

Article

Enhanced Removal of Hexavalent Chromium by Iron-Modified Biochar: Sorption Kinetics and Isotherm Studies

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Abstract

Hexavalent chromium Cr(VI) is a highly toxic and mobile contaminant commonly detected in industrial effluents and groundwater, requiring efficient and scalable treatment strategies. In this study, a commercial unmodified biochar (UB) and an iron-modified biochar (IMB) were evaluated for Cr(VI) removal from aqueous solutions. Iron modification via FeCl₃ impregnation and alkaline precipitation (pH 9) increased surface iron content from 0.2% to 3.3%, based on Energy Dispersive X-ray (EDX) analysis and extractable Fe from 0.009% to 0.108% (FerroVer). X-ray Diffraction (XRD) analysis suggested the presence of iron-containing phases and Fourier Transform Infrared (FTIR) analysis indicated the appearance of an Fe-O band at 564 cm⁻¹. BET analysis showed a slight decrease in surface area from 359 to 317 m² g⁻¹, consistent with partial pore blockage following iron modification. Batch adsorption experiments (pH 2–10; initial Cr(VI) concentration 5–600 mg L⁻¹; adsorbent dosage 2 g L⁻¹) revealed a maximum Langmuir adsorption capacity of 158 mg g⁻¹ for IMB, nearly double that of UB (82 mg g⁻¹), with optimal performance at pH 4–6. At equilibrium, removal efficiencies of ~60% and ~80% were obtained for UB and IMB, respectively (C₀ = 100 mg L⁻¹; adsorbent dose = 2 g L⁻¹). Kinetics followed a pseudo-second-order model, with IMB reaching equilibrium within 8 h compared to 50 h for UB. Isotherm analysis is consistent with Langmuir behavior for UB and Freundlich behavior for IMB. The improved adsorption performance of IMB is likely associated with the increased iron content introduced during modification, demonstrating its potential as an effective adsorbent for Cr(VI) removal from water.

Keywords: biochar; FeCl₃ modification; Cr(VI); adsorption capacity; groundwater remediation; permeable reactive barriers

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1. Introduction

Chromium is an emerging contaminant in aquatic environments that has attracted significant attention over recent decades due to its persistence and toxicity. It has been detected in a large proportion of hazardous waste sites, with approximately two-thirds of sites proposed for inclusion on the U.S. Environmental Protection Agency (EPA) National Priorities List (NPL) reported to contain chromium contamination [1]. In natural systems, chromium primarily exists in two oxidation states: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Cr(VI) is considered to be more toxic than Cr(III) due to its

high solubility and mobility and is widely recognized as carcinogenic and mutagenic [2,3]. Although Cr(III) is considered an essential micronutrient, its role remains a matter of ongoing debate, with some studies suggesting potential involvement in carcinogenic processes [3].

Human exposure to chromium occurs predominantly through ingestion of contaminated water and food. Chromium present in water bodies can directly enter the human body via drinking water or indirectly through bioaccumulation in crops such as vegetables and fruits [4]. As the 21st most abundant element in the Earth's crust, chromium is introduced into aquatic systems through both natural and anthropogenic pathways. Natural sources include the weathering of chromite ore and other chromium-bearing minerals, while major anthropogenic sources include industrial activities such as electroplating, alloy manufacturing, leather tanning, wood preservation, corrosion control [5] and mining operations (e.g., chromite and coal mining) [6,7]. Naturally occurring Cr(VI) concentrations in groundwater have been reported in the range of 0.002–0.700 mg L⁻¹ [5], whereas concentrations in industrial wastewater can reach 0.1–200 mg L⁻¹ [8].

Due to its adverse health effects, the EPA and WHO have established a maximum contaminant level (MCL) for total chromium in drinking water at 0.1 mg L⁻¹ and 0.05 mg L⁻¹, respectively [9,10]. The higher solubility and mobility of Cr(VI) facilitate its transport into subsurface environments, posing a significant risk to groundwater systems. Consequently, effective remediation strategies are required for both contaminated sites and industrial effluents. Depending on site-specific conditions such as contaminant concentration, flow regime, and hydrogeological characteristics, treatment approaches can be implemented either in situ or ex situ [11]. In situ technologies are commonly applied in contaminated aquifers and mining sites, for example through permeable reactive barriers (PRBs), whereas ex situ treatments are typically employed in engineered systems such as reactors in industrial facilities. Therefore, there is a growing need to develop versatile materials suitable for both applications.

Among the available Cr(VI) removal technologies, including chemical precipitation, ion exchange, electrochemical methods, biological treatments, and sorption, sorption has emerged as one of the most promising approaches due to its high efficiency, cost-effectiveness, and operational simplicity. Importantly, adsorption can be readily adapted for both in situ and ex situ applications. Biochar, a carbon-rich material produced via pyrolysis of biomass under oxygen-limited conditions, has gained considerable attention as an adsorbent owing to its low cost, high specific surface area, well-developed pore structure, and abundance of surface functional groups [12]. These properties enable biochar to effectively remove a wide range of contaminants.

Biochar contains various oxygen-containing functional groups (e.g., -COOH, -OH, -C=O) and inorganic mineral components (e.g., Si-O-Si, Al-O domains), which act as active sites for contaminant interactions [12,13]. In one study, organic components were estimated to account for up to 97% of the Cr(VI) adsorption capacity [14]. In particular, oxygen-containing functional groups and π -electron-rich aromatic structures facilitate the reduction of Cr(VI) to Cr(III), followed by immobilization through ion exchange or surface complexation [14–17]. However, raw biochar typically exhibits a negatively charged surface, which limits its ability to adsorb anionic species such as chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) [18]. As a result, although reduction and complexation mechanisms exist, the overall adsorption capacity and kinetics for Cr(VI) removal remain relatively low.

To overcome these limitations, various physical and chemical modification strategies have been developed to enhance biochar performance. Such modifications can alter functional groups, increase surface area and porosity, and, importantly, change the point of zero charge, pH_{ZPC}, thereby improving electrostatic attraction toward negatively charged

oxyanions [19]. Whether pH_{zpc} increases or decreases depends on the modification method. For instance, oxidation treatment can increase surface acidity and lower the pH_{zpc} [20], whereas the incorporation of metal oxides often increases the pH_{zpc} by introducing metal-hydroxyl groups [21]. Metal oxide modifications, particularly with iron, manganese, or copper, have been widely employed to enhance oxyanion adsorption capacity [22,23]. Iron is especially favored due to its natural abundance in the Earth's crust [24]. Iron-based modifications are particularly effective, as iron oxides/hydroxides not only increase adsorption sites but also facilitate redox reactions and electron transfer processes [12]. Iron-modified biochar is commonly prepared using two main approaches: co-pyrolysis of biomass with iron salts/oxides and post-pyrolysis surface deposition of iron species onto pre-produced biochar [24,25]. While co-pyrolysis can effectively incorporate iron into the carbon matrix, it requires high-temperature processing, resulting in greater energy consumption and the potential formation of undesirable gaseous emissions [26,27]. In contrast, post-pyrolysis surface deposition is a simpler and more controllable modification method that enables iron species to be introduced onto the biochar surface under mild reaction conditions. In the present study, FeCl_3 was precipitated under alkaline conditions (pH 9) to deposit iron hydroxide/oxide species on the biochar surface. This modification strategy was selected because the resulting iron-containing surface increases the biochar pH_{zpc} and provides amphoteric adsorption sites, thereby improving the adsorption of negatively charged chromate species over a broader pH range [19]. For instance, $\text{Fe}_2(\text{SO}_4)_3$ -modified biochar has been reported to enhance Cr(VI) removal capacity by up to seven-fold compared to raw biochar [28], while Sun et al. compared biochar and iron oxide-loaded biochar/attapulgite composite, which showed 54 mg g^{-1} and 107 mg g^{-1} Langmuir maximum adsorption capacities, respectively [29].

Although iron-modified biochar has been extensively investigated, the relationships between iron oxide mineral formation, the distribution of iron species on the biochar surface, and their influence on surface area, pore structure, adsorption kinetics, equilibrium behavior, and adsorption mechanisms remain insufficiently understood [30]. Elucidating these relationships is essential for optimizing iron-modified biochar for groundwater remediation and permeable reactive barrier applications. Furthermore, most previous studies have evaluated Cr(VI) adsorption under strongly acidic conditions [13,25] which are not representative of typical groundwater or natural water systems. Therefore, assessing adsorption performance under near-neutral pH conditions is critical for evaluating the practical applicability of iron-modified biochar in environmental remediation. Nevertheless, the efficiency of oxyanion removal strongly depends on the iron loading method, as it influences both the iron content and the nature of the iron oxide species formed on the biochar surface [24].

In this work, commercial biochar was chemically modified using ferric chloride (FeCl_3) to produce iron oxide/hydroxide-functionalized biochar through a simple and scalable procedure. The modification is expected to enhance surface functionality, increase positive surface charge, and improve the adsorption of negatively charged chromate species. The objectives of this work were to: (i) synthesize and characterize FeCl_3 -modified biochar; (ii) investigate the effects of key operational parameters, including contact time, pH, initial Cr(VI) concentration, and adsorbent dosage; and (iii) elucidate and compare the adsorption mechanisms of Cr(VI) on raw and modified biochar. In this study, we address these research gaps by reporting results with iron-modified biochar using a simple FeCl_3 alkaline precipitation method, conducting comprehensive material characterization, and reporting on batch adsorption experiments to compare the Cr(VI) removal performance of modified and unmodified biochar under environmentally relevant conditions.

2. Materials and Methods

2.1. Iron-Modified Biochar Preparation

Commercial biochar was obtained from Wakefield Biochar (Valdosta, GA, USA). First, 50 g of biochar was washed with deionized water until the water became clear. Then, the biochar was placed in an oven for 24 h at 70 ± 1 °C to dry. After drying, the biochar was sieved to obtain the 300–500 µm fraction. The biochar was kept in a desiccator to avoid water absorption. The product represented the unmodified biochar (UB) used in the experiments. For the iron modification, 20 g of UB was stirred with 200 mL of 0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (>97%) using a magnetic stirrer by keeping the solid-to-liquid ratio 1:10. The initial mixture was stirred at 60 °C for 2 h to ensure thorough mixing. Then, sodium hydroxide (5 M) was added until the mixture reached a pH of 9. After reaching pH 9, the solution was kept stirring for another 2 h at 60 °C. After 2 h, the biochar was washed with deionized water to wash out any residual ferric chloride solution. Then, the biochar was dried in an oven at 70 ± 1 °C for 12 h to obtain the iron-modified biochar (IMB).

2.2. Biochar Characterization

The following properties of biochar were quantified to interpret and assess the effect of biochar modification on hexavalent chromium sorption capacity: specific surface area, morphology, elemental composition, elemental distribution, and iron percentages. The morphology and elemental chemical composition of unmodified and iron-modified biochar were analyzed using an S-3400N II scanning electron microscope (SEM) equipped with an Energy-Dispersive X-ray spectrometer (EDX) (Hitachi, Tokyo, Japan). The X-ray diffraction of ground unmodified biochar and iron-modified biochar was measured using an X-ray diffractometer (MiniFlex II, PANalytical Empyrean X-Ray Diffractometer, Malvern, Worcestershire, UK) with Cu K α radiation (wavelength = 1.540 Å). The surface functional groups of unmodified and modified biochar were analyzed using a Thermo Fisher (Waltham, MA, USA) Nicolet iS10 Fourier Transform Infrared Spectrometer (FTIR) equipped with OMNIC software version 8.1.11. Spectra were recorded over the wavenumber range of 4000–400 cm^{-1} . Nitrogen adsorption/desorption isotherms were used to determine the Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore-size distribution of unmodified and iron-modified biochar using an ASAP 2050 micropore analyzer (Micromeritics, Norcross, GA, USA). The nitrogen adsorption was carried out at 77 K. The zeta potential of the sorbents was measured using a Malvern Zetasizer (Malvern Panalytical, Worcestershire, UK). Suspensions of UB and IMB were initially prepared at a concentration of 0.1 mg mL^{-1} . To evaluate the effect of pH on surface charge, a series of solutions with pH values of 2, 4, 4.5, 5, 5.5, 6, 8, and 10 were prepared using 0.01 M nitric acid (HNO_3) and 0.01 M sodium hydroxide (NaOH) to adjust the pH. Each pH condition was tested in replicate using the corresponding biochar suspension.

2.3. Chromium (VI) Sorption Experiments

Two 100 mg L^{-1} and 1000 mg L^{-1} dichromate stock solutions were prepared, dissolving analytical grade (99.5%) potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water. The pH was adjusted in all working solutions and mixtures using 0.1 M HNO_3 or 0.1 M NaOH solution.

Kinetic experiments were carried out at a constant pH of 6 with 100 mg L^{-1} chromium (VI) and a sorbent dose of 2 g L^{-1} at room temperature. The pH was adjusted to 6 whenever the pH drifted higher during the experiment. For each time interval (0.5, 1, 2, 4, 6, 12, 24 contact hours), a separate experimental setup was maintained to keep the same matrix and the chromate concentration. The effect of pH was studied by varying the pH of the solutions in the range of 2, 4, 6, 8, and 10 while keeping the chromium concentration at 5

mg L⁻¹ and biochar dose at 2 g L⁻¹. The effect of adsorbent dosage was studied in the range of 2 g L⁻¹ to 8 g L⁻¹, while keeping the chromium concentration at 5 mg L⁻¹ and pH 6.

Equilibrium isotherm experiments were conducted using 100 mL beakers with a sample volume of 60 mL. Concentrations of 5, 10, 25, 50, 100, 250, 300, 400, 500, and 600 mg L⁻¹ of Cr(VI) concentrations were used. All the samples were stirred using a magnetic stirrer at 200 rpm.

In all experiments, q_e , the amount of chromate adsorbed at equilibrium time, was calculated using Equation (1),

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

where C_o is the initial concentration of the Cr(VI) adsorbate (mg L⁻¹), C_e is the equilibrium concentration of adsorbate (mg L⁻¹), m is the mass of the adsorbent (g), and V is the volume of solution (L).

2.4. Kinetic Study

The pseudo-second-order kinetic model and its linearized formula are shown in Equations (2) and (3). The pseudo-second-order equation is derived from the assumption that sorbent capacity and sorbate dosage determine a substance's sorption rate [31].

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is a pseudo-second-order rate constant (g mg⁻¹ h⁻¹), and q_e and q_t represent the amount adsorbed at equilibrium time and time (t) in (mg g⁻¹).

2.5. Isotherm Study

Adsorption isotherms (Langmuir and Freundlich) were applied to the analysis of adsorption characteristics. Equations (4) and (5) show the Langmuir isotherm and the linearized Langmuir isotherm, respectively [32]. The expression for the Langmuir separation factor R_L , is given by Equation (6).

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (5)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

where q_{max} is the maximum adsorption capacity (mg g⁻¹) and K_L is the Langmuir isotherm constant (L mg⁻¹).

The Freundlich isotherm and its linearized form are shown in Equations (7) and (8) [33].

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

K_f is the Freundlich constant, reflecting the adsorption capacity of the adsorbent, and $1/n$ is the adsorption intensity.

2.6. Analytical Procedures

For chromium determinations, all the experiments were conducted in duplicate by collecting two samples at a time. Results were obtained by calculating mean values. All samples were preserved using trace metal-grade nitric acid (100 μ L acid in 10 mL of sample). The samples were then analyzed using ICP-OES (Perkin Elmer Avio 550 Max ICP-OES, PerkinElmer, Shelton, CT, USA) for total chromium concentration. It should be noted that ICP-OES measures total chromium (Cr(VI) + Cr(III)) and does not distinguish between chromium species. Therefore, the concentrations reported in this study represent total chromium rather than Cr(VI) alone.

Iron analysis was performed to determine the iron percentage in UB and IMB. A quantity of 0.1 g of both UB and IMB was placed in a 50 mL beaker. Then, 2 mL of 0.1 M HNO₃ was added to the beaker. Both samples were shaken well and allowed to stand for 10 min. Then, 0.2 mL of the solution was removed and added to the reagent vial. The sample was diluted by a factor of 50 to 10 mL total volume. Then, the contents of a FerroVer (HACH, Loveland, CO, USA) iron reagent powder pillow were added to the vial, making a final volume of 10 mL. If iron was present, the solution would turn orange. Another vial was filled with deionized water as a blank solution. After that, the solutions in the vials were analyzed with a 6000 N spectrophotometer (Hach, Loveland, CO, USA) under the FerroVer iron reagent program to obtain the iron concentration.

3. Results and Discussion

3.1. Characterization of Modified Biochar

3.1.1. Mineralogy of UB/IMB and SEM/EDX Results

The SEM analysis of UB and IMB showed that both biochars exhibited roughly irregularly shaped microscale aggregates (Figure 1). Part of the pore structure presented in IMB was blocked by iron particles after modification. The coverage of iron on the modified biochar surface was further confirmed by EDX analysis, and the surface iron content of IMB was much higher than that of UB (Table 1). Biochar is a carbon-rich material, and, as expected, carbon is the main component of biochar.

Table 1. Elemental composition of raw and modified adsorbents.

Biochar Type	C	O	Al	Si	K	Fe	Ca	Mg
UB	91.9	6.0	0.1	0.9	0.4	0.2	0.9	0.2
IMB	88.7	5.3	0.1	0.8	0.5	3.3	0.7	0.1

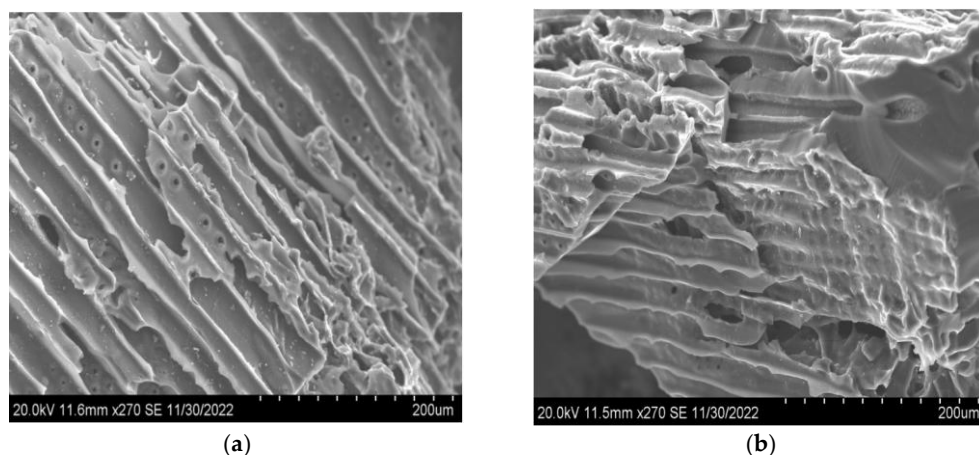


Figure 1. SEM images of (a) UB; (b) IMB.

3.1.2. FTIR Spectroscopy

FTIR spectroscopic analysis was conducted in the range of 400–4000 cm^{-1} to identify the functional groups present on the biochar surface (Figure 2). Changes in the FTIR spectra before and after modification were subsequently used to infer the possible involvement of these functional groups in the hexavalent chromium adsorption process. The peaks at 2918 and 2851 cm^{-1} can be attributed to alkane C-H stretching [34]. The peaks at 3500–3770 cm^{-1} indicate hydroxy (O-H) groups [35]. The band at 1601 cm^{-1} is mainly attributed to aromatic C=C or carbonyl (C=O) groups, while the band at 1370 cm^{-1} is assigned to O=C- [29,36,37]. A new band appeared in IMB at 564 cm^{-1} , which is attributed to Fe-O [38].

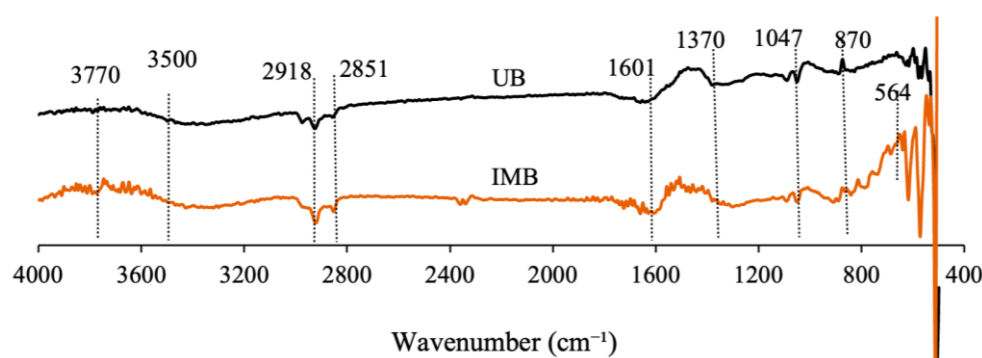


Figure 2. FTIR spectra for UB and IMB.

3.1.3. X-Ray Diffraction

Figure 3 shows the XRD spectra for UB and IMB. An intense, broad peak at $2\theta = 25^\circ$ confirms an amorphous carbon structure with poor crystallinity in the biochar [39]. These types of biochar, known as turbostratic chars, have poor crystal graphite structure. A sharp and small peak at $2\theta = 29^\circ$ is consistent with the presence of SiO_2 . The spectrum of the iron-modified biochar shows a similar XRD pattern but without the peak at $2\theta = 29^\circ$. A peak at $2\theta = 68^\circ$ in the iron-modified biochar may be associated with iron-containing phases introduced during modification [39]. The X-ray diffraction spectra of UB and IMB indicate that the biochar matrix is predominantly amorphous, as evidenced by the broad diffraction features. However, the characteristic magnetite peak near $2\theta = 35.5^\circ$ was not observed, suggesting that the precipitated iron species may have existed in poorly crystalline or amorphous forms.

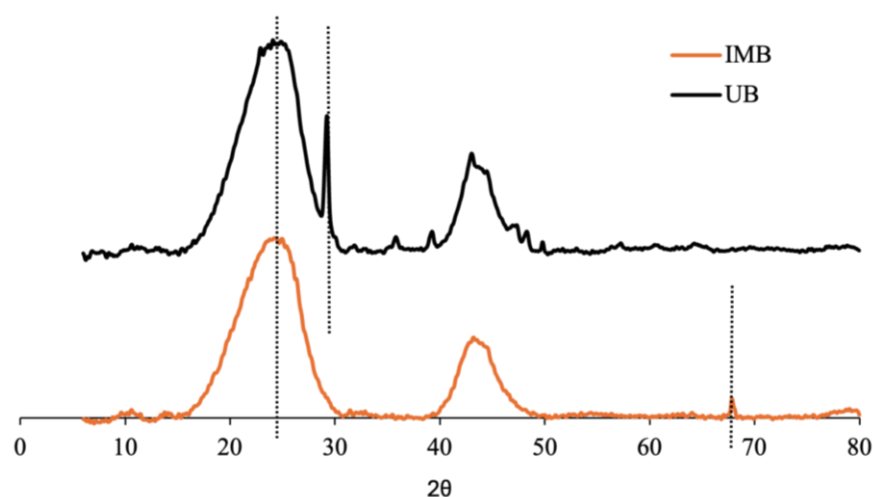


Figure 3. XRD spectra for UB and IMB.

3.1.4. FerroVer Iron Reagent

As summarized in Table 2, UB has 0.009% iron content, and IMB, which was modified with iron, has 0.108% iron content in 0.1 g of both UB and IMB, consistent with the fact that IMB has ten times more iron content compared with UB.

Table 2. Iron content (*w/w* %) in UB and IMB.

	UB	IMB
Iron content (<i>w/w</i> %)	0.009	0.108

3.1.5. BET Isotherms

The adsorption–desorption isotherms for N₂ gas on UB and IMB are shown in Figure 4. According to IUPAC classifications, these isotherms belong to type IV isotherms with type H4 hysteresis loops. The pore structures leading to H4 type hysteresis loops include narrow slit-like pores, particles with internal voids of irregular shape and broad size distribution, and hollow spheres with walls composed of ordered mesoporous carbon. Compared to UB, IMB has a higher average pore width and a smaller BET surface area (Table 3). The increase in average pore width accompanied by a decrease in BET surface area suggests that iron coating occupies or blocks micropores within the biochar structure. Because micropores contribute significantly to surface area, their blockage reduces the measured BET surface area while shifting the pore size distribution toward larger mesopores. Pore width analysis shows that most of the surface area of both UB and IMB is contributed by mesopores, which have a pore diameter between 2 and 50 nm. Mesoporous structures are advantageous for aqueous adsorption processes because they facilitate diffusion of contaminants into the internal structure of the adsorbent [40,41]. Hence, the reduction in specific surface area observed for IMB relative to UB reflects modification of the pore network rather than deterioration of the adsorption potential. In fact, the incorporation of iron hydroxide introduces chemically active Fe-OH sites that can enhance adsorption through surface complexation mechanisms. The large quantity of nitrogen sorbed at very low relative pressure is indicative of micropores, which have average pore size less than 2 nm. These micropores contribute significantly to the BET surface area of UB. However, some of these micropores may become partially occupied by iron hydroxide particles after modification, explaining the decrease in surface area observed for IMB.

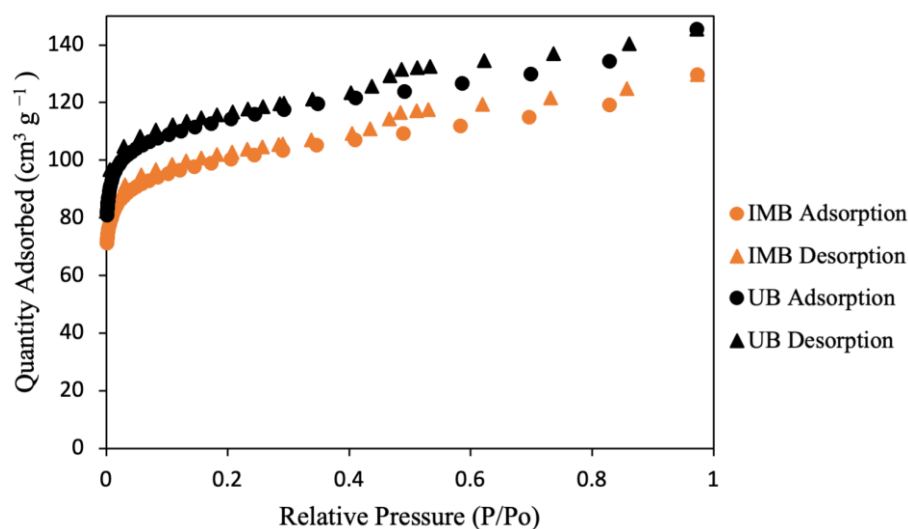


Figure 4. Nitrogen gas adsorption/desorption isotherms.

Table 3. Summary of specific surface area and porosity parameters of the adsorbents.

Biochar Type	Average Pore Width (Å)	Pore Volume (cm ³ g ⁻¹)	BET Surface Area (m ² g ⁻¹)	Langmuir Surface Area (m ² g ⁻¹)
UB	26.267	0.2356	359.072	452.651
IMB	26.548	0.2102	316.785	394.785

3.2. Chromate Sorption Characteristics

3.2.1. Effect of Time

Figure 5A shows the removal efficiency of chromium ($C_0 = 100 \text{ mg L}^{-1}$; adsorbent dose = 2 g L^{-1}) as a function of contact time for UB and IMB. For both adsorbents, removal efficiency increased with time, although IMB exhibited a much faster uptake compared to UB. A rapid increase in chromate removal was observed within the first two hours for IMB, followed by a gradual approach to equilibrium, whereas UB showed a slower and more continuous increase in removal over time. This difference is likely due to the presence of iron oxide coating on IMB, which provides readily accessible Fe-OH active sites on the external surface. Furthermore, the higher positive charge of IMB may lead to enhanced electrostatic attraction toward chromium species and promote surface interactions, including sorption and possible reduction. In contrast, UB contains more internal adsorption sites, requiring chromate ions to diffuse into the pore structure, which slows the overall adsorption process. The removal efficiency for IMB became nearly constant after approximately 8 h, indicating that equilibrium was reached. UB exhibited slower adsorption kinetics, requiring extended contact time beyond 2 h and approaching equilibrium only after approximately 50 h. At the selected equilibrium time, UB achieved around 60% removal, whereas IMB reached approximately 80%, indicating that a substantial fraction of adsorption occurred within this period. Notably, rapid adsorption was observed with IMB, with substantial removal achieved within 0.5 h, whereas up to 8 h was required by UB to attain a comparable level of chromate uptake. These results highlight the faster adsorption kinetics and higher efficiency on IMB relative to UB. The observed fast stage reflects the large number of available reduction/adsorption sites at the initial stage, whereas the slow stage is probably resulting from sorption/reduction on less easily accessible sites. However, the relative contributions of Cr(VI) adsorption and reduction to Cr(III) could not be distinguished in the present study as chromium concentrations were determined by ICP-OES, which measures total chromium. Therefore, the observed decrease in chromium concentration may reflect a combination of adsorption and reduction processes.

3.2.2. Effect of pH

As can be seen in Figure 5B, both UB and IMB showed higher removal at pH 4 and pH 6 ($C_0 = 5 \text{ mg L}^{-1}$; adsorbent dose = 2 g L^{-1}). The ionic forms of Cr and the pH_{zpc} of the adsorbent are important factors affecting hexavalent chromium removal. Cr(VI) is mainly present in the form of HCrO_4^- at pH values between 2 and 5, and this negatively charged ion can be easily adsorbed with lower free energy on positively charged surfaces. At pH values between 5 and 8, both HCrO_4^- and CrO_4^{2-} exist, and above pH 8, CrO_4^{2-} dominates [28]. The zeta potential of the modified biochar has significantly shifted towards higher pH in comparison to raw biochar (Figure 6). This suggests that the positive charge increased at the surface of the biochar after iron modification, indicating higher potential of removal efficiency for anionic hexavalent chromium through electrostatic interactions. The pH_{zpc} values of UB and IMB were approximately 3 and 5.5, respectively. These pH_{zpc} values are consistent with previously reported values [28,42]. When the pH is lower compared to the pH_{zpc} of the solid, functional groups such as hydroxyl groups will become

positively charged because of protonation. This positive charge helps to attract the oxyanions to the surface [43]. Chromate sorption decreases at pH values above 6; this can be attributed to competition with OH^- [44]. At pH 2, the reduced removal observed for both adsorbents may be attributed to partial dissolution of the Fe coating on the biochar surface under highly acidic conditions, as suggested in previous studies on Fe-based sorbents [45]. At $\text{pH} < 2$, undissociated H_2CrO_4 predominates. Hence, even though the adsorbent surface is positively charged, H_2CrO_4 is not electrostatically attracted to the adsorbent surface, which results in a decrease in adsorption [46]. At pH 4–6, although the UB surface is slightly negatively charged ($\text{pH}_{\text{zpc}} = 3$), oxygen-containing functional groups (like $-\text{OH}$ or $-\text{COOH}$) are deprotonated and become excellent electron donors, enhancing the reduction of Cr(VI) to Cr(III), and then adsorbing the reduced Cr(III) [47,48]. At pH 4–6, iron-modified biochar is near its zero-charge point or is slightly positively charged, which provides favorable electrostatic attraction for anionic Cr(VI). Simultaneously, iron oxides on the surface act as active sites for reducing Cr(VI) and complexing/exchanging reduced Cr(III) [46]. A pH of 6 was used for kinetic and isotherm experiments, as it is more relevant to conditions at contaminated sites.

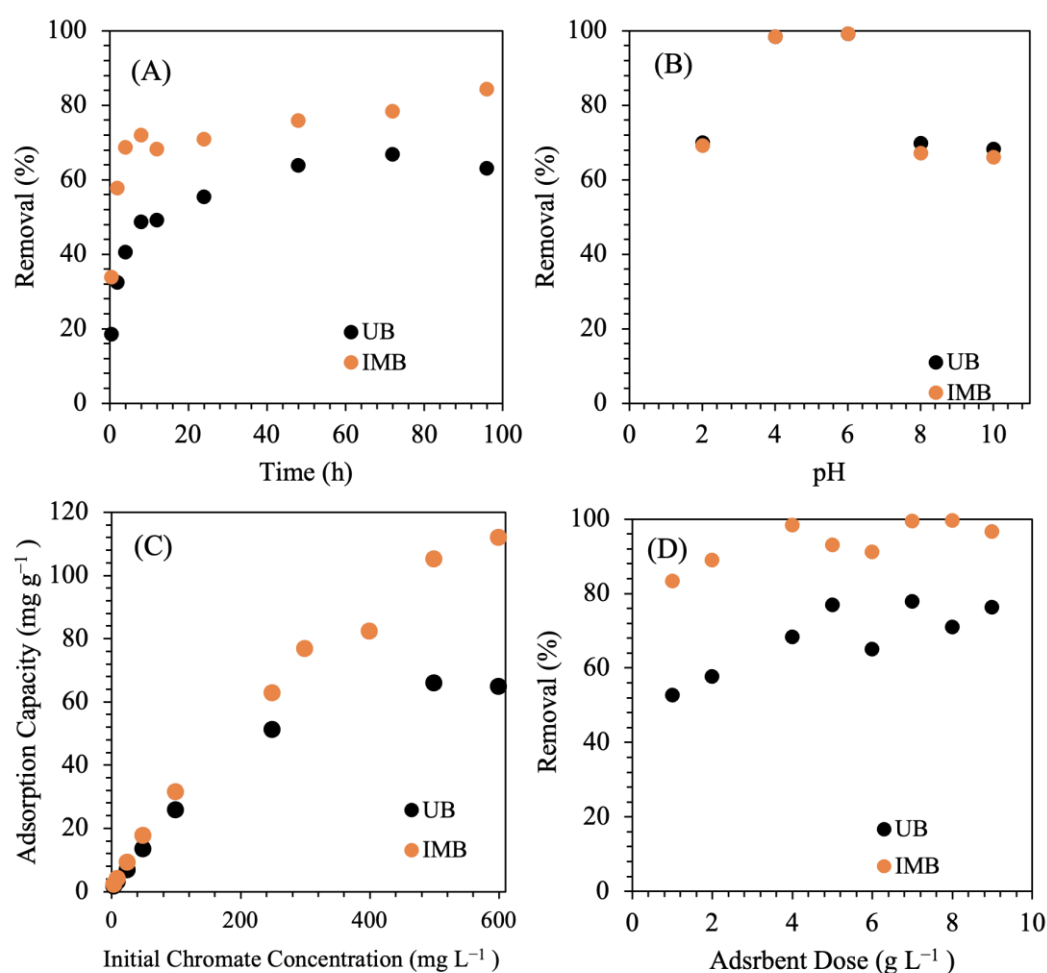


Figure 5. Hexavalent chromium sorption characteristics of UB and IMB. (A) Time vs. Removal ($C_0 = 100 \text{ mg L}^{-1}$, adsorbent dose = 2 g L^{-1} , $\text{pH} = 6$). (B) pH vs. Removal ($C_0 = 5 \text{ mg L}^{-1}$; adsorbent dose = 2 g L^{-1}). (C) Initial hexavalent chromium concentration vs. adsorption capacity (adsorbent dose = 2 g L^{-1} , $\text{pH} = 6$). (D) Adsorbent dose vs. removal ($C_0 = 5 \text{ mg L}^{-1}$; adsorbent dose = 2 g L^{-1}).

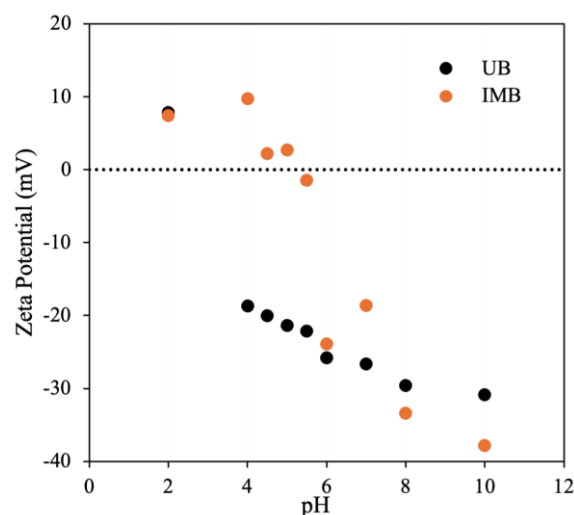


Figure 6. Zeta potentials of UB and IMB.

3.2.3. Effect of Initial Chromate Concentration

The adsorption capacity of UB and IMB increased with increasing initial Cr(VI) concentration (Figure 5C). This trend occurs because higher initial concentrations provide a stronger driving force for mass transfer between the solution and the adsorbent surface. The driving force increase as concentration rises results in more collisions between the Cr(VI) molecules and the active sites on the surface of the materials [49]. At an adsorbent dosage of 2 g L^{-1} and equilibrium contact time of 24 h, the q_e of UB increased from 1.55 to 64.77 mg g^{-1} as the initial concentration increased from 5 to 600 mg L^{-1} , approaching a plateau that indicates gradual saturation of available adsorption sites. In contrast, IMB showed significantly higher adsorption capacities, increasing from 2.04 to 111.9 mg g^{-1} , and did not reach a clear adsorption plateau within the range studied. The higher capacity of IMB is attributed to additional active sites introduced by iron hydroxide coating, which enhances chromate adsorption through a surface complexation mechanism.

3.2.4. Effect of Adsorbent Dosage

The effect of adsorbent dosage on Cr(VI) removal was investigated for UB and IMB (Figure 5D). The removal efficiency increased with increasing dosage due to the greater availability of adsorption sites. UB fractional sorption increased from 52.7% at 1 g L^{-1} to 78% at 5 g L^{-1} , reflecting the increased availability of active adsorption sites at higher dosages. In contrast, the fractional Cr(VI) removal using IMB was 83.3% removal at 1 g L^{-1} , with only slight improvement at higher dosages, indicating an abundance of adsorption sites, even at low dosage. Therefore, the optimal adsorbent dosage was established as 5 g L^{-1} for UB and 1 g L^{-1} for IMB. The higher removal efficiency using modified biochar at a lower dosage demonstrates the effectiveness of iron modification in enhancing adsorption performance.

3.2.5. Adsorption Kinetics

Kinetic studies of adsorption are essential for elucidating the rate of solute removal, the time required to attain equilibrium, and the underlying mechanisms governing the process, such as pore diffusion or surface-controlled reactions [50]. Identification of the rate-limiting step is particularly important, as it enables targeted optimization of adsorption performance through modification of the relevant physical or chemical controlling processes. In this study, pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were applied using nonlinear regression to evaluate the adsorption behavior of

Cr(VI) onto UB and IMB. The nonlinear model fits are presented in Figure 7, and the corresponding kinetic parameters are summarized in Table 4.

The nonlinear PFO model exhibited relatively poor agreement with the experimental data yielding lower coefficients of determination ($R^2 = 0.8347$ for UB and 0.8549 for IMB) and higher error functions (RMSE and χ^2), compared to PSO. In addition, the calculated equilibrium adsorption capacities deviated considerably from the experimentally determined values.

In contrast, the PSO model using nonlinear regression provided the best overall fit for both sorbents, yielding the highest R^2 values (0.9450 for UB and 0.9362 for IMB) along with the lowest RMSE and χ^2 values. Furthermore, the equilibrium adsorption capacities derived from the PSO model closely matched the experimental values. The experimentally determined q_e values for UB and IMB (32 and 39 mg g^{-1} , respectively) were in good agreement with the PSO-predicted values (31.89 ± 1.12 and 38.87 ± 0.90 mg g^{-1}), indicating that the PSO model adequately describes the adsorption kinetics of both sorbents.

The inadequate performance of the PFO model suggests that simple physisorption governed by weak van der Waals interactions is not the dominant mechanism. Instead, the superior fit of the PSO model suggests that adsorption is primarily controlled by surface-mediated processes such as chemisorption and surface complexation [51]. The PSO model assumes that the adsorption rate is proportional to the square of the number of unoccupied sites and is typically associated with chemisorption involving electron sharing or transfer between adsorbent and adsorbate [31]. In this context, Cr(VI) ions likely interact with oxygen-containing functional groups (e.g., hydroxyl and carboxyl groups) present on the biochar surface [52]. However, the good agreement with the PSO model alone does not provide definitive evidence of a chemisorption mechanism, as kinetic models are primarily empirical descriptions of adsorption behavior.

The Cr(VI) removal by biochar has been reported to involve several possible mechanisms including: (i) electrostatic attraction of negatively charged chromate species (e.g., HCrO_4^-) to protonated surface sites (e.g., $-\text{OH}_2^+$, $-\text{COOH}_2^+$), (ii) reduction of Cr(VI) to Cr(III) facilitated by electron-donating functional groups, and (iii) subsequent immobilization of Cr(III) through surface complexation or ion exchange [14,53]. Among these steps, chemisorption is likely the rate-limiting step due to the necessary bond formation and electron transfer, which typically require higher activation energy compared to physical adsorption processes [54,55].

Iron modification substantially increased the PSO rate constant, from 0.015 ± 0.003 $\text{g mg}^{-1} \text{h}^{-1}$ for UB to 0.038 ± 0.007 $\text{g mg}^{-1} \text{h}^{-1}$ for IMB, and improved the adsorption capacity. The enhanced kinetic performance of IMB may be attributed to the increased availability of Fe-OH surface groups, higher positive surface charge, and additional reactive sites introduced by iron modification, which may promote surface interactions with chromium species. These results confirm that iron modification improved both the sorption rate and overall chromium removal performance of the biochar. Although regeneration experiments were not conducted in this study, the reusability and long-term stability of the adsorbent are important factors that warrant further investigation.

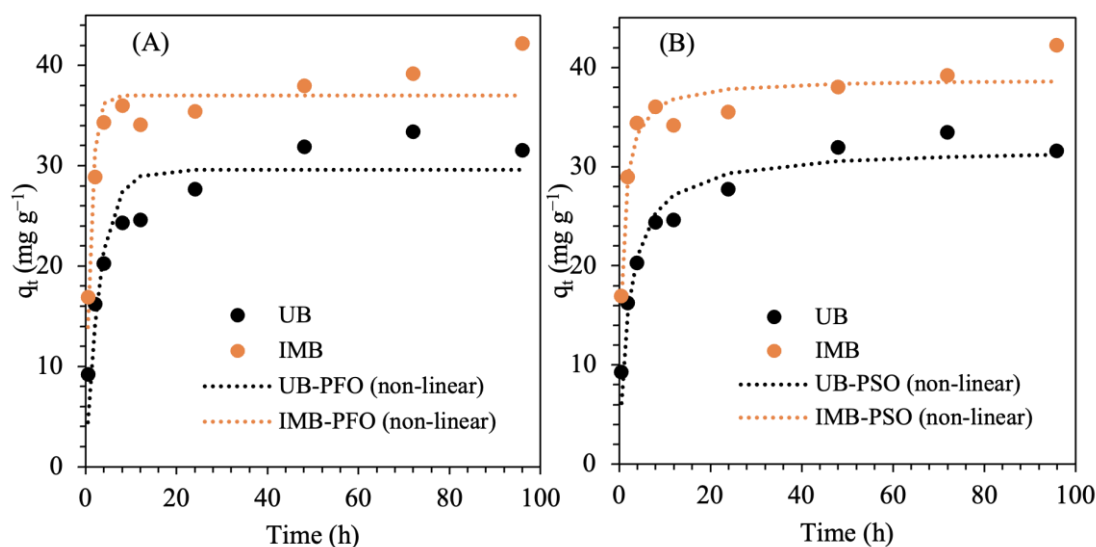


Figure 7. Kinetic analysis of Cr(VI) adsorption onto UB and IMB biochar at an initial Cr(VI) concentration of 100 mg L^{-1} , sorbent dose of 2 g L^{-1} , and pH 6. (A) Nonlinear pseudo-first-order and (B) nonlinear pseudo-second-order model fit to q_t vs. time (h) data.

Table 4. Parameters for the pseudo-first- and -second-order models.

Pseudo-First-Order (Non-Linear Fit)					
	$K_1 (\text{h}^{-1})$	$q_e (\text{mg g}^{-1})$	R^2	RMSE	χ^2
UB	0.324 ± 0.080	29.59 ± 1.56	0.8347	3.07	7.53
IMB	0.945 ± 0.197	37.03 ± 1.16	0.8549	2.12	2.13
Pseudo-Second-Order (Non-Linear Fit)					
	$K_2 (\text{g mg}^{-1} \text{ h}^{-1})$	$q_e (\text{mg g}^{-1})$	R^2	RMSE	χ^2
UB	0.015 ± 0.003	31.89 ± 1.12	0.9450	1.77	2.19
IMB	0.038 ± 0.007	38.87 ± 0.90	0.9362	1.75	0.74

3.2.6. Adsorption Isotherms

Fitting experimental equilibrium data to appropriate theoretical models is essential for quantifying adsorption capacity and optimizing adsorbent dosage for practical applications [56]. Isotherm modeling also provides a robust framework for comparing unmodified and modified adsorbents by elucidating changes in adsorption mechanisms, identifying shifts in surface behavior (e.g., transition between isotherm types), and verifying enhancements in maximum adsorption capacity. Furthermore, isotherm parameters enable systematic evaluation of adsorbent performance, facilitating process optimization and cost reduction in large-scale applications [57].

In this study, the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The Langmuir model describes monolayer adsorption on a homogeneous surface with a finite number of identical active sites, whereas the Freundlich model accounts for adsorption on heterogeneous surfaces with non-uniform energy distributions [58].

The fitted isotherms (non-linear regression) and corresponding parameters are presented in Figure 8 and Table 5. Overall, the results demonstrate a significant enhancement in Cr(VI) adsorption following biochar modification. For UB, the Langmuir model yielded the best statistical fit ($R^2 = 0.9955$; $\chi^2 = 0.846$), consistent with adsorption that predominantly occurs as a monolayer on relatively homogeneous sites. This behavior is consistent with the nature of chromate oxyanions, which typically do not form surface precipitates under the studied conditions and therefore do not promote multilayer adsorption. The dimensionless separation factor (R_L) ranged from 0.14 to 0.95 for UB and 0.22 to 0.97 for

iron-modified biochar (IMB) over the investigated concentration range (5–600 mg L⁻¹), confirming favorable adsorption behavior ($0 < R_L < 1$) [59]. These values indicate that the adsorption process is thermodynamically favorable and practically feasible across the studied concentration range, supporting the potential applicability of both materials for industrial water treatment.

In contrast, IMB exhibited the best fit with the Freundlich model ($R^2 = 0.9887$; $\chi^2 = 5.02$), suggesting adsorption on a heterogeneous surface with possible multilayer interactions. Furthermore, the results are consistent with changes in surface heterogeneity and distribution of adsorption sites following iron modification. The maximum adsorption capacity (q_{max}) increased substantially from 82 mg g⁻¹ for UB to 158 mg g⁻¹ for IMB, indicating that surface modification significantly enhanced the number and/or accessibility of active sites.

The improved performance of IMB is primarily attributed to the incorporation of iron oxide/hydroxide functional groups, which introduce additional reactive sites and enhance electrostatic attraction toward anionic chromate species (e.g., HCrO₄⁻ at pH 6) [25]. In addition to electrostatic interactions, these iron-containing functional groups may facilitate surface complexation and potentially promote redox transformations, which have been reported in previous studies, including the reduction of Cr(VI) to Cr(III), followed by precipitation or immobilization on the adsorbent surface. However, because chromium concentrations were determined using ICP-OES, which measures total chromium and does not distinguish between Cr(VI) and Cr(III), the occurrence of Cr(VI) reduction could not be directly confirmed in the present study. Therefore, these mechanisms should be regarded as possible pathways rather than definitive mechanisms responsible for the enhanced performance of IMB.

The Freundlich constant ($1/n$) values for both adsorbents were within the range of 0–1 (UB = 0.48; IMB = 0.56), indicating favorable adsorption [60]. Moreover, the increase in K_f from 3.65 (UB) to 4.24 (IMB) further confirms improved adsorption affinity on heterogeneous surfaces. This behavior reflects the contribution of multiple concurrent mechanisms, including electrostatic attraction, ligand exchange, surface complexation, redox reactions, and diffusion-controlled processes. At pH 6, where HCrO₄⁻ is the dominant chromium species, these mechanisms are particularly effective due to the enhanced interaction between negatively charged chromate ions and positively charged iron-modified surfaces, as well as the redox activity of iron species.

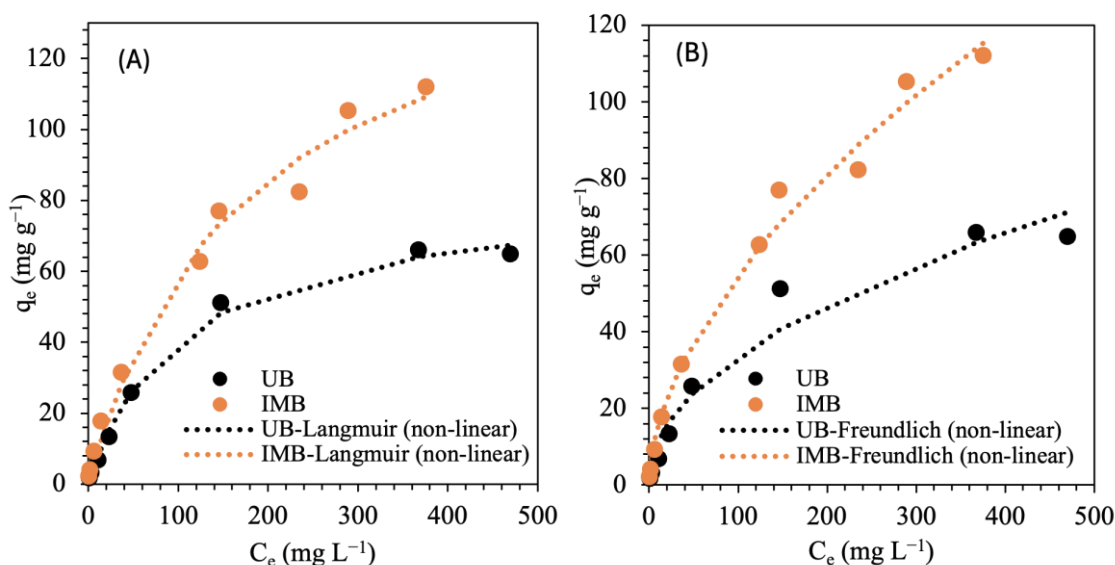


Figure 8. Cr(VI) sorption onto UB and IMB at pH 6 and adsorbent dosage 2 g L⁻¹ in the initial Cr(VI) concentration range 5–600 mg L⁻¹; nonlinear regression fit into (A) Langmuir model, and (B) Freun-

dlich model. C_e is the chromium concentration in the solution at equilibrium, and q_e is the adsorption capacity of the adsorbents at equilibrium.

Table 5. Parameters for isotherm models.

Adsorbent	Langmuir (Non-Linear Fit)				
	q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R ²	RMSE	χ^2
UB	82.22	0.0096	0.9955	1.72	0.846
IMB	158.33	0.0059	0.9871	4.59	8.875
	Freundlich (Non-Linear Fit)				
	1/n	K_F	R ²	RMSE	χ^2
UB	0.48	3.65	0.9575	5.31	11.01
IMB	0.56	4.24	0.9887	4.29	5.02

The maximum Langmuir adsorption capacity of the modified biochar (158.33 mg g⁻¹) compares favorably with previously reported Cr(VI) adsorbents under comparable experimental conditions. For similar initial concentration ranges and solution pH, conventional unmodified biochars typically exhibit Langmuir adsorption capacities in the range of 20–80 mg g⁻¹ [18,29], whereas activated carbons generally fall within 50–200 mg g⁻¹ depending on the extent of surface activation and functionalization [61]. However, direct comparison of Langmuir-derived adsorption capacities across different studies should be approached with caution, as these values are strongly influenced by the selected concentration range, experimental conditions, and model fitting approach [62]. It should be noted that the maximum experimental adsorption capacity observed for IMB was approximately 112 mg g⁻¹, which was lower than the Langmuir-predicted q_{max} value. This difference reflects the fact that complete saturation of the adsorbent was not attained within the investigated concentration range.

For instance, a previous study conducted with a concentration up to 450 mg L⁻¹ reported a maximum adsorption capacity of 63.1 mg g⁻¹ for distiller grain biochar, which increased to 157.9 mg g⁻¹ following phosphogypsum modification, highlighting the significant role of surface engineering in enhancing adsorption performance. In general, modified biochars incorporating oxygen-containing or metal-based functional groups typically exhibit capacities in the range of 100–200 mg g⁻¹ [18], consistent with the value obtained in the present study.

The enhanced performance observed here positions the modified biochar within the upper range of high-efficiency carbonaceous adsorbents, underscoring the effectiveness of the applied surface modification strategy in increasing the density of reactive sites and promoting surface heterogeneity. Notably, the relatively high adsorption capacity of the unmodified biochar compared to values reported in the literature may be attributed to differences in precursor material, particle size distribution, and pyrolysis conditions, all of which significantly influence surface area, pore structure, and functional group availability.

4. Conclusions

A significant enhancement in the Cr(VI) removal performance of commercial biochar was achieved through iron modification, which altered its physicochemical properties and introduced Fe-OH reactive sites. Quantitative characterization confirmed successful modification, with EDX showing an increase in iron elemental composition from 0.2% to 3.3%, supported by FerroVer measurements, which also showed iron content increase of w/w % (0.009 to 0.108). XRD analysis and FTIR results indicated structural transformation through the introduction of iron oxide into biochar surface. Despite a reduction in BET surface area (from 359 to 317 m² g⁻¹), the modified biochar exhibited superior adsorption

performance, indicating that chemical functionality rather than surface area governs Cr(VI) removal.

Iron modification altered the adsorption behavior, resulting in faster adsorption kinetics and a transition from homogenous adsorption to heterogeneous surface adsorption. Improved Cr(VI) removal is attributed to the combined effects of enhanced electrostatic interactions, surface complexation, and possible redox transformation governed by iron-mediated functional groups available in biochar. These findings emphasize that targeted surface engineering can overcome limitations associated with conventional biochar, even when surface area decreases.

Although adsorption isotherm modeling indicated enhanced adsorption capacity, complete sorbent saturation was not achieved within the investigated concentration range, and the estimated maximum adsorption capacity should therefore be regarded as model-derived. Future work should focus on evaluating the performance, regeneration, and long-term stability of iron-modified biochar under environmentally relevant conditions, including lower Cr(VI) concentrations, and competing ions in continuous flow systems representative of groundwater remediation applications.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

UB	Unmodified biochar
IMB	Iron-modified biochar
XRD	X-ray diffraction
FTIR	Fourier-transform infrared
SEM	Scanning electron microscopy

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