



Remediation of Chromium (VI)-Contaminated Water Using Biochar: A Performance and Mechanistic Study

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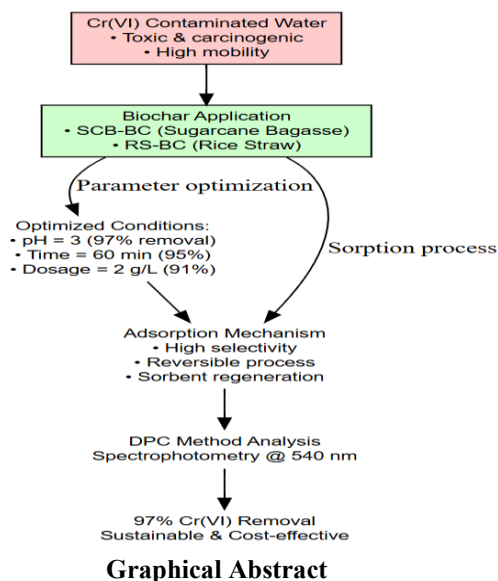
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Abstract

Chromium (Cr), particularly its hexavalent form Cr(VI), is a hazardous heavy metal and a recognized human carcinogen. Compared to trivalent Cr (III), Cr (VI) exhibits higher mobility and solubility in water, posing a greater environmental and health risk. Among various remediation techniques, adsorption is recognized for its operational simplicity, cost-effectiveness, and high selectivity. This study evaluated the efficacy of different biochars, an eco-friendly and abundant sorbent, for removing Cr (VI) from contaminated water. Batch sorption experiments were conducted to investigate the influence of key parameters, including solution pH, contact time, and sorbent dosage. Cr (VI) concentration was quantified spectrophotometrically at 540 nm using the diphenylcarbazide (DPC) method. Results demonstrated that a maximum sorption capacity of 97% was achieved using sugarcane bagasse biochar (SCB-BC) at pH 3. The same sorbent also showed maximum sorption (95%) after a contact time of 60 minutes. In terms of dosage, rice straw biochar (RS-BC) achieved 91% removal at a concentration of 2 g L⁻¹. Kinetic modeling provided further insight into the adsorption mechanism. The process also proved to be reversible, allowing for sorbent regeneration and recovery, thereby minimizing solid waste. This study concludes that biochar, particularly SCB-BC under optimized conditions, is a highly effective and sustainable sorbent for the remediation of Cr (VI)-contaminated water.

1. Introduction

Water is a crucial natural resource essential for human activity and ecosystem stability, requiring prudent management for long-term sustainability. However, industrialization has led to the discharge of inadequately treated pollutants into aquatic systems, causing a significant accumulation of harmful contaminants, including non-biodegradable heavy metals (Younas et al., 2022). These metals are of particular concern due to their toxicity, persistence, and ability to bioaccumulate within food chains, ultimately threatening environmental health and human safety. Chromium (Cr), especially in its hexavalent form Cr(VI), is a prime example, ranked by the World Health Organization as a top-priority hazardous heavy metal and classified as a Group A human carcinogen by the USEPA (Yuan, Wei, Yang, Wang, & Hussain, 2025). While chromium occurs naturally through processes like rock weathering and volcanic activity, anthropogenic activities



such as electroplating, leather tanning, pigment production, and ore smelting are the primary sources of environmental contamination (Xie et al., 2023). The toxicity and mobility of chromium are highly dependent on its speciation; under oxidized conditions, Cr (VI) exists as highly soluble and mobile oxyanions like chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), facilitating its widespread dispersal in groundwater and soils (Zhao et al., 2023). In contrast, trivalent chromium (Cr (III)) is less soluble, less toxic, and readily precipitates as hydroxides, making its remediation less challenging (Yuan et al., 2025). This stark difference in behavior underpins the primary treatment strategy for Cr(VI)-contaminated water: its reduction to Cr (III) followed by immobilization.

Various technologies, including chemical precipitation, ion exchange, and reverse osmosis, have been employed to remove Cr (VI) from wastewater. However, the adsorption process is often favored due to its operational simplicity, cost-effectiveness, and high selectivity for target contaminants (Younas et al., 2023). Among the diverse range of adsorbents, biochar has emerged as a particularly promising, eco-friendly, and economically viable material (Bashir, Niazi, Saqib, & Hussain, 2025). Produced through the pyrolysis of biomass in an oxygen-limited environment, biochar possesses a highly porous structure, large surface area, and a rich array of surface functional groups (Bashir et al., 2025). The mechanism of Cr (VI) removal by biochar is complex and can involve simultaneous adsorption, reduction, and precipitation. Key processes include (1) the electrostatic attraction of Cr (VI) oxyanions to positively charged surface sites on the biochar, particularly at low pH; (2) the reduction of Cr (VI) to Cr (III) by electron-donating functional groups (e.g., phenolic -OH) or inherent reducing agents in the biochar matrix; and (3) the subsequent complexation or precipitation of the formed Cr (III) onto the biochar surface (Chang, Li, Liu, Liu, & Yao, 2016). The efficacy of this process is highly influenced by operational parameters such as solution pH, contact time, and adsorbent dosage, which govern the surface chemistry and the availability of active sites.

Therefore, this study aims to systematically evaluate the efficacy of various biochars derived from abundant agricultural wastes for the removal of Cr (VI) from aqueous solutions. We hypothesize that the specific physicochemical properties of different biochars, influenced by their biomass feedstock and production conditions, will dictate their performance in removing Cr (VI) through a combination of adsorption and reduction mechanisms, and that this removal efficiency can be optimized by controlling key parameters like pH, contact time, and adsorbent dose. The specific objectives of this research are to investigate the effect of different biochar types on the remediation of Cr (VI) from wastewater and to determine the optimal conditions for removal by assessing the influence of pH, sorbent dosage, and contact time.

2. Materials and Methods

2.1. Collection and Characterization of Wastewater

A batch sorption experiment was conducted to evaluate the efficacy of various biochars for removing Cr (VI) from wastewater. The wastewater sample was collected from the inlet of the Chokera wastewater treatment plant (WWTP) in Faisalabad. To characterize the matrix, the wastewater was analyzed for key physicochemical parameters. The pH and electrical conductivity (EC) were measured using a digital pH and conductivity meter, respectively. The carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) content were determined by titration with sulfuric acid. Concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) were ascertained using an atomic absorption spectrophotometer (AAS), while chloride (Cl^-) was measured by argentometric titration. Additional parameters, including total soluble salts (TSS), redox potential, and dissolved oxygen (DO), were also analyzed using standard methods (APHA, 2017). The initial concentration of Cr (VI) and other heavy metals of concern was determined to establish the baseline contamination level.

2.2. Collection of Biomass and Biochar Preparation

Five different types of biomass—rice husk (RH), sugarcane bagasse (SB), rice straw (RS), cotton stick (CS), and corn cob (CC)—were sourced from local agricultural markets in Faisalabad. The feedstocks were thoroughly washed with deionized water to remove soil and other adhering impurities and subsequently sun-dried to a constant weight. The pyrolysis process was carried out in a muffle furnace under an oxygen-limited environment created by purging with nitrogen gas. The temperature was ramped to a final range of 450–500 °C and maintained for a residence time of one hour. The resulting biochars were allowed to cool to room temperature within the closed furnace, then ground to a fine powder and passed through a 150- μm sieve to ensure homogeneity for subsequent experiments. The prepared biochars were labeled as RH-BC, SB-BC, RS-BC, CS-BC, and CC-BC, respectively.

2.3. Batch Sorption Experiments

Batch experiments were conducted in 50 mL polypropylene centrifuge tubes by agitating the mixtures on a mechanical shaker at a constant speed of 150 rpm. All treatments were performed in triplicate to ensure statistical reliability. The effects of three critical parameters—pH, contact time, and sorbent dose—on Cr (VI) removal efficiency were investigated.

2.3.1. Effect of Initial pH

The impact of solution pH on sorption efficiency was studied across a pH range of 3 to 10. The pH of the wastewater was adjusted using 0.1 M NaOH or 0.1 M HNO_3 solutions. A constant sorbent dose of 1 g L^{-1} of each biochar was added to the pH-adjusted wastewater, and the suspensions were shaken for a contact time of 2 hours.

2.3.2. Effect of Contact Time

The kinetics of Cr (VI) sorption were evaluated by varying the contact time from 0 to 1440 minutes (24 hours). For these experiments, a constant sorbent dose of 1 g L⁻¹ was used, and the initial pH of the wastewater was left unadjusted (its native pH) to isolate the time variable.

2.3.3. Effect of Sorbent Dose

To determine the optimal adsorbent quantity, different doses of each biochar (1, 2, 4, 6, 8, and 10 g L⁻¹) were tested. These experiments were conducted at a neutral pH of 7.0 and a constant shaking time of 2 hours.

Following each experiment, the suspensions were centrifuged at 4000 rpm for 15 minutes to separate the solid biochar from the liquid. The supernatant was then filtered through a 0.45-μm membrane filter. The concentration of Cr (VI) in the filtrate was quantified using the diphenylcarbazide (DPC) method on a UV-Vis spectrophotometer at a wavelength of 540 nm (Clesceri et al., 1999). The removal efficiency (R, %) was calculated using the formula:

$$R (\%) = [(C_0 - C_e) / C_0] \times 100$$

where C₀ and C_e (mg L⁻¹) are the initial and equilibrium concentrations of Cr (VI) in the solution, respectively.

2.4. Chemical Analysis

Hexavalent Cr was measured by spectrophotometer by DPC method at 540nm. Hexavalent Cr standards was prepared of 0, 0.5, 1, 2, 3, 4, and 5 mg L⁻¹ from a Cr stock solution. Five mL of Cr containing samples was pipetted in 10 mL test tubes. The samples was diluted, in which concentration was high. The 0.1 mg L⁻¹ of 2.5 M H₂SO₄ was added to each standard and samples followed by 0.1 mg L⁻¹ of 0.5% DPC solution. The lids was put on and keep the samples and standards for 5 minutes. Hexavalent Cr absorbance were measured on spectrophotometer.

Removal of Cr (VI) from the solution as a percentage (%) was calculated as given below:

$$\% \text{ Cr removal} = \frac{C_0 - C_e}{C_0} \times 100$$

In the above formula, initial Cr (VI) concentration in solution (mg L⁻¹) are represented by C₀, while the final Cr (VI) concentration in solution (mg L⁻¹) are represented by C_e. The sorption capacity (q_e) at equilibrium was considered by using the following equation.

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

Where m is the oven-dried sorbent weight (g), V is the volume of solution (L), and C₀ and C_e are as shown previously.

2.5. Kinetics modeling

Kinetic constants are used to extend the adsorption phase's residence duration in order to estimate the adsorption kinetics. The rate of Cr (VI) adsorption on adsorbents was assessed using pseudo-first order and pseudo-second order

kinetic models. According to Tiadi et al. (2017), the solid sorbent potential is described by the pseudo-first order model.

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

Where k₁ is the rate constant of equation (min⁻¹) and q_t is the sorbed Cr (VI) at any time t (mg g⁻¹). Here, q_e represents the sorbed Cr (VI) (mg g⁻¹). Plotting log (q_e - q_t)/t allows for the experimental calculation of k₁. Additionally, the pseudo-second order model was applied, demonstrating that chemisorption is regarded as a sorption mechanism and that the rate of adsorption is related to the square of the number of free sorption sites that remain. The equation below provides an illustration of the model (Liang et al., 2009).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

In the above equation, k₂ is the sorption rate constant at equilibrium (g mg⁻¹ min⁻¹). With an intercept of 1/(k₂q_e²) and a slope of 1/q_e, the relationship between t/q_t and t is linear (Bashir et al., 2025).

3. Results and discussion

A variety of biochar types were gathered from the Institute of Soil and Environmental Sciences (ISES) soil and water chemistry laboratory at the University of Agriculture Faisalabad (UAF). The plastic and glassware used in the batch sorption studies were thoroughly cleaned in 2% HNO₃, then twice in deionized water.

3.1. Effect of Solution pH

The pH of the aqueous solution is a critical operational parameter governing heavy metal sorption efficiency, as it simultaneously influences the surface charge of the sorbent and the chemical speciation of the sorbate. In this study, the sorption behavior of Cr (VI) onto five different biochars—rice husk biochar (RHB), sugarcane bagasse biochar (SBB), rice straw biochar (RSB), coconut stick biochar (CSB), and corn cob biochar (CCB)—was systematically evaluated across a pH range of 3 to 10 (Figure 1).

A consistent and pronounced trend was observed across all biochar types: Cr (VI) sorption was maximized under strongly acidic conditions and decreased progressively as the pH became more alkaline. The optimal sorption for all sorbents occurred at pH 3. SBB demonstrated the highest sorption capacity at this pH (0.97 mg/g), closely followed by CCB (0.95 mg/g), RHB (0.93 mg/g), RSB (0.92 mg/g), and CSB (0.83 mg/g). As the pH increased from 3 to 10, a steady decline in sorption efficiency was recorded. For instance, the sorption capacity of SBB decreased by approximately 36% (from 0.97 mg/g to 0.62 mg/g), a trend mirrored by the other biochars, with RHB, RSB, CSB, and CCB showing reductions of 30%, 39%, 33%, and 35%, respectively. The most significant decrease for most biochars was typically noted between pH 7 and 10.

This universal pH-dependent behavior is mechanistically explained by the interplay of electrostatic interactions and surface chemistry. Under highly acidic conditions (low pH),

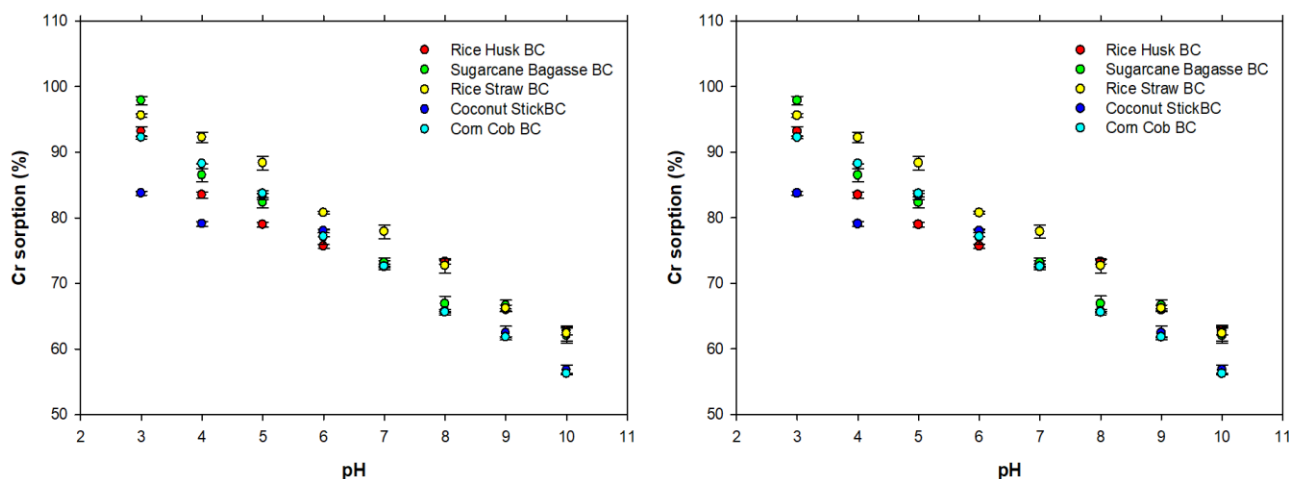


Figure 1: Impact of pH on chromium sorption removal percentage and chromium sorption capacity by rice husk biochar, sugarcane bagasse biochar, coconut stick biochar, rice straw biochar, and corn cob biochar, at sorbent dose of 2 g L^{-1} and 2 h contact time

the biochar surface becomes extensively protonated, acquiring a net positive charge. This favors the strong electrostatic attraction of the anionic Cr (VI) species predominant in solution (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$). Furthermore, the abundant H^+ ions facilitate the reduction of Cr (VI) to Cr (III) by acting as a proton source for redox reactions with electron-donating functional groups on the biochar surface. Conversely, as the pH increases, the biochar surface undergoes deprotonation, resulting in a net negative charge. This leads to electrostatic repulsion of the chromate anions and increased competition with OH^- ions for sorption sites, thereby significantly suppressing Cr (VI) removal (Ashraf et al., 2016; Bashir et al., 2025).

The superior performance of SBB and CCB, particularly at low pH, suggests they possess a greater density of proton-active functional groups or a more favorable porous structure for ion access compared to CSB (Adebayo, Adegoke, & Fauzeeyat, 2020; Adegoke, AmooAdekola, Fatoki, & Ximba, 2014). The results conclusively demonstrate that an acidic environment (pH ~ 3) is essential for maximizing the efficiency of Cr (VI) removal by biochar, underscoring the critical role of pH control in treatment processes for chromium-laden wastewater.

3.2. Effect of Contact Time on Chromium Sorption

The kinetics of Cr (VI) sorption were investigated for all five biochars over a 1440-minute period, revealing distinct temporal patterns and sorption capacities. A nearly universal trend was observed, characterized by a rapid initial sorption phase followed by a plateau and a subsequent decline over extended periods, though the specific kinetics and optimal contact times varied between sorbents (Figure 2).

Sugarcane bagasse biochar (SBB) demonstrated the most rapid and effective sorption, reaching its peak capacity

of 0.95 mg/g within the first 60 minutes. This was closely followed by corn cob biochar (CCB), which also showed rapid initial uptake. Rice husk biochar (RHB) and coconut stick biochar (CSB) achieved their maximum sorption (0.88 mg/g and 0.83 mg/g , respectively) at 120 minutes, while rice straw biochar (RSB) exhibited a more stable but lower plateau between 60 and 480 minutes. A critical finding across all biochars was the significant decrease in sorption capacity observed at the 1440-minute (24-hour) mark. For instance, SBB and RSB experienced substantial reductions of approximately 23% and 21%, respectively, from their peak values.

The initial rapid sorption phase can be attributed to the high availability of active sites on the biochar surface and a strong concentration gradient, which provides a significant driving force for mass transfer. The subsequent plateau indicates the approach of equilibrium, where the rate of sorption equals the rate of desorption. The notable decline in sorption after extended contact time, particularly evident at 1440 minutes, suggests the potential occurrence of desorption or a secondary process such as surface reconfiguration, dissolution of biochar components, or the microbial reduction of sorbed Cr (VI) to more soluble forms. This phenomenon underscores that exceeding critical contact time can be counterproductive for removal efficiency.

From an application perspective, these results highlight that the optimal contact time is biochar specific. While SBB achieves maximum efficiency within 60 minutes, RHB and CSB require up to 120 minutes. Crucially, for all biochars tested, prolonged agitation beyond 480 minutes should be avoided to prevent a significant loss of the bound chromium. The superior kinetic performance of SBB and CCB suggests they possess a more accessible pore structure or surface chemistry that facilitates faster attachment and potentially

stronger binding of Cr (VI) ions (Chakraborty, Asthana, Singh, Jain, & Susan, 2020; Chang et al., 2016; Choppala et al., 2018).

3.3. Effect of Sorbent Dosage on Chromium Sorption

The influence of sorbent dosage on Cr (VI) removal efficiency was evaluated across a range from 0.5 to 8 g/L, revealing a clear optimal dosage for each biochar type. The results demonstrate a non-linear relationship where increasing the adsorbent mass initially enhances removal efficiency up to a critical point, beyond which diminished returns or decreased performance is observed (Figure 3).

the highest sorption capacity (0.92 mg/g), followed by RHB and CSB (both 0.87 mg/g), and SBB (0.68 mg/g). In contrast, corn cob biochar (CCB) displayed a unique profile, achieving its peak sorption capacity earlier, at a lower dosage of 1 g/L (0.88 mg/g). For all biochars, a further increase in dosage to 4 g/L and 8 g/L resulted in a progressive decline in the amount of Cr (VI) sorbed per unit mass of biochar (mg/g). This trend is mechanistically explained by the interplay of active site availability and particle interactions. The initial increase in sorption with dosage is attributed to the greater surface area and a proportional increase in the number of available binding sites for Cr (VI) ions. However, after the

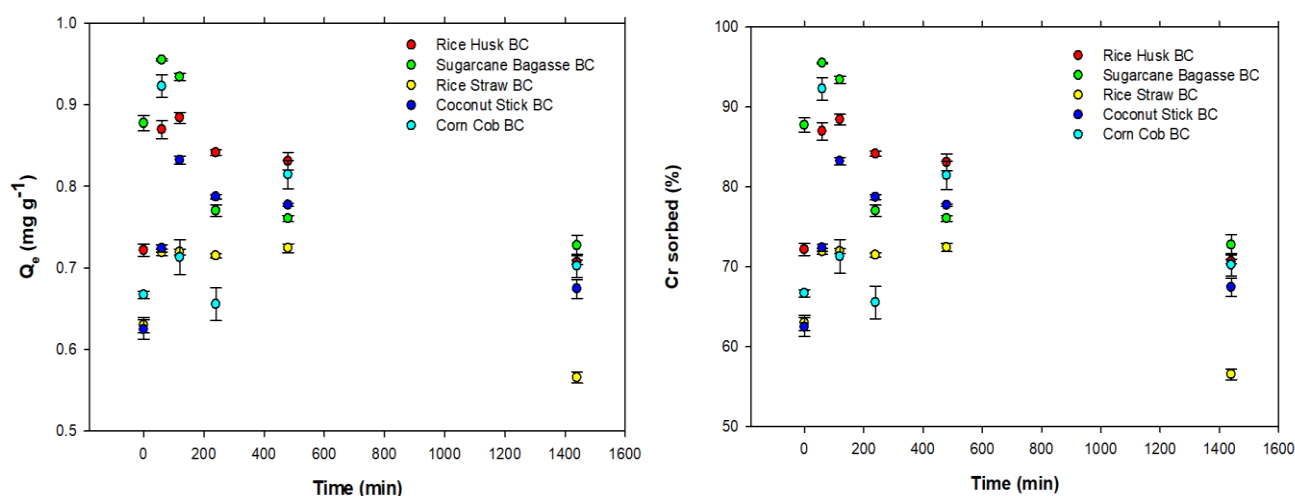


Figure 2: Effect of contact time on chromium sorption and removal percentage by rice husk biochar, sugarcane bagasse biochar, coconut stick biochar, rice straw biochar, and corn cob biochar, at sorbent dose of 2 g L^{-1} and pH 7.

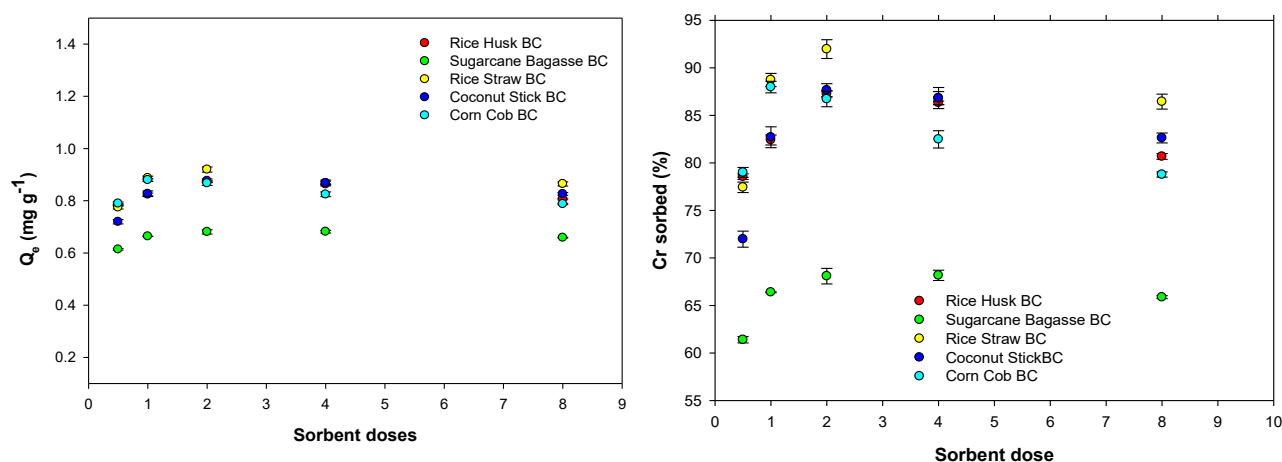


Figure 3: Impact of sorbent dose on chromium sorption and removal percentage by rice husk biochar, sugarcane bagasse biochar, coconut stick biochar, rice straw biochar, and corn cob biochar, at 7 pH and 2 h contact time.

A consistent optimal dosage of 2 g/L was identified for four of the five biochars: rice husk biochar (RHB), sugarcane bagasse biochar (SBB), rice straw biochar (RSB), and coconut stick biochar (CSB). At this dosage, RSB exhibited

optimal dosage is reached, the phenomenon of site saturation occurs. Further additions of biochar lead to overlapping of adsorption sites and potential agglomeration of particles, which reduces the total effective surface area and can block

pores, limiting diffusion and access to internal sites. This is often coupled with a "screening effect," where the high solid concentration creates a diffusion barrier for the solute. Additionally, at very high sorbent masses, the leaching of soluble organic components from the biochar could compete with Cr (VI) for binding sites or promote desorption (Goharshadi & Moghaddam, 2015; Huang, Hou, Song, Zhao, & Zhang, 2016; Jiang et al., 2014).

The superior performance of RSB at its optimal dosage suggests a higher density of active sites or a more favorable pore structure for Cr (VI) uptake. The distinct behavior of CCB, peaking at a lower dose, may indicate either a faster saturation of its specific active sites or a greater propensity for particle aggregation at higher concentrations. These findings are critical for application, establishing that a dosage of 2 g/L is generally optimal for most tested biochars, while highlighting the need for sorbent-specific calibration to avoid inefficiency and unnecessary material costs in treatment processes (Liang, Guo, & Tian, 2011; Lima et al., 2022; Liu, Chen, & Yongmei, 2013).

3.4. Sorption Kinetic Modeling

The mechanism and rate of Cr (VI) sorption onto the five biochars were investigated by fitting the experimental data to pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models. The correlation coefficients (R^2) revealed a definitive trend across all sorbents. The PSO model demonstrated a superior fit, with significantly higher R^2 values (RHB: 0.99, SBB: 0.99, RSB: 0.99, CSB: 0.99, CCB: 0.99) compared to the PFO model (RHB: 0.66, SBB: 0.53, RSB: 0.48, CSB: 0.05, CCB: 0.02). The near-unity R^2 values for the PSO model indicate that it accurately describes the sorption process for all biochars (**Figure 4,5; Table 1**).

The superior applicability of the PSO model suggests that the rate-limiting step of Cr (VI) removal is chemisorption. This involves the sharing or exchange of electrons between the Cr (VI) oxyanions and the functional groups on the biochar surface. Key mechanisms include:

1. Redox Reaction: The dominant chemisorption process is likely the reduction of Cr (VI) to Cr (III) by electron-donating functional groups (e.g., phenolic -OH) on the biochar, a process that follows second-order kinetics based on the concentration of both the sorbate and the sorption sites.
2. Surface Complexation: The formation of strong, covalent inner-sphere complexes between Cr (VI) ions and protonated oxygen-containing groups (e.g., carboxylates) on the biochar surface.

The poor fit of the PFO model, which typically describes physical sorption or diffusion-controlled processes, further confirms that physisorption (e.g., van der Waals forces) is not the primary mechanism. The high consistency of the PSO fit across all five biochars, despite their different feedstocks, implies a universal chemisorption-dominated mechanism for Cr (VI) removal, likely centered on the redox reaction that transforms the highly toxic and mobile Cr (VI) into the less

hazardous and immobile Cr (III). This finding is critical for process optimization, as it confirms that the sorption efficiency is governed by the chemical affinity and electron-donating capacity of the biochar surface rather than mere physical attachment (Bashir et al., 2025).

3.5. Desorption

Desorption experiments estimated sorbent reuse for polluted water treatment. In three cycles 0.2 M NaOH was used as a desorbing agent (Masood ul Hassan et al., 2023). Results showed that in the first desorption cycle, the removal of Cr was 94% (CC-BC and RH-BC), 94% (RS-BC), 90% (CS-BC), and 79% (SCB-BC). While in the second cycle Cr removal was 91% by RH-BC, CS-BC, and CC-BC, 71% by SCB-BC. In the third desorption cycle the removal of Cr was 89% (RS-BC), 86% (CS-BC), 84% (RH-BC and CC-BC), and 67% (SCB-BC) (Fig. 4.32). Black bar showed 1st cycle, gray bar showed 2nd cycle and white bar showed 3rd cycle of desorption.

4. Discussion

The efficacy of Cr (VI) removal by biochar is critically governed by several experimental parameters, primarily solution pH, contact time, and sorbent dosage, each influencing the underlying adsorption mechanisms. The pH of the solution is arguably the most crucial factor, as it directly dictates the surface charge of the biochar, the speciation of Cr (VI) in aqueous solution, and the subsequent electrostatic interactions between them. In this study, maximum sorption was observed at lower pH levels (pH 3), a finding consistent with established literature. Under acidic conditions (pH 2-6), the biochar surface becomes protonated, acquiring a positive charge that favors the electrostatic attraction of negatively charged Cr (VI) oxyanions, primarily HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ (Abdel-Fattah et al., 2015; Zhang et al., 2013). Furthermore, the high concentration of H^+ ions in the solution facilitates the reduction of Cr (VI) to the less toxic and less mobile Cr (III) by electron-donating functional groups on the biochar, such as phenols and carboxylic acids (Deng and Stone, 1996; Jiang et al., 2014). In contrast, at higher pH values (alkaline conditions), the biochar surface becomes deprotonated and carries a net negative charge, leading to electrostatic repulsion of Cr (VI) anions and competition with excess OH^- ions for sorption sites, resulting in a marked decrease in removal efficiency (Dong et al., 2011). Given that many industrial effluents contaminated with Cr (VI) are acidic, biochar presents a highly suitable treatment option for such waste streams.

The kinetics of Cr (VI) sorption revealed a rapid initial phase, with a significant portion of the removal occurring within the first 480 minutes. This rapid uptake can be attributed to the high availability of active sorption sites and a strong concentration gradient driving force at the beginning of the process (Nguyen et al., 2015). As these sites became occupied and the Cr (VI) concentration in the solution decreased, the sorption rate gradually slowed until a state of

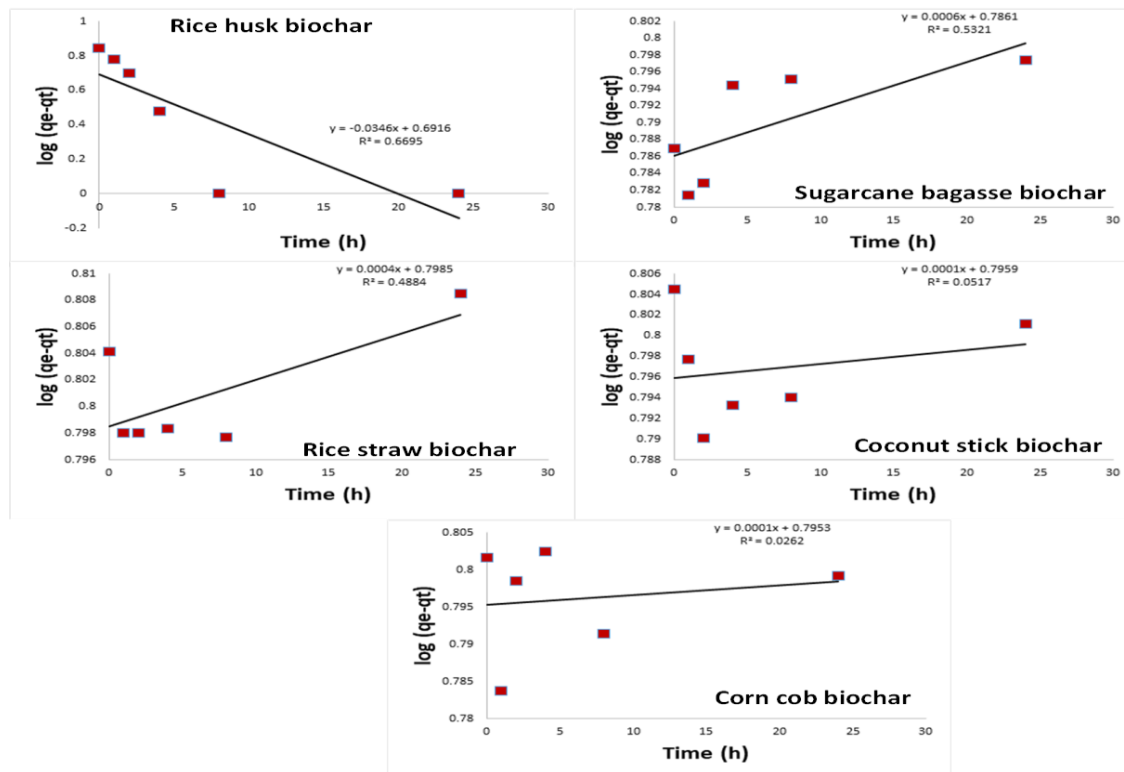


Figure 4: Plots Linearized for kinetic pseudo-first order kinetic models for Chromium sorption

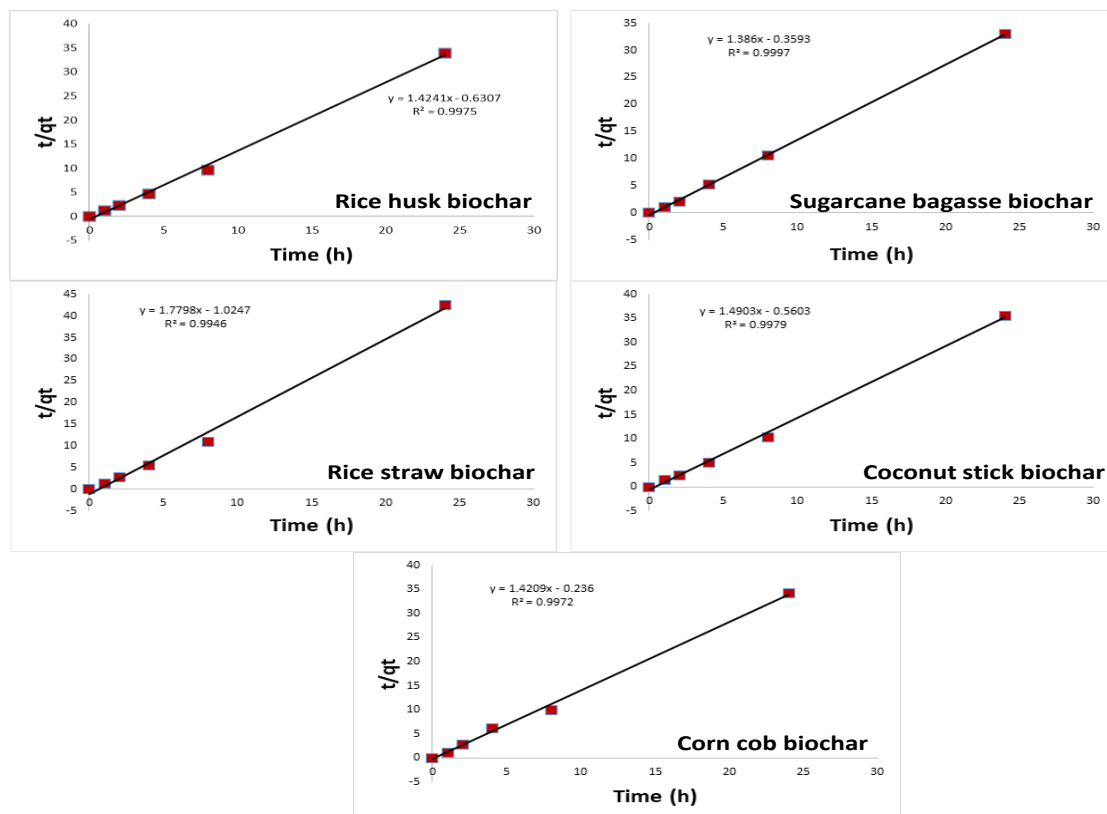


Figure 5: Plots Linearized for kinetic pseudo-second order models chromium sorption.

Table 1. Kinetics non- Linear variables pseudo-first model then pseudo-second order models 2 g L⁻¹ sorbent dose Cr sorption to rice husk biochar, sugarcane bagasse biochar, rice straw biochar, coconut stick biochar and corn cob biochar at 25 C°.

Sorbents	Pseudo first-order model			Pseudo second-order model		
	q _e (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _e (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
Rice Husk Biochar	4.91	-0.03	0.66	0.70	1.42	0.99
Sugarcane Bagasse Biochar	6.11	0.0006	0.53	0.72	1.38	0.99
Rice Straw Biochar	6.28	0.0004	0.48	0.56	1.77	0.99
Coconut Stick Biochar	6.25	0.0001	0.05	0.67	1.49	0.99
Corn Cob Biochar	6.24	0.001	0.02	0.70	1.42	0.99

dynamic equilibrium was reached, where the rate of adsorption equaled the rate of desorption. The eventual plateau in sorption capacity at higher contact times can be explained by the saturation of binding sites and increased repulsive forces between the solute molecules already adsorbed on the surface and those remaining in the solution (A ul Haq et al., 2019; Hassoon and Najem, 2017).

The impact of sorbent dosage further elucidates the adsorption process. The observed increase in Cr (VI) removal efficiency with an increase in biochar dose from 1 to 4 g L⁻¹ is a direct consequence of the greater surface area and the corresponding increase in the number of available active sites for a fixed initial Cr (VI) concentration (Xu et al., 2012). However, the diminishing returns and eventual decrease in removal efficiency at very high doses (6-10 g L⁻¹) suggest the phenomenon of site saturation and particle interactions. At excessive dosages, overlapping adsorption sites and potential pore blockage can occur, reducing the overall effective surface area. Additionally, interference from soluble organic compounds or ions released from the biochar at high masses might compete with Cr (VI) for sorption sites or even promote the desorption of already-bound chromium (Li et al., 2002).

In summary, the superior performance of SCB-BC (sugarcane bagasse biochar) at low pH and its rapid kinetics highlight its potential as an effective sorbent. The overall removal mechanism is not limited to a single process but is a combination of electrostatic attraction of Cr (VI) oxyanions to the protonated biochar surface, followed by its reduction

to Cr (III) by surface functional groups, and the subsequent complexation or precipitation of the Cr (III) species. This multi-mechanistic approach, governed by the optimized parameters of pH, contact time, and dosage, underscores the viability of biochar as a efficient and multifaceted agent for the remediation of Cr (VI)-contaminated water.

5. Conclusion

This study comprehensively demonstrates that biochar, particularly sugarcane bagasse biochar (SCB-BC), is a highly effective and viable sorbent for the remediation of Cr (VI)-contaminated water. The removal process is a complex, multi-mechanistic sequence dominated by chemisorption, initiated by the electrostatic attraction of anionic Cr(VI) species to the positively charged biochar surface under acidic conditions (optimally at pH 3), followed by its reduction to the less toxic and immobile Cr(III). The kinetics of sorption are best described by a pseudo-second-order model, confirming that chemical interaction is the rate-limiting step. Furthermore, the process is highly dependent on operational parameters, with an optimal contact time of 60-120 minutes for most biochars and a clearly defined optimal sorbent dosage (e.g., 2 g L⁻¹), beyond which efficiency declines due to site saturation and particle interactions. The superior performance of SCB-BC underscores the importance of feedstock selection. In summary, biochar presents a cost-effective, efficient, and environmentally friendly solution for treating Cr (VI)-laden wastewater, aligning well with the

characteristics of typical industrial effluents and offering a promising alternative to conventional treatment technologies.

6. Future Studies

While this study confirms the high potential of biochar for Cr (VI) removal, several avenues for further research are recommended to facilitate its practical application and enhance its efficacy:

1. Advanced Biochar Engineering: Future work should focus on the chemical or physical modification of biochar (e.g., magnetization with Fe_3O_4 , impregnation with zero-valent iron, or activation with acids/bases) to enhance its sorption capacity, stability, and selectivity for Cr (VI) across a broader pH range.
2. Investigation of Real Wastewater Matrices: Testing the optimized biochars on real industrial effluents is crucial. This will evaluate their performance in the presence of competing ions (e.g., Cl^- , SO_4^{2-} , NO_3^-) and organic matter, which can significantly influence removal efficiency and mechanism.
3. Regeneration, Reusability, and Safe Disposal: A critical step for economic viability is developing efficient regeneration protocols for spent biochar. Studies on multiple sorption-desorption cycles are needed. Furthermore, the long-term stability of the immobilized Cr (III) and the safe disposal method for the spent sorbent must be thoroughly investigated to prevent secondary environmental pollution.
4. Column Studies and Scalability: Batch experiments should be scaled up to continuous-flow column studies to simulate real-world treatment systems, such as fixed-bed adsorbers. This will provide essential data on breakthrough curves, hydraulic loading rates, and operational longevity for pilot-scale design.
5. In-Depth Mechanistic Elucidation: Advanced spectroscopic techniques, such as X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Near Edge Structure (XANES), should be employed to quantitatively speciate the chromium on the biochar surface, unequivocally confirming the reduction from Cr (VI) to Cr (III) and identifying the specific functional groups involved.

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10. Conflict of Interest:

Authors declare no conflict of interest.

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