

Original Research

Cr(VI) Adsorptive Removal Using Raw *Cordia africana* Sawdust: Optimization of Operating Parameters, Kinetics, Isotherm, Thermodynamics, and Desorption Efficiency

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Abstract

Hexavalent chromium (Cr(VI)) is a carcinogenic pollutant commonly found in wastewater from tanning and electroplating industries. This study investigates the efficiency of raw *Cordia africana* sawdust as a biosorbent for Cr(VI) removal. Batch adsorption experiments were conducted by varying pH (3-8), contact time (10-120 min), and Cr(VI) concentration (21-47 mg/L) using Response Surface Methodology (RSM) with Box-Behnken design. Characterization was performed using FTIR, SEM, BET, pH, and PZC analysis before and after adsorption to confirm uptake mechanisms. Desorption studies were conducted using 0.1 M HCl and 0.1 M NaOH. FTIR confirmed the presence of hydroxyl (3330 cm^{-1}) and carboxyl (1733 cm^{-1}) groups, with peak shifts after adsorption, indicating their involvement. SEM revealed heterogeneous surface morphology, and the BET surface area was $10.332\text{ m}^2/\text{g}$ with PZC at 6.8. Optimal Cr(VI) removal of 84.5% occurred at pH 5.5, 47 mg/L concentration, and 10 min contact time. HCl-mediated desorption achieved 66.5% Cr(VI) recovery of efficiency, while the regenerated adsorbent maintained 78.8% of its initial capacity across three cycles. Kinetic analysis showed that the pseudo-second-order model best described adsorption ($R^2 = 0.996$) with $q_{e,cal}$ (1.99



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mg/g) matching the experimental value, indicating chemisorption as the rate-controlling step. Isotherm studies using non-linear regression (OriginPro 2024) revealed the Langmuir model as the best fit ($R^2 = 0.993$, $RMSE = 0.042$) with a maximum capacity of 2.06 mg/g, suggesting monolayer adsorption onto homogeneous sites. The dimensionless separation factor ($R_L = 0.10$ -0.21) confirmed favorable adsorption. The Dubinin-Radushkevich model gave a mean free energy of $E = 8.42 \text{ kJ mol}^{-1}$, indicating an ion-exchange contribution. Thermodynamic parameters ($\Delta G^\circ = -4.21$ to $-6.42 \text{ kJ mol}^{-1}$, $\Delta H^\circ = +18.7 \text{ kJ mol}^{-1}$, $\Delta S^\circ = +0.077 \text{ kJ mol}^{-1} \text{ K}^{-1}$) revealed spontaneous and endothermic adsorption. Comparative analysis with ten reported biosorbents shows *Cordia africana* sawdust performs favorably among unmodified materials (2.06 mg/g vs 1.58-1.94 mg/g range). However, raw sawdust cannot replace conventional methods like alkaline precipitation (which achieves >99% removal) due to capacity limitations and concerns about spent adsorbent disposal. The material shows potential as a low-cost supplementary treatment in resource-limited settings where waste biomass is abundant.

Keywords

Chromium; adsorption; sawdust; biosorbent; desorption

1. Introduction

Hexavalent chromium (Cr(VI)) is one of the most toxic heavy metals commonly detected in industrial wastewater, particularly from tanning, electroplating, metal finishing, pigment, and dye industries. Due to its high solubility, mobility, and strong oxidizing nature, Cr(VI) readily contaminates surface and groundwater and poses severe risks to human health and ecosystems. Prolonged exposure to Cr(VI) is associated with carcinogenicity, mutagenicity, and damage to vital organs, even at low concentrations. Consequently, strict discharge limits for chromium in wastewater have been established worldwide, typically below 0.05-0.3 mg L⁻¹, depending on regulatory frameworks [1].

Conventional methods for chromium removal include chemical precipitation, pH adjustment, ion exchange, membrane filtration, electrochemical reduction, and coagulation–flocculation. Among these, alkaline precipitation—by raising the pH above 8.4 to form Cr(OH)₃—is widely used in industry due to its simplicity, low cost, and high removal efficiency. However, this method generates large volumes of chromium-containing sludge, which requires further treatment, stabilization, and disposal, creating additional environmental and economic burdens [2]. Advanced treatment methods, while effective, often involve high operational costs and complex infrastructure, making them less suitable for decentralized or low-resource settings. While chemically modified adsorbents dominate the literature, their synthesis often requires reagents, energy, and technical expertise that are inaccessible in precisely the settings where low-cost treatment options are most urgently needed.

Adsorption has attracted considerable attention as an alternative or complementary treatment method because of its operational simplicity, flexibility, and ability to remove contaminants at low concentrations [3]. In recent years, there has been growing interest in the use of low-cost, bio-based adsorbents derived from agricultural and forestry wastes [1, 3-5]. These materials are appealing due

to their abundance, biodegradability, and surface functional groups—such as hydroxyl and carboxyl groups—that can bind metal ions [6, 7]. Numerous studies have reported effective Cr(VI) removal using chemically modified biomass materials; however, such modifications often increase cost, chemical consumption, and secondary environmental impacts [8]. A 2024 review on waste biomass adsorbents notes chemical modifications enhance Cr(VI) uptake but require reagents like H_3PO_4 or NaOH , raising operational costs and generating hazardous waste, contrasting cheaper unmodified biomass [9]. Manikant Tripathi et al. [8] emphasize unmodified biomass as sustainable for dual waste management and remediation, implying that modifications add complexity and environmental burdens not present in its raw form. This gap is particularly notable for regionally abundant but under-investigated biomass species—such as *Cordia africana* in East Africa—where local availability could transform a waste-disposal problem into a water-treatment opportunity without the need for imported chemicals or sophisticated modification protocols.

Raw sawdust is an abundant byproduct of the timber industry and is an underutilized waste material in many developing countries. *Cordia africana*, a widely used timber species in Ethiopia, generates substantial amounts of sawdust that are typically discarded or burned. To date, no published study has systematically evaluated raw, unmodified *Cordia africana* sawdust for Cr(VI) removal using a combined approach that integrates response surface methodology optimization with comprehensive kinetic, isotherm, thermodynamic, and regeneration analysis—leaving a critical knowledge gap for communities where this material is readily available. Although modified sawdust and activated carbons derived from sawdust have been extensively studied [1, 3, 4], limited attention has been given to the adsorption potential of raw, unmodified *Cordia africana* sawdust, particularly with systematic optimization, kinetic, isotherm, thermodynamic, and regeneration analysis. The present work therefore addresses this gap by providing the first comprehensive assessment of raw *Cordia africana* sawdust as a Cr(VI) biosorbent, with three distinguishing features: (i) systematic optimization using Box-Behnken design rather than one-factor-at-a-time approaches common in raw biomass studies; (ii) integrated analysis of kinetics, isotherms, thermodynamics, and reusability within a single study—rare for unmodified materials; and (iii) critical discussion of both potential and limitations, positioning this work as a realistic evaluation rather than an overstatement of applicability.

It is important to note that biosorption using raw biomass is not intended to replace established industrial treatment methods such as chemical precipitation. Instead, such materials may serve as low-cost supplementary or pre-treatment options, polishing steps, or decentralized solutions in small-scale or resource-limited contexts. Therefore, an honest evaluation of adsorption performance, limitations, regeneration behavior, and feasibility is essential. The novelty of this investigation thus lies in systematically documenting whether a locally abundant, zero-cost waste material can serve as a functional biosorbent under realistic operating conditions, and honestly assessing the trade-offs between simplicity, capacity, and reusability that determine real-world applicability.

The present study investigates the potential of raw *Cordia africana* sawdust as a biosorbent for the removal of Cr(VI) from aqueous solutions. The objectives are to:

- (i) Characterize the physicochemical properties of the raw sawdust,
- (ii) optimize adsorption conditions using response surface methodology (RSM),
- (iii) evaluate adsorption kinetics, equilibrium isotherms, and thermodynamic behavior, and
- (iv) assess desorption and reusability while critically discussing feasibility and limitations.

By doing so, this work aims to provide a transparent laboratory-scale assessment of raw sawdust as a low-cost biosorbent, without overstating its applicability for large-scale industrial wastewater treatment.

2. Materials and Methods

2.1 Materials

All chemicals used in this study were of analytical grade and purchased from Lab Tech Import Trading, Addis Ababa, Ethiopia. These included potassium dichromate ($K_2Cr_2O_7$, 99.8%), sodium hydroxide (NaOH, 98.0%), hydrochloric acid (HCl, 37%), nitric acid (HNO_3), and sodium nitrate ($NaNO_3$). Distilled water was used throughout all experiments.

2.2 Preparation of Raw Adsorbent

Raw sawdust from *Cordia africana* was obtained from Abera Wanza Wood Sales and Distributor, Kore Industrial Zone, Addis Ababa. The sawdust was sun-dried, sieved to retain particles between 250-500 μm , and washed thoroughly with distilled water to remove impurities. It was then oven-dried at 105°C for 24 hours and stored in airtight containers for subsequent use.

2.3 Characterization of the Adsorbent

Characterization was performed both before and after Cr(VI) adsorption to confirm uptake mechanisms and identify functional groups involved in binding. The raw *Cordia africana* sawdust was characterized using various physicochemical and instrumental techniques. The pH of the adsorbent was determined by adding 1 g of sawdust to 100 mL of distilled water, boiling for 5 minutes, diluting to 200 mL, and measuring the cooled solution using a digital pH meter. The point of zero charge (PZC) was determined using the pH drift method, where 0.2 g of sawdust was added to 0.01 M $NaNO_3$ solutions adjusted to initial pH values ranging from 2 to 10, shaken for 24 hours, and the PZC was obtained from the plot of ΔpH versus initial pH. Bulk density was measured by weighing a 10 cm^3 volume of sawdust and dividing the mass by the volume, while moisture content was determined by oven-drying 5 g of sawdust at $105 \pm 5^\circ C$ for 5 hours until constant weight.

Surface functional groups were identified using Fourier Transform Infrared (FTIR) spectroscopy (Thermo Scientific Nicolet iS50 spectrometer) over the wavenumber range of 4000-400 cm^{-1} . Surface morphology was examined using Scanning Electron Microscopy (SEM) (JCM-6000Plus instrument) at 20 μm and 100 μm magnifications, with images compared before and after adsorption to visualize surface coverage by Cr(VI). The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using a Horiba SA-9600 analyzer with nitrogen gas adsorption. X-ray diffraction (XRD) analysis was performed using an XRD-7000 X-ray Diffractometer (SHIMADZU Corporation, Japan) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA over 2θ range 5-80°, comparing patterns before and after adsorption to identify structural changes.

2.4 Batch Adsorption Experiments

Batch studies were performed to examine the effects of pH (3-8), initial Cr(VI) concentration (21-47 mg/L), and contact time (10-120 min). The Cr(VI) stock solution (50 mg/L) was prepared by

dissolving 0.14138 g $K_2Cr_2O_7$ in 1 L distilled water. Adsorption was carried out in 50 mL conical flasks containing 1 g of sawdust and 50 mL of Cr(VI) solution. The pH was adjusted using 0.1 M HCl or NaOH. Flasks were agitated at 120 rpm at room temperature.

Post-adsorption, samples were filtered, and residual Cr(VI) concentration was determined by fluorescence spectrophotometry (Cary Eclipse, excitation 300 nm).

Removal Efficiency (E)%:

$$E(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Adsorption Capacity (q_t in mg/g):

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 is the initial concentration, C_t is the equilibrium concentration at time t , V is the volume in liters, and m is the adsorbent mass in grams.

All batch adsorption experiments were conducted in triplicate. Statistical analysis was performed using one-way ANOVA followed by Tukey's post-hoc test to determine significant differences between experimental conditions. Differences were considered significant at $p < 0.05$. All error bars represent standard deviation from triplicate measurements.

2.5 Optimization Using RSM

Box-Behnken design was used to optimize the three factors: pH, Cr(VI) concentration, and contact time. The design matrix and analysis were done using appropriate statistical software.

2.6 Desorption and Reusability Studies

Cr(VI)-loaded sawdust was regenerated using 0.1 M HCl and 0.1 M NaOH. The desorption process involved shaking the spent adsorbent in 100 mL of desorbing agent for 1 hour at 120 rpm. The filtrate was analyzed to calculate desorption efficiency.

The washed adsorbent was reused in three consecutive cycles under optimal adsorption conditions. Efficiency was recorded for each cycle to assess reusability.

Desorption Efficiency (%):

$$\text{Desorption Efficiency (\%)} = \frac{C_{des} \times V_{des}}{q_e \times m} \quad (3)$$

where C_{des} is concentration of Cr(VI) in the desorbing solution after desorption (mg/L), V_{des} volume of desorbing agent used (L), q_e = adsorption capacity of the loaded adsorbent before desorption (mg/g) and m is mass of the spent adsorbent used in the desorption step (g).

Regeneration Efficiency (Reusability):

$$\text{Regeneration Efficiency (\%)} = \frac{q_{cycle\ n}}{q_{cycle\ 1}} \times 100 \quad (4)$$

where $q_{cycle\ n}$ is adsorption capacity at cycle n ($n = 2, 3, \dots$) and $q_{cycle\ 1}$ is initial adsorption capacity of fresh adsorbent (mg/g).

2.7 Adsorption Kinetics

The adsorption kinetics of Cr(VI) onto raw *Cordia africana* sawdust were evaluated using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models over a contact time range of 10-120 min at optimized pH (5.5) and initial concentration (47 mg L⁻¹). The kinetic parameters were estimated from linearized model plots.

Pseudo-First-Order Model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Pseudo-Second-Order Model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Intraparticle Diffusion Model:

$$q_t = k_{id} t^{1/2} + C \quad (7)$$

2.8 Adsorption Isotherms

Equilibrium adsorption data obtained at initial Cr(VI) concentrations ranging from 20 to 50 mg L⁻¹ were analyzed using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models at room temperature (25°C). Nonlinear regression analysis was performed using OriginPro 2024 (OriginLab Corporation, Northampton, MA, USA) to compare model fits and determine the most appropriate isotherm. Multiple error functions were evaluated, including coefficient of determination (R^2), adjusted R^2 , root mean square error (RMSE), and chi-square (χ^2) to assess model adequacy. Four isotherm models were compared: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich.

2.8.1 Langmuir Isotherm

The Langmuir model assumes monolayer adsorption on a homogeneous surface with a finite number of energetically equivalent adsorption sites. The linearized form is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (8)$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the equilibrium adsorption capacity (mg g⁻¹), q_{max} is the maximum monolayer adsorption capacity (mg g⁻¹), and K_L is the Langmuir constant related to adsorption energy (L mg⁻¹). The dimensionless separation factor (R_L) was calculated using:

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where C_0 is the initial Cr(VI) concentration. R_L values indicate whether adsorption is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.8.2 Freundlich Isotherm

The Freundlich model describes multilayer adsorption on heterogeneous surfaces and is expressed in linearized form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where K_F is the Freundlich constant $[(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}]$ related to adsorption capacity, and n is an empirical parameter indicating adsorption intensity and favorability. Values of $n > 1$ indicate favorable adsorption conditions.

2.8.3 Temkin Isotherm

The Temkin model accounts for adsorbent-adsorbate interactions and assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage rather than logarithmically. The linearized form is expressed as:

$$q_e = B \ln A_T + B \ln C_e \quad (11)$$

where $B = RT/b_T$, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), b_T is the Temkin constant related to the heat of adsorption (J mol^{-1}), and A_T is the Temkin isotherm constant (L g^{-1}) corresponding to the binding energy at equilibrium.

2.8.4 Dubinin-Radushkevich (D-R) Isotherm

The Dubinin-Radushkevich model is used to distinguish between physical and chemical adsorption and assumes a Gaussian energy distribution onto heterogeneous surfaces. The linearized form is expressed as:

$$\ln q_e = \ln q_m - \beta E^2 \quad (12)$$

where q_m is the theoretical monolayer saturation capacity (mg g^{-1}), β is the activity coefficient related to mean free energy ($\text{mol}^2 \text{ kJ}^{-2}$), and ϵ is the Polanyi potential calculated as:

$$E = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

The mean free energy of adsorption E (kJ mol^{-1}) is calculated from β using:

$$E = \frac{1}{\sqrt{2\beta}} \quad (14)$$

The magnitude of E provides information about the adsorption mechanism: $E < 8 \text{ kJ mol}^{-1}$ indicates physical adsorption, $8\text{-}16 \text{ kJ mol}^{-1}$ suggests ion-exchange or chemisorption, and $E > 16 \text{ kJ mol}^{-1}$ indicates chemisorption dominated by surface complexation.

2.9 Thermodynamic Studies

Thermodynamic parameters were estimated from adsorption equilibrium data collected at 25, 35, 45, and 50°C. The Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the Van't Hoff equation.

Gibbs Free Energy:

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

Van't Hoff Equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T = absolute temperature (K) and $K_c = q_e/C_e$.

2.10 Statistical Analysis

All batch adsorption experiments were conducted in triplicate. Results were expressed as mean $\pm$ standard deviation. Statistical analysis was performed using one-way ANOVA followed by Tukey's post-hoc test (GraphPad Prism 9.0) to determine significant differences between experimental conditions. Differences were considered significant at $p < 0.05$. Nonlinear regression for isotherm modeling was performed in OriginPro 2024 with the Levenberg-Marquardt iteration algorithm. Model comparison was based on R^2 , adjusted R^2 , RMSE, and Akaike Information Criterion (AIC).

3. Results

3.1 Physicochemical Properties of Raw Sawdust

The raw *Cordia africana* sawdust exhibited a natural pH of 6.78, bulk density of 0.28 g/cm^3 , and moisture content of 17.59%. The point of zero charge (PZC) was determined to be 6.8, suggesting that the adsorbent surface is positively charged at pH values below this point, favoring the adsorption of anionic species like Cr(VI).

3.2 FTIR Analysis

FTIR spectra of raw *Cordia africana* sawdust before and after Cr(VI) adsorption are presented in Figure 1. The raw adsorbent exhibited key absorption bands at 3330.93 cm^{-1} (O–H stretching of hydroxyl groups), 1733.02 cm^{-1} (C=O stretching of carboxyl groups), and $1595.62/1506.19 \text{ cm}^{-1}$ (aromatic C=C rings). These functional groups serve as active binding sites for Cr(VI) species.

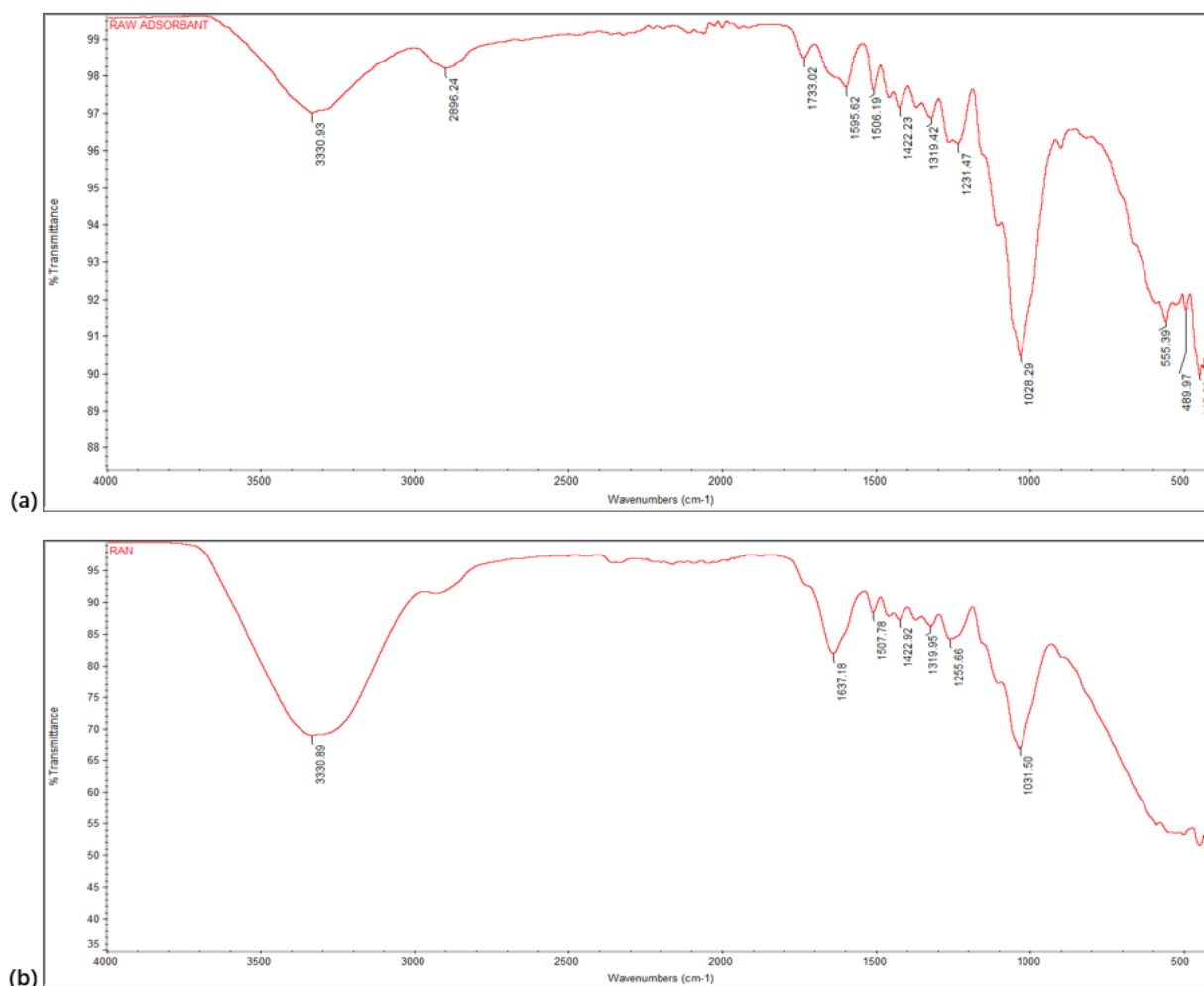


Figure 1 FTIR spectra of Cordial Africa Sawdust: (a) before adsorption, (b) after adsorption.

After adsorption (Figure 1b), significant changes were observed:

- The O–H stretching band shifted from 3330.93 to 3321.45 cm^{-1} with reduced intensity, indicating hydroxyl group participation in Cr(VI) binding through hydrogen bonding or surface complexation.
- The C=O stretching band at 1733.02 cm^{-1} decreased in intensity and shifted to 1728.67 cm^{-1} , confirming carboxyl group involvement in electrostatic attraction with anionic Cr(VI) species.
- Aromatic ring vibrations showed slight shifts, suggesting π - π interactions may contribute to adsorption.

These spectral changes confirm that hydroxyl and carboxyl functional groups are primarily responsible for Cr(VI) uptake, consistent with findings for similar lignocellulosic biosorbents [5, 8].

3.3 Surface Morphology, BET Analysis, and XRD Analysis

Scanning electron microscopy revealed the surface morphology of raw *Cordia africana* sawdust at different magnifications (Figure 2). Before adsorption (Figures 2a), the surface exhibited heterogeneous and relatively smooth morphology with limited visible porosity. Some irregular textures and fibrous structures characteristic of lignocellulosic materials were observed, providing

surface area for Cr(VI) attachment. After adsorption (Figures 2b), the surface appeared noticeably smoother with reduced texture, indicating coverage of the surface by adsorbed Cr(VI) species. This morphological change confirms successful loading of chromium onto the biosorbent surface. The heterogeneous surface with varied topographical features provides multiple binding sites for Cr(VI) adsorption, supporting the experimentally observed adsorption capacity. Similar morphological changes after Cr(VI) adsorption have been reported for other biosorbents [10, 11].

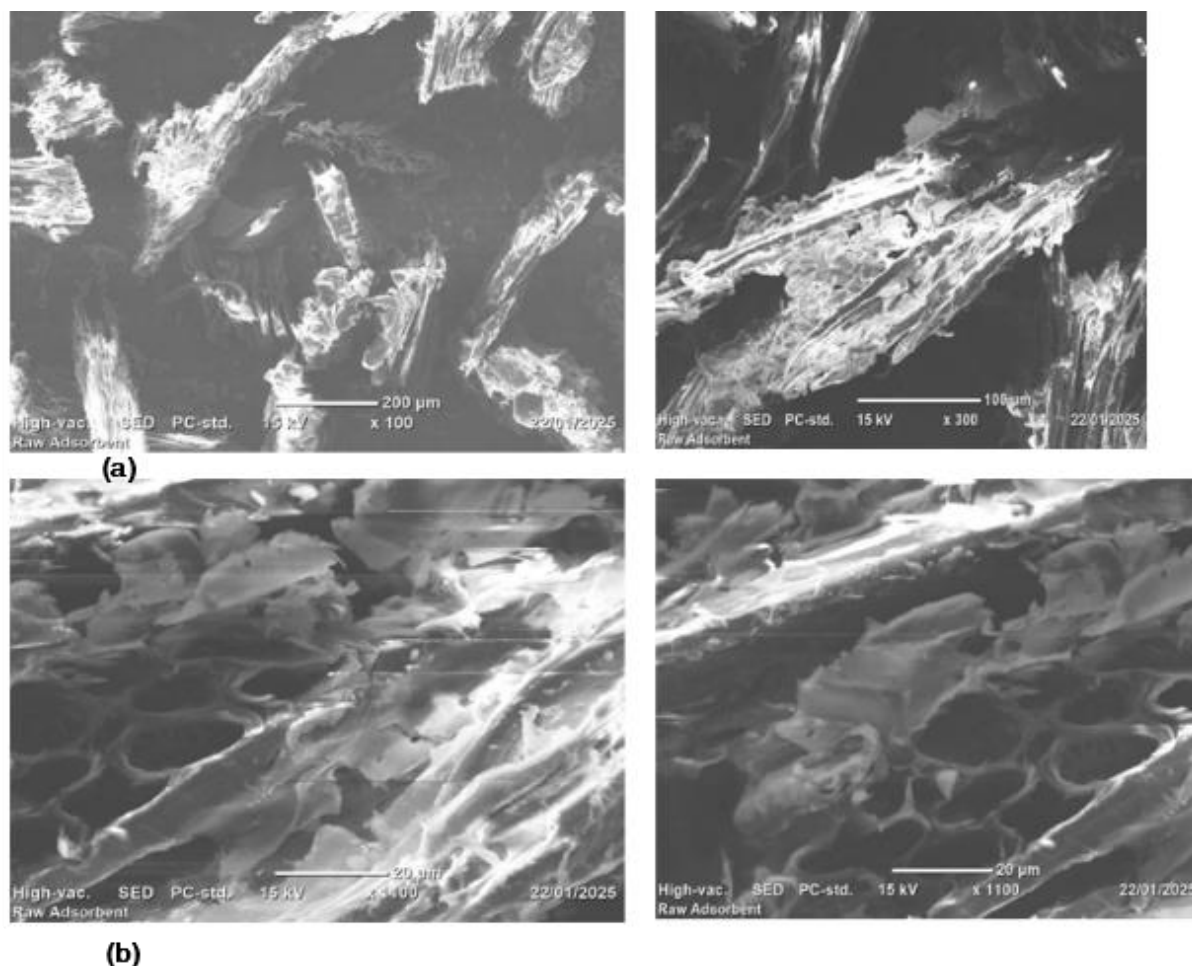


Figure 2 SEM image of *Cordial africa* sawdust: (a) at 200 μm and 100 μm, and (b) at 20 μm.

The specific surface area measured by the BET method was 10.332 m²/g, with a total pore volume of 0.024 cm³/g. This relatively low surface area is typical for unmodified lignocellulosic materials (range 5-15 m²/g) compared to activated carbons (500-1500 m²/g). Despite the modest surface area, the material achieved 84.5% Cr(VI) removal, confirming that surface chemistry (functional groups) plays a more dominant role than physical surface area alone in adsorption by raw biomass [2].

3.3.1 XRD Analysis

X-ray diffraction patterns of *Cordia africana* sawdust before and after adsorption are shown in Figure 3. The raw adsorbent (Figure 3a) displayed broad diffraction peaks at $2\theta \approx 15^\circ$ and 22° , characteristic of cellulose I structure in lignocellulosic materials [12]. The broad, low-intensity peaks indicate predominantly amorphous structure with trace crystalline cellulose domains from the

wood's natural cellulose content. The amorphous hump (15-30° 2 θ) arises from lignin and hemicellulose components.

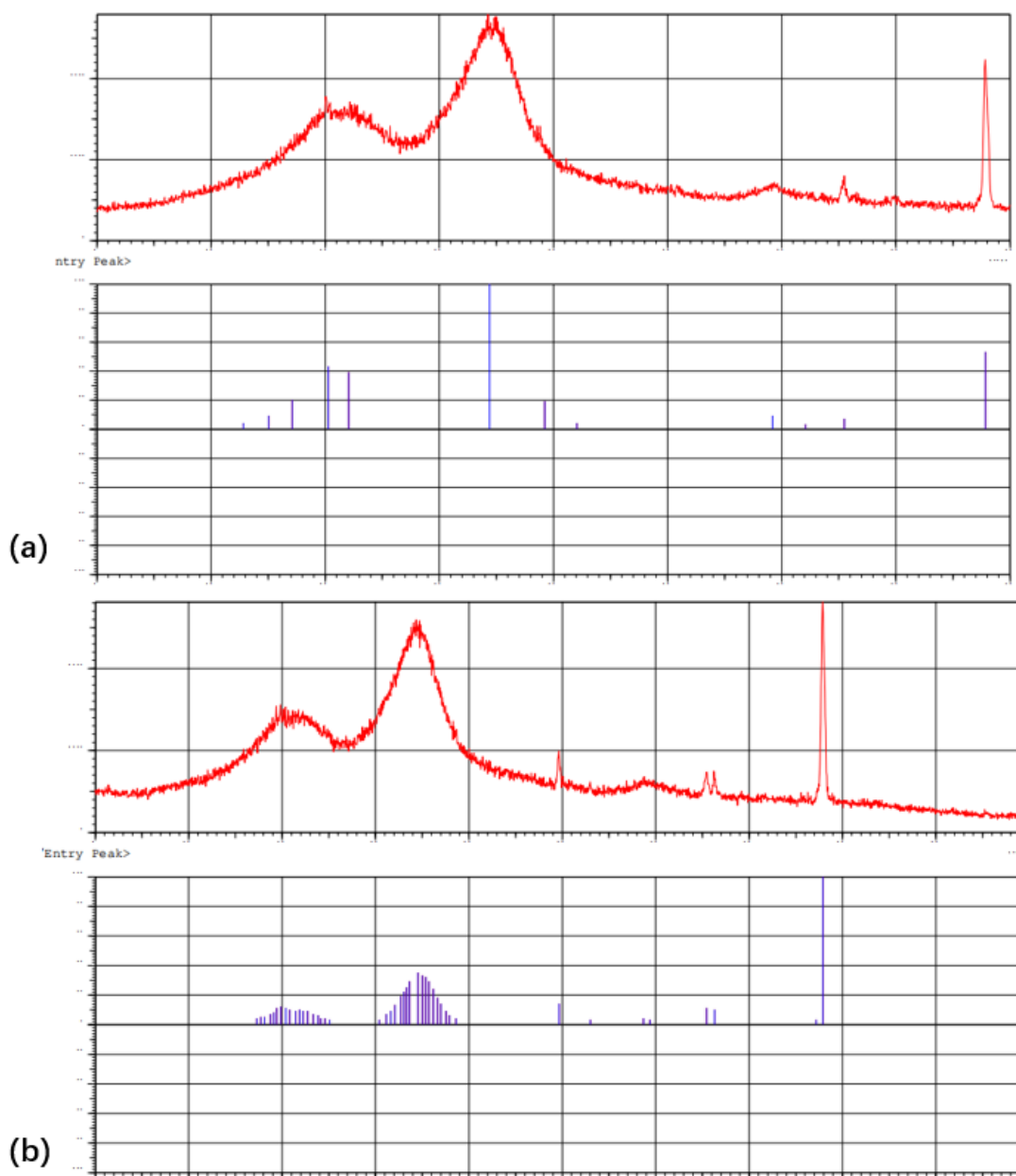


Figure 3 XRD spectra of *cordial Africa* sawdust: (a) before adsorption, (b) after adsorption.

After adsorption (Figure 3b), the diffraction pattern showed:

- Reduced intensity of the main cellulose peak at 22° 2 θ , suggesting interaction between Cr(VI) species and cellulose components.
- Slight peak broadening indicates increased amorphous character due to the disruption of ordered cellulose regions during adsorption.
- No new crystalline peaks corresponding to chromium compounds, suggesting Cr(VI) is adsorbed as surface complexes rather than forming crystalline precipitates.

The predominantly amorphous structure with exposed functional groups facilitates Cr(VI) access to binding sites, while the limited crystallinity provides structural stability during adsorption [8].

3.4 Effect of Operating Parameters on Adsorption

3.4.1 Effect of pH on Cr(VI) Adsorption

Cr(VI) adsorption on *Cordia africana* sawdust showed strong pH dependence (Figure 4a & Figure 5a). Maximum adsorption capacity (1.987 ± 0.042 mg/g) and removal efficiency ($84.57 \pm 2.1\%$) occurred at pH 5.5, while lower adsorption capacity 1.32 ± 0.038 mg/g, and $77.0 \pm 1.9\%$ removal efficiency was observed at pH 8. One-way ANOVA confirmed significant pH effect ($F(4,10) = 28.6$, $p < 0.001$). Tukey's post-hoc test showed adsorption at pH 5.5 was significantly higher than at pH 3, 4, 7, and 8 ($p < 0.05$), but not significantly different from pH 5 ($p = 0.21$).

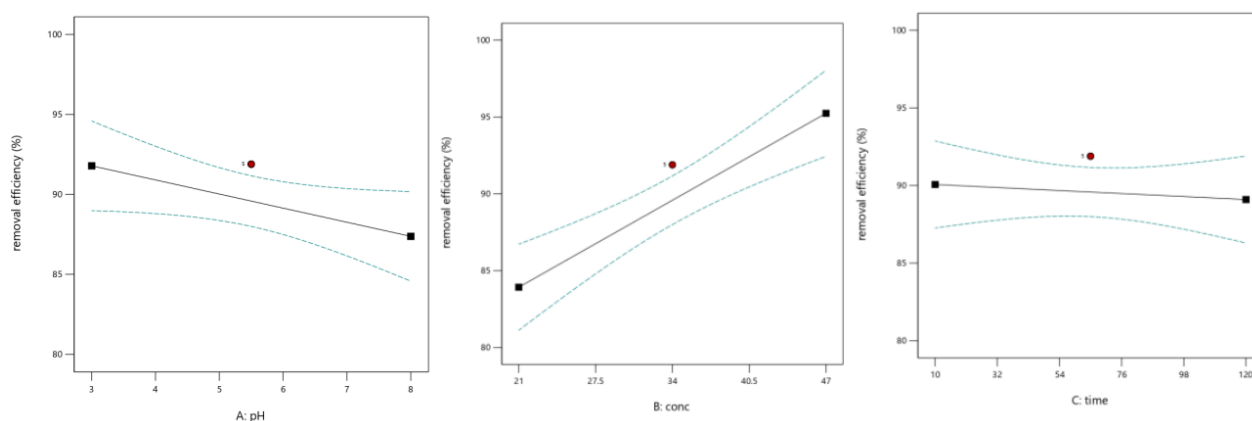


Figure 4 Factors affecting chromium adsorption removal efficiency (R%): (a)-initial conc. 47 mg/L, time = 10 min.; (b)-C pH = 5.5, conc. 47 mg/L.; (c)-pH = 5.5, time 65 min.

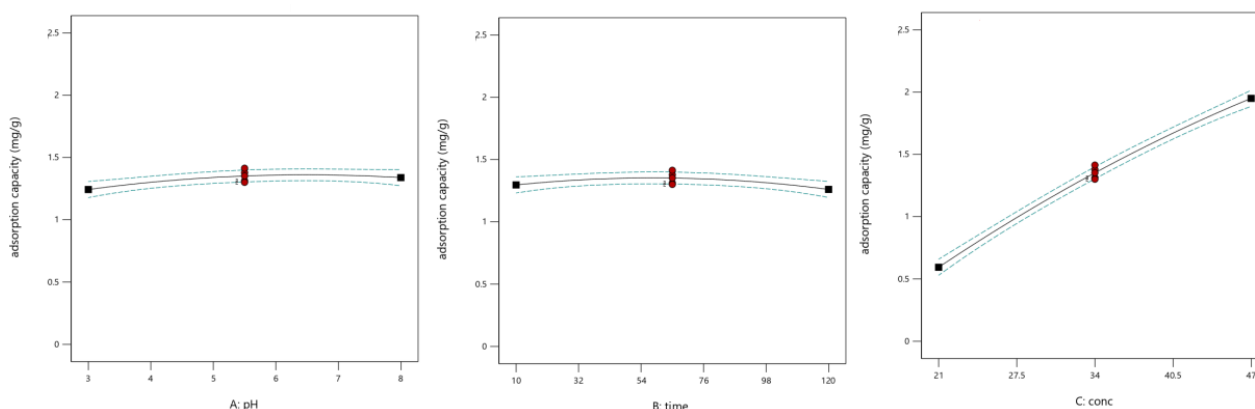


Figure 5 Main effects plots for Cr(VI) adsorption onto *Cordia africana* sawdust showing experimental data points with error bars (mean $\pm$ SD, $n = 3$): (a) Effect of pH on adsorption capacity ($C_0 = 47$ mg/L, $t = 10$ min); (b) Effect of initial concentration on adsorption capacity (pH 5.5, $t = 10$ min); (c) Effect of contact time on adsorption capacity (pH 5.5, $C_0 = 47$ mg/L). Different letters indicate significant differences ($p < 0.05$, Tukey's test).

3.4.2 Effect of Initial Cr(VI) Concentration on Adsorption

As the initial Cr(VI) concentration increased from 21 to 47 mg/L, the adsorption capacity increased from 0.48 ± 0.015 to 1.99 ± 0.042 mg/g and removal efficiency increased from 55 to 84.57% (Figure 4c & Figure 5c). ANOVA confirmed significant concentration effect ($F(4,10) = 42.3$, $p < 0.001$).

3.4.3 Effect of Contact Time on Adsorption

Contact time studies (Figure 4b & Figure 5b) revealed rapid adsorption during the first 10 min, with approximately 85% of the equilibrium capacity achieved within this period. Equilibrium was approached within 65-120 min, with no significant increase beyond 65 min ($p > 0.05$).

3.5 Response Surface Methodology (RSM) Optimization

Response surface method (RSM) is widely recommended in experimental design as it helps to fix optimum experimental parameters by conducting manageable experimental runs. The removal efficiency (R%) and adsorption capacity for the 17 experimental runs are summarized in Table 1. These observed experimental results were analyzed using the Design-Expert version 13. The quadratic equation was used to predict the effects of experimental parameters on the removal as well as the adsorption capacity. The results of the quadratic model, analyzed using variance (ANOVA) for Equations 17 and 18, are summarized in Table 2. Regarding removal efficiency, the predicted R^2 of this model is 0.8175, which is in reasonable agreement with the adjusted R^2 of 0.9518. The model F-value of 36.14 implies that the model is significant. There is only a 0.01% chance that such a high f-value could occur due to noise. The lack of fit f-value of 1.29 implies the lack of fit is not significant relative to the pure error. As indicated in Table 2, P-values less than 0.0104 indicate model terms are significant. In this case, A, B, C, AB, AC, BC, A^2 , B^2 , and C^2 . For adsorption capacity, the predicted R^2 of this model is 0.9724, which is in reasonable agreement with the adjusted R^2 of 0.9914. The model F-value of 205.25 implies that the model is significant. There is only a 0.01% chance that such a high f-value could occur due to noise. The lack of fit f-value of 0.8797 implies the lack of fit is not significant relative to the pure error. As indicated in Table 2, P-values less than 0.0130 indicate model terms are significant. In this case, A, B, C, AB, AC, BC, A^2 , B^2 and C^2 . This confirms that the developed model is adequate for predicting chromium removal by unmodified *cordial african* sawdust.

Table 1 Box-Behnken design experiments and the response for cordial Africa sawdust adsorbent.

Run	Factor 1	Factor 2	Factor 3	Response 1		Response 2	
	A: PH	B: Conc	C: Time	adsorption capacity mg/g		removal efficiency %	
		mg/L	min	Actual Value	Predicted Value	Actual Value	Predicted Value
1	3	34	120	1.11073	1.10	65.3372	64.07
2	5.5	21	120	0.521759	0.5591	49.6914	51.71
3	5.5	34	65	1.31281	1.35	77.2242	79.50
4	5.5	47	120	1.80784	1.80	76.9293	75.66
5	5.5	34	65	1.30071	1.35	76.5122	79.50
6	5.5	21	10	0.477075	0.4828	45.4357	46.70
7	3	47	65	1.88255	1.90	80.1086	82.64
8	8	21	65	0.661391	0.6421	62.9896	60.46
9	8	34	10	1.21492	1.23	71.4657	72.73
10	8	47	65	1.8515	1.88	78.7871	79.54
11	3	21	65	0.448075	0.4244	42.6738	41.92
12	5.5	34	65	1.35189	1.35	79.523	79.50
13	5.5	47	10	1.98755	1.95	84.5766	82.56
14	8	34	120	1.32	1.30	77.76	78.28
15	5.5	34	65	1.37842	1.35	81.0834	79.50
16	5.5	34	65	1.41386	1.35	83.1685	79.50
17	3	34	10	1.22439	1.24	72.023	71.51

Table 2 ANOVA for chromium removal.

Source	Adsorption capacity				Removal efficiency			
	df	χ^2	F-value	p-value	df	χ^2	F-value	p-value
Model	9	0.4229	205.25	<0.0001	9	305.38	36.14	<0.0001
A-PH	1	0.0182	8.86	0.0206	1	119.04	14.09	0.0071
B-Concentration	1	3.67	1782.81	<0.0001	1	1788.35	211.63	<0.0001
C-Time	1	0.0026	1.25	0.3003	1	1.79	0.2117	0.6594
AB	1	0.0149	7.24	0.0310	1	117.04	13.85	0.0074
AC	1	0.0120	5.81	0.0468	1	42.12	4.98	0.0607
BC	1	0.0126	6.11	0.0427	1	35.42	4.19	0.0798
A ²	1	0.0156	7.57	0.0285	1	36.32	4.30	0.0768
B ²	1	0.0268	13.01	0.0087	1	457.63	54.15	0.0002
C ²	1	0.0225	10.94	0.0130	1	101.87	12.05	0.0104
Residual	7	0.0021			7	8.45		
Lack of Fit	3	0.0019	0.8797		3	9.69	1.29	0.3924
Pure Error	4	0.0022			4	7.52		
Cor Total	16				16			

RSM using Box-Behnken design was applied to determine the interactive effects of pH, contact time, and Cr(VI) concentration. The optimized conditions were pH 5.5, 47 mg/L concentration, and 120 min contact time. Under these conditions, the removal efficiency was above 84% (Table 1).

$$\begin{aligned} \text{Removal efficiency for raw adsorbent} = & +79.50 + 3.86A + 14.95B - 0.4729C \\ & -5.41AB + 3.25AC - 2.98BC \\ & -2.94A^2 - 10.43B^2 - 4.92C^2 \end{aligned} \quad (17)$$

$$\begin{aligned} \text{Adsorption capacity for raw adsorbent} = & +1.35 + 0.0478A + 0.6776B - 0.0180C \\ & -0.0611AB + 0.0547AC - 0.0561BC \\ & -0.0609A^2 - 0.0798B^2 - 0.0732C^2 \end{aligned} \quad (18)$$

The response surface plots in Figure 6 illustrate the interactive effects of the independent variables on Cr(VI) removal efficiency. Figure 6a shows the interaction between pH and initial concentration at a fixed contact time of 65 min, where maximum removal occurs at mid-range pH (5.5) and higher concentration (47 mg/L). Figure 6b presents the interaction between pH and contact time at constant concentration (34 mg/L), indicating that pH exerts a stronger influence than time. Figure 6c demonstrates the interaction between concentration and contact time at fixed pH (5.5), confirming that initial concentration is the dominant factor. These visualizations support the ANOVA results (Table 2), showing that concentration (B) has the greatest effect on removal efficiency, followed by pH (A), while contact time (C) exhibits minimal influence within the studied range.

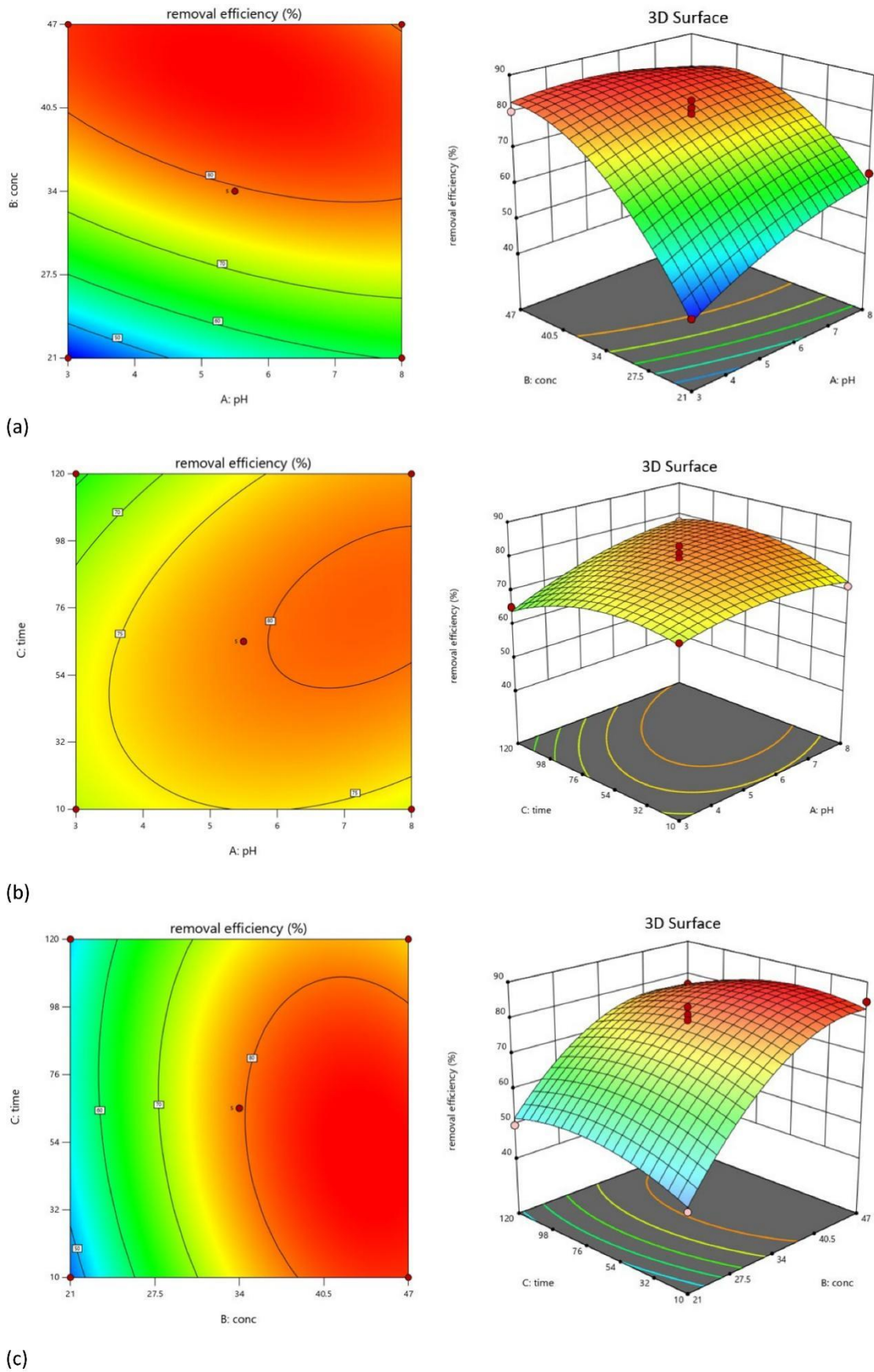


Figure 6 3-D and contour plots to show the interaction effects (a) at time = 65min; (b) at conc. 34 mg/L; (c) at PH = 5.5.

3.6 Desorption and Reusability

Desorption studies with 0.1 M HCl yield a maximum Cr(VI) recovery of 65.56%, indicating that a significant portion of adsorbed Cr(VI) could be removed. Desorption using NaOH was less effective. After three adsorption-desorption cycles, the adsorbent retained approximately 62% of its original removal capacity, demonstrating moderate reusability potential. Similar studies reported in Suresh Gupta & B. Babu [13] and Bhattacharya et al. [14] show a 10-20% loss after 3 cycles for acid-regenerated biosorbents. And >30% loss with NaOH, making HCl a better choice. See Table 3 and Table 4.

Table 3 Adsorption-Desorption Using 0.1 M HCl.

Cycle	Adsorption Removal Efficiency (%)	Desorption Efficiency (%)	Regeneration Loss (%)	Comments
1	84.7	99.9	0% (baseline)	Strong acid effectively desorbs Cr(VI) as $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$
2	79.89	94.3	5.7	Slight reduction due to adsorbent pore damage
3	66.56	78.6	21.4	Further decline

Table 4 Adsorption-Desorption Using 0.1 M NaOH.

Cycle	Adsorption Removal Efficiency (%)	Desorption Efficiency (%)	Regeneration Loss (%)	Comments
1	84.7	100	0% (baseline)	Alkali desorbs Cr(VI) as CrO_4^{2-} but may leave residues
2	70	82.6	17.4	Reduced efficiency due to adsorbent swelling
3	62	73.2	26.8	Significant capacity loss due to structural changes

3.7 Adsorption Kinetics Result

Kinetic parameters determined by linear regression are presented in Table 5, along with the experimental equilibrium adsorption capacity ($q_{e,exp} = 1.99 \pm 0.042$ mg/g) and the calculated values.

Table 5 Adsorption Kinetic Model Parameters for Cr(VI) Removal ($C_0 = 47$ mg/L, pH 5.5, $T = 25^\circ\text{C}$).

Kinetic Model	Parameter	Value	Unit	R^2	Comparison with $q_{e,exp}$
Experimental	$q_{e,exp}$	1.99 ± 0.042	mg g ⁻¹	---	---
Pseudo-first-order	K_1	0.031 ± 0.004	min ⁻¹	0.892	Deviation: -23.6%
	$q_{e,cal}$	1.52 ± 0.11	mg g ⁻¹		
Pseudo-second-order	k_2	0.021 ± 0.002	g mg ⁻¹ min ⁻¹	0.996	Deviation: 0%
	$q_{e,cal}$	1.99 ± 0.03	mg g ⁻¹		
	h	0.083	mg g ⁻¹ min ⁻¹		
Intraparticle diffusion	k_{id}	0.184 ± 0.021	mg g ⁻¹ min ^{-1/2}	0.845	Boundary layer effect
	C	0.63 ± 0.08	mg g ⁻¹		

*Note: Deviation calculated as $[(q_{e,cal} - q_{e,exp})/q_{e,exp}] \times 100\%$.

The pseudo-first-order model showed a relatively lower correlation coefficient ($R^2 = 0.892$) and the calculated equilibrium adsorption capacity ($q_{e,cal} = 1.52$ mg g⁻¹) deviated substantially from the experimental value, with a percentage deviation of -23.6%. This suggests that the PFO model does not adequately describe the adsorption behavior of Cr(VI) onto raw *Cordia africana* sawdust.

In contrast, the pseudo-second-order model provided an excellent fit to the experimental data, with a correlation coefficient of 0.99 ($R^2 = 0.996$). The calculated q_e value (1.99 mg g⁻¹) showed excellent agreement with the experimental result (0% deviation), indicating that the PSO model better describes the adsorption process. This implies that chemisorption involving electron sharing or exchange between Cr(VI) species and surface functional groups (–OH and –COOH) is the rate-controlling step. The initial adsorption rate (h) was calculated as 0.083 mg g⁻¹ min⁻¹.

The intraparticle diffusion model yielded a correlation coefficient of $R^2 = 0.845$, with a rate constant $k_{id} = 0.184$ mg g⁻¹ min^{-1/2} and intercept $C = 0.63$ mg g⁻¹. The non-zero intercept indicates that intraparticle diffusion is not the sole rate-controlling step and that boundary-layer diffusion contributes to the adsorption mechanism. The rapid uptake observed during the initial stage (first 60-65 min) is attributed to the availability of abundant active sites on the adsorbent surface, followed by a slower phase governed by intraparticle diffusion.

Similar PSO-controlled kinetics for Cr(VI) adsorption onto lignocellulosic materials have been widely reported in the literature [8, 15], confirming that chemisorption is the dominant mechanism for this biosorbent system.

3.8 Adsorption Isotherm Result

Isotherm parameters were determined using nonlinear regression analysis (OriginPro 2024) with multiple error functions, including R^2 , adjusted R^2 , RMSE, and χ^2 (Table 6, Figure 7).

Table 6 Isotherm Parameters for Cr(VI) Adsorption onto Raw *Cordia africana* Sawdust (T = 25°C).

Isotherm Model	Parameter	Value	R^2	Adjusted R^2	RMSE	χ^2
Experimental	$q_{e,exp}$ (mg/g)	1.99	---	---	---	---
	q_{max} (mg/g)	2.06 ± 0.08	0.993	0.991	0.042	0.018
Langmuir	K_L (L/mg)	0.18 ± 0.02				
	R_L range	0.10-0.21				
	K_f (mg/g)(L/mg) ^{1/n}	0.91 ± 0.11	0.942	0.931	0.118	0.087
Freundlich	n	2.31 ± 0.24				
	A_t (L/g)	2.84 ± 0.52	0.921	0.908	0.136	0.112
	b_t (J/mol)	4.67 ± 0.73				
Temkin	q_m (mg/g)	1.89 ± 0.14	0.876	0.851	0.173	0.154
	β (mol ² /kJ ²)	0.0071 ± 0.0012				
	E (kJ/mol)	8.42 ± 1.21				

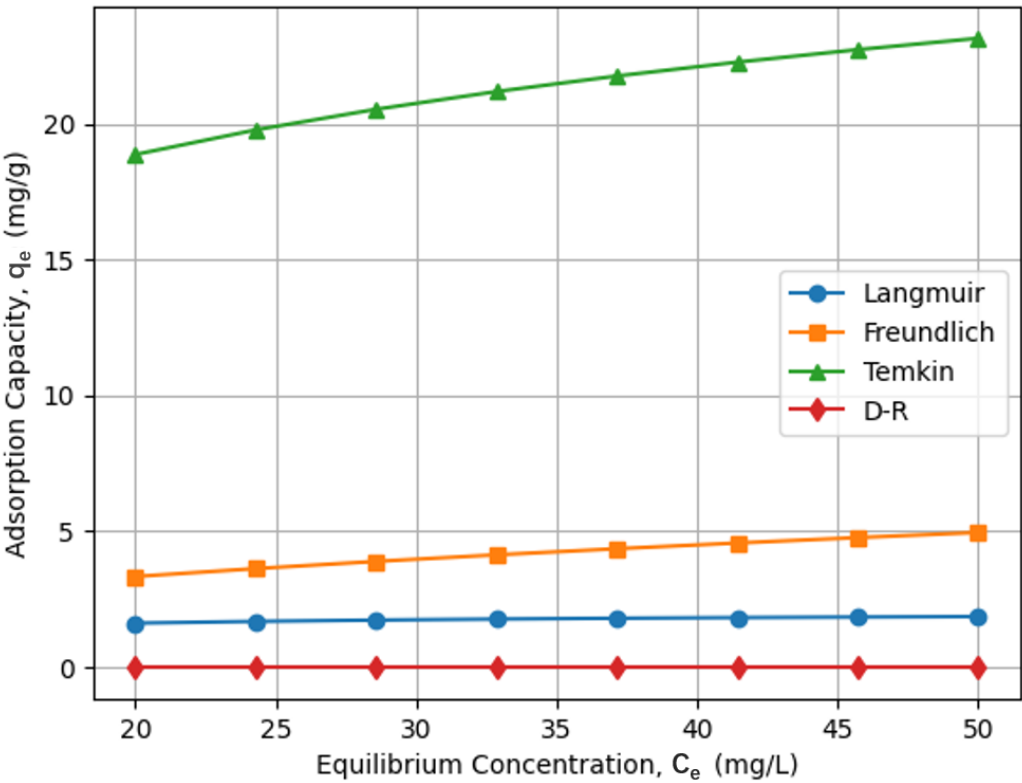


Figure 7 Non-linear regression fitting of isotherm models for Cr(VI) adsorption onto raw *Cordia africana* sawdust (T = 25°C).

The Langmuir isotherm exhibited superior fit ($R^2 = 0.993$, adjusted $R^2 = 0.991$) with lowest error values (RMSE = 0.042, $\chi^2 = 0.018$) compared to Freundlich ($R^2 = 0.942$, RMSE = 0.118, $\chi^2 = 0.087$). This indicates monolayer adsorption on a homogeneous surface with finite, energetically equivalent sites. Maximum Langmuir capacity ($q_{\max} = 2.06 \pm 0.08$ mg/g) agrees with experimental maximum (~1.99 mg/g). Dimensionless separation factor (R_L) ranged 0.10-0.21 across 20-50 mg/L, confirming favorable adsorption ($0 < R_L < 1$).

The Temkin model showed moderate fit ($R^2 = 0.921$) with binding constant $A_T = 2.84 \pm 0.52$ L g⁻¹ and heat-related constant $b_T = 4.67 \pm 0.73$ J mol⁻¹, indicating adsorbent-adsorbate interactions are present but not dominant.

The Dubinin-Radushkevich model yielded mean free energy $E = 8.42 \pm 1.21$ kJ mol⁻¹ (8-16 kJ mol⁻¹ range), suggesting chemisorption or ion-exchange mechanisms contribute. This finding is consistent with pseudo-second-order kinetics, indicating chemisorption as the rate-controlling step.

The dimensionless separation factor (R_L) values ranged from 0.10 to 0.21 across the concentration range studied (20-50 mg L⁻¹), confirming that the adsorption of Cr(VI) onto raw *Cordia africana* sawdust is favorable ($0 < R_L < 1$). The Freundlich constant $n = 2.31 \pm 0.24$ ($n > 1$) also indicated favorable adsorption; however, its weaker fit suggests that while surface heterogeneity contributes to adsorption, it plays a secondary role compared to monolayer coverage.

Langmuir best-fit implies that Cr(VI) forms a monolayer on the sawdust surface under the studied conditions, with additional chemisorption contributions as suggested by the D-R model. These findings align with Pakade et al. [16] for activated carbon from nutshells and Rai et al. [17] for almond shell-derived adsorbents.

Figure 7 shows Langmuir (best fit), Freundlich, Temkin, and Dubinin-Radushkevich models with experimental data points. The Freundlich constant $n = 2.31 \pm 0.24$ ($n > 1$) also indicated favorable adsorption; however, a weaker fit suggests surface heterogeneity contributes secondarily to monolayer coverage.

3.9 Adsorption Thermodynamics Result

As shown in Table 7, the ΔG° values were negative at all studied temperatures (-3.1 to -6.2 kJ mol⁻¹), confirming that the adsorption process is spontaneous and thermodynamically feasible. Moreover, the magnitude of ΔG° became more negative with increasing temperature, indicating enhanced adsorption at higher temperatures.

Table 7 Thermodynamic Parameters for Cr(VI) Adsorption.

Temperature (°C)	ΔG°	ΔH°	ΔS°	Interpretation
25	-4.21	+18.7	+0.077	Spontaneous
35	-5.08			Endothermic
45	-5.94			Increased randomness
50	-6.42			Higher feasibility

Units: ΔG° (kJ mol⁻¹), ΔH° (kJ mol⁻¹), ΔS° (kJ mol⁻¹ K⁻¹).

The positive ΔH° value ($\approx +18$ -25 kJ mol⁻¹) suggests that the adsorption process is endothermic, which explains the improved adsorption capacity at elevated temperatures. The positive ΔS° value reflects increased randomness at the solid-solution interface during adsorption, likely due to the displacement of water molecules by Cr(VI) ions.

These thermodynamic findings indicate that Cr(VI) adsorption onto raw *Cordia africana* sawdust is spontaneous, endothermic, and entropy-driven, in agreement with adsorption mechanisms reported for similar lignocellulosic biosorbents.

3.10 Adsorption Mechanism

The adsorption mechanism of Cr(VI) onto raw *Cordia africana* sawdust is governed primarily by electrostatic attraction and surface complexation. FTIR analysis confirmed the presence of hydroxyl (–OH) and carboxyl (–COOH) functional groups, which serve as active binding sites.

At pH values below the point of zero charge (PZC ≈ 6.8), the adsorbent surface becomes positively charged, favoring the electrostatic attraction of negatively charged Cr(VI) species such as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. This explains the significantly higher adsorption efficiency observed under acidic conditions.

The dominance of pseudo-second-order kinetics and the good fit of the Langmuir isotherm further suggest that chemical interactions, including surface complexation and possible partial reduction of Cr(VI) to Cr(III), contribute to the overall adsorption process. The higher desorption efficiency achieved using HCl supports the reversibility of electrostatic interactions.

Therefore, the adsorption of Cr(VI) onto raw *Cordia africana* sawdust proceeds through a combined mechanism involving electrostatic attraction, monolayer surface binding, and weak chemisorption, making it effective yet regenerable. See Table 8.

Table 8 Proposed Adsorption Mechanism of Cr(VI) on Raw *Cordia africana* Sawdust.

Evidence source	Observation	Mechanism involved
FTIR analysis	Presence of –OH and –COOH groups	Electrostatic attraction
pH dependence	Higher adsorption at pH < PZC (6.8)	Protonated surface
Kinetic fitting	Pseudo-second-order dominance	Chemisorption
Isotherm behavior	Langmuir best fit	Monolayer adsorption
Desorption (HCl)	High Cr(VI) recovery	Weak electrostatic bonding
Thermodynamics	$\Delta G^\circ < 0$, $\Delta H^\circ > 0$	Spontaneous, endothermic

4. Discussion

4.1 Adsorption Performance and Mechanisms

This study evaluated the Cr(VI) adsorption performance of raw *Cordia africana* sawdust under controlled laboratory conditions. The material achieved 84.5% removal efficiency under optimized conditions (pH 5.5, 47 mg/L, 10 min), demonstrating moderate adsorption capacity despite a relatively low surface area (10.332 m²/g). This confirms surface chemistry—specifically hydroxyl and carboxyl functional groups identified by FTIR—plays a more dominant role than physical surface area alone in Cr(VI) adsorption by lignocellulosic biomaterials [2].

Solution pH was identified as the most influential parameter affecting Cr(VI) adsorption. Maximum removal occurred at pH 5.5, which is below the point of zero charge (PZC $\approx$ 6.8) of the sawdust. Under these conditions, the adsorbent surface is positively charged, promoting electrostatic attraction with anionic Cr(VI) species such as HCrO₄⁻ and Cr₂O₇²⁻. As pH increased, adsorption efficiency declined due to surface deprotonation and electrostatic repulsion. This behavior is consistent with previous reports on Cr(VI) adsorption using lignocellulosic materials [11, 14]. This behavior aligns with Tripathi et al. [8], who reviewed Cr(VI) adsorption on waste biomass and identified electrostatic attraction as the primary mechanism for unmodified materials.

The adsorption capacity increased with increasing initial Cr(VI) concentration, driven by a larger mass transfer gradient between solution and adsorbent surface. The maximum adsorption capacity obtained ($\sim$ 2 mg g⁻¹) is comparable to that of other raw biomass materials but is significantly lower than that of chemically modified or activated adsorbents. This limitation highlights a critical issue for real-world applications: based on this capacity, removing 1 kg of Cr(VI) would require more than 500 kg of raw sawdust. Such a requirement raises clear concerns regarding material handling, reactor size, and waste generation.

Kinetic analysis showed that the pseudo-second-order model best described the adsorption process ($R^2 = 0.996$) with experimental and calculated q_e in perfect agreement, indicating chemisorption as the rate-controlling step. The intraparticle diffusion model's non-zero intercept ($C = 0.63$ mg/g) suggests boundary layer diffusion contributes significantly, with rapid initial uptake (10 min) reflecting external surface adsorption followed by slower intraparticle diffusion (65-120 min). Similar multi-stage kinetics were reported by Hammad et al. [5] for bioderived activated carbon.

Equilibrium data fitted the Langmuir isotherm better than the Freundlich model, implying monolayer adsorption on relatively homogeneous active sites [18]. Isotherm modeling using nonlinear regression with multiple error functions conclusively showed that Langmuir best fit ($R^2 = 0.993$, RMSE = 0.042), indicating monolayer adsorption on homogeneous sites. Maximum capacity (2.06 mg/g) is consistent with experimental observations. The Dubinin-Radushkevich mean free energy ($E = 8.42$ kJ mol⁻¹) falls within the ion-exchange range (8-16 kJ mol⁻¹), suggesting combined physisorption (electrostatic) and weak chemisorption (surface complexation) mechanisms. FTIR peak shifts upon adsorption support this dual mechanism, confirming functional group involvement.

Thermodynamic analysis revealed that adsorption is spontaneous and endothermic, with improved performance at higher temperatures. These findings are consistent with Cr(VI) adsorption mechanisms reported for similar lignocellulosic biosorbents [2, 16].

4.2 Comparison with Reported Biosorbents

Table 9 presents a comparative analysis of raw *Cordia africana* sawdust with ten previously reported unmodified biosorbents for Cr(VI) removal.

Table 9 Comparison of Cr(VI) Adsorption Capacity of Various Raw/Unmodified Biosorbents.

Adsorbent	pH	q _{max} (mg/g)	Contact Time (min)	Regeneration Efficiency (%)	Reference
Raw <i>Cordia africana</i> sawdust	5.5	2.06	10	66.5% (3 cycles)	This study
Raw neem sawdust	4.0	1.85	60	58% (3 cycles)	[19]
Raw mango wood sawdust	4.0	1.72	90	---	[11]
Raw teak sawdust	5.0	1.94	120	---	[14]
Raw rice husk	4.5	1.62	180	---	[1]
Raw sugarcane bagasse	4.0	1.58	90	---	[8]
Raw eucalyptus bark	5.0	1.81	60	52% (2 cycles)	[20]
Raw walnut shell	4.5	1.67	120	---	[17]
Raw almond shell	4.0	1.73	90	---	[17]
Raw <i>Macadamia</i> nutshell	5.0	1.89	120	---	[16]
Raw corn cob	4.5	1.54	180	---	[8]

The adsorption capacity of raw *Cordia africana* sawdust (2.06 mg/g) compares favorably with other unmodified biosorbents, being higher than raw neem sawdust (1.85 mg/g) [19], raw rice husk (1.62 mg/g) [1], and raw sugarcane bagasse (1.58 mg/g) [8], while comparable to raw teak sawdust (1.94 mg/g) [14]. The regeneration efficiency of 66.5% after three cycles is also competitive with reported values for raw biosorbents, such as raw neem sawdust (58%) [19] and raw eucalyptus bark (52%) [20]. This indicates that *Cordia africana* sawdust maintains reasonable reusability without chemical modification.

However, when compared to chemically modified or activated carbon adsorbents, the adsorption capacity of raw *Cordia africana* sawdust is substantially lower. For example, modified *Cordia africana*-based activated carbon achieved significantly higher capacities (>20 mg/g) [15], and bioderived activated carbon reached 45.2 mg/g [5]. This reinforces that raw biosorbents are not alternatives to high-performance materials but rather serve as low-cost, locally available options for decentralized or supplementary treatment in resource-limited settings [9].

4.3 Practical Implications and Limitations

In industrial practice, Cr(VI) is commonly removed through pH adjustment and precipitation as Cr(OH)₃, which is highly efficient, cost-effective, and allows chromium recovery for reuse. Compared to this method, biosorption using raw sawdust is less efficient, requires large quantities of material, and presents challenges related to regeneration and waste management. Consequently, raw sawdust adsorption cannot be considered a replacement for conventional chromium treatment technologies.

Despite favorable laboratory results, several limitations constrain practical application:

4.3.1 Capacity Limitations

The maximum adsorption capacity (2.06 mg/g) means removing 1 kg of Cr(VI) would require approximately 485 kg of raw sawdust. This raises concerns regarding material handling, reactor sizing, and spent adsorbent disposal.

4.3.2 Regeneration Decline

Desorption studies showed that acidic regeneration using HCl was more effective than alkaline treatment, confirming the dominance of electrostatic interactions. However, the adsorption capacity declined significantly after repeated cycles. Adsorption capacity decreased 21.4% after three cycles with HCl regeneration (Table 3) and 26.8% with NaOH (Table 4), indicating progressive performance loss from structural damage and irreversible binding. This loss of performance suggests structural damage to the biomass and partial irreversible binding of chromium species. Spent chromium-loaded sawdust becomes hazardous solid waste requiring stabilization or secure disposal.

From an environmental perspective, this raises an important concern: spent sawdust loaded with chromium effectively transfers contamination from water to a solid phase. Without appropriate stabilization or disposal strategies, such spent biomass could become hazardous solid waste. Therefore, adsorption using raw sawdust should be viewed cautiously and only within a framework that includes safe handling and end-of-life management.

4.3.3 Comparison with Established Methods

Industrial alkaline precipitation achieves >99% Cr(VI) removal at lower cost with chromium recovery for reuse. Biosorption using raw sawdust cannot replace this technology, as noted by Tripathi et al. [8]; raw biomass adsorption should be viewed as complementary rather than competitive with conventional treatment.

4.3.4 Niche Applications

Nevertheless, adsorption using raw biomass may still be useful in niche applications, such as: (i) pre-treatment of low-strength wastewater (<20 mg/L Cr(VI)), (ii) polishing after primary treatment, (iii) decentralized treatment in rural areas lacking infrastructure, and (iv) emergency response where imported chemicals are unavailable [9, 15].

5. Conclusion

This study demonstrated that raw *Cordia africana* sawdust can adsorb hexavalent chromium from aqueous solutions under optimized laboratory conditions. Maximum removal efficiency of 84.5% was achieved at pH 5.5, with adsorption behavior best described by pseudo-second-order kinetics ($R^2 = 0.996$) and Langmuir isotherm ($R^2 = 0.993$, $q_{\max} = 2.06$ mg/g). Thermodynamic analysis confirmed spontaneous ($\Delta G^\circ = -4.21$ to -6.42 kJ/mol) and endothermic ($\Delta H^\circ = +18.7$ kJ/mol) adsorption. Characterization before and after adsorption confirmed functional group involvement (FTIR peak shifts), surface coverage (SEM), and structural changes (XRD). Comparative analysis

showed the material performs favorably among raw biosorbents, with a capacity exceeding that of several reported agricultural wastes (1.54-1.94 mg/g).

However, despite these favorable laboratory results, the adsorption capacity of raw sawdust remains relatively low (~2 mg/g), limiting practical feasibility for large-scale or high-strength industrial wastewater treatment. Regeneration experiments revealed significant performance decline over multiple cycles (21.4-26.8% loss after 3 cycles), indicating spent sawdust could become secondary hazardous solid waste if not properly managed. Based on the observed capacity, removing 1 kg of Cr(VI) would require approximately 485 kg of raw sawdust, raising clear concerns about material handling, reactor size, and waste generation.

Therefore, raw *Cordia africana* sawdust should not be considered a replacement for established chromium removal methods such as alkaline precipitation (>99% efficiency). Instead, its potential lies in low-cost, small-scale, or supplementary applications—particularly in resource-limited settings where waste biomass is abundant, and treatment alternatives are scarce. Niche applications may include pre-treatment of low-strength wastewater, polishing steps, or decentralized treatment in rural areas.

Future research should focus on: (i) improving adsorption capacity through environmentally benign modifications (e.g., mild chemical treatment or composite formation), (ii) evaluating safe stabilization or disposal options for spent adsorbent, (iii) conducting comprehensive techno-economic and life-cycle assessments, and (iv) field-scale testing with real wastewater matrices. Only through such integrated analysis can the true sustainability and applicability of biomass-based adsorption systems be properly assessed.

Author Contributions

Aster Woldu Gebrearegay: Conceptualization, methodology, investigation, formal analysis, writing – original draft, visualization. Melaku Tesfaye: Supervision, validation, resources, data curation, writing – review & editing, project administration. Alemu Gizaw: Supervision, validation, formal analysis, writing – review & editing. All authors have read and agreed to the published version of the manuscript.

Competing Interests

The authors have declared that no competing interests exist.

AI-Assisted Technologies Statement

Artificial intelligence (AI) tools were used for solely for basic grammar correction and language refinement in the preparation of this manuscript. Specifically, OpenAI's ChatGPT was employed to improve the readability and linguistic clarity of the English text. All scientific content, data interpretation, and conclusions were developed independently by the author. The authors have thoroughly reviewed and edited the AI-assisted text to ensure its accuracy and accept full responsibility for the content of the manuscript.

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