RESEARCH PAPER

# Evaluation of Chromium and Cadmium Contamination and Remediation in Wastewater from Industrial Areas of Faridabad: A Determinative Analysis

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**Abstract**
One of the primary ecological issues in modern times is industrial contamination of wastewater. The manufacturing plants located in the industrial hub of Faridabad discharge their wastewater into nearby water bodies. To evaluate how these industrial releases affect water quality, we investigated the levels of heavy metals in water samples collected from various locations throughout Faridabad. We employed Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to analyze the heavy metal concentrations in the gathered water samples. We observed the levels of Chromium (Cr) and Cadmium (Cd) contamination vary between 2.17 to 27.80 mg/L and 1.86 to 24.16 mg/L, respectively. Based on pH analysis, the samples were found mostly alkaline and their densities were observed in the range of 1.349 mg. The values of total dissolved solids ranged between 691-9931 ppm. In this study, we observed Cr and Cd cadmium concentrations in several wastewater samples exceeded permissible limits. Using batch adsorption methods, this work examines the effective use of biochar (derived from agricultural waste) for the removal of 46% to 63% of Cr and 47 to 57% of Cd from industrial wastewater. Biochar was prepared from onion, garlic, and citrus peels and was chemically activated with $H_3PO_4$. The biochar was also characterized post-compositing with hydroxyapatite (HAP) using FTIR and XRD to evaluate the potential for future adsorption studies. The results suggest that activated biochar from peel is a useful, cost-effective, and sustainable adsorbent for the partial removal of Cr and Cd-contaminated wastewater. The characterization of HAP–biochar composite provides a basis for future work on efficiency improvement.

**Keywords:** Heavy metal contamination, industrial wastewater, ICP-MS, Ecological concerns
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## Introduction

Faridabad serves as a significant industrial hub within the National Capital Region. Geographically, it is bordered by Uttar Pradesh to the east and south, the capital city of India and its union territory, Delhi, to the north, and Gurugram district to the west. Faridabad is Haryana's most populated city with geographic area 742.9 square kilometres [1]. The rapid urbanization and industrialization have raised concerns about the effects on the environment, particularly heavy metal contamination of wastewater. Effluents from agricultural, municipal, and industrial activities release various contaminants, including dyes, heavy metals, surfactants, personal care items, pesticides, and pharmaceuticals. These pollutants significantly change water characteristics such as odor, color, chemical oxygen demand (COD), biochemical oxygen demand (BOD), turbidity, pH levels, and total dissolved solids (TDS) [2]. These changes seriously harm aquatic life and people's health, upsetting the balance of ecosystems.

Water quality is greatly impacted by industrial waste, which limits its use for household purposes. Unwanted concentrations of dissolved chemicals in industrial wastewater can infiltrate into groundwater and endanger public health [3]. The buildup of organic materials and heavy metals in both surface water and groundwater is influenced by a variety of elements. These factors include unregulated pollution stemming from urban and semi-urban developments, the excessive disposal of untreated or inadequately processed domestic waste, inadequate drainage infrastructure, illegal mining operations, and sediment accumulation in urban waterways [4]. The levels of heavy metals namely Cadmium, Chromium, Iron and Nickel in the water, sediments and aquatic plants growing along this stretch from Haryana to Delhi showed that significant enrichment of Cd and Ni were confined to the sediments having sources from industries which make the water quality exceed drinkable acceptable limits particularly at downstream locations near industrial areas while highest content of Fe was observed at all sites tested and some uptake by plants for other metals have also been seen to be dependent on contamination status. Heavy metal contamination of the environment from industrial effluents is an increasing global concern due to water scarcity and lack of proper treatment systems, especially for electroplating industries. Much chromium (Cr(VI)) (1000 mg/L) in such effluents [5] is highly toxic and poses major health risks as it bioaccumulates. Industrial effluent, which contains hazardous heavy metals such as Cu, As, Cr, Cd, Ni, Zn, Pb, and Hg, contaminates water bodies and land alike. Due to the very high solubility of these metals in aquatic ecosystems, they pose a potential for bioaccumulation. Chemical precipitation,

adsorption, ion flotation, ion exchange, coagulation/flocculation, and electrochemistry have been used for decades to remove these heavy metals [6].

For the environment, toxic heavy metal complexes (HMCs) in water and waste must be efficiently reduced. Common techniques for removal of heavy metal pollutants, physical separation and chemical decomplexation (HMC) removal, are concisely [7], previously addressed. Enzyme-treated biochar and other simple biomaterials may strip more than 90% heavy metals out of electroplating effluent in minutes, presenting a practical, reusable solution [8]. Treatment of heavy metals from wastewater is important to reduce pollution as it reduces contamination & clean water runs low. Industries such as electroplating release high Cr (VI) (up to 1000 mg/L) and other metals go far up the rivers and endanger human health and ecosystems. By providing suggestions for long-term solutions to alleviate the environmental impacts of industrial effluent, the research presented here is part of a wider discussion concerning wastewater treatment. The project uses adsorbents, as it compares to traditional heavy metal cleanup techniques, in a bid to fill the void in the literature and provide feasible solutions for sustainable environmental preservation with practical means of remediation and public health issues. This method gives an overview of the system of nature in terms of how its interactions play in, in this case some heavy metals in the region, illustrating the need to combine environmental science, population health, and new urban growth technologies. Rising environmental awareness has led to an increasing demand for environmentally-friendly, regulatory-compliant adsorbents for cost-effective sources such as local industrial wastes, mineral residues, and agricultural waste [9]. The porous nature, high surface area and a great number of functional groups of biochar contribute for its relatively good removal through complexation which promotes their adsorption of heavy metals. ion exchange, and, electrostatic attraction. A large percentage of the particles in the media are metal-sensitive, as the adsorbents are more sensitive to oxygenation. A similar result is demonstrated by [10], which demonstrated this means that under pristine conditions biochar is capable of removing up to 90% Cd and Cr. Moreover, activated biochar ($KOH/H_3PO_4$-treated) improve heavy metal sorption by providing porosity and functional sites, allowing a low-cost alternative for wastewater disposal [11]. The results also illustrate the significance of wastewater pH for the adsorption process. According to [12] stated that biosorbents are excellent to eliminate Cr (VI) at acidic pH. [13] mentioned that the high metal ion removal between $4.5 < pH < 5.2$ is attributed to deprotonation of surface sites on the adsorbent material. [14] assessed onion peel as a biosorbent for divalent cobalt ($Co^{2+}$) and shows its application as an economical agro-industrial waste-based alternative.

The research optimized the parameters to a temperature of 30°C, a pH of 7.0, and a particle size range of 300–800 µm. This optimization achieved a peak capacity of 59.88 mg $g^{-1}$ at an initial concentration of 380 mg $L^{-1}$ within a duration of 120 minutes. According to [15], removal efficiency may also be lowered by competition between heavy metals and other ions in actual wastewater conditions. Adsorption-based treatment using modified biochar has emerged as an effective approach for removing toxic metals from wastewater. The removal efficiency is highly dependent on process variables, since increasing biochar dosage increases the number of active sites, while higher temperatures enhances surface activity and ion diffusion, jointly promoting metal uptake [16]. Therefore, it is essential to optimise contact time, temperature, and adsorbent dosage when designing biochar-based systems for chromium and cadmium removal. The research aimed to refine the conditions at a temperature of 30°C, with a pH of 7.0 and a particle size ranging from 300 to 800 µm. This optimization resulted in a peak capacity of 59.88 mg $g^{-1}$ at an initial concentration of 380 mg $L^{-1}$ over a duration of 120 minutes. Additionally, our investigation intends to deliver an in-depth evaluation of heavy metal pollution in the industrial zones of Faridabad. The focus will primarily be on Chromium (Cr) and Cadmium (Cd), both of which are recognized for their harmful impacts on environmental quality and human health. In our study, we find the total concentrations of Cr and Cd in wastewater, evaluating the possible ecological risks related to heavy metal contamination, looking into the health effects on the local population, and investigating novel remediation techniques, which are the main objectives of this study. In the context of the use of ICP-MS, the sophisticated versions, including ICP-MS/MS, ICP-TOF-MS, HR-ICP-MS, MH-ICP-MS, and MC-ICP-MS, which are used in conjunction with microwave micro-digestion technologies, allow speciation for the quantification of hazardous metals ($As^{3+}$, $Cr^{6+}$, methylmercury) in wastewater at concentrations lower than 0.1 µg/L, thereby achieving the recommendations of WHO [17].

## 2. Materials and methods

### 2.1. Sample location and collection

Faridabad lies between 28.4211° N latitude and 77.3078° E longitude, covering an area of approximately 189.9 $km^2$ [18], is a major industrial hub in the National Capital Region of India. Considerable water pollution has arisen due to the region's closeness to Delhi and substantial industrial operations, particularly from heavy metals such as chromium and cadmium. Additionally, Faridabad, being an industrial hub, encompasses a Wide Range of Industries, Including Plastic, rubber, aluminium,

chemicals, glass, iron and steel, petrochemicals, pharmaceuticals, soaps, soft drinks, textiles, and wires, among others, in its active industrial units. Without adequate treatment, these operational units released a significant volume of wastewater. For the past decades, nearby agricultural fields have been irrigated with industrial wastewater due to the scarcity of irrigation water. The water quality of the city has received lots of attention because of its environmental vulnerability. But still, there remains room for clearer and more authentic experimentation. This study aims to address this gap, providing critical insights into contamination levels and supporting strategies.

The sampling area is depicted in Figure 1, which shows the position of Faridabad within India. The wastewater samples were collected from 15 different wastewater sources of Faridabad district, Haryana, during two sampling periods. Ten samples were collected from 10 different locations in June 2024 and five additional samples were collected from five different locations in January 2025. Each site was sampled once, resulting in 15 independent grab samples in total. Details of different collection sites with sample codes are given in Table 1.

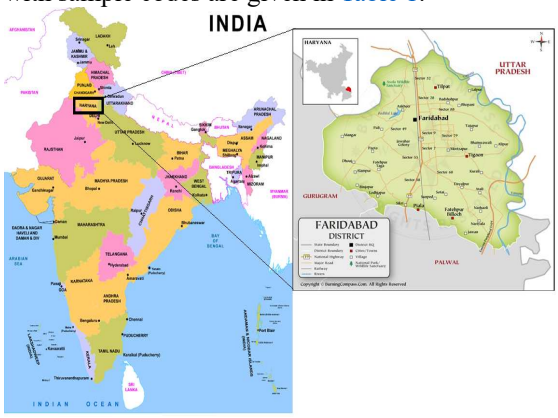



**Figure 1.** Location of Faridabad district in Haryana, India, showing the geographical setting of the study area.

### 2.2. Site Description



**Figure 2.** Representative photographs of wastewater sources and sample collection during the field survey.

**Table 1. Details of the sample collection sites**

| Sr. No. | Location | Code |
|---|---|---|
| 1. | Sector-23 (Industrial Sector) | W1 |
| 2. | Sector-22 (Whirlpool Chowk) | W2 |
| 3. | Jawahar Colony (Adjacent to Industrial Units) | W3 |
| 4. | Sector 25 (HIL LMD Complex) | W4 |
| 5. | Sector 25 (Krishna Colony) | W5 |
| 6. | Sector 25 (Sterling pool, Industrial Zone) | W6 |
| 7. | Sector-58 (Central Industrial Area) | W7 |
| 8. | Sector-58 (Ramco Steel, Industrial Region) | W8 |
| 9. | Sector 25 (Adjacent Industrial Zone) | W9 |
| 10. | Sector-58 (Manufacturing & Processing Area) | W10 |
| 11. | Sector- 31 (Manufacturing & engineering) | W11 |
| 12. | Sector-31 Industrial Region (NIT area) | W12 |
| 13. | DLF Phase II Industrial Area | W13 |
| 14. | Sector-32 (Auto Parts & Light Engineering) | W14 |
| 15. | Sector-32 (Textile & Garments) | W15 |

### 2.3. Sample Collection

Wastewater samples were gathered from targeted locations using clean, acid-washed containers to avoid contamination. After sealing, they were transported to the laboratory in a cold box to keep them fresh. In the lab, samples were filtered through a 0.45 µm membrane to eliminate solids and impurities before testing and analysis.

### 2.4. Sample Preparation

Microwave pyrolysis (MWP) or microwave digestion effectively treated sewage sludge (SS), using microwave energy for rapid, uniform volumetric heating through dielectric loss that decomposes organic matter and oxygen-containing functional groups [19]. A closed-vessel method for full mineralization at regulated temperatures of 200°C under high pressure, reducing analyte loss and matrix interferences compared to traditional hot plate digestion. The process improves the recovery of heavy metals for accurate ICP-MS quantification while shortening digestion times from hours to minutes. Figure 3 illustrates the complete analytical workflow from sample collection through ICP-MS analysis. The process was performed at the laboratory using dilute nitric acid solution with a standard heating program, followed by appropriate dilution before ICP-MS analysis (adapted from [20]).

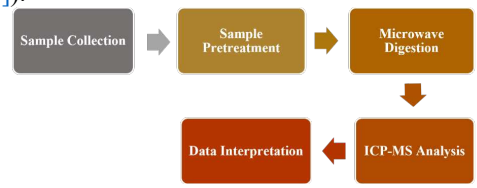



**Figure 3.** Method for Wastewater Analysis by ICP-MS Using Microwave Digestion

### 2.5. Sample pretreatment

After being weighed, a known volume (25 mL) of the wastewater sample was transferred to a Teflon PFA digestion vessel. Wastewater samples were gathered from designated sites utilizing clean, acid-washed containers to prevent any contamination. Once sealed, the samples were transported in a cold box to preserve their integrity. In the laboratory, these samples underwent filtration through a 0.45 µm membrane to eliminate solids and impurities prior to testing and analysis. Subsequently, 5 mL of concentrated nitric acid ($HNO_3$, 69-70%) and 2 mL of hydrogen peroxide ($H_2O_2$, 30%) were introduced into the vessel. The container was securely sealed and placed in a microwave digestion system, where an internal pressure of 20 bar was maintained for 25 minutes while the temperature was raised to 180°C; afterward, the samples were allowed to cool to room temperature.

**2.6. Preparation of Biochar**

Biochar was prepared by peeling onion, garlic, and orange/lemon peels and washing the biomass thoroughly to eliminate impurities. To enhance pyrolysis efficiency, the cleaned biomass was dried in an oven at 105°C to remove moisture from the biomass. Pyrolysis was performed in a muffle furnace under low oxygen atmosphere at a heating rate of 10°C/min. The temperature was increased to 400-600 °C and maintained for 4 h to obtain fine, porous, carbon-rich biochar. After pyrolysis, the biochar was allowed to cool gradually in the furnace under a low oxygen condition. The cooled biochar was ground and sieved to a particle size < 0.5 mm. The biochar yield was approximately 30% by weight. This was achieved at Oatman Overseas Private Limited, Ghaziabad, India providing both quality and repeatability. Impregnation with phosphoric acid ($H_3PO_4$) changed chemical properties as described above for biochar activation. The biochar was impregnated with 85% $H_3PO_4$ at a ratio of 1:3 (w/v) and kept at room temperature for 24 h for activation. As illustrated in Figure 4a, after impregnation, the activated biochar was filtered, washed extensively with distilled water until neutral pH and dried in an oven at 105 °C for 12 h, which acted as the activated substance used in adsorption testing.

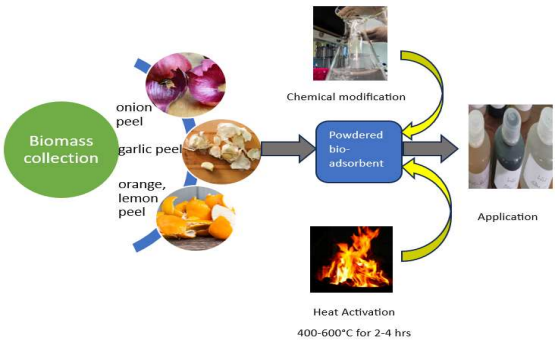



**Figure 4a**. Schematic representation of Biochar synthesis from agricultural peel waste. The activated biochar produced was used in batch adsorption experiments for Cr and Cd removal.

**2.7. Laboratory Preparation of Hydroxyapatite (HAP)**

Hydroxyapatite (HAP) was prepared by a wet chemical precipitation method. The solution is made up of an initial 0.3 M diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), dissolved in 100 mL of distilled water (solution A), and also a 0.5 M calcium nitrate tetrahydrate ($Ca(NO_3)_2$), dissolved in 100 mL of distilled water (solution B); the pH of solution A was adjusted by carefully adding ammonium hydroxide solution. Solution B was then added gradually to solution A, followed by continuous stirring at room temperature for 2 to 4 h, per the procedure described in [21]. This mixture was also allowed to age overnight in order to facilitate precipitation of hydroxyapatite. Following was the white precipitate of HAP, which was washed three to four times with distilled water and once with ethanol before drying in an oven at 60°C to 80°C for about 12 h. Hydroxyapatite powder and biochar were mixed in a 1:1 mass ratio using a mortar and pestle. The mixture was slightly moistened with ethanol to improve uniform blending. After thorough mixing, the composite powder was dried at 60°C to remove residual ethanol and moisture. The dried HAP-biochar composite was kept in borosilicate bottles for further experiments, as illustrated in Figure 4b.

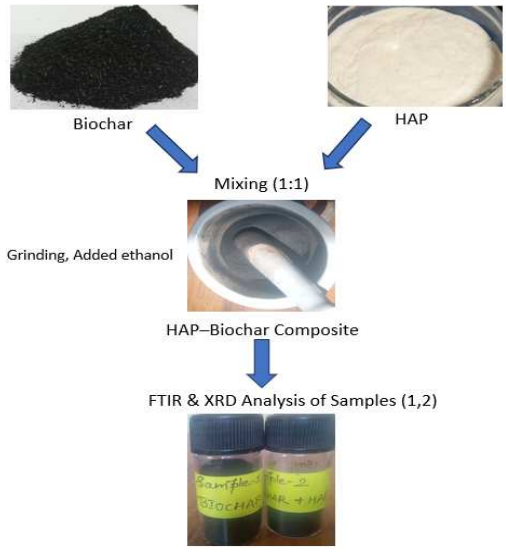



**Figure 4b.** Process flow for preparation of HAP-Biochar Composite. This composite was characterized by FTIR and XRD; adsorption experiments were not performed with this material in the current study.

**3. Results and discussion**

**3.1. ICP-MS Data**

Wastewater heavy metals (Cd, Cr, etc.) were analyzed using ICP-MS. Pretreated samples were stored at 4 °C until analysis. Each sample (25 mL) was digested in a microwave digester with $HNO_3$ and $H_2O_2$ at 180 °C and 20 bar for 25 min (Section

2.5). Digested solutions were cooled, filtered and diluted to 50 mL with deionized water. Calibration employed 0.1–10 µg/mL multi-element standards with internal standards (Rh, In, Y) achieving $R^2 \geq 0.995$. Quality control was maintained through the analysis of blanks, duplicates, spikes (80-120% recovery), and NIST-traceable certified reference materials. Duplicate precision (relative percent difference) was <20%. Instrument operating conditions were RF power 1200-1550 W and plasma Ar flow 15 L/min. Method detection limits were Cr 0.2 µg/L and Cd 0.05 µg/L. Concentrations were calculated from instrument response and dilution factors and are reported in mg/L.

The experimental data for all physicochemical parameters are summarized in Table 2 and illustrated in Figure 5-8.

**Table 2. Results of all physicochemical characteristics on all the sample lots**

| S. No. | pH | Density (g/mL) | TDS (ppm) | Chromium (mg/L) | Cadmium (mg/L) |
|---|---|---|---|---|---|
| **1.** | 9.35 | 1.349 | 2845 | 11.45 | 9.27 |
| **2.** | 8.65 | 1.245 | 1763 | 9.80 | 4.90 |
| **3.** | 7.86 | 1.273 | 1889 | 9.28 | 5.27 |
| **4.** | 9.45 | 1.345 | 3779 | 14.27 | 7.26 |
| **5.** | 7.15 | 1.342 | 691 | 9.26 | 4.17 |
| **6.** | 7.35 | 1.362 | 2717 | 17.25 | 22.45 |
| **7.** | 8.25 | 1.212 | 2863 | 3.39 | 2.12 |
| **8.** | 1.42 | 1.278 | 9931 | 13.87 | 12.18 |
| **9.** | 7.92 | 1.126 | 3779 | 2.17 | 1.86 |
| **10.** | 1.59 | 1.102 | 7206 | 13.28 | 24.16 |
| **11.** | 7.90 | 1.102 | 1850 | 19.20 | 3.60 |
| **12.** | 8.19 | 1.130 | 1690 | 27.80 | 4.35 |
| **13.** | 7.34 | 1.126 | 1588 | 7.40 | 3.50 |
| **14.** | 8.34 | 1.105 | 1960 | 4.37 | 2.85 |
| **15.** | 5.70 | 1.129 | 1785 | 4.37 | 2.85 |

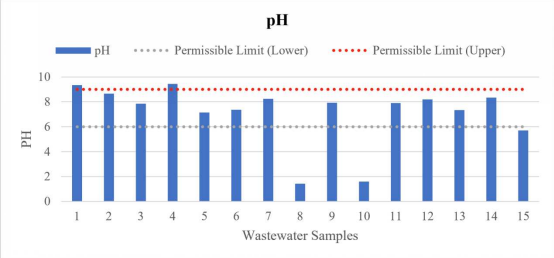



**Figure 5.** Graphical representation of pH variations in wastewater samples.

### 3.2. Water quality characteristics

- **pH**

As presented in Table 2 and Figure 5. It is visible that the pH was above 7 in all the samples, except in W8, W10 and W15 where the value was observed to be 1.42, 1.59 and 5.07, respectively. The results indicate that 12 out of 15 samples were observed to be alkaline in nature (pH>7). Samples W8 and W10 exhibited very acidic pH values of 1.42 and 1.59, respectively, which are consistent with the influence of acid-intensive industrial activities such as metal plating and acid pickling. Because industrial discharges are diverse, industrial wastewater usually exhibits a wide range of pH values. For example, wastewater from the food processing and textile industries is frequently alkaline, whereas effluents from chemical and metal plating processes are associated with extremely acidic pH values [22], which is consistent with the observed variation in pH found in previous studies. Central Pollution Control Board (CPCB) [23] specifies a pH range of 6.5–8.5 (IS: 10500) for safe effluent discharge. Values below 6.5 cause pipe corrosion and aquatic toxicity, while values above 8.5 lead to scaling, reduced oxygen levels, and harm to receiving water ecosystems.

- **Density**

The differences in density between the samples are shown in Table 2 and Figure 6. Samples W10 and W11 showed the same density value, likely due to their origin from similar sources, reflecting consistent wastewater characteristics: they had the lowest density (1.102 g/mL), while sample W1 had the highest density (1.349 g/mL). Consistent physical characteristics of the wastewater are suggested by the observed range of density values, which show slight variations across all samples collected. According to studies on industrial discharges, relatively uniform physicochemical parameters across samples can indicate a common effluent source or similar treatment conditions [24].

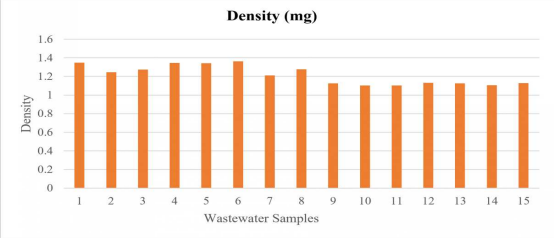



**Figure 6.** Graphical representation of Density variations in wastewater samples.

- **Total Dissolved Solids (TDS)**

As per the results depicted in Table 2 and Figure 7. The samples analyzed exhibited a significant concentration of total dissolved solids (TDS), with measurements varying from 691 ppm in sample W5 to 9931 ppm in sample W8. There was a visible difference in TDS at different locations of sample collection. Excessive levels of Total Dissolved Solids (TDS) in industrial wastewater are frequently a sign of contaminants and are frequently impacted by the type of industry. The dilution capacity of receiving water bodies and localized effluent discharge are usually the causes of variations in TDS levels at various sampling locations. Our focus is on gathering data and characterizing the effluents from the textile industry to evaluate the physicochemical load discharged into natural wastewater streams, similar to the approach adopted by [25]. Extreme TDS levels, the range between (691–9931 ppm), are also a sign of industrial areas with inadequate waste management, which can harm both environmental integrity and public health. Studies have shown that TDS levels exceeding 500 ppm can significantly impact aquatic ecosystems and the suitability of water for household use; concentrations above 1,000 ppm are classified as unsafe for untreated consumption according to WHO Guidelines [26]. Industrial wastewater treatment requires strict management of total dissolved solids (TDS) because high TDS increases the bioavailability of heavy metals. According to [27], TDS levels up to 8300 ppm may be tolerated by livestock, but due to human health risks, it is essential to reduce TDS below 500 ppm in combination with effective heavy metal removal.

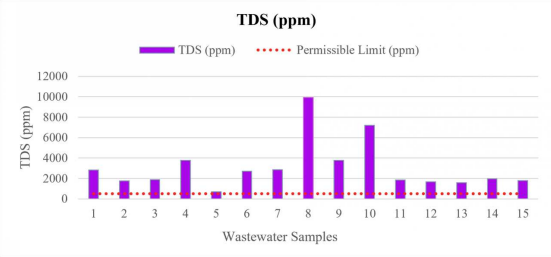



**Figure 7.** Graphical representation of TDS variations in wastewater samples

- **Chromium**

During the study period the average range of chromium we found was 2.17 to 27.80 mg/L as shown in Figure 8. This level exceeds the permissible threshold established by Indian standards. Chromium is considered one of the most harmful substances for environmental health. Throughout all research locations during the entire study period, the concentration of chromium consistently surpassed the maximum acceptable limit set by the Central Pollution Control Board (CPCB) for industrial effluent discharge (0.5 mg/L). For context, the IS:10500 drinking water standard for chromium is 0.05 mg/L, which is relevant if untreated effluent enters drinking water sources [23].

- **Cadmium**

Throughout the duration of the study, cadmium concentrations in wastewater samples varied from 1.86 to 24.16 mg/L across the 15 sampling locations. All sites exhibited cadmium levels that significantly exceeded the permissible limit established by the Central Pollution Control Board (CPCB), which is set at 2 mg/L for effluent discharge, thereby resulting in environmental toxicity. As illustrated in Table 2 and Figure 8, Chromium (Cr) and cadmium (Cd), particularly in its hexavalent form, are acknowledged for their high toxicity and carcinogenic properties. When found at increased concentrations in water intended for drinking or irrigation, they present dangers including kidney damage, DNA harm, and an elevated cancer risk [28].

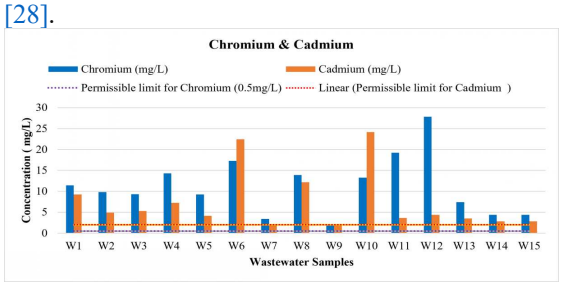



**Figure 8.** Graphical representation of Chromium and Cadmium variations in wastewater samples

The levels of chromium (Cr) in industrial wastewater ranged from 2.17 to 27.80 mg/L, while cadmium (Cd) concentrations were between 1.86 and 24.16 mg/L, both of which significantly exceed the permissible limits established by regulatory standards for wastewater quality. The alkaline pH as shown indicates that basic substances might be present in some industrial effluents and require special treatment to neutralize the water. Moreover, excessive concentration of dissolved substances can damage the environment with adverse effects on aquatic organisms and water quality. This is indicated by the density of 1.349 mg/L and their total dissolved solids (TDS) are between 691 and 9931 ppm which is highly significant. High TDS, high pH and high metal concentrations reflect the need for remediation methods in order to counter the harmful impact of these pollutants on the environment.

Chromium and cadmium concentrations in the tested sites were also the lowest concentrations. At W7 (Sector-58, Central Industrial Area) Cr was recorded as 3.39 and Cd 2.12 mg/L, respectively, whereas the comparable low Cd is again obtained at W9 (Sector-25, Adjacent Industrial Zone; 1.86 mg/L). Low concentrations in these regions indicate that effluents may be released at W7 and W9 from lower metal-density industrial processes (such as mixed light manufacturing, not metal plating or tanning) and/or from facilities that use dilution, partial recycling, or pre-discharge primary treatment. And W6, W8, W10 and W12 have much higher Cr and

Cd levels, most commonly associated with metal finishing, dyeing and other heavy metal processes, which might be evidence of more anthropogenic input or at least inferior treatment at those sites in comparison. These inadequately treated discharges from textile, paper and pulp, oil processing, breweries, and food and drinks industry can harm our aquatic ecosystems and leave receiving waters uninhabitable or unsuitable for homes or farms. Recent review studies [29] stress requirements of integrated sustainable treatment trains consisting of physical, chemical and biological systems to manage such contaminants and to recover and reuse treated wastewater.

### 3.3. Chromium (Cr) and Cadmium (Cd) removal by biochar

Heavy metals (e.g., chromium and cadmium are readily and effectively extracted from wastewater by biochar, which is derived from the pyrolysis of organic biomass. It can be used to adsorb toxic metals as they are separated using ion exchange, complexation and electrostatic interaction due to different specific properties like high surface area, porous nature and chemical groups. To find this balance, [30] emphasizes that optimizing water and sewage treatment approaches is vital to promote agricultural productivity while conserving resources and ensuring environmental security. The expansion of water reuse needs to take into account the most suitable possible impact on soil, crops and ecosystems and, therefore, sustainability efforts must incorporate novel, ecological technologies.

### 3.4. Strategy for Application of Biochar

The powdered bio-adsorbent was exposed to the chromium and cadmium-contaminated wastewater samples in the application step, and the residual metal concentrations were read to monitor treatment properties. This simple application demonstrates the potential of the prepared biochar as a practical, low-cost option for wastewater purification.

Sample 1 (activated biochar) and Sample 2 (HAP-biochar composite) were characterized by Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). To assess the functional groups and the chemical bonds on the surface of the materials, FTIR analysis was performed. XRD analysis provided information about the crystalline structure and phase composition of each sample, confirming the successful synthesis and modification of the biochar. Adsorption experiments were conducted using activated biochar (Sample 1) only; the HAP-biochar composite (Sample 2) was characterized to assess its potential for future adsorption studies.

### 3.5. Characterization of Bio-adsorbent

The surface chemistry of the sorbent is influenced significantly by chemical treatments like acid and base modification that facilitate enhanced total chromium removal efficiency, as reported by FTIR and thermogravimetric investigations [31]. The different functional groups for heavy metal adsorption were identified by FTIR analysis of biochar samples in Figures 9a and 9b.

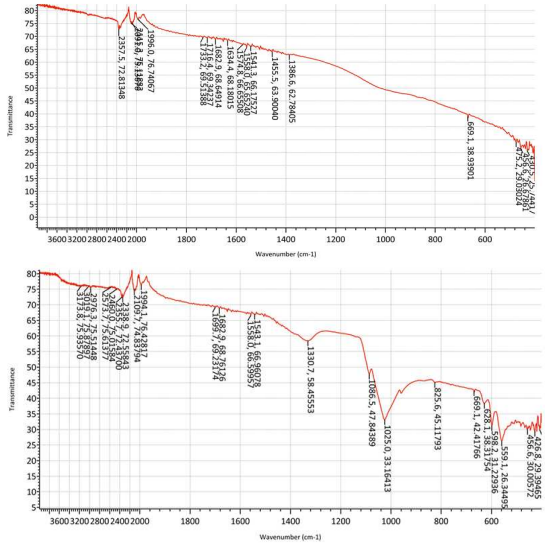
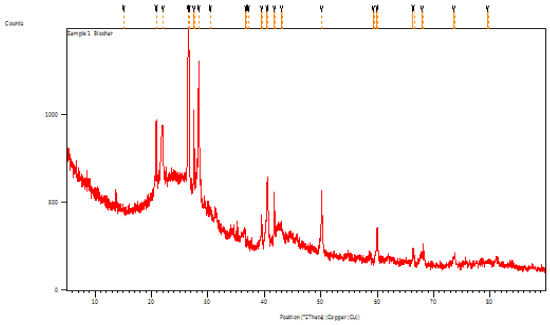



**Figure 9.** FTIR spectra of raw biochar (a) and HAP-biochar composite (b)

Peaks at 430.5, 456.6, and 669.1 $cm^{-1}$ can be seen for sample 1, indicating a relationship of aromatic ring skeletal vibrations with metal-oxygen bonding. Important peaks at 1386.6, 1455.5, and 1541.3 $cm^{-1}$ are indicative of C-H bending and aromatic C=C stretching vibrations, indicating the presence of aromatic carbon. High peaks around 1634.4 $cm^{-1}$ in conjunction with a band near 1558 $cm^{-1}$ represent carbonyl (C=O/CHO) functionalities and lead to the conclusion that carbonyl-containing groups play the role of binding metal ions. Additional broad bands in 1996-2115 $cm^{-1}$ imply complex organic functionalities that could result in an additional biochar adsorption capacity. Note specifically, the addition of hydroxyapatite (HAP) seems to accentuate some peaks, suggesting surface modifications that would increase heavy metal binding performance. These results supported that the functional group is active for the adsorption mechanism and the surface modification will be useful for the wastewater treatment.

X-ray diffraction (XRD) analysis was carried out on Sample 1 (biochar) and Sample 2 (HAP-biochar composite), and the results are presented in Figures 9c and 9d.



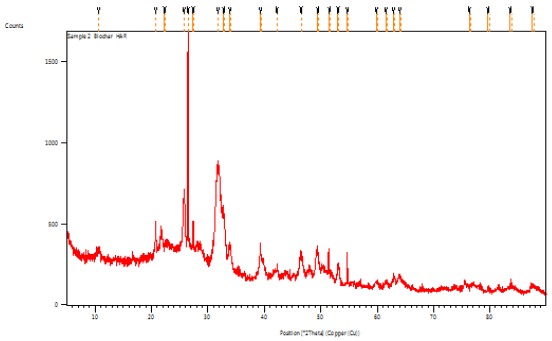


**Figure 9.** XRD patterns of raw biochar (c) and HAP-biochar composite (d)

Sample 1 (biochar) exhibited typical broad peaks from 20° to 30° 2θ, consistent with amorphous carbon structure. Sharp peaks at 26.5°, 27.5°, and 28.0° 2θ indicated graphitic carbon phases, while minor peaks at approximately 15° and 22° 2θ suggested residual mineral impurities such as quartz. Sample 2 showed more distinct peaks at 10.6°, 20.7°, 22.3°, 25.7°, and strong peaks near 26.5°, indicating hydroxyapatite (HAP) and other mineral phases. These sharper peaks in Sample 2 point to higher crystallinity due to HAP addition. Overall, both samples have layered carbon structures, but Sample 2's mineral content may enhance metal adsorption efficiency.

### 3.7. Estimation of Response Surface for Optimal Removal of Chromium and Cadmium

The results from twenty experiments carried out using Central Composite Design (CCD) analysis [32] demonstrate that the removal efficiencies for Chromium and Cadmium were notably high. In a comparative study, [33] assessed the effectiveness of zinc chloride (ACZ)- and calcium chloride (ACC)-activated walnut shell charcoal in removing cadmium from aqueous solutions using Response Surface Methodology (RSM) optimization. Additionally, [34] investigated various biomass-derived and nanostructured materials, including metal oxide-modified biochar and activated carbons, for their capacity to remove divalent heavy metals such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, and $Ni^{2+}$ from aqueous environments. The efficiencies in removing chromium and cadmium

### 3.6. Adsorption performance and optimization

A total number of 15 wastewater samples (Sites 1–15) were collected, but adsorption experiments with raw biochar were carried out only with samples 11–15 (Table 3). The removal efficiency (%) of chromium and cadmium was calculated by using the following equation:

$$\textbf{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

where $C_0$ is the initial concentration (mg/L) before adsorption,

$C_e$ is the equilibrium concentration (mg/L) after adsorption

For Samples 11 to 15, the calculated chromium removal ranged from approximately 46% to 63%, while cadmium removal ranged from about 47% to 57%, indicating only moderate performance of the raw biochar. These results were further used to construct a site-wise bar diagram, with sample sites on the x-axis and removal efficiency for chromium and cadmium on the y-axis, to visualize the variation in adsorption behaviour before comparing it with the subsequently developed HAP–biochar composite.

**Table 3. Physicochemical characteristics of wastewater samples (W11–W15) before and after biochar + $H_3PO_4$ treatment**

| Sample No. | pH (Initial→Final) | TDS (Initial→Final) | Cr (Initial→Final) | Cd (Initial→Final) |
|---|---|---|---|---|
| W11 | 7.90→7.19 | 1850→1003 | 19.20→10.42 | 3.60→1.89 |
| W12 | 8.19→7.95 | 1690→897 | 27.80→10.42 | 4.35→1.89 |
| W13 | 7.34→7.11 | 1588→840 | 7.40→3.96 | 3.50→1.86 |
| W14 | 8.34→8.13 | 1960→1065 | 4.37→2.39 | 2.85→1.47 |
| W15 | 5.70→5.90 | 1785→939 | 4.37→2.33 | 2.85→1.27 |
| Average | 7.49→7.26 | 1734→949 | 12.63→6.10 | 3.43→1.68 |

were calculated among the dependent response variables compared with important independent process factors, which included pH, initial metal concentration, contact time, temperature, and adsorbent dosage.

This analysis was conducted within the Central Composite Design (CCD) framework. The coded and actual levels of the chosen factors used for optimization by CCD-based response surface methodology are outlined in Table 4. Table 5 lists the experimental design matrix together with the observed chromium and cadmium removal efficiencies obtained in each CCD-RSM optimization run using raw biochar.

- **Factors and Levels**

**Table 4. Specifications of Response Surface Methodology (Central Composite Design) Optimization**

| Factor | Low (-1) | Central (0) | High (+1) | -α | +α |
|---|---|---|---|---|---|
| Contact time (hours) | 12 | 24 | 36 | 3.81 | 44.18 |
| Temperature (°C) | 15 | 25 | 35 | 8.18 | 41.81 |
| Biochar Dose (%w/v) | 1.5 | 2.5 | 3.5 | 0.81 | 4.18 |

**Table 5: Experimental design and observed chromium and cadmium**

**removal efficiencies obtained from the CCD-RSM optimization runs using raw biochar**

| Run | Contact Time (h) | Temperature (°C) | Biochar Dosage (%w/v) | Chromium Removal (%) | %Cadmium Removal (%) |
|---|---|---|---|---|---|
| 1 | 12 | 12 | 1.5 | 40 | 42 |
| 2 | 36 | 12 | 1.5 | 44 | 46 |
| 3 | 12 | 24 | 1.5 | 42 | 44 |
| 4 | 36 | 24 | 1.5 | 46 | 48 |
| 5 | 12 | 12 | 3.5 | 43 | 45 |
| 6 | 36 | 12 | 3.5 | 47 | 49 |
| 7 | 12 | 24 | 3.5 | 45.7 | 47.5 |
| 8 | 36 | 24 | 3.5 | 50 | 52 |
| 9 | 24 | 18 | 2.5 | 62.5 | 56.6 |
| 10 | 24 | 18 | 2.5 | 46.7 | 55.4 |
| 11 | 24 | 18 | 2.5 | 45.7 | 48.4 |
| 12 | 24 | 18 | 2.5 | 47 | 51 |
| 13 | 12 | 18 | 2.5 | 43 | 45 |
| 14 | 36 | 18 | 2.5 | 49 | 53 |
| 15 | 24 | 8.18 | 2.5 | 38 | 40 |
| 16 | 24 | 27.82 | 2.5 | 51 | 54 |
| 17 | 24 | 18 | 0.82 | 39 | 41 |
| 18 | 24 | 18 | 4.18 | 52 | 55 |
| 19 | 3.82 | 18 | 2.5 | 41 | 43 |
| 20 | 44.18 | 18 | 2.5 | 53 | 56 |

- **ANOVA Analysis for Chromium and Cadmium Removal**

The evaluation of the linear model for heavy metal removal was conducted through analysis of variance (ANOVA) using Design-Expert software (Stat-Ease Inc., Minneapolis, MN, USA) to determine its significance. Tables 6-8 present the fit statistics, regression coefficients, and ANOVA results for both chromium and cadmium removal. In the context of chromium removal, which averaged at 46.26%, the linear model demonstrated a moderate fit with an $R^2$ value of 0.4504, suggesting that the model accounted for 45.04% of the variation in chromium removal efficiency. The adjusted $R^2$ value of 0.3473 and the predicted $R^2$ value of 0.3058 were in close agreement (with a difference of less than 0.2), However, the relatively low $R^2$ value suggests that other factors not included in this model may affect chromium removal. An adequate precision ratio of 7.395 (greater than 4) was observed, which was considered an adequate signal-to-noise ratio for navigating the design space. The sequential model sum of squares (Table 8) confirmed the linear model as the best fit ($p = 0.0199$), with higher-order terms (2FI, quadratic, cubic) showing non-significant improvement ($p > 0.05$). Regression coefficients (Table 7) revealed that temperature had the highest positive effect ($\beta = 3.87$), followed by biochar dosage ($\beta = 2.60$) and contact time ($\beta = 2.71$). Notably, the 95% confidence interval for temperature includes zero (-0.5998 to 8.33), suggesting that this effect may not be statistically significant at the 95% confidence level. All factors showed low variance inflation factors (VIF = 1.00), confirming no multicollinearity.

**Table 6. Fit Statistics for Chromium and Cadmium Removal Using Linear Model**

| Parameter | Chromium | Cadmium |
|---|---|---|
| **Standard Deviation** | 4.62 | 3.69 |
| **Mean** | 46.26 | 48.59 |
| **C.V. %** | 9.98 | 7.59 |
| **$R^2$** | 0.4504 | 0.5924 |
| **Adjusted $R^2$** | 0.3473 | 0.5160 |
| **Predicted $R^2$** | 0.3058 | 0.4175 |
| **Adequate Precision** | 7.3949 | 9.8225 |

**Table 7. Regression Coefficients for Chromium and Cadmium Removal**

| Factors | Coefficient (Cr) | 95% CI Low (Cr) | 95% CI High (Cr) | Coefficient (Cd) | 95% CI Low (Cd) | 95% CI High (Cd) |
|---|---|---|---|---|---|---|
| **Intercept** | 48.97 | 45.15 | 52.78 | 51.43 | 48.38 | 54.47 |
| **A-Contact Time** | 2.71 | 0.2389 | 5.19 | 2.96 | 0.9852 | 4.94 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **B-Temperature** | 3.87 | -0.5998 | 8.33 | 4.04 | 0.4787 | 7.61 |
| **C-Biochar Dosage** | 2.60 | -0.0459 | 5.26 | 2.71 | 0.5964 | 4.83 |

**Table 8. ANOVA (Sequential Model Sum of Squares) for Chromium and Cadmium Removal**

| Model Comparison | Cr F-value | Cr p-value | Cd F-value | Cd p-value |
|---|---|---|---|---|
| **Linear vs Mean** | 4.37 | 0.0199 | 7.75 | 0.0020 |
| **2FI vs Linear** | 0.0049 | 0.9995 | 0.0069 | 0.9992 |
| **Quadratic vs 2FI** | 1.02 | 0.4236 | 2.65 | 0.1062 |
| **Cubic vs Quadratic** | 0.2241 | 0.9368 | 1.13 | 0.4484 |
| **Lack of Fit** | 0.2241 | 0.9368 | 1.13 | 0.4484 |

**Regression Equations (Coded Factors):**

- Cr Removal (%) = 48.97 + 2.71A + 3.87B + 2.60C
- Cd Removal (%) = 51.43 + 2.96A + 4.04B + 2.71C

For cadmium removal (mean = 48.59%), the model showed better fit with $R^2$ = 0.5924 (59.24% variability explained). Adjusted $R^2$ (0.5160) and predicted $R^2$ (0.4175) were reasonably aligned, with adequate precision of 9.822. The linear model was highly significant (p = 0.0020), with temperature showing the strongest influence (β = 4.04).

### 3.8. Combined effects of process variables

**Effect of Temperature and Contact Time on Adsorption:** The combined influence of temperature and contact time affected cadmium removal more strongly than chromium removal (Figure 10B and Figure 11B). Both metals exhibited relatively low removal at low temperature (around 12 °C) and short contact time (12 h), and their removal increased by increasing the temperature up to 24 °C and extending the contact time. The steeper response surface of cadmium could be seen as the result of the positive regression coefficients of both factors, and this indicates that adsorption is endothermic and kinetically favoured at higher temperature, because greater diffusion of metal ions into the pores and stronger interaction with surface functional groups leads to increased uptake.

**Effect of Biochar Dosage and Temperature on Adsorption:** Moreover, the combined effect of biochar dosage and temperature significantly positively affected removal of chromium and cadmium (Figure 10C and Figure 11C). At 24h contact time, transitioning from low dose of 1.5% w/v and low temperature (12°C) to high dose of 3.5% w/v and high temperature of 24°C resulted in a notable increase in removal at a fixed contact time, with the highest zones of surfaces corresponding to the maximum responses obtained the CCD of the runs (about 62–63% chromium and around 56–57% cadmium). This behaviour is ascribed to the enhanced number of active sites at higher biochar loading and increased surface functionality and ion mobility at increased temperature, which facilitates metal absorption.

**Effect of Biochar Dosage and Contact Time on Adsorption:** Based on the 3D response surface plots (Figure 10C-D and Figure 11C-D), biochar dosage, contact time, and removal of chromium and cadmium were investigated. At 18°C and a constant temperature, contact time was increased from 12 h to 36 h, and the biochar dosage of 1.5–3.5% (w/v) also presented a gradual enhancement in removal efficiency for both metals. Each surface rises towards the high dosage and larger contact time before the top reaches all those, suggesting that at that point most adsorption sites are used up, and at increasing time or dosage, the little additional removal is achieved by higher dosage and a longer contact time only.

**Validation of the response surface methodology**

Figures 10 and 11 present the model performance and response surface plots for chromium and cadmium removal by the biochar adsorbent. In both cases, the predicted-versus-actual plots (Figure 10A and 11A) show that most data points cluster around the diagonal line, indicating good agreement between experimental and model-predicted removal efficiencies. The fitted regression models yield positive coefficients for contact time, temperature and biochar dosage, with comparatively stronger effects for cadmium, which is consistent with the steeper response surfaces obtained for this metal. The three-dimensional plots (10B-D and 11B-D) further demonstrate that chromium and cadmium removal increase when contact time, temperature and biochar dosage are simultaneously raised within the investigated range, after which the surfaces tend to level off. This levelling behaviour suggests that the process approaches saturation of the available active sites on the biochar at the upper experimental conditions. Taken together, the close correspondence between predicted and observed responses, the non-significant lack-of-fit and adequate precision values greater than 4 indicate that the CCD-based response surface methodology provides a reasonable description of the system and is suitable for identifying operating conditions that improve chromium and cadmium removal in wastewater treatment. However, the moderate $R^2$ values (Cr: 0.4504; Cd: 0.5924) suggest that

additional factors not included in this model may also influence metal removal efficiency.

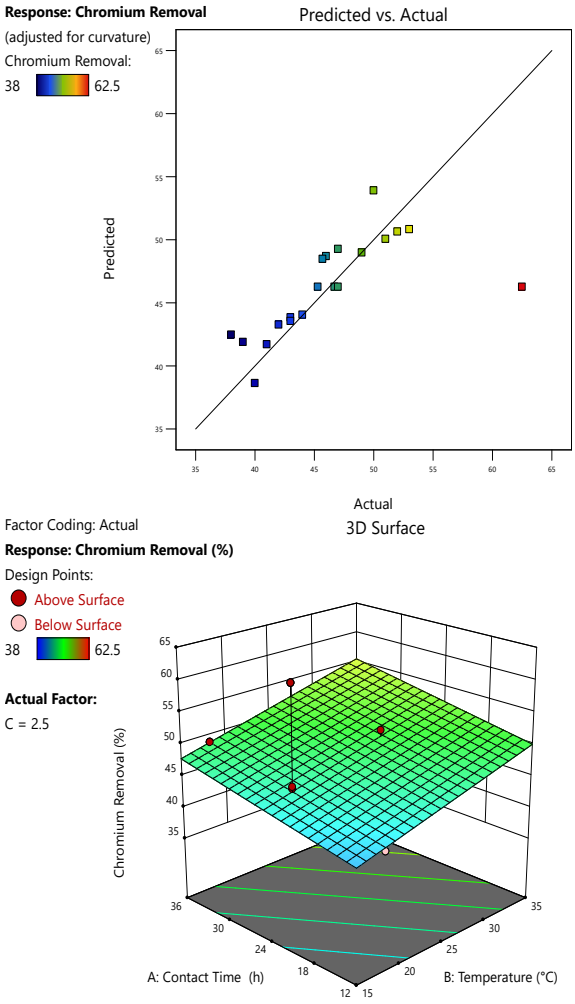



**Figure 10.** Results of RSM Analysis for Chromium Removal Using Biochar. (A) Predicted versus actual values; (B) combined influence of temperature and contact time; (C) combined influence of biochar dosage and temperature; (D) combined influence of biochar dosage and contact time.

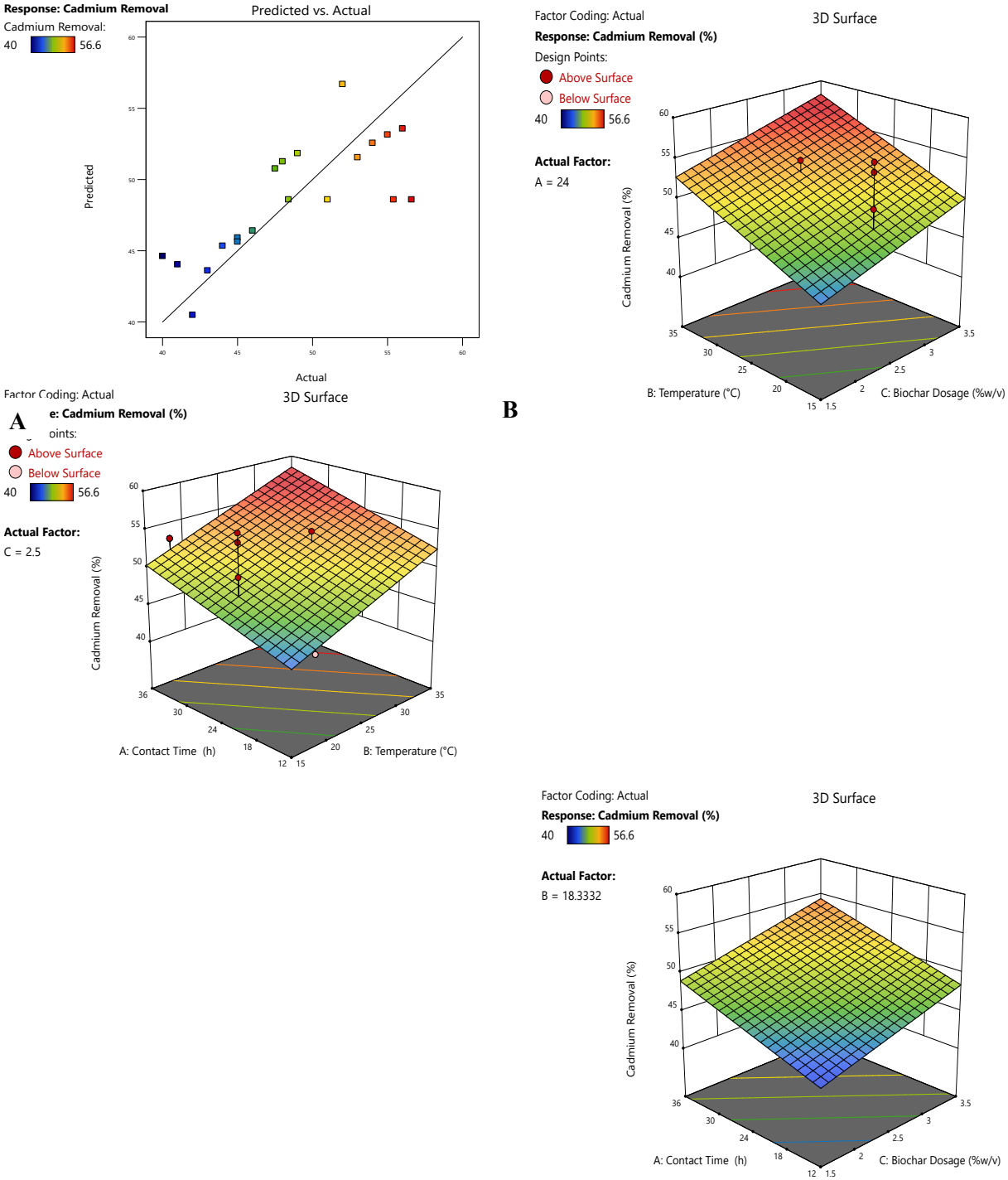



**Figure 11.** Results of RSM Analysis for Cadmium Removal Using Biochar. (A) Predicted versus actual values; (B) combined influence of temperature and contact time; (C) combined influence of biochar dosage and temperature; (D) combined influence of biochar dosage and contact time.

## 4. Conclusion

This study shows that the biochar prepared from the selected precursor can remove chromium and cadmium from wastewater in an efficient, low-cost and environment-friendly way. The adsorption experiments and model results indicate that by adjusting simple operating conditions such as contact time, temperature and biochar dosage, a

considerable part of the metal load can be removed from the water. Because the raw material is inexpensive and locally available, this type of biochar offers a practical option for treating industrial effluents from areas like Faridabad, where conventional treatment is often too costly or difficult to operate. Overall, the work suggests that biochar-based adsorption can play a useful role in reducing heavy-metal pollution and in improving the quality of discharged or reused wastewater.

**Future Aspects**

In future work, HAP-biochar composite can be modified to increase pores and active sites for Cr/Cd binding, to improve adsorption capacity and kinetics after design modification. HAP efficiency will be evaluated by an established batch protocol with synthetic/real wastewater for HAP reaction conditions and then pilot-scale trials to evaluate performance amid competing ions, pH variations, and matrix effects. Reusability through multiple adsorption-desorption cycles, techno-economic analysis (cost, energy, and commercial comparison), ecological risk, and human health risk assessments of treated effluents will be conducted, considering Nala discharge risks. Finally, integration with biological treatment and long-term carbon sequestration studies will result in the development of sustainable remediation methods that contribute substantially to the mitigation of climate change.

**CRediT Authorship Contributions Statement**

**Sonia Bisht:** Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing-review & editing. **Pratibha Sharma:** Writing-original draft, Validation, Supervision, Project administration.

**Declaration of Competing Interest**

The authors declare no financial or personal conflicts that might influence this research.

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