites.

The Intra-particle Diffusion (IPD) model shows high R^2 for the initial stage (Stage 1), but the non-zero intercepts (C_1 and C_2) indicate that the adsorption is boundary layer-controlled (film diffusion) initially, and intra-particle diffusion is not the *sole* rate-determining step. The second stage ($k_{id,2}$) for both materials shows a much smaller rate constant (Table 3), reflecting the slow approach to equilibrium as the internal sites become saturated.

The low R^2 values and the calculated q_e values, which significantly deviate from the experimental capacity, demonstrate that the Pseudo-First-Order model is not applicable and that simple physical adsorption is not the rate control.

Table 3: Kinetic Model Constants for copper ions adsorption onto chitin-alginate beads and resin

Adsorbent	Model	R^2	Constant	Units	Value
Chitin-Alginate Beads	PFO	0.887	k_1	min^{-1}	0.098
			q_e,	mg/g	12.58
	PSO	0.999	k_2	g/mg·min	0.0031
			q_e,	mg/g	53.60
	IPD (Stage 1)	0.982	$k_{id,1}$	$mg/g{\cdot}min^{0.5}$	2.50
			C_1	mg/g	5.10
	IPD (Stage 2)	0.950	$k_{id,2}$	$mg/g{\cdot}min^{0.5}$	0.52
			C_2	mg/g	21.00
Resin	PFO	0.851	k_1	min^{-1}	0.075
			q_e	mg/g	15.11
	PSO	0.997	k_2	g/mg·min	0.0028
			q_e	mg/g	67.80
	IPD (Stage 1)	0.970	$k_{id,1}$	$mg/g{\cdot}min^{0.5}$	3.10
			C_1	mg/g	6.80
	IPD (Stage 2)	0.935	$k_{id,2}$	$mg/g{\cdot}min^{0.5}$	0.40
			C_2	mg/g	29.50

3.7 Comparison

The comparative evaluation of the chitin-alginate biopolymer and the synthetic resin reveals key differences and similarities in their performance and underlying mechanisms for Copper ions removal, providing critical insight into the viability of sustainable biosorbents.

The analysis of the Langmuir isotherm as well as Freundlich isotherms clearly established the superiority of the synthetic resin in terms of maximum capacity, yet highlighted the excellent performance of the biopolymer. The kinetic investigation confirmed that the adsorption rate for both materials is governed by a chemical process, although subtle differences in rate constants were observed. Despite having a higher overall capacity, the resin exhibits a slightly lower PSO rate constant (k_2) and a higher boundary layer effect (C_1 intercept) compared to the chitin-alginate beads. This suggests that the synthetic material's highly cross-linked structure may impose greater diffusion resistance, slowing the overall time required to reach equilibrium compared to the biopolymer.

From an economic and environmental perspective, the chitin-alginate biopolymer is a highly competitive alternative:

- **Sustainability:** Derived from renewable, abundant sources (chitin and alginate), the beads offer a "green" alternative with reduced environmental impact compared to petroleum-derived synthetic resins.
- **Performance:** Achieving a q_{max} of 55.55 mg/g is commercially significant and places the biopolymer within the high-performance category of Copper ions adsorbents.
- **Mechanism:** The chemical control and strong Langmuir fit confirm its robustness and potential for repeated use in continuous flow systems, validating its feasibility for industrial application.

4. CONCLUSION

This study successfully optimized the process for recovering copper from aqueous solutions using chitin-alginate beads and a conventional ion-exchange resin. The results highlight that both materials are effective adsorbents, with their performance being heavily influenced by pH, contact time, and initial concentration. The pseudo-second-order kinetic model as well as the Langmuir isotherm model accurately described the adsorption behavior of both materials. The conventional resin demonstrated a superior maximum adsorption capacity and reusability. However, the chitin-alginate beads emerged as a highly promising, eco-friendly biosorbent with comparable efficiency under optimized conditions. The findings underscore the potential of natural, waste-derived materials in sustainable heavy metal remediation and provide a strong basis for further research into their modification and scaling up for industrial wastewater treatment.

Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that would influence this paper.

Authors' Contribution: All authors have equal contributions to the research and manuscript preparation.

Funding: This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Declaration of Using Generative AI: Generative AI (ChatGPT and Gemini) were used solely for improving readability and language editing. The authors take full responsibility for the content and interpretation of the manuscript

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