

# KOH-Activated Iron-Modified Corn Straw Biochar for Nitrate Removal: Preparation, Adsorption Performance, and Mechanism

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**Abstract:** Nitrate contamination of groundwater requires low-cost adsorbents with strong affinity for anionic species. This study developed an iron-modified corn straw biochar (Fe-BC) by coupling KOH activation with FeCl<sub>3</sub> impregnation and secondary pyrolysis, thereby integrating a porous carbon framework with iron-derived adsorption sites. The optimal Fe-BC was obtained at an iron-to-biochar mass ratio of 1:3 and a secondary pyrolysis temperature of 600 °C. It contained uniformly dispersed crystalline Fe<sub>3</sub>O<sub>4</sub>, had a Brunauer–Emmett–Teller (BET) surface area of 550.20 m<sup>2</sup>/g, and exhibited a point of zero charge of 7.3. Fe-BC maintained an adsorption capacity above 5 mg/g at pH 2–7 and reached a Langmuir maximum capacity of 12.74 mg/g at 313 K, nearly fivefold that of pristine biochar. The pseudo-second-order model showed higher R<sup>2</sup> values (0.978–0.980) than the pseudo-first-order model, while the Langmuir model yielded R<sup>2</sup> values of 0.970–0.986. Thermodynamic parameters ( $\Delta G = -17.77$  to  $-19.47$  kJ/mol,  $\Delta H = 7.11$  kJ/mol, and  $\Delta S = 84.89$  J/(mol·K)) indicated spontaneous and mildly endothermic adsorption. Phosphate produced the strongest competitive inhibition, whereas chloride and sulfate had smaller effects. Characterization results support a combined mechanism involving pH-dependent electrostatic attraction, association with Fe–OH sites, and pore filling. The principal contribution is the deliberate coupling of KOH-generated porosity and Fe<sub>3</sub>O<sub>4</sub> functionalization in an agricultural-waste matrix, which provides a balanced improvement in accessible surface area, near-neutral-pH performance, and resistance to common anions. Regeneration and flow-through performance require further verification.

**Keywords:** corn straw biochar; KOH activation; iron modification; nitrate nitrogen; adsorption mechanism

## 1. Introduction

With global population growth and intensified agricultural production, nitrate pollution caused by excessive fertilizer application has become a widespread groundwater-quality challenge [1–3]. Owing to its high solubility,



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chemical stability, and mobility, nitrate ( $\text{NO}_3^-$ ) can persist in aquifers and is difficult to remove through natural attenuation. Long-term consumption of nitrate-contaminated water is associated with methemoglobinemia and other potential health risks [1,3]. Consequently, developing efficient, economical, and environmentally compatible nitrate-removal technologies remains an important objective in water treatment.

Biochar is a carbon-rich material produced by pyrolyzing biomass under oxygen-limited conditions. Its adjustable pore structure, surface functionality, abundant feedstocks, and relatively low production cost have promoted extensive research on contaminant adsorption [4–6]. Nevertheless, pristine biochar generally carries a negative surface charge and therefore exhibits weak affinity for nitrate and other anionic pollutants [7,8]. Coexisting anions in groundwater may further compete for the limited positively charged or protonated sites, reducing nitrate uptake under realistic water-chemistry conditions [7,8].

To address these limitations, biochar has been modified with metal oxides, layered double hydroxides, and nitrogen- or cationic-functionalized components [9–13]. Iron modification is particularly attractive because iron oxides can increase the point of zero charge, provide protonatable Fe–OH groups, and facilitate magnetic separation [9–11]. Zhang et al. reported an adsorption capacity of 9.35 mg/g for acid-protonated iron-based biochar and attributed the improvement to increased surface area, positive charge, and oxygen-containing functional groups [10]. Biochar-supported nanoscale zero-valent iron has also achieved efficient nitrate conversion, although its dominant pathway involves reductive transformation rather than adsorption alone [14–16]. More recently, iron-modified barley-straw biochar showed a nitrate capacity of approximately 2.0 mg/g, with electrostatic interaction identified as an important mechanism [17]. These studies demonstrate the value of iron-containing biochars but also show that performance depends strongly on precursor, activation route, iron phase, solution chemistry, and whether nitrate is adsorbed or chemically reduced.

Recent  $\text{Fe}_3\text{O}_4$ /biochar studies have additionally emphasized the importance of combining accessible porosity, surface functionality, and recoverability. For example, Verma et al. prepared a corn-silk biochar@ $\text{Fe}_3\text{O}_4$  composite for malachite-green adsorption and demonstrated strong adsorption and multicycle recovery [18]. However, adsorption of a cationic organic dye differs fundamentally from nitrate uptake, and the corresponding interaction mechanisms cannot be directly transferred to anionic groundwater contaminants. For nitrate removal, many reported materials rely on iron loading without deliberate predevelopment of the carbon pore network, whereas aggressive iron loading may block pores and reduce accessible active sites. A remaining need is therefore to coordinate pore activation and iron-oxide functionalization and to link preparation conditions quantitatively to surface charge, pore structure, adsorption behavior, and competitive-anion effects.

Accordingly, this study aimed to prepare a KOH-activated, iron-modified corn straw biochar and clarify the structure–performance relationships governing nitrate adsorption. The specific objectives were to: (i) screen biomass-derived activated biochars and optimize the iron-to-biochar ratio and secondary pyrolysis temperature; (ii) characterize crystalline phases, pore structure, surface functional groups, morphology, and surface charge; (iii) quantify the effects of pH, adsorbent dosage, initial nitrate concentration, temperature, and coexisting anions; (iv) evaluate kinetic, isotherm, and thermodynamic behavior; and (v) develop an evidence-based adsorption mechanism while explicitly identifying the limits of the available characterization. The novelty lies in coupling KOH-generated hierarchical porosity with  $\text{Fe}_3\text{O}_4$ -derived anion-binding sites in a corn-straw matrix and evaluating their combined contribution under near-neutral and competitive conditions.

## 2. Materials and Methods

### 2.1. Materials and Reagents

Corn straw was collected from local farmland in Hebei Province, China. The biomass was thoroughly washed to remove adhering impurities, oven-dried at 80 °C for 24 h, pulverized, passed through a 100-mesh sieve, and sealed for subsequent use. The following analytical-grade reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification: ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ), potassium hydroxide (KOH,  $\geq 85.0\%$ ), potassium nitrate ( $\text{KNO}_3$ ,  $\geq 99.0\%$ ), hydrochloric acid (HCl, 36.0–38.0%), sodium hydroxide (NaOH,  $\geq 96.0\%$ ), sodium chloride (NaCl,  $\geq 99.5\%$ ), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ,  $\geq 99.0\%$ ), anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ,  $\geq 99.8\%$ ), and potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ,  $\geq 99.5\%$ ). Deionized water was used in all preparation and adsorption experiments.

### 2.2. Characterization Instruments

The crystalline phases of the synthesized materials were examined using an X-ray diffractometer (XRD; D8 Advance, Bruker, Karlsruhe, Germany) with Cu K $\alpha$  radiation over a  $2\theta$  range of 10–90° at a scan rate of 5°/min. Specific surface area and pore structure were measured using an ASAP 2460 analyzer (Micromeritics, Norcross,



GA, USA). Samples were degassed at 110 °C for 12 h; the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model were used to estimate surface area and pore-size distribution, respectively. Fourier-transform infrared (FTIR) spectra were recorded using a Spectrum One spectrometer (PerkinElmer, Waltham, MA, USA) with KBr pellets over 4000–400  $\text{cm}^{-1}$ . Surface charge was measured using a Zetasizer Nano ZS (Malvern, Malvern, UK) in 0.01 mol/L NaCl background electrolyte. Morphology was observed using a Sigma 300 scanning electron microscope (Zeiss, Oberkochen, Germany) at 5 kV.  $\text{NO}_3^-$ -N concentration was determined using a UV–visible spectrophotometer (UV-1000I, Shimadzu, Kyoto, Japan).

### 2.3. Preparation of Adsorbents

#### 2.3.1. Preparation of KOH-Activated Biochar Base

A chemical activation method was used to prepare the porous biochar base. Briefly, 10 g of pulverized corn straw was mixed with KOH solution at an alkali-to-biomass mass ratio of 2:1 and a liquid-to-solid ratio of 5:1. The suspension was stirred at 450 r/min for 2 h at room temperature and then aged for 24 h to promote penetration of KOH into the biomass matrix. The slurry was subsequently dried at 105 °C to constant mass to obtain the activated precursor. This activation strategy follows established principles of alkali activation and activated-carbon pore development [19,20].

The precursor was transferred into a quartz boat and placed inside a tube furnace (OTF-1200X-S, Hefei Kejing Materials Technology Co., Ltd., Hefei, China). High-purity nitrogen ( $\text{N}_2$ , 99.999%) was introduced at a flow rate of 200 mL/min for 30 min to purge residual air. The furnace was then heated to 750 °C at a ramp rate of 5 °C/min and maintained for 1 h. After naturally cooling to room temperature, the pyrolyzed product was immersed and washed with 1 mol/L HCl for 2 h to eliminate ash content, followed by rinsing with DI water until the filtrate reached a neutral pH. The final product was dried at 105 °C for 12 h, ground, and sieved through a 100-mesh screen to yield the KOH-activated corn straw biochar, designated as BC. Following the identical procedure, bamboo powder biochar (ZBC) and coffee ground biochar (CBC) were prepared as parallel candidates for the substrate screening experiment.

#### 2.3.2. Synthesis of Iron-Modified Biochar (Fe-BC)

Iron oxide was loaded through impregnation followed by secondary pyrolysis. A fixed mass of BC was dispersed in  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution at iron-to-biochar mass ratios of 1:5, 1:4, 1:3, 1:2, and 1:1, while maintaining a solid-to-liquid ratio of 1:10. The suspension was ultrasonicated at 25 °C for 2 h and magnetically stirred at 450 r/min for 24 h. It was then concentrated in an 85 °C water bath and vacuum-dried at 60 °C for 12 h.

The dried precursor was placed in the tube furnace and heated under  $\text{N}_2$  to secondary pyrolysis temperatures of 300, 400, 500, 600, or 700 °C at 6 °C/min, followed by a 2 h holding period. After cooling under  $\text{N}_2$ , the products were ground and passed through a 100-mesh sieve. The resulting iron-modified biochar was designated Fe-BC.

### 2.4. Batch Adsorption Experiments

Batch adsorption experiments were conducted in 100 mL Erlenmeyer flasks under continuous agitation at 450 r/min using a thermostatic magnetic stirrer (DF-101S, Gongyi Yuhua Instrument Co., Ltd., Gongyi, China). Unless otherwise specified, the baseline conditions were an initial  $\text{NO}_3^-$ -N concentration of 20 mg/L, an adsorbent dosage of 1 g/L, a solution volume of 100 mL, a temperature of 25 °C, an initial pH of 7, and a contact time of 24 h. After reaction, the supernatant was filtered through a 0.45  $\mu\text{m}$  aqueous membrane.  $\text{NO}_3^-$ -N was measured by UV spectrophotometry according to HJ/T 346-2007 using absorbance at 220 and 275 nm. All experiments were performed in triplicate, and results are reported as mean values with standard deviations.

#### 2.4.1. Single-Factor Optimization and Influence Experiments

- (1) Effect of pH on  $\text{NO}_3^-$ -N Removal: To determine the optimal pH window for adsorption, 100 mg of either pristine BC or Fe-BC was added to 100 mL of  $\text{KNO}_3$  solution in 250 mL Erlenmeyer flasks. The initial pH values of the solution were adjusted across a range of 2, 4, 6, 8, 10, and 12 using dilute HCl or NaOH solutions. The mixtures were agitated at 25 °C and 450 r/min for 24 h. The filtrate was collected to evaluate the equilibrium  $\text{NO}_3^-$ -N mass concentration.
- (2) Effect of Adsorbent Dosage: Varying masses of BC and Fe-BC (20, 40, 60, 80, 100, 150, and 200 mg) were introduced into 100 mL of  $\text{KNO}_3$  solution with the pH adjusted to 7. The systems were agitated at 25 °C. To track the kinetics under different dosages, 1 mL aliquots of the solution were extracted at predetermined intervals (5, 15, 45, 105, and 240 min) via syringes, filtered, diluted, and analyzed for  $\text{NO}_3^-$ -N content.

- (3) Effect of Initial  $\text{NO}_3^-$ -N Concentration: Batch tests were performed by dosing 100 mg of BC or Fe-BC into 100 mL of nitrate solutions with varying initial concentrations (5, 10, 20, 40, 60, 80, and 100 mg/L) at pH 7. The solutions were shaken at 25 °C, and 1 mL samples were collected at 5, 15, 45, 105, and 240 min to monitor the concentrations.
- (4) Effect of Coexisting Anions: To examine the competitive effects of background ions commonly found in natural waters, individual coexisting anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) were introduced into the system. The experiments were conducted by adding 100 mg of adsorbent to 100 mL of nitrate solution (20 mg/L, pH 7) containing either 0.1 mmol/L or 0.2 mmol/L of the respective interfering anions.

#### 2.4.2. Adsorption Kinetics

Based on the pH-dependent adsorption tests, pH 2 was selected for the kinetic analysis because Fe-BC exhibited its highest adsorption performance under this condition. Using this high-adsorption condition allowed the time-dependent uptake behavior and fitted kinetic parameters to be evaluated under a consistent surface-charge state. Kinetic studies were performed at an initial pH of 2, an adsorbent dosage of 1 g/L, and an initial  $\text{NO}_3^-$ -N concentration of 20 mg/L. The experiments were carried out across three temperature levels (293, 303, and 313 K). Water samples were taken at specified time intervals (5, 20, 65, 125, 185, 245, 480, and 1440 min). The obtained data were simulated using the pseudo-first-order and pseudo-second-order kinetic models. Model fitting and interpretation followed established guidance for adsorption-model analysis and the avoidance of common fitting inconsistencies [21,22].

The pseudo-first-order kinetic model is commonly used as an empirical description of adsorption-rate behavior and is expressed as [23]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

The pseudo-second-order kinetic model provides an alternative empirical rate expression that is often associated with surface-reaction-controlled uptake, although model fit alone does not establish a unique mechanism [24]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

#### 2.4.3. Adsorption Isotherms

For consistency with the kinetic experiments, the isotherm measurements were also conducted at pH 2 so that equilibrium adsorption and thermodynamic behavior could be evaluated under the same high-adsorption condition. For isotherm evaluations, the initial  $\text{NO}_3^-$ -N concentration was varied from 5 to 100 mg/L at pH 2 with an adsorbent dosage of 1 g/L. The systems were thoroughly shaken for 24 h to reach equilibrium at temperatures of 293, 303, and 313 K, respectively. The equilibrium data were modeled using the Langmuir and Freundlich isotherm equations.

The Langmuir isotherm represents adsorption on a finite population of equivalent sites and is expressed as [25]:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}$$

The Freundlich isotherm is an empirical model for adsorption on energetically heterogeneous surfaces and is expressed as [26]:

$$Q_e = K_F C_e^{1/n}$$

Thermodynamic parameters, including the Gibbs free-energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ), were calculated to assess the thermodynamic tendency and temperature dependence of nitrate adsorption [27,28]. The Gibbs free-energy change was calculated using:

$$\Delta G = -RT \ln K_c$$

The van't Hoff equation was adopted to derive the enthalpy change and entropy change by fitting equilibrium data at different temperatures:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

## 2.5. Statistical Analysis

Each adsorption condition was tested in triplicate, and numerical results are presented as mean  $\pm$  standard deviation; error bars in the figures represent one standard deviation. Kinetic and isotherm parameters were estimated by nonlinear regression using OriginPro 2025 (OriginLab Corporation, Northampton, MA, USA). Model performance was evaluated using the coefficient of determination ( $R^2$ ) together with the agreement between experimental and model-calculated equilibrium capacities. Because the experiments were designed primarily to evaluate continuous factor–response trends rather than prespecified pairwise hypotheses, no inferential significance test was applied. Model assignment was therefore treated as empirical evidence and interpreted jointly with physicochemical characterization rather than as stand-alone proof of an adsorption mechanism.

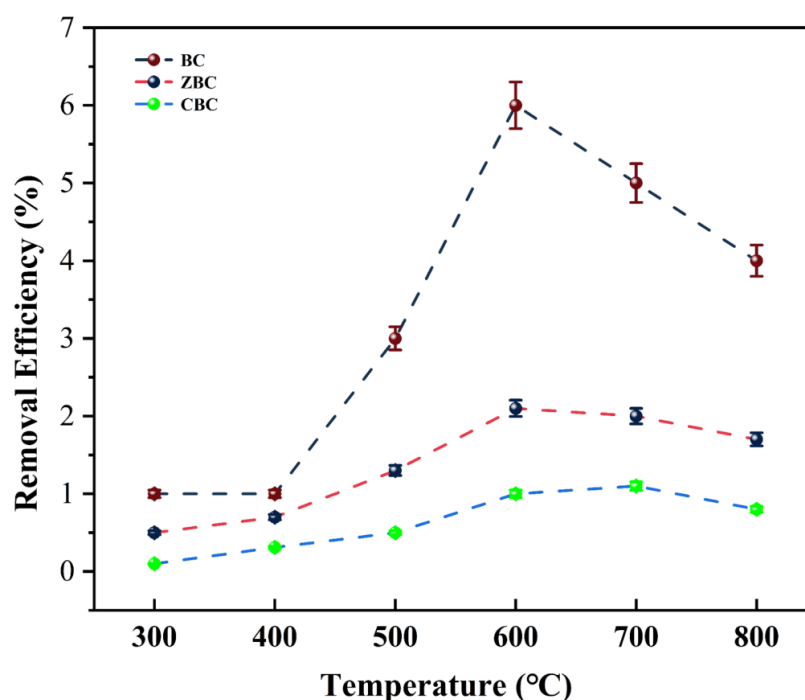
## 3. Results

### 3.1. Substrate Screening of Biochar

The nitrate adsorption performance of three KOH-activated biochars derived from corn straw (BC), bamboo powder (ZBC), and coffee grounds (CBC) was evaluated after secondary pyrolysis at temperatures ranging from 300 to 800 °C (Figure 1).

For all three biochar samples, nitrate adsorption efficiency first increased and then decreased with rising pyrolysis temperature, with the maximum value observed at 600 °C. At 600 °C, BC achieved an adsorption efficiency of approximately 6%, which was markedly higher than those of ZBC (~2%) and CBC (nearly 0%).

Corn straw-derived activated biochar (BC) was selected as the optimal substrate for subsequent iron modification. The substrate-screening results are shown in Figure 1.



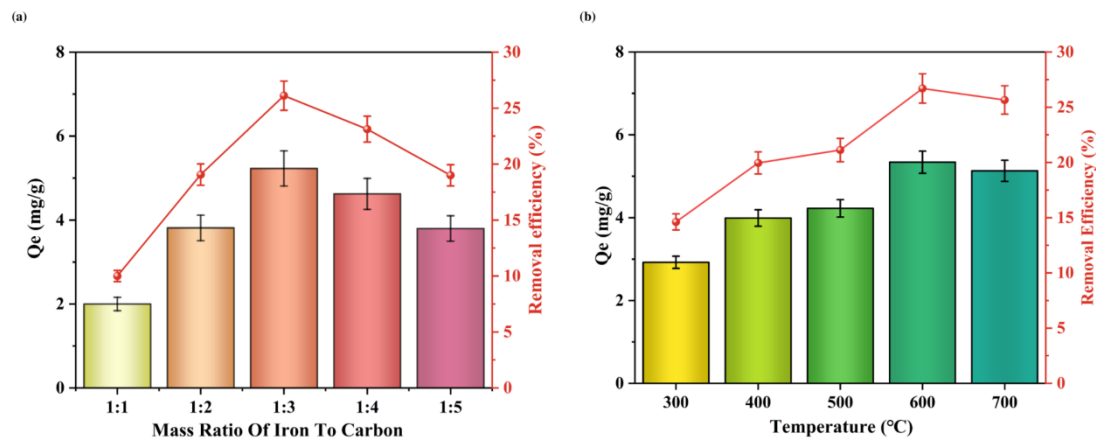
**Figure 1.** Nitrate adsorption efficiencies of BC, ZBC and CBC as a function of secondary pyrolysis temperature.

### 3.2. Optimization of Fe-BC Preparation Process

Two key preparation variables, iron-to-biochar mass ratio and secondary pyrolysis temperature, were optimized with equilibrium  $\text{NO}_3^-$ -N adsorption capacity as the evaluation index.

As the iron-to-biochar mass ratio increased from 1:5 to 1:3, the equilibrium adsorption capacity of Fe-BC increased significantly from 3.8 mg/g to 5.2 mg/g. A further increase in the ratio to 1:1 resulted in a sharp decrease in adsorption capacity to approximately 2 mg/g. The optimal iron-to-biochar mass ratio was determined to be 1:3.

With the rise of secondary pyrolysis temperature from 300 °C to 600 °C, the adsorption capacity of Fe-BC increased continuously and reached a maximum of 5.3 mg/g at 600 °C, followed by a slight decrease at 700 °C. The optimal secondary pyrolysis temperature was determined to be 600 °C. The effects of the two preparation parameters are shown in Figure 2.



**Figure 2.** Effects of preparation parameters on  $\text{NO}_3^-$ -N adsorption capacity of Fe-BC: (a) iron-to-biochar mass ratio and (b) secondary pyrolysis temperature.

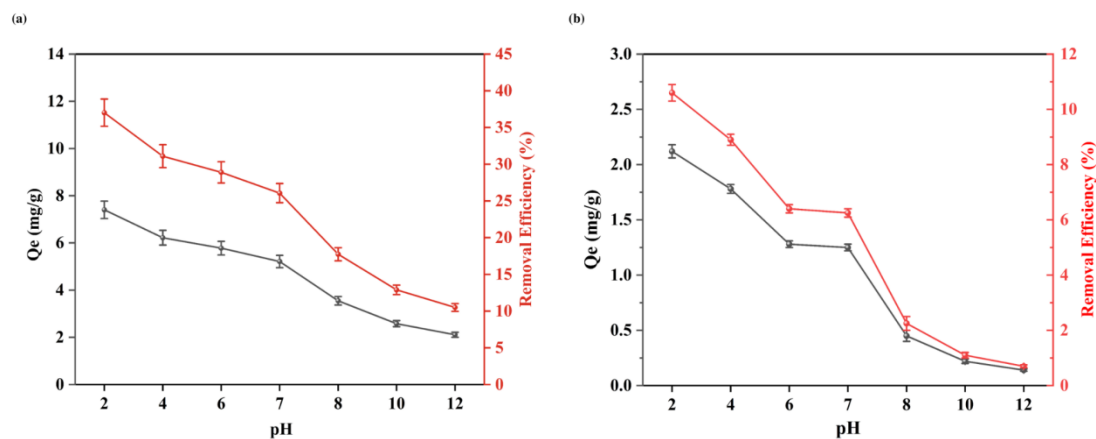
### 3.3. Factors Influencing Nitrate Adsorption on Fe-BC

#### 3.3.1. Effect of Solution pH

The  $\text{NO}_3^-$ -N adsorption performance of Fe-BC and pristine BC was investigated at an initial pH range of 2–12.

Fe-BC exhibited substantially higher nitrate adsorption capacity than pristine BC across the entire pH range. At pH 2–7, the adsorption capacity of Fe-BC remained above 5 mg/g, corresponding to a removal efficiency of nearly 25%, which was approximately 5 times that of pristine BC under the same conditions. The adsorption capacity of Fe-BC decreased gradually with increasing pH within 2–7, and declined more obviously under alkaline conditions (pH > 7), reaching the minimum at pH 10–12.

Given the stable adsorption performance in the near-neutral range, pH 7 was selected as the standard condition for subsequent experiments. The effects of initial solution pH on nitrate adsorption by Fe-BC and pristine BC are shown in Figure 3.



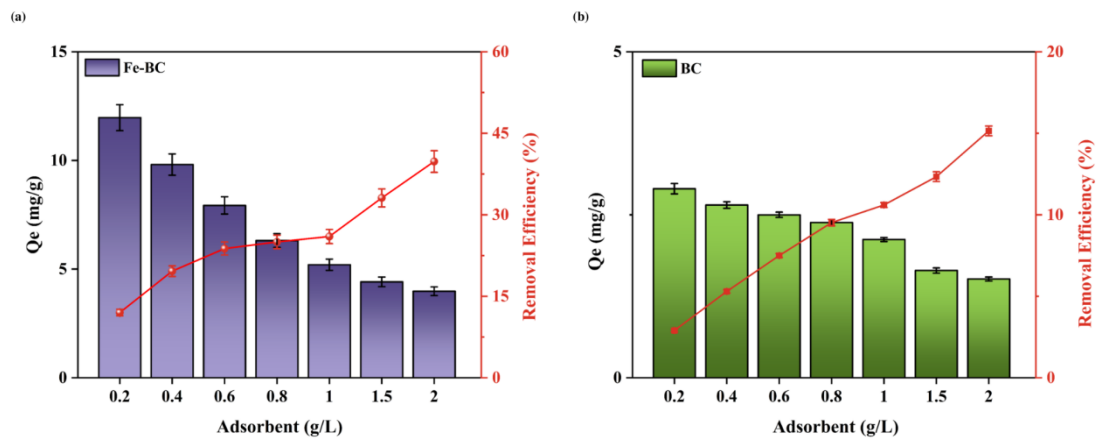
**Figure 3.** Effect of initial solution pH on nitrate adsorption capacity and removal efficiency: (a) Fe-BC and (b) pristine BC.

#### 3.3.2. Effect of Adsorbent Dosage

The effect of adsorbent dosage on adsorption performance was examined in the range of 0.2–2 g/L.

With increasing Fe-BC dosage from 0.2 g/L to 2 g/L, the nitrate removal efficiency increased continuously and approached 43% at 2 g/L, while the unit adsorption capacity decreased gradually. The maximum unit adsorption capacity of approximately 12.2 mg/g was obtained at the dosage of 0.2 g/L. The growth rate of removal efficiency slowed down significantly when the dosage exceeded 1 g/L.

The unit adsorption capacity of Fe-BC was approximately 5 times that of pristine BC at the lowest dosage. A dosage of 1 g/L was selected as the standard condition for subsequent experiments. The effects of adsorbent dosage on nitrate adsorption by Fe-BC and pristine BC are shown in Figure 4.



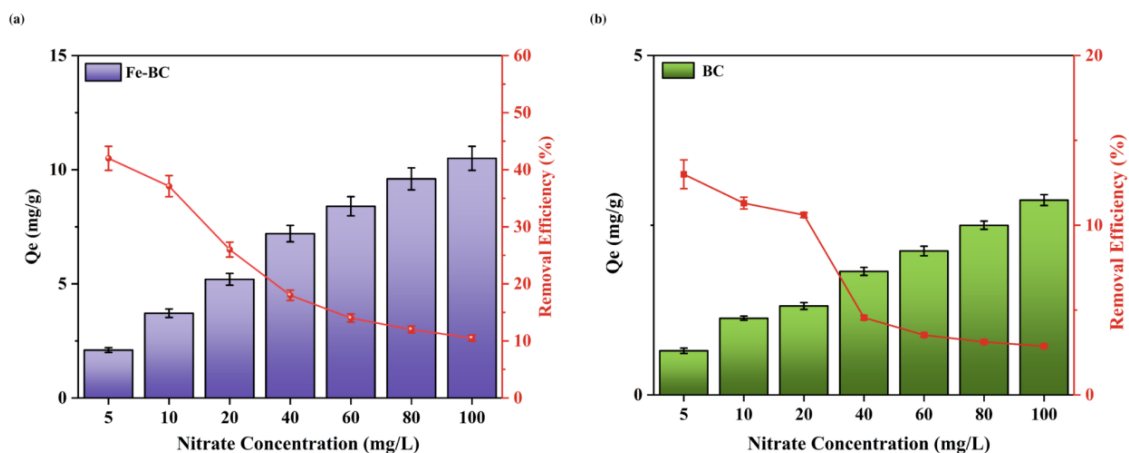
**Figure 4.** Effect of adsorbent dosage on nitrate adsorption capacity and removal efficiency: (a) Fe-BC and (b) pristine BC.

### 3.3.3. Effect of Initial Nitrate Concentration

The adsorption performance was evaluated at initial NO<sub>3</sub><sup>−</sup>-N concentrations ranging from 5 mg/L to 100 mg/L.

The unit adsorption capacity of Fe-BC increased prominently with increasing initial nitrate concentration, while the removal efficiency showed a decreasing trend. At an initial concentration of 100 mg/L, the adsorption capacity of Fe-BC was 4 times that of pristine BC. At low concentrations (5–20 mg/L), Fe-BC maintained high removal efficiency. The effects of initial nitrate concentration on nitrate adsorption by Fe-BC and pristine BC are shown in Figure 5.

An initial concentration of 20 mg/L was selected as the standard condition for subsequent kinetic and thermodynamic tests.



**Figure 5.** Effect of initial nitrate concentration on nitrate adsorption capacity and removal efficiency: (a) Fe-BC and (b) pristine BC.

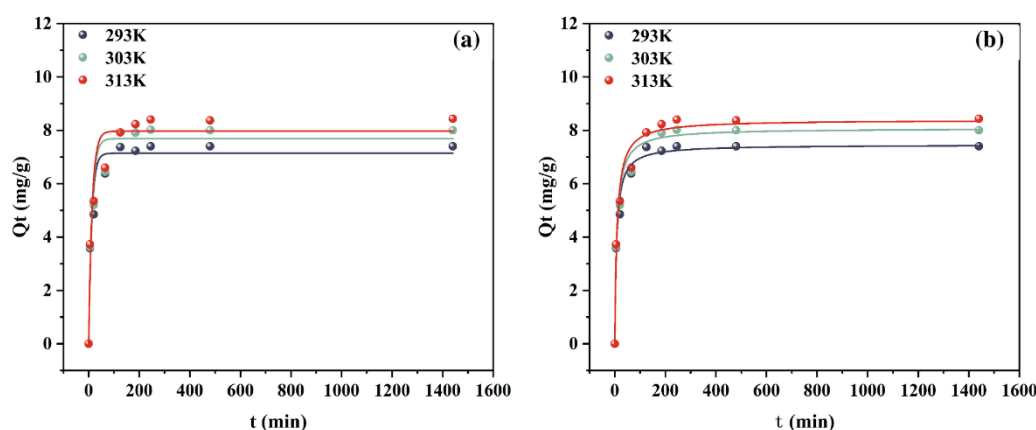
## 3.4. Adsorption Kinetics, Isotherms, and Thermodynamics

### 3.4.1. Adsorption Kinetics

Unlike the near-neutral baseline tests conducted at pH 7, the kinetic and isotherm experiments were performed at pH 2 to characterize adsorption behavior under the high-affinity condition identified by the pH experiment. The adsorption kinetics of nitrate onto Fe-BC were investigated at 293 K, 303 K and 313 K, and the experimental data were fitted by pseudo-first-order and pseudo-second-order kinetic models. The kinetic fitting results are shown in Figure 6.

The adsorption process could be divided into two distinct stages: a rapid adsorption stage within 0–200 min, and a slow equilibrium stage after 200 min, with adsorption equilibrium reached at approximately 600 min. The equilibrium adsorption capacity increased with rising temperature.

The correlation coefficients ( $R^2$ ) of the pseudo-second-order model were all above 0.975, which were higher than those of the pseudo-first-order model (0.92–0.94). The fitted kinetic parameters are summarized in Tables 1 and 2.



**Figure 6.** Adsorption kinetics of  $\text{NO}_3^-$ -N onto Fe-BC at different temperatures (293, 303, and 313 K): (a) pseudo-first-order kinetic fitting; (b) pseudo-second-order kinetic fitting.

**Table 1.** Pseudo-first-order kinetic parameters for nitrate adsorption on Fe-BC. Nitrate concentration and adsorption-capacity terms are expressed on an  $\text{NO}_3^-$ -N basis.

| Temperature (K) | $q_e$ , exp (mg/g) | $q_e$ , cal (mg/g) | $k_1$ ( $\text{min}^{-1}$ ) | $R^2$   |
|-----------------|--------------------|--------------------|-----------------------------|---------|
| 293             | 7.13               | 7.14               | 0.08348                     | 0.9341  |
| 303             | 7.68               | 7.69               | 0.07604                     | 0.92835 |
| 313             | 7.96               | 7.97               | 0.07421                     | 0.92172 |

**Table 2.** Pseudo-second-order kinetic parameters for nitrate adsorption on Fe-BC. Nitrate concentration and adsorption-capacity terms are expressed on an  $\text{NO}_3^-$ -N basis.

| Temperature (K) | $q_e$ , exp (mg/g) | $q_e$ , cal (mg/g) | $k_2$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) | $R^2$   |
|-----------------|--------------------|--------------------|-----------------------------------------------------------------|---------|
| 293             | 7.2                | 7.46               | 0.01856                                                         | 0.97982 |
| 303             | 7.9                | 8.07               | 0.01489                                                         | 0.97887 |
| 313             | 8.2                | 8.39               | 0.01358                                                         | 0.97759 |

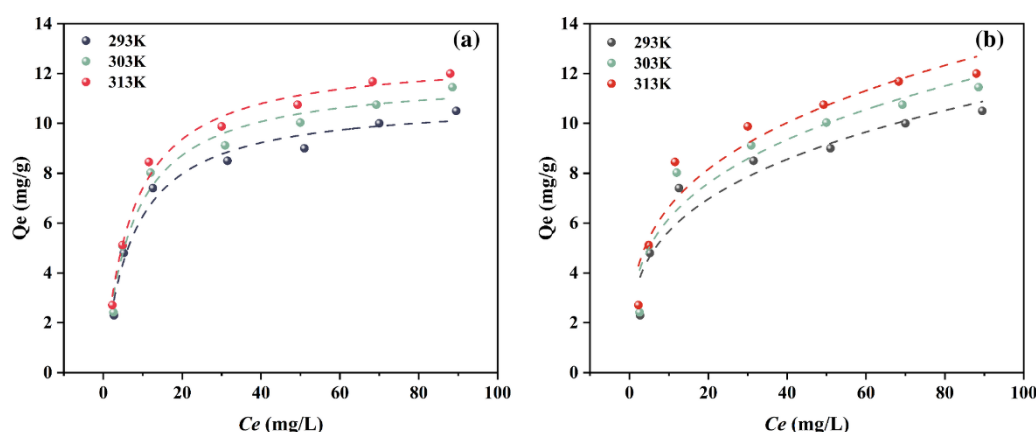
Across 293–313 K, the pseudo-second-order model yielded  $R^2$  values of 0.97759–0.97982, compared with 0.92172–0.93410 for the pseudo-first-order model. In contrast, the pseudo-first-order model produced  $q_e$ , cal values that were numerically closer to the experimental  $q_e$  values. The higher  $R^2$  of the pseudo-second-order model is consistent with an important contribution from surface-reaction-controlled adsorption, whereas the closer  $q_e$  agreement of the pseudo-first-order model indicates that non-surface-reaction contributions, including diffusion-related uptake, should not be excluded. Combined with the FTIR, zeta-potential, pore-structure, and competitive-ion results, nitrate adsorption on Fe-BC is interpreted as a physicochemical process involving electrostatic attraction, Fe–OH-associated interactions, and pore filling/diffusion rather than as a purely chemisorption-controlled process. The fitted  $k_2$  decreased from 0.01856 to 0.01358  $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$  as temperature increased, while equilibrium capacity increased. This inverse trend may reflect covariance among fitted parameters and should not be interpreted independently as evidence of a change in the elementary adsorption pathway.

### 3.4.2. Adsorption Isotherms

Adsorption isotherm tests were conducted at 293 K, 303 K and 313 K, and the equilibrium data were fitted by Langmuir and Freundlich models. The adsorption isotherm fitting results are shown in Figure 7.

The theoretical maximum monolayer adsorption capacity increased from 10.94 to 12.74  $\text{mg NO}_3^-$ -N/g as temperature rose from 293 K to 313 K. The Langmuir model yielded  $R^2$  values ranging from 0.96968 to 0.98606, consistently higher than those of the Freundlich model (0.89471–0.90662). The fitted Langmuir and Freundlich parameters are summarized in Tables 3 and 4.

The Langmuir model produced higher  $R^2$  values (0.96968–0.98606) than the Freundlich model (0.89471–0.90662). The Langmuir constant  $K_L$  increased slightly from 0.1342 to 0.1389 L/mg, while  $q_{\text{max}}$  increased from 10.94 to 12.74  $\text{mg/g}$  with temperature. Freundlich  $1/n$  values remained close to 0.30, indicating favorable uptake over the tested concentration range. These fits support a saturable adsorption process, but they are empirical and do not, by themselves, prove a perfectly homogeneous monolayer surface.



**Figure 7.** Adsorption isotherms for  $\text{NO}_3^-$ -N onto Fe-BC at different temperatures (293, 303, and 313 K): (a) Langmuir isotherm model fitting; (b) Freundlich isotherm model fitting.

**Table 3.** Langmuir isotherm parameters for nitrate adsorption on Fe-BC. Nitrate concentration and adsorption-capacity terms are expressed on an  $\text{NO}_3^-$ -N basis.

| Temperature (K) | qmax (mg/g) | K <sub>L</sub> (L/mg) | R <sup>2</sup> |
|-----------------|-------------|-----------------------|----------------|
| 293 K           | 10.94       | 0.1342                | 0.96968        |
| 303 K           | 11.92       | 0.1364                | 0.97139        |
| 313 K           | 12.74       | 0.1389                | 0.98606        |

**Table 4.** Freundlich isotherm parameters for nitrate adsorption on Fe-BC. Nitrate concentration and adsorption-capacity terms are expressed on an  $\text{NO}_3^-$ -N basis.

| Temperature (K) | K <sub>F</sub> [(mg/g)(L/mg) <sup>1/n</sup> ] | 1/n     | R <sup>2</sup> |
|-----------------|-----------------------------------------------|---------|----------------|
| 293 K           | 2.8588                                        | 0.29727 | 0.89471        |
| 303 K           | 3.1014                                        | 0.29913 | 0.89561        |
| 313 K           | 3.3476                                        | 0.29744 | 0.90662        |

### 3.4.3. Adsorption Thermodynamics

Thermodynamic parameters including Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated to reveal the spontaneity, thermal effect and driving force of nitrate adsorption onto Fe-BC [27,28]. The thermodynamic parameters were calculated using the equations described in Section 2.4.3.

The Gibbs free energy change ( $\Delta G$ ) was negative at all tested temperatures, and its absolute value increased with rising temperature, ranging from  $-17.77$  kJ/mol to  $-19.47$  kJ/mol. The enthalpy change ( $\Delta H$ ) was  $7.11$  kJ/mol, and the entropy change ( $\Delta S$ ) was  $84.89$  J/(mol·K), both of which were positive. The calculated thermodynamic parameters are summarized in Table 5.

**Table 5.** Thermodynamic parameters for nitrate adsorption on Fe-BC. Nitrate concentration and adsorption-capacity terms are expressed on an  $\text{NO}_3^-$ -N basis.

| Temperature (K) | ln K <sub>c</sub> | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ [J/(mol·K)] | R <sup>2</sup> |
|-----------------|-------------------|---------------------|---------------------|------------------------|----------------|
| 293 K           | 7.292             | $-17.77$            | 7.11                | 84.89                  | 0.9989         |
| 303 K           | 7.394             | $-18.63$            |                     |                        |                |
| 313 K           | 7.478             | $-19.47$            |                     |                        |                |

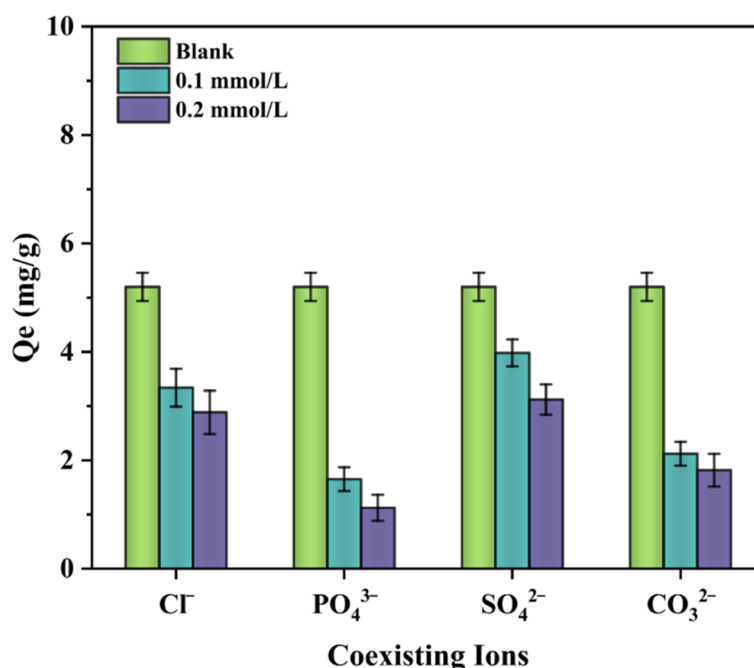
### 3.5. Effect of Coexisting Anions

Natural water matrices typically contain multiple background anions that can reduce adsorbent performance through competition for charged or metal-associated sites. The effects of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  were evaluated at 0.1 and 0.2 mmol/L. The observed inhibitory order was  $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{SO}_4^{2-}$ .

$\text{PO}_4^{3-}$  produced the strongest inhibition. At 0.2 mmol/L, the nitrate adsorption capacity decreased from 5.2 mg/g in the blank control to approximately 1.1 mg/g. This result is consistent with the high charge density and strong affinity of phosphate for iron-(hydr)oxide surface sites, which can preferentially occupy sites otherwise available to nitrate. Fe-BC nevertheless retained a nitrate capacity of approximately 2.4 mg/g in the presence of



$\text{Cl}^-$ , twice the capacity of pristine BC in the ion-free control (1.2 mg/g), demonstrating a marked improvement in resistance to chloride interference. The effects of common coexisting anions on nitrate adsorption by Fe-BC are shown in Figure 8.



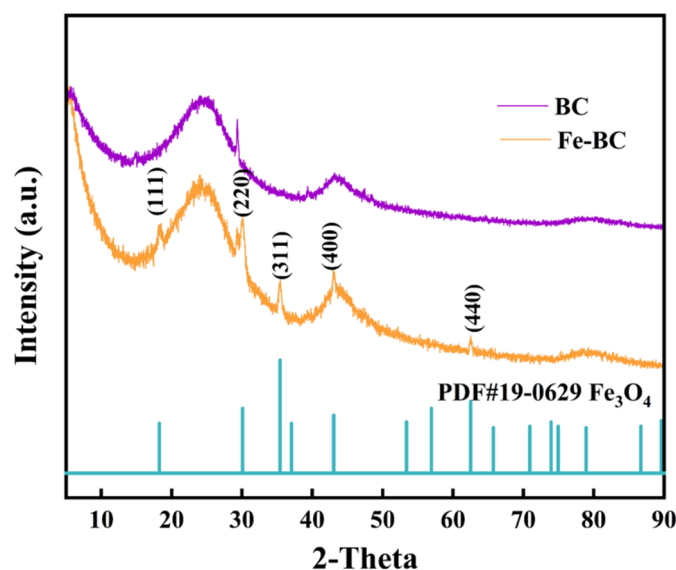
**Figure 8.** Effect of common coexisting anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) at different concentrations on the nitrate adsorption capacity of Fe-BC.

### 3.6. Microstructural Characterization and Mechanism Analysis

#### 3.6.1. XRD Crystalline Phase Analysis

The crystalline phases of BC and Fe-BC were characterized by X-ray diffraction, following common interpretations of iron oxide crystalline phases [29,30].

Pristine BC only showed a broad diffraction halo at  $2\theta = 20\text{--}30^\circ$ , corresponding to an amorphous carbon structure. In contrast, Fe-BC exhibited sharp diffraction peaks at  $2\theta = 18.3^\circ$ ,  $30.1^\circ$ ,  $35.5^\circ$ ,  $43^\circ$  and  $62.6^\circ$ , which were consistent with the standard PDF card of magnetite (PDF#19-0629). The XRD patterns of pristine BC and Fe-BC are shown in Figure 9.

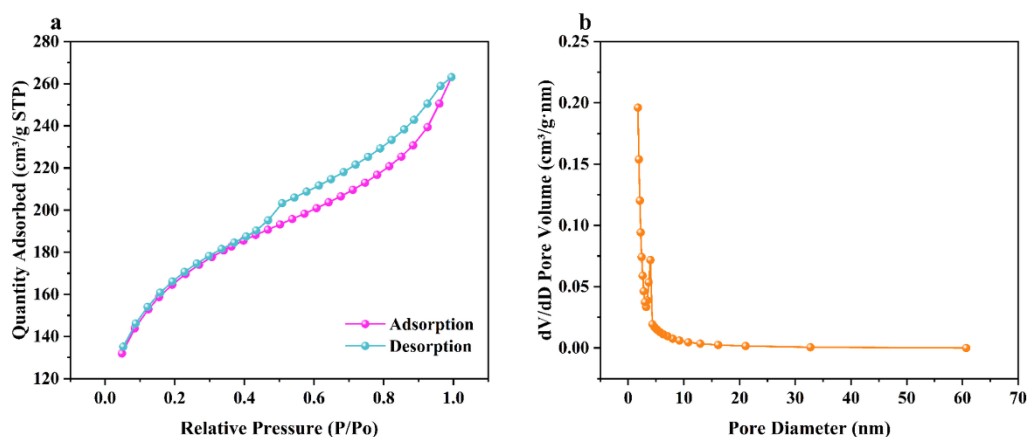


**Figure 9.** XRD patterns of pristine biochar (BC) and iron-modified biochar (Fe-BC).

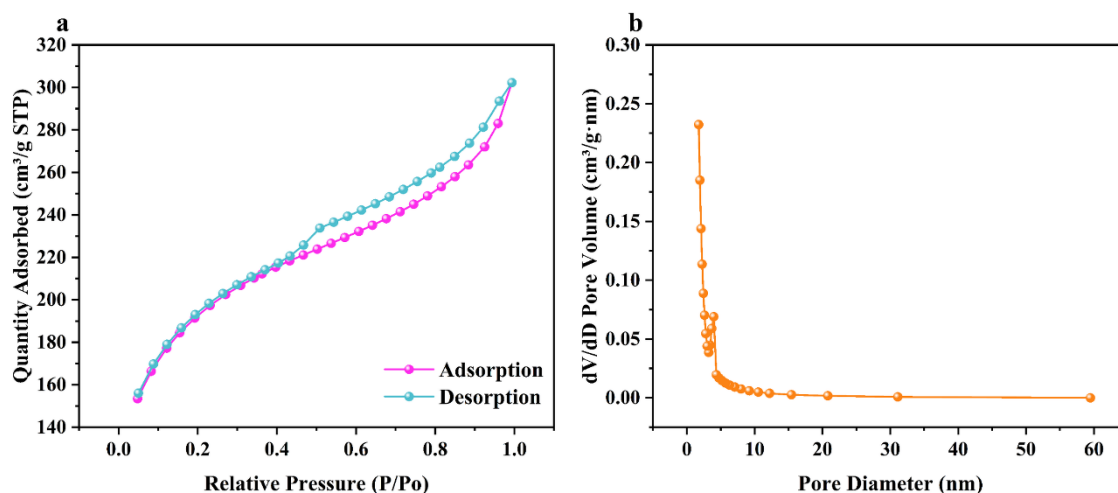
### 3.6.2. Pore Structure Analysis by BET

The specific surface area and pore structure of the materials were analyzed by N<sub>2</sub> adsorption–desorption tests at 77 K.

Both BC and Fe-BC exhibited Type IV isotherms with H4-type hysteresis loops in the relative pressure range of 0.4–1.0, indicating the coexistence of micropores and mesopores. After iron modification, the BET specific surface area decreased from 642.75 m<sup>2</sup>/g to 550.20 m<sup>2</sup>/g, with a corresponding decrease in total pore volume. The dominant mesopore size remained centered at approximately 4.59 nm. The N<sub>2</sub> adsorption–desorption isotherms and pore-size distribution curves of Fe-BC and BC are shown in Figures 10 and 11, respectively.



**Figure 10.** Pore structure analysis: (a) N<sub>2</sub> adsorption–desorption isotherms and (b) BJH pore size distribution curves of Fe-BC.

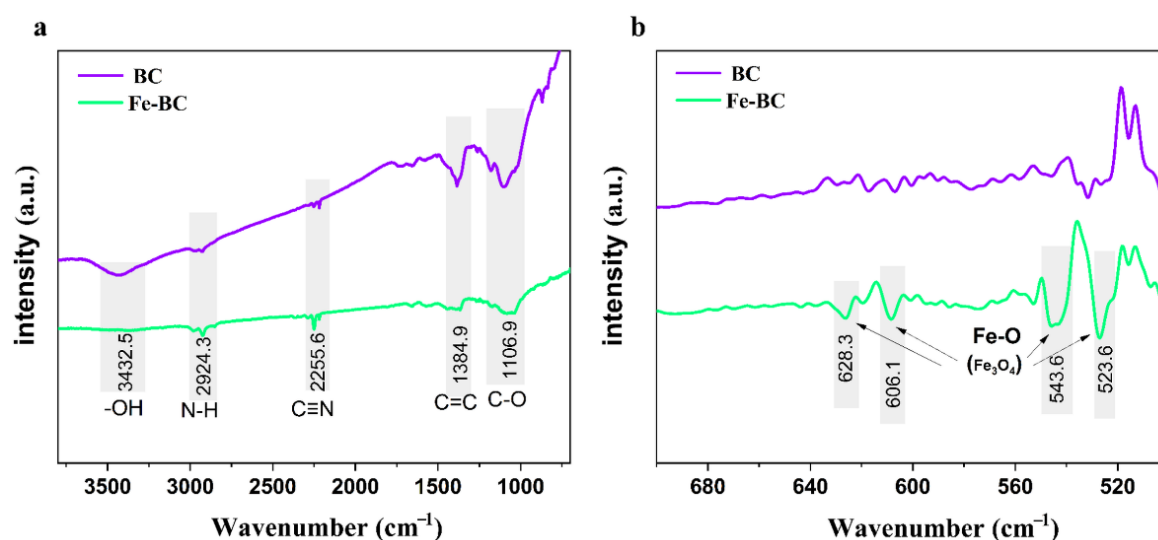


**Figure 11.** Pore structure analysis: (a) N<sub>2</sub> adsorption–desorption isotherms and (b) BJH pore size distribution curves of BC.

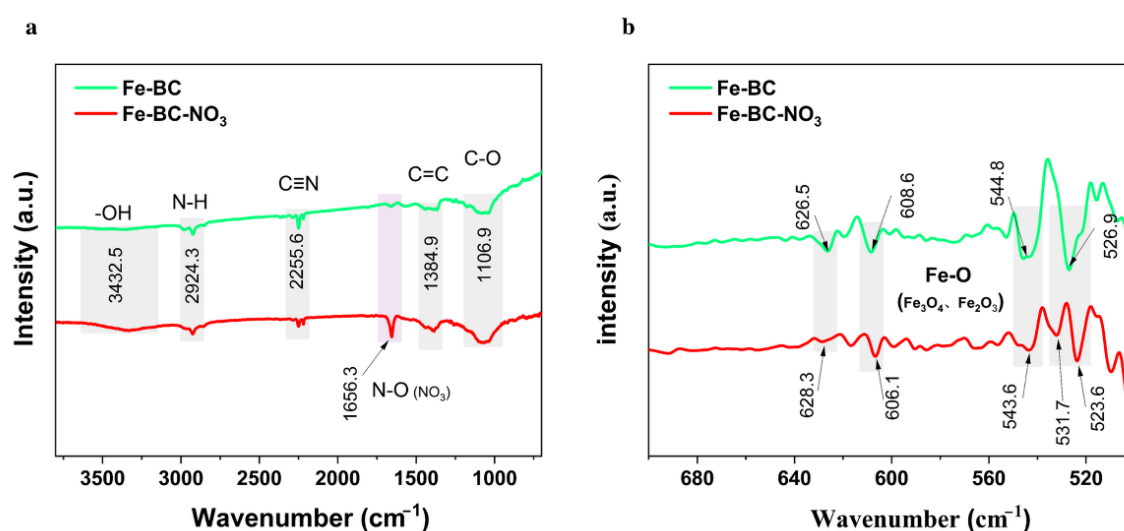
### 3.6.3. Functional Group Analysis by FTIR

The surface functional groups of the materials before and after modification and adsorption were characterized by Fourier transform infrared spectroscopy [31]. The FTIR spectra of pristine BC and Fe-BC, as well as Fe-BC before and after nitrate adsorption, are shown in Figures 12 and 13, respectively.

Compared with pristine BC, Fe-BC displayed a new absorption band at 520–640 cm<sup>−1</sup>, assigned to Fe–O vibrations and consistent with iron-oxide loading. After nitrate adsorption, a distinct band appeared at approximately 1656.3 cm<sup>−1</sup> and was attributed to N–O-related vibrations of surface-coordinated nitrate. Similar bands at approximately 1655–1658 cm<sup>−1</sup> have been reported for bridging nitrate species on metal-oxide surfaces [32,33]. Concurrent shifts in the Fe–O region further indicate interaction between nitrate and iron-associated surface sites (Figure 13). These spectral changes support nitrate association with Fe-BC but do not alone establish a unique adsorption geometry.



**Figure 12.** FTIR spectra of pristine BC and Fe-BC: (a) full spectra over 4000–800 cm<sup>-1</sup> and (b) enlarged Fe–O vibration region over 680–500 cm<sup>-1</sup>.



**Figure 13.** FTIR spectra of Fe-BC before and after nitrate adsorption: (a) full spectra over 4000–800 cm<sup>-1</sup> and (b) enlarged Fe–O vibration region over 680–500 cm<sup>-1</sup>.

### 3.6.4. Morphological Observation by SEM

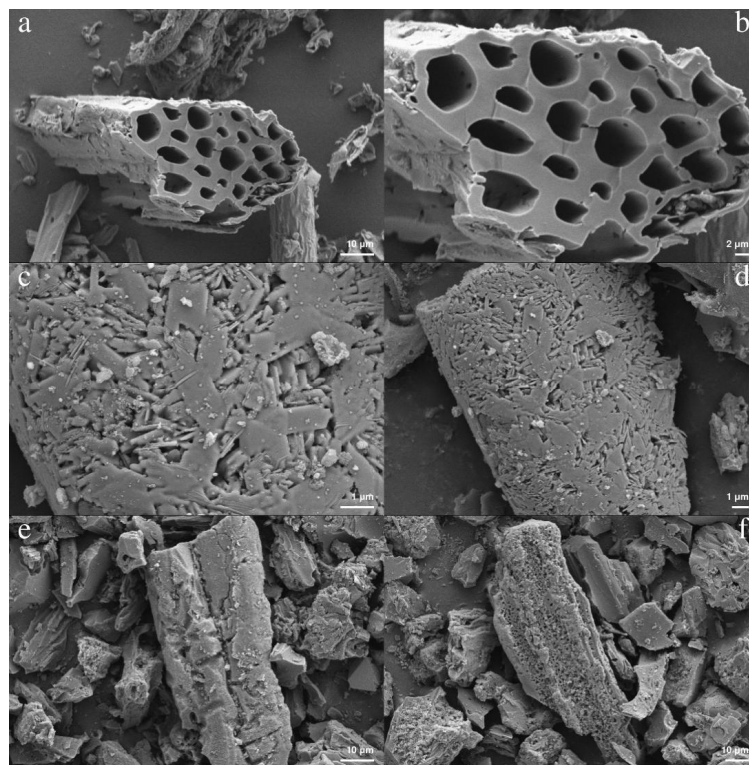
The surface morphology of the materials was observed by scanning electron microscopy.

Pristine BC retained the honeycomb-like multichannel tubular structure inherited from corn straw vascular bundles, with abundant pore structures. After iron modification, the surface of biochar was uniformly covered with nanoscale spherical Fe<sub>3</sub>O<sub>4</sub> aggregates. The SEM morphologies of pristine BC, Fe-BC, and nitrate-loaded Fe-BC are shown in Figure 14.

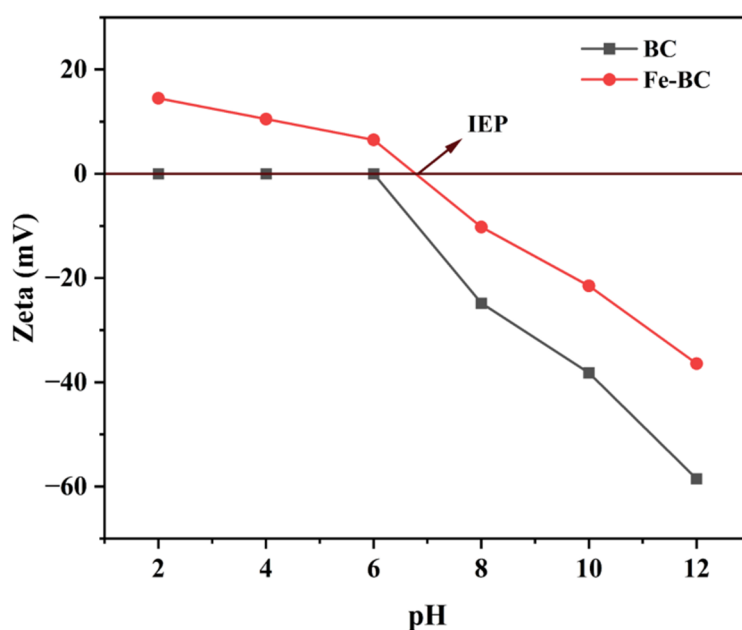
### 3.6.5. Zeta Potential Analysis

The surface charge properties of the materials were characterized by zeta potential measurements.

Pristine BC exhibited a continuously negative zeta potential across the pH range of 4–12. After iron modification, the point of zero charge (pH<sub>pzc</sub>) increased to approximately 7.3. At pH 2, the zeta potential of Fe-BC reached +18 mV. The zeta potentials of pristine BC and Fe-BC as a function of solution pH are shown in Figure 15.



**Figure 14.** SEM micrographs of the adsorbents: (a,b) pristine BC; (c,d) Fe-BC; and (e,f) nitrate-loaded Fe-BC.



**Figure 15.** Zeta potentials of pristine biochar (BC) and iron-modified biochar (Fe-BC) as a function of solution pH.

## 4. Discussion

### 4.1. Mechanism Underlying Preparation Parameter Optimization

The dependence of adsorption performance on iron loading can be interpreted as a balance between the creation of iron-associated sites and the preservation of accessible porosity. Increasing the iron-to-biochar ratio from 1:5 to 1:3 increased nitrate uptake, consistent with a greater density of protonatable Fe–OH sites. Above the optimum, iron-oxide aggregation and pore-mouth blockage likely reduced the fraction of accessible sites. This interpretation is supported by the lower BET surface area after iron modification and by SEM evidence of iron-rich particles on the carbon surface, although direct quantification of iron dispersion would require elemental mapping or surface-sensitive spectroscopy.

The increase in adsorption capacity between 300 and 600 °C likely reflects improved conversion of the iron precursor to crystalline Fe<sub>3</sub>O<sub>4</sub> together with stabilization of the activated carbon framework. At temperatures above 600 °C, particle sintering, loss of oxygen-containing groups, and partial collapse or coalescence of fine pores may offset the benefit of increased crystallinity. Thus, the optimum at 600 °C represents a compromise among iron-phase formation, surface hydroxyl availability, and pore accessibility rather than a simple maximum in either crystallinity or surface area alone.

#### 4.2. Mechanism of Environmental Factor Effects on Adsorption

The pH dependence of nitrate adsorption is closely related to the surface charge of Fe-BC. The measured  $pH_{pzc}$  was approximately 7.3. Below this value, protonation of Fe–OH groups generate Fe–OH<sub>2</sub><sup>+</sup> sites and increases electrostatic attraction toward NO<sub>3</sub><sup>−</sup>. Above pH 7.3, deprotonation reduces positive charge, while OH<sup>−</sup> competes for surface sites, leading to lower uptake. Pristine BC remained negatively charged over the measured range and consequently showed substantially weaker nitrate adsorption. The persistence of some adsorption above the  $pH_{pzc}$  suggests that pore confinement and localized iron-associated interactions may contribute in addition to bulk electrostatics.

For adsorbent dosage, the increase in removal efficiency and the decrease in unit adsorption capacity are typical mass balance phenomena. With the increase of dosage, the total number of available adsorption sites increases, so more nitrate can be removed; however, under a fixed total solute amount, the adsorption sites cannot be fully saturated at high dosage, leading to a decline in unit utilization efficiency. The slowdown of removal efficiency growth above 1 g/L is due to the reduction of bulk solution concentration, which increases the mass transfer resistance and lowers the marginal utilization of adsorption sites.

For initial concentration, a higher initial nitrate concentration creates a larger concentration gradient at the solid–liquid interface, which provides a stronger mass transfer driving force to overcome liquid film resistance and promote nitrate diffusion into internal pore channels. Therefore, the unit adsorption capacity increases with initial concentration. Since the total number of active sites on the adsorbent is fixed, the sites gradually reach saturation at high pollutant loads, resulting in a gradual decrease in removal efficiency.

#### 4.3. Essence of Adsorption Kinetics and Thermodynamics

The pseudo-second-order model yielded higher R<sup>2</sup> values than the pseudo-first-order model, whereas the pseudo-first-order model produced calculated equilibrium capacities closer to the experimental values. This combination suggests that surface-reaction-controlled uptake is important but not exclusive. The rapid initial stage is consistent with external mass transfer and occupation of readily accessible surface sites, whereas the later stage may involve intraparticle diffusion and progressive filling of less accessible pores. Mechanistic interpretation therefore relies on the combined kinetic, surface-charge, FTIR, XRD, pore-structure, and competitive-ion evidence and supports a physicochemical adsorption process involving electrostatic attraction, Fe–OH-associated interactions, and pore filling/diffusion rather than a purely chemisorption-controlled pathway.

The higher Langmuir R<sup>2</sup> values and the increase in  $q_{max}$  from 10.94 to 12.74 mg/g indicate a saturable uptake process whose apparent capacity increases with temperature. Freundlich 1/n values near 0.30 indicate favorable adsorption over the tested concentration range. However, Fe-BC is structurally heterogeneous, and the Langmuir fit should be understood as an effective representation rather than proof that all sites are energetically identical. The observed behavior likely reflects the collective saturation of Fe-associated sites and accessible pore domains.

The negative  $\Delta G$  values indicate thermodynamic favorability under the tested conditions, and their increasing magnitude with temperature is consistent with enhanced uptake at higher temperatures. The positive  $\Delta H$  value (7.11 kJ/mol) indicates a mildly endothermic process. Its relatively small magnitude does not independently support strong chemical bond formation; instead, it is compatible with a combination of electrostatic association, desolvation, weak surface interactions, and pore filling. The positive  $\Delta S$  may reflect release or rearrangement of interfacial water and counterions during nitrate uptake. These thermodynamic parameters should be viewed as apparent values because the equilibrium constant and standard-state treatment strongly influence adsorption thermodynamics [27,28].

#### 4.4. Competitive Adsorption Mechanism of Coexisting Anions

The interference order can be explained by differences in charge density, acid–base speciation, hydration, and affinity for iron-(hydr)oxide surfaces. Phosphate is strongly adsorbed by ligand exchange and can form stable inner-sphere Fe–O–P complexes; carbonate can also interact strongly with positively charged or metal-associated sites.

Their higher affinity accounts for the pronounced inhibition of nitrate uptake. In contrast, chloride and sulfate caused smaller changes under the tested conditions, indicating weaker competition at the concentrations investigated.

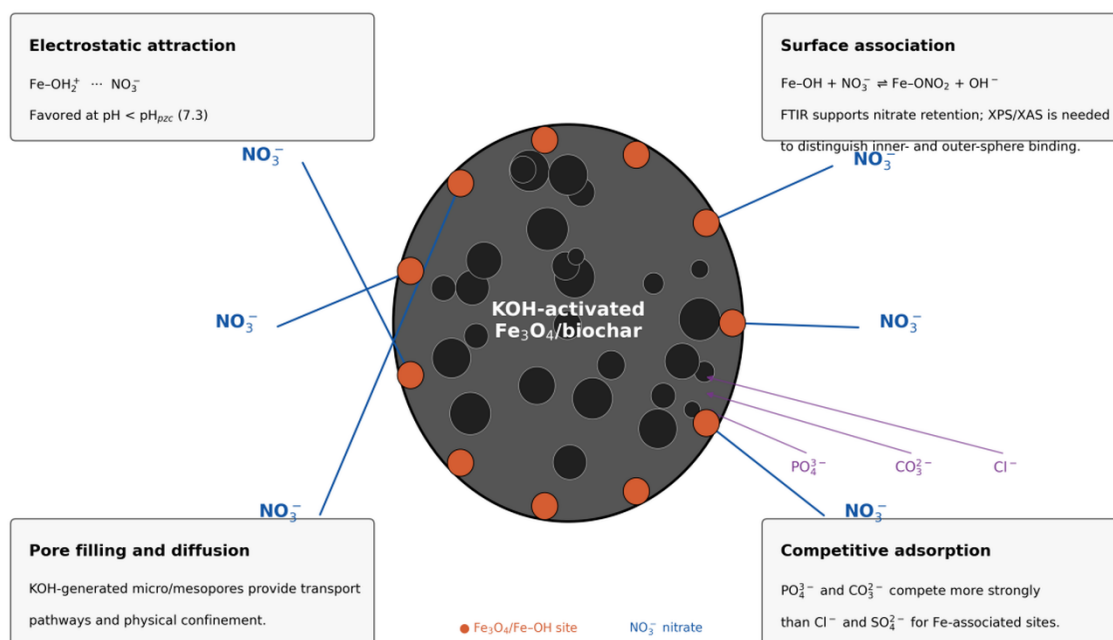
The competitive-ion results support a mechanism in which electrostatic attraction to protonated surfaces is important but not the only contribution. The particularly strong effect of phosphate shows that high-affinity occupation of iron-associated sites can suppress nitrate uptake. For nitrate itself, the present FTIR and zeta-potential data are consistent with surface association, but they are insufficient to establish that inner-sphere complexation is dominant. Direct differentiation among inner-sphere, outer-sphere, and hydrogen-bonded configurations would require XPS, X-ray absorption spectroscopy, or molecular-scale calculations.

#### 4.5. Comprehensive Adsorption Mechanism

Integration of the XRD, BET, SEM, FTIR, zeta-potential, kinetic, isotherm, and competitive-ion results supports a multicomponent nitrate-removal mechanism rather than a single controlling interaction.

First, pH-dependent electrostatic attraction occurs when Fe–OH groups are protonated below the  $pH_{pzc}$ , producing positively charged Fe–OH<sub>2</sub><sup>+</sup> sites. Second, nitrate can associate with iron-oxide surface hydroxyls through outer-sphere attraction, hydrogen bonding, and potentially ligand exchange; the enhanced N–O band after adsorption is consistent with nitrate retention, although direct evidence for a specific coordination geometry is not available. Third, the KOH-developed micro/mesoporous network provides transport pathways and physical confinement. These processes operate concurrently, while phosphate and carbonate compete strongly for iron-associated sites. The proposed adsorption mechanism is summarized schematically in Figure 16.

The maximum Langmuir capacity of Fe-BC (12.74 mg/g) is higher than the 9.35 mg/g reported for acid-protonated iron-based biochar [10] and the approximately 2.0 mg/g reported for iron-modified barley-straw biochar [17]. Nevertheless, some zero-valent-iron/biochar systems show higher apparent nitrate removal because adsorption is coupled with chemical reduction [14–16], so direct capacity comparisons must account for reaction pathway, pH, initial concentration, temperature, adsorbate basis, and model selection. The value of the present material is therefore not solely a record capacity; it lies in the coordinated use of KOH pore development and Fe<sub>3</sub>O<sub>4</sub> functionalization, the systematic optimization of both preparation variables, and the demonstrated operation across pH 2–7 with limited interference from chloride and sulfate.



**Figure 16.** Schematic illustration of the proposed nitrate adsorption mechanisms on Fe-BC, including electrostatic attraction, association with Fe–OH sites, pore filling and diffusion, and competitive adsorption by coexisting anions.

#### 4.6. Research Limitations

Despite the favorable batch adsorption performance and the mechanistic evidence obtained in this study, several limitations restrict direct extrapolation to engineering applications.

First, all adsorption experiments were conducted in well-mixed batch systems under controlled laboratory conditions; dynamic groundwater flow, hydraulic residence time, and porous-medium transport may produce different mass-transfer behavior. Second, the competitive experiments evaluated individual inorganic anions rather than complex mixtures containing natural organic matter, metals, and microorganisms. Third, regeneration and cyclic adsorption were not evaluated in the present study. Accordingly, this work does not claim demonstrated reusability or long-term operational stability. Fourth, iron leaching, spent-adsorbent management, and full preparation costs were not quantified. Finally, the proposed surface-association mechanism is based on conventional characterization and model fitting; direct molecular-scale evidence for nitrate coordination remains unavailable.

#### 4.7. Future Research Directions

Future work should address these limitations before field application of Fe-BC is considered.

Dynamic fixed-bed column experiments should be conducted to obtain breakthrough curves, bed capacities, and service-life estimates under groundwater-relevant flow rates. Regeneration studies should first screen mild alkaline, salt, and other environmentally acceptable desorption solutions and then evaluate at least five adsorption–desorption cycles, reporting capacity retention, mass recovery, iron leaching, and post-cycle XRD/FTIR or surface analysis. Tests in real groundwater should examine combined effects of dissolved organic matter, competing ions, metals, and microorganisms. Finally, XPS, X-ray absorption spectroscopy, and density-functional-theory calculations could be used to resolve adsorption geometry, binding energy, and charge transfer, while life-cycle and economic analyses should evaluate whether the material remains advantageous at scale.

### 5. Conclusions

This study developed an iron-modified, KOH-activated corn straw biochar through chemical activation,  $\text{FeCl}_3$  impregnation, and secondary pyrolysis. The optimal iron-to-biochar mass ratio and secondary pyrolysis temperature were 1:3 and 600 °C, respectively. Under these conditions, crystalline  $\text{Fe}_3\text{O}_4$  was dispersed on a porous carbon matrix with a BET surface area of 550.20  $\text{m}^2/\text{g}$  and a  $\text{pH}_{\text{pzc}}$  of 7.3. Fe-BC achieved a Langmuir maximum nitrate capacity of 12.74  $\text{mg/g}$  at 313 K, nearly fivefold that of pristine biochar, and maintained capacities above 5  $\text{mg/g}$  between pH 2 and 7. Kinetic, isotherm, and thermodynamic analyses indicated a saturable, temperature-favored adsorption process, while phosphate was the strongest competing anion.

The main scientific contribution is the coordinated coupling of KOH-generated pore accessibility with  $\text{Fe}_3\text{O}_4$ -derived surface-charge and hydroxyl functionality in an agricultural-residue adsorbent. The combined evidence supports electrostatic attraction, nitrate association with Fe–OH sites, and pore filling, while also showing that the available data cannot uniquely prove inner-sphere complexation. Thus, Fe-BC is a promising candidate for further development rather than a fully validated engineering material. Regeneration, iron-leaching, multicomponent-water, and continuous-flow studies remain necessary to establish long-term practicality and environmental safety.

#### Author Contributions

Y.L.: conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing—original draft, writing—review & editing. X.L.: investigation, validation, writing—review & editing. C.W.: methodology, validation, writing—review & editing. K.L.: investigation, data curation, writing—review & editing. A.Y.: investigation, resources, writing—review & editing. S.Y.: investigation, data curation, validation, writing—review & editing. H.W.: conceptualization, supervision, project administration, writing—review & editing. C.L.: supervision, validation, writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Not applicable.

#### Informed Consent Statement

Not applicable.



## Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of Interest

The authors declare no conflict of interest.

## Use of AI and AI-Assisted Technologies

The authors confirm that ChatGPT (OpenAI) was used solely as a language-editing and proofreading aid. Its use was limited to improving English grammar, sentence structure, clarity, conciseness, and readability. The tool was not used to generate experimental data, fabricate or alter results, perform statistical analyses, prepare figures, or independently formulate the scientific interpretations and conclusions of the study. Every AI-assisted language revision was carefully reviewed, corrected where necessary, and approved by the authors. The authors take full responsibility for the accuracy, originality, and integrity of the manuscript.

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