

Article

Enhanced Removal of Hexavalent Chromium from Water by Nitrogen-Doped Wheat Straw Biochar Loaded with Nanoscale Zero-Valent Iron: Adsorption Characteristics and Mechanisms

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Abstract: The widespread industrial use of chromium has exacerbated water contamination issues globally. In this study, a nitrogen-doped wheat straw biochar loaded with nanoscale zero-valent iron composite (nZVI/N-KBC) was synthesized via a liquid-phase reduction method, and its adsorption properties for hexavalent chromium (Cr(VI)) in aqueous solutions were systematically investigated. The material was characterized using SEM, XRD, Raman spectroscopy, FTIR, and XPS. Experimental results demonstrated that under optimal conditions (pH 2, 0.05 g adsorbent dosage, and 50 mg/L initial Cr(VI) concentration), the adsorption capacity reached 41.29 mg/g. Isothermal adsorption analysis revealed that the process followed the Langmuir model, indicating monolayer adsorption with a maximum capacity of 100.9 mg/g. Kinetic studies show that the adsorption conforms to the pseudo-second-order kinetic model, and thermodynamic and XPS analyses jointly prove that chemical adsorption is dominant. Thermodynamic analyses confirmed the endothermic and entropy-driven nature of adsorption. Mechanistic studies via XPS and FTIR revealed a dual mechanism: (1) partial adsorption of Cr(VI) onto the nZVI/N-KBC surface, and (2) predominant reduction in Cr(VI) to Cr(III) mediated by Fe⁰ and Fe²⁺. This study highlights the synergistic role of nitrogen doping and nZVI loading in enhancing Cr(VI) removal, offering a promising approach for remediating chromium-contaminated water.

Keywords: hexavalent chromium; biochar; nanoscale zero-valent iron (nZVI); adsorption; reduction



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1. Introduction

Heavy metal contamination in wastewater remains a critical global environmental challenge, with chromium emerging as a particularly problematic contaminant due to its extensive industrial applications and associated health risks [1]. Chromium is widely used in various industrial production processes such as papermaking, dyeing, leather manufacturing, and electroplating. The widespread use of chromium compounds in industrial processes generates substantial quantities of chromium-laden wastewater, containing both trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium species [2]. Notably, Cr(VI) poses severe threats to human health through dermal, respiratory, and gastrointestinal expo-

sure pathways, with documented associations to carcinogenic, mutagenic, and teratogenic effects [3].

Current chromium removal technologies encompass adsorption [4], electrocoagulation [5], membrane separation [6], and ion exchange [7]. Among these, adsorption stands out as the most widely adopted approach due to its cost-effectiveness, operational simplicity, and environmental compatibility [8]. The efficacy of adsorption systems primarily depends on adsorbent characteristics such as surface functionality, porosity, and regeneration potential. Biochar, a carbon-rich material derived from pyrolyzed biomass waste (e.g., agricultural residues, forestry byproducts, and organic municipal waste), has gained prominence as a sustainable adsorbent owing to its high specific surface area, porous structure, and abundant oxygen-containing functional groups [9–11].

To enhance adsorption performance, biochar modifications have been extensively explored. Nitrogen atoms have an atomic radius closer to that of carbon atoms, making it easier for them to substitute carbon in the surface structure of biochar. This substitution can also alter the distribution of π electrons on the biochar surface, generating more adsorption potential [12,13]. Cai et al. [14] confirmed that the introduction of nitrogen into biochar significantly increases the amino group content on the biochar surface. Through electrostatic interactions, it can more effectively capture anionic Cr(VI). Meanwhile, it was found that the pore structure of nitrogen-doped biochar was also affected by the nitrogen doping process. This change in the pore structure, together with the increased adsorption potential, jointly contributes to the enhanced adsorption performance of nitrogen-doped biochar for Cr(VI). Recent studies demonstrate that nitrogen-doped biochar (NBCs) exhibits superior Cr(VI) removal capabilities compared to pristine biochar, attributed to nitrogen-induced electron-rich sites and enhanced π - π interactions with chromium species [15–17]. Innovative composite materials such as mesoporous Fe/N-OB synthesized through carbothermal reduction and NH_3 treatment [18], as well as Fe/N-doped biochar catalysts developed via biomass pyrolysis [19,20], have demonstrated exceptional chromium removal efficiencies.

The integration of nanoscale zero-valent iron (nZVI) with biochar has emerged as a promising strategy to address chromium contamination. While nZVI demonstrates high reactivity as a reducing agent for heavy metal remediation, its practical application is limited by particle aggregation and oxidative instability [21,22]. Biochar-supported nZVI composites effectively mitigate these limitations while synergistically combining adsorption and reduction mechanisms. For instance, sludge-derived biochar loaded with nZVI achieved a Cr(VI) adsorption capacity of 64.13 mg/g [23], while Fe/Ni nanoparticle-modified biochar demonstrated 99.36% Cr(VI) removal efficiency in contaminated soils [24]. Notably, Fang et al. [25] developed a chicken manure-derived biochar/nZVI composite with a remarkable removal capacity of 124.12 mg/g, highlighting the potential of iron-nitrogen co-doped biochar systems for multifunctional pollutant remediation [26].

However, a comprehensive understanding of the synergistic effects between nitrogen doping and nZVI loading on biochar for Cr(VI) removal is still lacking. Most existing studies either focus solely on nitrogen doping or nZVI loading, without fully exploring the combined impact of these two modifications. Additionally, the detailed mechanisms governing the adsorption-reduction processes under different environmental conditions, such as varying pH, initial Cr(VI) concentrations, and adsorbent dosages, remain incompletely understood. This knowledge gap limits the development of highly efficient and sustainable biochar-based materials for chromium-contaminated water treatment. Against this backdrop, the present study aims to bridge these gaps. We synthesized a nitrogen-enhanced nanocomposite (nZVI/N-KBC) by incorporating urea-derived nitrogen dopants into wheat straw biochar and loading it with nZVI. The novelty of our approach lies in the simultaneous utilization of nitrogen doping and nZVI loading, which creates a unique

material with multiple active sites and enhanced reactivity. This dual-modification strategy not only increases the adsorption capacity of the biochar but also promotes the reduction in Cr(VI) to the less toxic Cr(III), offering a more efficient and comprehensive solution for chromium removal.

We systematically investigated the Cr(VI) removal performance of nZVI/N-KBC under different pH values, initial Cr(VI) concentrations, and adsorbent dosages. Through in-depth characterization using techniques such as SEM, XRD, Raman spectroscopy, FTIR, and XPS, we were able to provide a detailed mechanistic understanding of the synergistic adsorption-reduction processes. Our findings are expected to contribute to the development of advanced biochar-based composites for the effective treatment of chromium-contaminated water, filling a crucial void in the current research landscape.

2. Materials and Methods

2.1. Chemicals and Materials

Detailed information about the chemicals has been listed in Section S1.1 of the Supplementary Materials.

2.2. Synthesis of Materials

2.2.1. Material Preparation

The wheat straw was initially washed three times with tap water and twice with deionized water, followed by air drying and subsequent drying in an oven at 80 °C. The dried wheat straw was then pulverized using a crusher and sieved through a 100-mesh sieve. The processed straw was stored in a glass bottle for subsequent use. A specific mass of the wheat straw powder was subjected to pyrolysis in a tubular furnace, with the temperature ramped at a rate of 10 °C/min to 500 °C and maintained for 2 h. Upon completion of the carbonization process and cooling to room temperature, the resulting biochar was collected, sealed in a bag, and designated as the original biochar (BC).

2.2.2. Activation and Doping Process

For activation, KOH was employed as an activating agent. Biochar, KOH, and water were combined in a mass ratio of 1:1:25 [27], dissolved in deionized water, and mechanically stirred for 30 min before allowing the mixture to stand for 24 h. The activated biochar (designated as KBC) was then filtered, thoroughly washed, and dried. Subsequently, KBC was mixed with urea in a mass ratio of 1:1 in a 500 mL beaker, dissolved in deionized water, and mechanically stirred for 30 min. The mixture was then incubated in a 60 °C water bath for 24 h. Post incubation, the material was filtered, dried, ground, and stored in a sealed bag, labeled as nitrogen-doped biochar (N-KBC).

2.2.3. nZVI Loading

In a three-neck flask, 50 mL of 0.1 mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was mixed with 2 g of N-KBC and nitrogen gas was purged through the mixture. The mixture was mechanically stirred for 2 h. Subsequently, 50 mL of an ethanol-water solution (1:1) was added, followed by the dropwise addition of 50 mL of 0.25 mol/L NaBH_4 solution. The reaction mixture was stirred for an additional 30 min until the solution turned black, indicating the formation of nanoscale zero-valent iron (nZVI). The resulting nZVI/N-KBC composite was vacuum-filtered, rinsed multiple times with distilled water and anhydrous ethanol, and then dried in a vacuum oven at 80 °C for 12 h. The final product was collected, sealed in a bag, and labeled as nZVI/N-KBC.

2.3. Characterization

Detailed information about the characterization has been listed in Section S1.2 of the Supplementary Materials.

2.4. Analytical Determination Method

Detailed information about the Analytical Determination Method has been listed in Section S2 of the Supplementary Materials.

3. Results and Discussion

3.1. Characterization Analysis

The morphological and structural evolution of biochar before and after modification, as well as post-reaction, was systematically investigated through comparative SEM characterization (Figure 1). As evidenced by Figure 1a–c, the pristine biochar exhibited underdeveloped pore architecture, whereas the activated nitrogen-doped biochar demonstrated significantly enhanced porosity with improved structural integrity and collapse resistance. This structural enhancement can be attributed to the exceptional intercalation capability of potassium hydroxide, which effectively expands the specific surface area of biochar—a critical factor for optimizing hexavalent chromium adsorption from aqueous solutions [28].

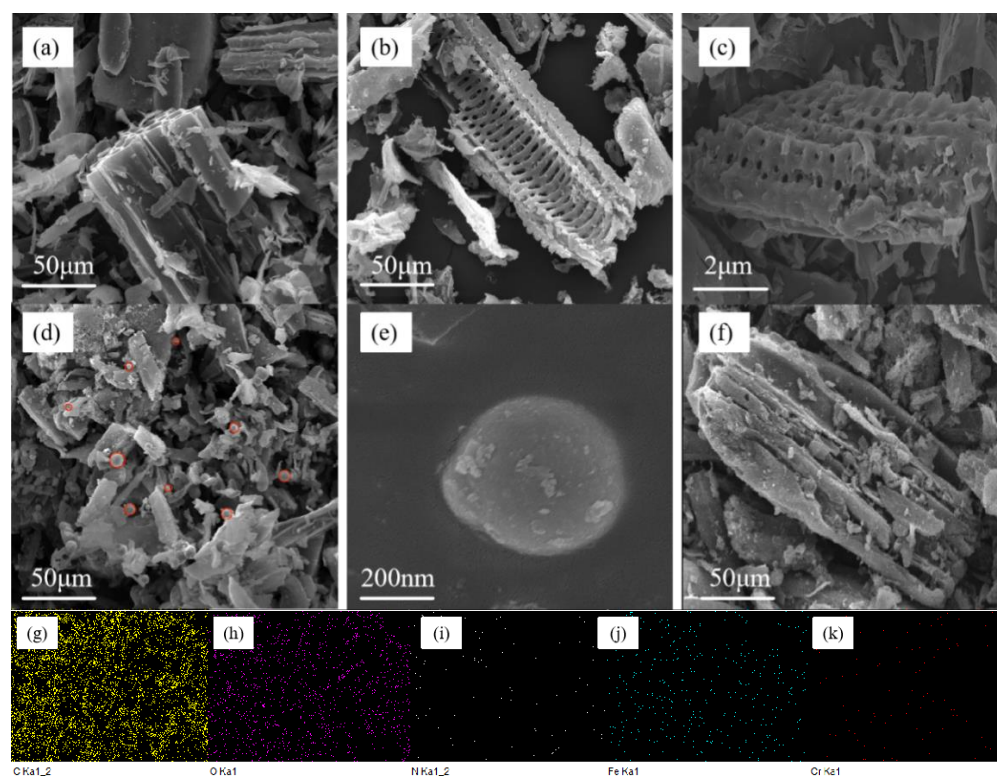


Figure 1. (a) Scanning electron microscope (SEM) image of BC, (b,c) SEM images of N-KBC, (d,e) SEM images of nZVI/N-KBC before the reaction, (f) SEM image of nZVI/N-KBC after the reaction, (g–k) corresponding elemental distribution maps of nZVI/N-KBC after the reaction.

Subsequent loading of nano-zero-valent iron (nZVI) yielded a well-distributed dispersion of nZVI particles across the biochar matrix, as clearly observed in Figure 1d,e. This homogeneous distribution confirms successful nZVI immobilization while effectively mitigating nanoparticle aggregation through the carbonaceous support. Post-reaction analysis (Figure 1f) revealed substantial pore collapse and blockage phenomena, likely caused by chromium species accumulation within the porous structure. Elemental mapping analysis

(Figure 1j,k) provided compelling evidence for the adsorption mechanism, demonstrating co-localization of C, O, N, Fe, and Cr elements. The presence of chromium confirms successful contaminant sequestration, while the persistent detection of nitrogen and iron validates the structural stability of the composite material throughout the reaction process.

Figure 2a presents the Raman spectral profiles of pristine biochar (BC) and the nZVI/N-KBC composite, displaying characteristic D (disordered carbon) and G (graphitic carbon) bands at 1350 cm^{-1} and 1590 cm^{-1} , respectively [29]. The I_D/I_G ratio reflects the defect degree of carbon structures, where a higher I_D/I_G value typically indicates greater structural defects in biochar [30].

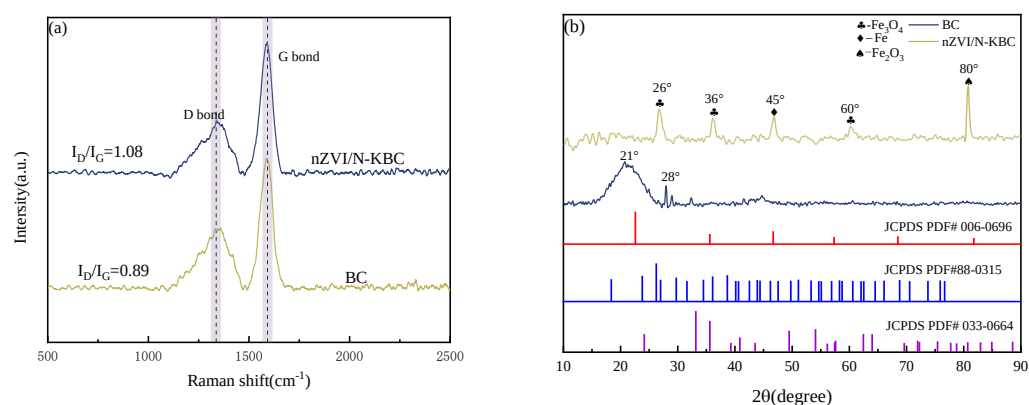


Figure 2. (a) Raman spectra of different adsorption materials; (b) X-ray diffraction patterns of different adsorption materials.

As clearly observed, the I_D/I_G ratio increased from 0.89 for pristine biochar to 1.08 for nZVI/N-KBC, demonstrating enhanced structural defects in the modified biochar. This phenomenon can be attributed to several factors: First, KOH activation effectively improves the porosity of biochar [31]. Second, nitrogen doping disrupts the carbon lattice, generating additional structural defects that create more active sites for Cr(VI) capture in aqueous solutions [2,32]. Finally, the surface defects induced by nano zero-valent iron (nZVI) particles loaded on the biochar matrix may also contribute to this structural alteration.

Figure 2b presents the XRD patterns of pristine biochar (BC) and the nZVI/N-KBC composite. BC exhibits a prominent diffraction peak at 21° , which serves as a distinctive marker of biochar [33]. The composite spectrum reveals three crystalline phases: (1) A Fe_2O_3 peak at 80° (JCPDS 033-0664) indicating surface iron oxidation [34], (2) Fe_3O_4 reflections at 26° , 36° , and 60° (JCPDS 88-0315), and (3) A distinct Fe^0 (110) peak at 45° (JCPDS 06-0696) confirming nZVI preservation [18]. These phase identifications collectively demonstrate successful iron loading and mineral retention during synthesis.

The coexistence of Fe^0 and Fe_2O_3 suggests a protective oxide layer on metallic iron cores—a configuration enhancing both nanoparticle stability and redox reactivity [18,34]. While atmospheric exposure caused partial iron oxidation, the maintained zero-valent iron signature confirms effective nZVI immobilization within the nitrogen-doped biochar matrix, fulfilling critical requirements for chromium remediation applications.

3.2. Selection of Adsorbent

To identify the optimal adsorbent, the Cr(VI) adsorption performances of BC, N-KBC, and nZVI/N-KBC were evaluated in aqueous solutions under identical conditions (Figure 3a). Notably, nZVI/N-KBC exhibited superior adsorption capacity for Cr(VI) compared to the other two materials. The pristine BC demonstrated limited removal efficiency of only 19% at equilibrium. Although nitrogen incorporation (N-KBC) moderately enhanced the Cr(VI) removal efficiency to 23.6%, the improvement remained unsatisfactory.

In contrast, nZVI/N-KBC achieved a remarkable removal efficiency of 30.8% with an adsorption capacity of 15.4 mg/g, representing a 62.1% enhancement over pristine BC. This significant performance improvement confirms the synergistic effects of iron-nitrogen co-doping in optimizing adsorption sites and surface reactivity. Based on these results, nZVI/N-KBC was selected for subsequent single-factor experiments to systematically investigate the influence of operational parameters on its adsorption behavior.

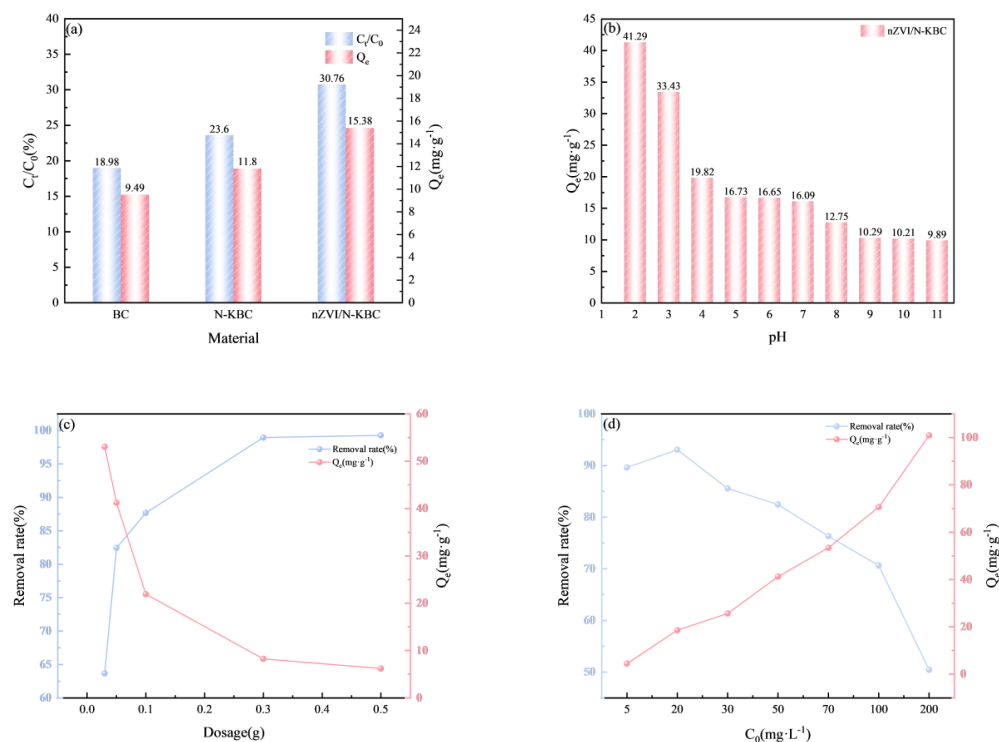


Figure 3. (a) Comparison of adsorption effects by different materials, Reaction conditions: $T = 25^\circ\text{C}$, $\text{pH} = 5$, dosage = 1 g/L, $C_0 = 50\text{ mg/L}$. (b) Comparison of adsorption effects at different pH levels, reaction conditions: $T = 25^\circ\text{C}$, dosage = 1 g/L, $C_0 = 50\text{ mg/L}$. (c) Comparison of adsorption effects with different dosages, reaction conditions: $T = 25^\circ\text{C}$, $\text{pH} = 2$, $C_0 = 50\text{ mg/L}$. (d) comparison of adsorption effects at different initial concentrations. Reaction conditions: $T = 25^\circ\text{C}$, $\text{pH} = 2$, dosage = 1 g/L.

3.3. Study on the Adsorption Characteristics of Cr(VI)

3.3.1. Different pH

The initial pH of the solution significantly influences Cr(VI) adsorption by governing the speciation of metal ions and the surface charge of the adsorbent [35]. As depicted in Figure 3b, the adsorption capacity of nZVI/N-KBC for Cr(VI) decreased sharply from 41.29 mg/g to 9.89 mg/g as pH increased from 2 to 11, indicating stronger adsorption affinity under acidic conditions. This pH-dependent behavior arises from multiple factors: At low pH values, Cr(VI) primarily exists as HCrO_4^- species [36], while the abundant H^+ ions protonate the nZVI/N-KBC surface, enhancing electrostatic attraction between the positively charged adsorbent and anionic chromate ions [18]. Additionally, HCrO_4^- exhibits lower free energy than other Cr(VI) species, favoring adsorption [37]. Conversely, at elevated pH levels, the reduced H^+ concentration causes surface deprotonation of nZVI/N-KBC, leading to electrostatic repulsion against Cr(VI) oxyanions. Simultaneously, competition arises between OH^- ions and Cr(VI) species for adsorption sites [38]. Moreover, alkaline conditions promote the formation of Fe-Cr (oxy)hydroxides on the adsorbent surface, which passivates active sites and hinders Cr(VI) accessibility [39]. Consequently, all subsequent experiments were conducted under $\text{pH} = 2$ to optimize adsorption performance.

3.3.2. Different Dosages

The effect of nZVI/N-KBC dosage on Cr(VI) removal was investigated at pH 2, as shown in Figure 3c. When the dosage increased from 0.03 g to 0.3 g, the Cr(VI) removal efficiency significantly improved from 63.66% to 98.96%, while the adsorption capacity decreased from 53.05 mg/g to 8.25 mg/g. This is attributed to the limited active sites available at lower dosages; increasing the dosage provides more active sites for Cr(VI) sequestration, thereby enhancing removal efficiency but decreasing adsorption capacity due to site underutilization [40]. However, further increasing the dosage to 0.5 g resulted in less than 1% additional removal efficiency. This phenomenon likely occurs due to particle agglomeration caused by excessive nZVI/N-KBC loading, which reduces the accessibility of active sites [41].

3.3.3. Different Initial Concentrations of Cr(VI)

The influence of initial Cr(VI) concentration on adsorption performance was systematically investigated under fixed conditions (25 °C, pH 2, 0.05 g nZVI/N-KBC dosage), as presented in Figure 3d. The equilibrium adsorption capacity increased from 4.48 mg/g to 100.9 mg/g as the initial Cr(VI) concentration rose from 5 mg/L to 200 mg/L, while the removal efficiency exhibited an inverse trend. These observations suggest two plausible mechanisms: First, the formation of chromium-iron oxide/hydroxide passivation layers on nZVI/N-KBC surfaces may block active sites and hinder electron transfer between Fe(0) and Cr(VI), thereby suppressing removal efficiency at higher concentrations [42,43]. Second, the fixed adsorbent dosage (0.05 g) likely becomes insufficient to effectively treat high-concentration Cr(VI) solutions, resulting in reduced removal percentages despite increased absolute adsorption.

3.3.4. Adsorption Kinetics Experiment

The adsorption kinetics of Cr(VI) onto nZVI/N-KBC were investigated, as shown in Figure 4a. The adsorption capacity increased rapidly during the initial 90 min and subsequently plateaued, reaching an equilibrium value of 41.21 mg/g. This indicates that most active sites were occupied during the early adsorption stage, with subsequent saturation limiting further Cr(VI) uptake. To elucidate the adsorption mechanism, four kinetic models—pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich models—were applied to fit the experimental data (Tables S1 and S2, Figure 4b–e).

The pseudo-second-order model demonstrated superior applicability, exhibiting a correlation coefficient (R^2) of 0.9999 and yielding a calculated equilibrium adsorption capacity ($Q_e = 41.271$ mg/g) that closely matched the experimental value (41.21 mg/g). These results, in conjunction with the thermodynamic results ($\Delta H^0 > 40$ KJ/mol) (Table S4) and XPS analysis, jointly demonstrate that chemical adsorption plays a dominant role in the removal process of Cr(VI) [44,45]. To elaborate on the adsorption mechanism in more detail, the intraparticle diffusion model was used to further analyze the kinetic experimental data and perform fitting. The fitting curve of the model for Cr(VI) shows a multi-segment linear relationship, indicating that the adsorption process consists of multiple process adsorption stages. In the first stage, the adsorption capacity increases rapidly with the passage of time and then approaches equilibrium. This suggests that the adsorption process includes the dispersion process inside the particles. Moreover, the fitting curve is a straight line that does not pass through the origin, indicating that intra-particle diffusion is not the only rate-limiting step in the adsorption process. The rate of the entire adsorption process is jointly controlled by the surface diffusion process and the intraparticle diffusion process [46–48].

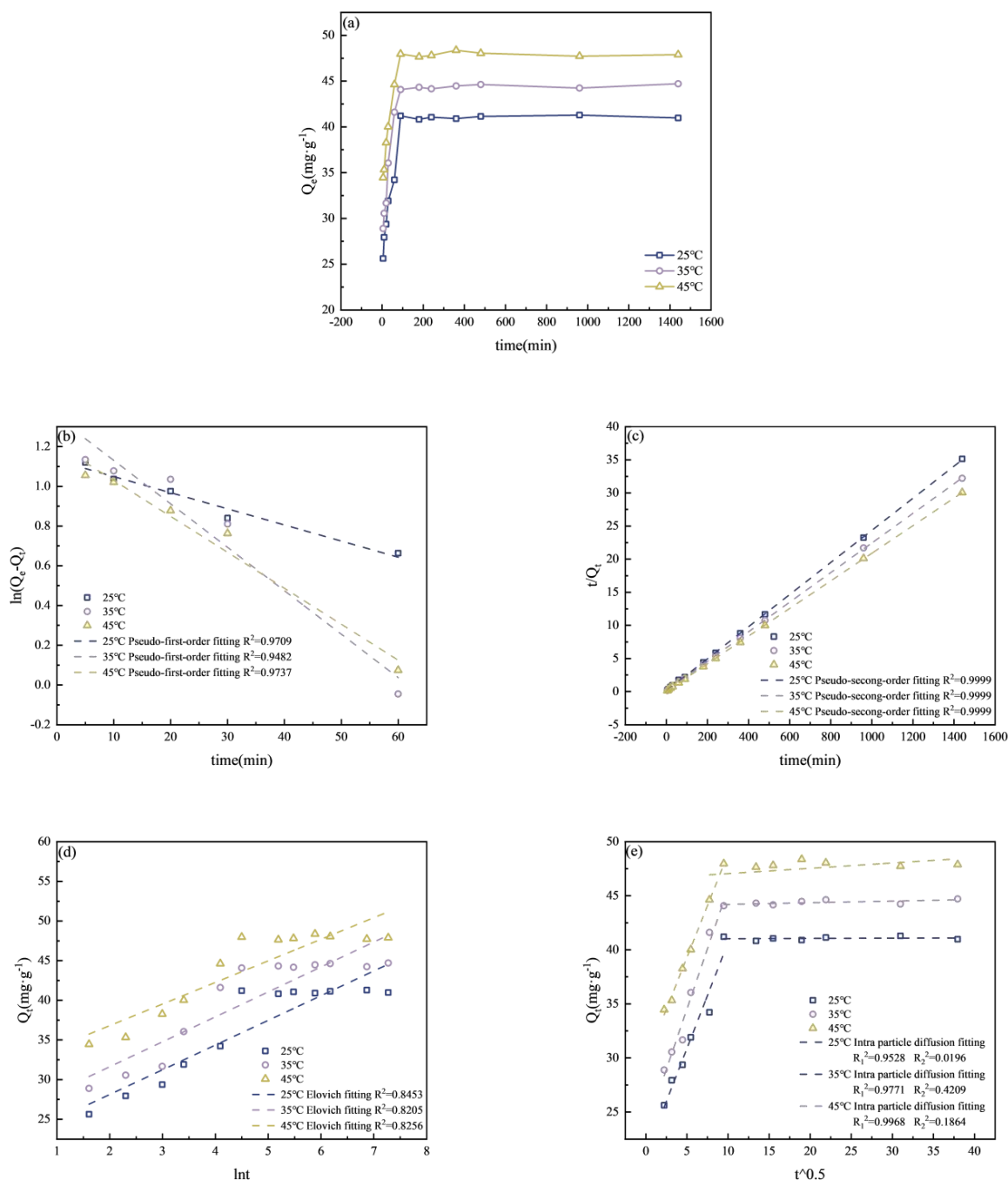


Figure 4. (a) Adsorption kinetics at different temperatures. (b–e) Adsorption kinetics fitting linear plots at different temperatures. Reaction conditions: pH = 2, Dosage = 1 g/L, $C_0 = 50$ mg/L.

3.3.5. Isotherm

The adsorption isotherms elucidate the equilibrium relationship between the Cr(VI) adsorption capacity of nZVI/N-KBC and the residual Cr(VI) concentration [49]. As shown in Figure 5a, the initial concentration of the Cr(VI) solution is directly proportional to the adsorption capacity. For the material, within the range of 0–200 mg/L, the maximum adsorption capacity is 100.9 mg/g. Moreover, as the temperature rises, the adsorption capacity also increases, indicating that the increase in the reaction temperature promotes the adsorption of Cr(VI) by the nZVI/N-KBC composite material. Increasing temperatures enhanced Cr(VI) adsorption, confirming the endothermic nature of the process [50,51].

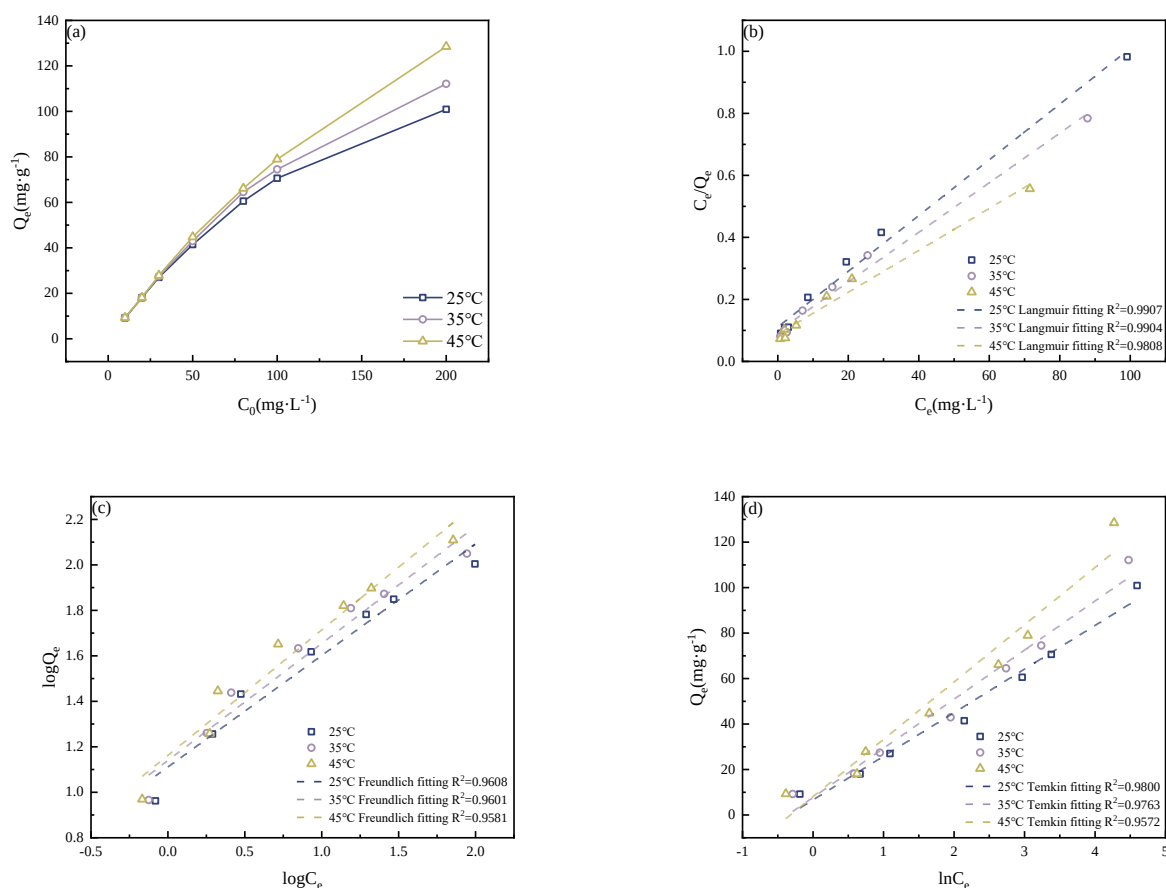


Figure 5. Isotherm adsorption effect diagram (a). Isotherm adsorption fitting linear plots (b–d). Reaction conditions: pH = 2, Dosage = 1 g/L, $C_0 = 50$ mg/L.

Three isotherm models—Langmuir, Freundlich, and Temkin—were employed to analyze the equilibrium adsorption behavior (Table S3, Figure 5b–d). By comparing the correlation coefficients (R^2), it can be seen that among the three isothermal adsorption models, comprehensively, the correlation coefficient of the Langmuir model is relatively high at three different temperatures, and the maximum equilibrium adsorption capacity Q_m obtained from the fitting results is 111.23 mg/g. This indicates that the Langmuir model is more suitable for describing the adsorption isotherm of the composite material for Cr(VI). It shows that the adsorption process is mainly monolayer adsorption, Cr(VI) is adsorbed on the surface of the material in a single layer, and there is no interaction between the adsorbed substances [51,52].

3.3.6. Thermodynamic Analysis

Thermodynamic analysis was employed to determine the spontaneity and feasibility of Cr(VI) removal by nZVI/N-KBC through energy exchange characterization [49]. As calculated in Table S4, the negative ΔG^0 values at all tested temperatures (25 °C, 35 °C, 45 °C) confirm the spontaneous nature of the adsorption process. The decreasing ΔG^0 magnitudes with rising temperature indicate enhanced thermodynamic favorability under elevated thermal conditions [41,53]. Furthermore, the positive ΔH^0 value confirms the endothermic nature of adsorption, while the positive ΔS^0 value suggests increased interfacial randomness during the process [54,55].

3.3.7. Recycling of nZVI/N-KBC

The reusability of the adsorbent is an important evaluation parameter for the industrial application of the adsorbent. The nZVI/N-KBC adsorbed by Cr(VI) was collected by

filtration, and the iron-chromium oxides on the surface of nZVI/N-KBC were dissolved with dilute hydrochloric acid. The results of the three-cycle experiment are shown in Figure 6, and the removal rate can reach about 57% after three cycles, which proves that nZVI/N-KBC has good stability.

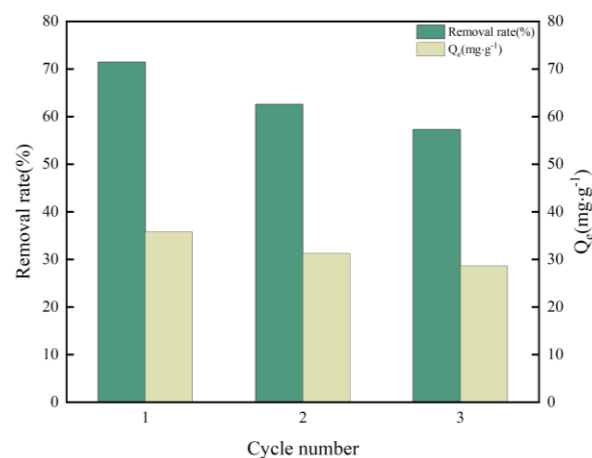


Figure 6. Reusability of nZVI/N-KBC. Reaction conditions: pH = 2; dosage = 1 g/L; C_0 = 50 mg/L.

3.4. Mechanism Analysis

3.4.1. FTIR Analysis

FTIR analysis was performed to identify functional group changes in nZVI/N-KBC before and after Cr(VI) adsorption, as shown in Figure 7. Both pristine and modified materials exhibited characteristic peaks at 3500 cm^{-1} (O-H stretching vibration) [56] and 2930 cm^{-1} (C-H stretching vibration) [57], confirming structural integrity preservation. A new absorption peak emerged at 1630 cm^{-1} , corresponding to either N-H scissoring deformation or C=N stretching vibrations, verifying successful nitrogen doping and the presence of reactive -NH_2 groups [58]. The appearance of a Fe-O bond vibration peak at 640 cm^{-1} [59] confirms iron oxide formation or chemical bonding between Fe atoms and oxygen-containing functional groups on the N-doped biochar surface. Post-adsorption spectral comparisons revealed noticeable shifts in C-H and C=N stretching vibrations, suggesting their participation in Cr(VI) adsorption mechanisms [18].

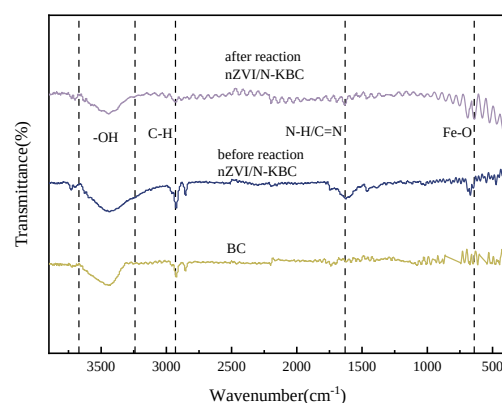


Figure 7. FTIR spectra before and after the adsorption reaction.

3.4.2. XPS Analysis

To determine the elemental composition and chemical states of nZVI/N-KBC composites before and after adsorption, XPS analysis was conducted, and the results are shown in Figure 8.

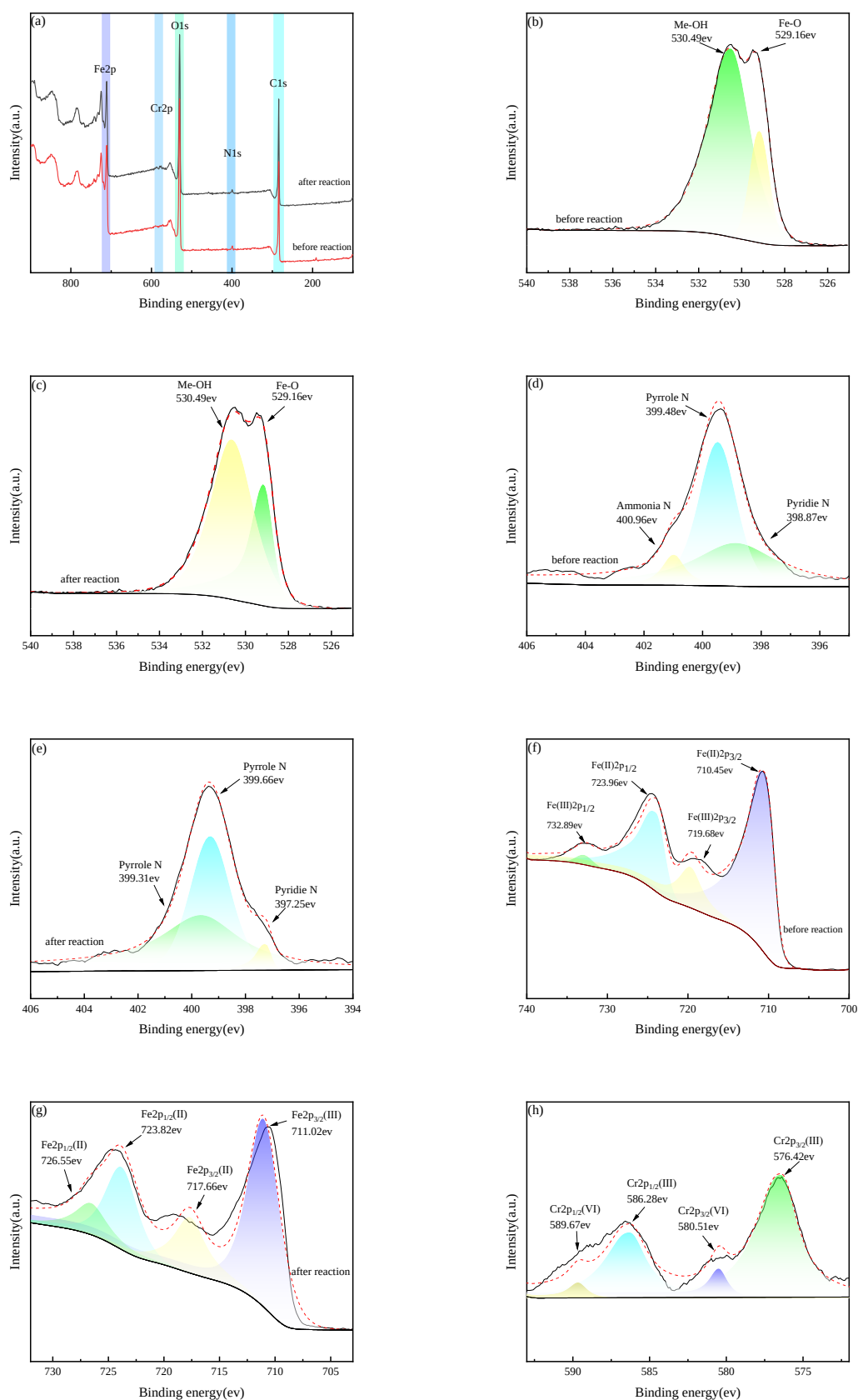


Figure 8. The high-resolution XPS spectra of O1s before (a) and after (b) the adsorption reaction, the high-resolution XPS spectra of N1s before (c) and after (d) the adsorption reaction, the high-resolution XPS spectra of Fe2p before (g) and after (h) the adsorption reaction, the full XPS spectra before and after the adsorption reaction (e), and the XPS spectrum of Cr2p after the adsorption reaction (f).

Figure 8a displays the full survey spectra of nZVI/N-KBC before and after adsorption, indicating the presence of C, N, O, and Fe in both spectra. The C and O originated from biochar (BC), N was derived from nitrogen doping modification of BC, and Fe was attributed to the loaded nano zero-valent iron (nZVI). These results confirm the successful nitrogen doping and nZVI loading, demonstrating the effective preparation of the composite. Notably, the emergence of a Cr peak after adsorption confirms the successful adsorption and reaction of Cr(VI).

As shown in Figure 8b,c, the O 1s spectra before and after adsorption reveal two oxygen states: surface hydroxyl oxygen (Me-OH) at 530.49 eV and lattice oxygen of metal oxides at 529.16 eV [60]. Although no peak shifts were observed, the proportion of lattice oxygen decreased from 33.66% to 20.18%, while hydroxyl oxygen increased from 66.34% to 79.82%, suggesting extensive hydroxylation of Fe during the reaction [61]. This indicates the participation of oxygen-containing functional groups from metal oxides in the reaction.

Figure 8d,e present the N 1s spectra of nZVI/N-KBC before and after adsorption. Three fitted peaks were identified in the pre-adsorption spectrum: pyrrolic-N (399.48 eV, 53.51%), pyridinic-N (398.87 eV, 38.38%), and amino-N (400.96 eV, 8.11%) [62]. This demonstrates that nitrogen doping primarily enhanced amino (-NH₂) groups on the biochar surface [63], consistent with FTIR results. Post-adsorption, only pyrrolic-N peaks (399.31 eV and 399.66 eV, 96.2%) and a diminished pyridinic-N peak (397.25 eV, 3.8%) remained. The reduction in pyridinic-N content is attributed to its unhybridized lone electron pairs, which provide Lewis basic sites with strong electron-donating capacity for redox reactions [26]. The disappearance of amino-N peaks suggests protonation of -NH₂ to -NH₃⁺ under acidic conditions, enabling electrostatic adsorption of CrO₄²⁻ anions [10].

The Fe 2p spectra (Figure 8f,g) exhibit two pre-adsorption peaks deconvoluted into four components: Fe(II) at 710.45 eV and 723.96 eV, and Fe(III) at 719.68 eV and 732.89 eV [64,65]. The absence of zero-valent iron peaks is likely due to oxidation during air exposure [66]. Post-adsorption, the Fe(II) peak shifted to 711.02 eV (Fe(III)), with additional Fe(II) peaks at 717.66 eV, 723.82 eV, and 726.55 eV. Quantitative analysis shows Fe(II) content decreased from 81.44% to 46.05%, confirming Fe(II) oxidation and occurrence of redox reactions [67].

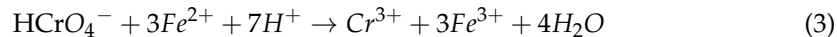
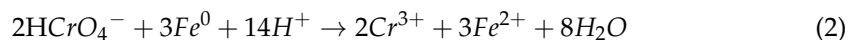
Figure 8h displays the post-adsorption Cr 2p spectrum, deconvoluted into four peaks: Cr(III) at 576.42 eV and 586.28 eV, and residual Cr(VI) at 580.51 eV and 589.67 eV [68]. The Cr(VI)/Cr(III) peak area ratio of 0.18 indicates that most Cr(VI) was reduced to Cr(III) by Fe(0) and Fe(II), with minor physical adsorption [69].

3.4.3. Adsorption Mechanism

The kinetic study on Cr(VI) adsorption by nZVI/N-KBC indicates that the adsorption process is predominantly governed by chemical adsorption. Isothermal adsorption model analysis reveals that the adsorption of Cr(VI) onto nZVI/N-KBC follows monolayer adsorption behavior without interactions between adsorbed species. Thermodynamic investigations demonstrate that the adsorption of Cr(VI) by nZVI/N-KBC is an endothermic, entropy-increasing spontaneous process.

Based on characterization analyses of nZVI/N-KBC before and after adsorption, combined with studies on its Cr(VI) adsorption behavior, the primary mechanisms for Cr(VI) removal by nZVI/N-KBC are identified as adsorption and reduction reactions, with the reduction reaction serving as the principal mechanism. The porous structure and functional groups on nZVI/N-KBC facilitate the adsorption of Cr(VI) onto the material surface, followed by subsequent reactions with nZVI and Fe(II) on the material surface. A small fraction of nZVI/N-KBC is oxidized to Fe(II) Equation (1) [70]. Cr(VI) is reduced to

Cr(III) under the action of zero-valent iron (ZVI) and Fe(II) Equations (2) and (3) [71]. The oxidized Fe(II) from nZVI further participates in the reduction of Cr(VI) to Cr(III).



The reaction mechanism is illustrated in Figure 9.

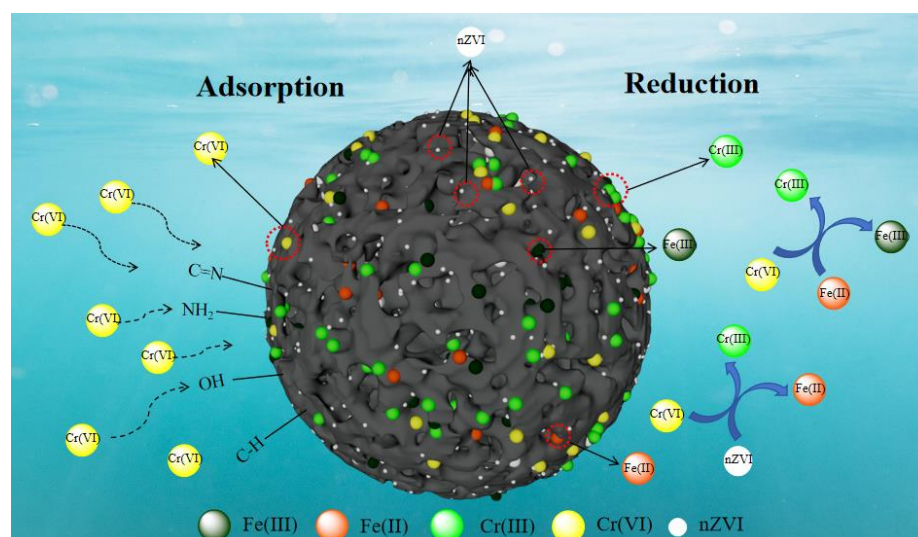


Figure 9. Adsorption mechanism of Cr(VI).

4. Conclusions

In this study, a nitrogen-doped wheat straw biochar-supported nano zero-valent iron composite (nZVI/N-KBC) was synthesized via a liquid-phase reduction method using agricultural waste (wheat straw) as the raw material. The composite demonstrated exceptional Cr(VI) removal performance with a maximum Langmuir adsorption capacity of 100.9 mg/g at pH 2, surpassing conventional nZVI-biochar systems such as sludge-derived biochar/nZVI (64.13 mg/g [23]). Characterization analyses (SEM, XRD, XPS) confirmed the synergistic role of nitrogen doping in stabilizing Fe^0 nanoparticles and enhancing electron transfer, while KOH activation generated hierarchical pores for efficient Cr(VI) accessibility. Kinetic and thermodynamic studies revealed a chemisorption-dominated process (pseudo-second-order $R^2 = 0.9999$) driven by spontaneous endothermic reactions ($\Delta H^0 > 40$ kJ/mol). Mechanistically, a majority of Cr(VI) was reduced to less toxic Cr(III) via $\text{Fe}^0/\text{Fe}^{2+}$ redox pathways, while a small fraction of Cr(VI) was adsorbed through electrostatic interactions with protonated $-\text{NH}_3^+$ groups and other functional groups, as evidenced by XPS and FTIR. The Langmuir model provided the best fit, suggesting monolayer adsorption dominated the Cr(VI) removal process. Due to its simple preparation and high efficiency, this material shows potential as a promising candidate for chromium-contaminated water remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr13061714/s1>, Section S1.1: Chemicals and Materials, Section S1.2: Adsorbents characterization; Section S2: Analytical Determination Method; Table S1: Quasi-first-order, quasi-second-order, and Elovich kinetic fitting parameters; Table S2: Intraparticle diffusion kinetic fitting parameters; Table S3: Isothermal fitting parameter table at different temperatures; Table S4: Thermodynamic parameters.

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Abbreviations

The following abbreviations are used in this manuscript:

nZVI/N-KBC	Nitrogen-doped wheat straw biochar loaded with nanoscale zero-valent iron
Cr(VI)	Hexavalent chromium
nZVI	Nanoscale zero-valent iron
Cr(III)	Trivalent chromium
N-KBC	Nitrogen-doped biochar
KBC	Biochar modified by KOH
BC	Original biochar
SEM	Scanning electron microscope
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier transform infrared spectroscopy

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