

## Article

# Synergistic Effect of Potassium Ferrate and Sodium Hydroxide in Lowering Carbothermal Reduction Temperature: Preparation of Magnetic Zero-Valent Iron-Doped Biochar for Antibiotic Removal

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## Abstract

In this study, a novel low-temperature (300–500 °C) carbothermal reduction route employing potassium ferrate and sodium hydroxide was developed to synthesize magnetic zero-valent iron-doped biochar for removing tetracycline and ciprofloxacin from aqueous solutions. Carbothermal reduction occurred effectively at 400 °C, generating sufficient small reductive molecules for the reduction of iron species into zero-valent iron. This process led to the impregnation of abundant zero-valent iron along with nano-magnetite into the carbon matrix, while nano-magnetite was also dispersed and stabilized on zero-valent iron. Simultaneously, abundant functional groups were formed, contributing to anchoring iron species and adsorbing pollutants. The magnetic biochar exhibited high adsorption capacities for tetracycline (1106.25 mg/g) and ciprofloxacin (182.03 mg/g), along with high saturation magnetization (56.3 emu/g) and superior reusability. Moreover, the magnetic biochar showed broad applicability for efficient removal of tetracycline and ciprofloxacin derivatives. Overall, carbothermal reduction efficiently transformed iron oxides into zero-valent iron at a relatively low temperature, providing a viable approach for manufacturing magnetic biochar doped with zero-valent iron.

**Keywords:** magnetic biochar; tetracyclines; fluoroquinolones



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## 1. Introduction

Antibiotic contamination has posed growing threats to both human health and ecological systems owing to the toxicity, persistence, and bio-incompatibility of antibiotics in aqueous solution [1]. Tetracycline (TC) and ciprofloxacin (CIP) are broad-spectrum antibacterial drugs widely used in the healthcare, animal husbandry, and aquaculture industries [2,3]. To address this issue, banana pseudostem—a widely available agricultural residue rich in lignocellulose—was selected as the biomass precursor for biochar synthesis due to its renewability, low cost, and high carbon content, which favor the generation of porous structures and surface functional groups suitable for adsorption [4]. Effluents containing these contaminants are often discharged into aquatic environments, where they

have been detected in various natural water systems at concentrations ranging from  $\mu\text{g/L}$  to  $\text{mg/L}$ . Adsorption is widely regarded as an effective and eco-friendly approach for contaminant elimination owing to its simple operation, cost-effectiveness, and minimal generation of secondary pollutants.

Zero-valent iron (ZVI)-doped magnetic biochar has garnered significant attention as a cost-effective and efficient adsorbent with superior magnetism, strong affinity, and excellent reducibility [5], rendering it a notable emerging material for wastewater remediation [6]. Significant progress has been made in the synthesis of magnetic nano-ZVI ( $n\text{ZVI}$ )-doped biochar, primarily via impregnation of iron species onto a biochar matrix followed by the reduction of sodium borohydride ( $\text{NaBH}_4$ ) [7]. However, the use of  $\text{NaBH}_4$  poses notable challenges due to its inherent high toxicity [8], flammability, and potential environmental risks. Alternatively, carbothermal reduction provides an environmentally friendly approach involving the reduction of high-valence iron into ZVI during thermal decomposition [9,10], where in situ-generated carbon monoxide ( $\text{CO}$ ), hydrogen ( $\text{H}_2$ ), methane ( $\text{CH}_4$ ), ethylene ( $\text{CH}_2=\text{CH}_2$ ), and small molecules play a crucial role in the reduction [6]. Several magnetic  $n\text{ZVI}$ -doped biochars have been synthesized by direct carbothermal reduction at  $900^\circ\text{C}$  using different iron precursors for the removal of Arsenic (V) ( $\text{As}^{5+}$ ) [11] and Uranium (VI) ( $\text{U}^{6+}$ ) [12,13];  $n\text{ZVI}$  participated in their adsorptions via a reduction mechanism. However, only moderate adsorption capabilities were achieved for these magnetic  $n\text{ZVI}$ -doped biochars, limiting their broader applicability in wastewater treatment systems.

Over the past decade, adsorption-inspired engineering has advanced the potential of magnetic ZVI-doped biochar for aqueous contaminant removal by incorporating additional adsorption sites that can work synergistically with the magnetic biochar's inherent active sites. For instance, ball-milling was applied to engineer magnetic  $\text{Fe}^0$ -doped biochar prepared by pyrolyzing corn straw biomass and potassium ferrate ( $\text{K}_2\text{FeO}_4$ ) at  $700^\circ\text{C}$  for the removal of Chromium (VI) ( $\text{Cr}^{6+}$ ) and TC. This process simultaneously enhanced the specific surface area and iron species exposure, achieving adsorption capabilities of  $117.49$  ( $\text{Cr}^{6+}$ ) and  $90.31$   $\text{mg/g}$  (TC) [14].  $\text{NH}_3$ -inducing N-doping was employed to enhance the adsorption performance of  $n\text{ZVI}$ -doped magnetic biochar prepared at  $1000^\circ\text{C}$  for Chromate ion ( $\text{CrO}_4^{2-}$ ) removal, in which  $n\text{ZVI}/\text{-NH-}$  contributed to the reduction of  $\text{CrO}_4^{2-}$  and positively charged  $\text{-N}^+=$  adsorbed  $\text{CrO}_4^{2-}$  via electrostatic interaction [15]. Ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) and lignin were calcined at  $900^\circ\text{C}$  to prepare  $\text{Fe}_3\text{C}$ -doped magnetic ZVI biochar for trichloroethene removal from anaerobic water [16].  $\text{Fe}_3\text{C}$  served as the predominant species for the reductive dechlorination of trichloroethene, thereby facilitating its effective removal. Notably, high temperatures are necessary to generate sufficient reductive molecules for ZVI formation, which concurrently reduce surface functionality and increase the energy input required. This limitation restricts the broad application potential of magnetic ZVI biochar for removing polyfunctional pollutants, particularly antibiotics.

Herein, we propose a novel low-energy pyrolysis magnetization method using  $\text{K}_2\text{FeO}_4$  and  $\text{NaOH}$  to synthesize versatile magnetic ZVI-doped biochar for TC and CIP removal.  $\text{NaOH}$  was expected to promote biomass degradation and reductive molecule formation at moderately low temperatures [17,18], thereby enabling efficient transformation of iron oxides into ZVI.  $\text{K}_2\text{FeO}_4$  could facilitate the oxidative degradation of biomass, introducing oxygen-containing groups during pyrolysis. Meanwhile, the inherent basicity of  $\text{K}_2\text{FeO}_4$  could also accelerate the regeneration of reductive molecules for reducing iron species into ZVI. Moreover,  $\text{NaOH}$  might stabilize  $\text{K}_2\text{FeO}_4$  while enhancing its oxidative function, leading to a synergistic effect in this pyrolysis system for producing magnetic ZVI-doped biochar. This study focused on fabricating magnetic ZVI-doped biochar through carbothermal reduction at a relatively low temperature, aiming to minimize energy consumption while improving the potential for antibiotic adsorption. The

findings will provide guidance for preparing diverse magnetic biochars via oxidative pyrolysis magnetization and advance our understanding of ZVI-doped magnetic biochar synthesis through carbothermal reduction.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

All chemicals and materials used in this study are listed in the Supplementary Materials (SM).

### 2.2. Magnetic Biochar Preparation and Characterization

The full experimental protocols for magnetic biochar preparation and characterization are provided in the Supplementary Materials.

### 2.3. The Adsorption and Regeneration of Magnetic Biochar

The detailed experimental procedures for the adsorption and regeneration of magnetic biochars are presented in the Supplementary Materials.

## 3. Results and Discussion

### 3.1. Properties of Magnetic Biochars

#### 3.1.1. Chemical Composition and Surface Property

As expected, as well as K, other common elements (C, H, N, O, Fe) were detected on the magnetic biochars (Table 1). Additional Na was also found on MMB400, on which it is believed to exist as -ONa and -CO<sub>2</sub>Na [19]. This suggests that NaOH plays an important role in the regulation of the acid–base properties of magnetic biochar in pyrolysis. Obviously, MMB400 has a higher Fe content than MB400, with lower content of O, accounting for increased Fe<sup>0</sup> formation. Moreover, MMB400 possessed a lower H/C ratio compared to MB400 ( $1.12/20.19 = 0.055$  vs.  $1.75/28.56 = 0.061$ ); therefore, an increased degree of aromatization was achieved during pyrolysis with NaOH even at a relatively low temperature. Comparable N/C ratios ( $0.081/28.56 = 0.028$  vs.  $0.55/20.19 = 0.027$ ) were obtained for both magnetic biochars, suggesting N-functional groups were less influenced by NaOH during pyrolysis.

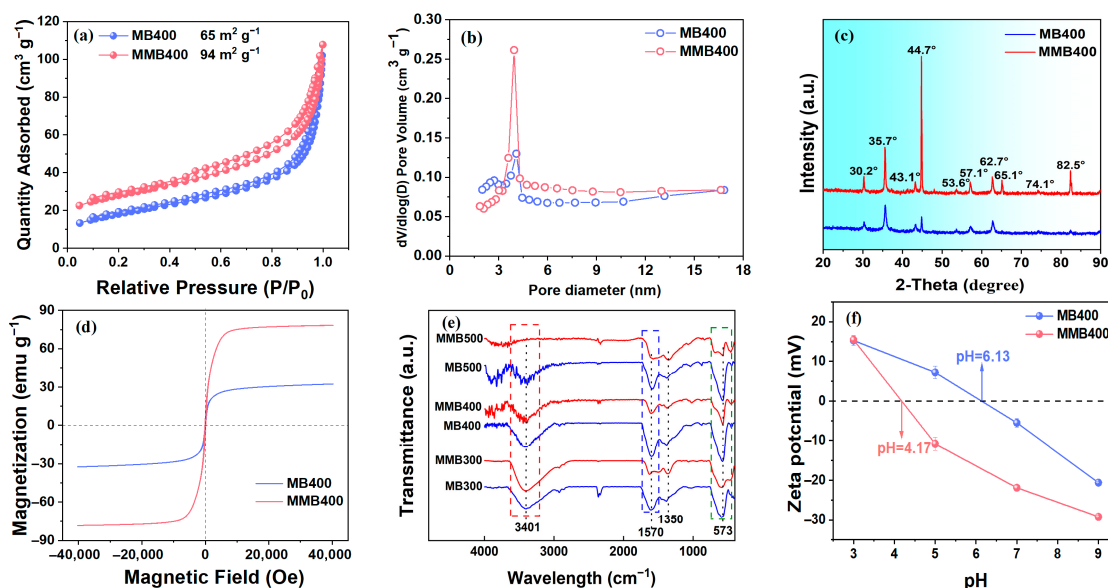
**Table 1.** Element composition, surface area, and pore characteristics of the magnetic biochars.

| Biochar | Elements (wt%) |      |       |      |       |      |      | Surface Parameters      |                         |         |
|---------|----------------|------|-------|------|-------|------|------|-------------------------|-------------------------|---------|
|         | C              | H    | O     | N    | Fe    | Na   | K    | SSA (m <sup>2</sup> /g) | PV (cm <sup>3</sup> /g) | PD (nm) |
| MB400   | 28.56          | 1.75 | 26.79 | 0.81 | 40.54 | 0.00 | 0.35 | 65.14                   | 0.0808                  | 4.57    |
| MMB400  | 20.19          | 1.12 | 18.22 | 0.55 | 53.79 | 0.21 | 0.20 | 94.44                   | 0.0914                  | 4.71    |

(SSA: Specific surface area, PV: Pore volume, PD: Pore diameter).

The surface area and porosity of the adsorbent are critical factors influencing adsorption efficiency. In this study, the specific surface areas and pore characteristics of the magnetic biochars were evaluated using Brunauer–Emmett–Teller (BET) analysis. The findings are detailed in Table 1 and illustrated in Figure 1a. MB400 and MMB400 possessed type III adsorption/desorption isotherms, which are specific to mesoporous adsorbents according to the IUPAC classification [20]. Slightly increased specific surface area and pore volume were found in MMB400 compared to MB400. Meanwhile, a slightly higher pore diameter was observed for MMB400 than MB400. Pore size distribution curves (Figure 1b) revealed that mesoporous structures (>3.20 nm) were created on MMB400 due to NaOH-induced expansion during pyrolysis, with the predominant pore size centered

around 4.08 nm. These results indicate that NaOH co-pyrolysis moderately enhances the physical properties of magnetic biochar, as substantial volatiles were generated for pore formation [18]. These improvements should be conducive to pollutant adsorption, as mass transfer is strengthened and the number of active adsorption sites is increased.



**Figure 1.** Characterization of magnetic biochars MB400 and MMB400. N<sub>2</sub> physisorption isotherms (a), pore diameter distribution plots (b), XRD spectra (c), hysteresis loops (d), FTIR spectra (e), Zeta potentials (f).

### 3.1.2. Crystalline and Magnetism

The XRD spectra are shown in Figure 1c. The diffraction peaks at 30.2°, 35.7°, 43.1°, 53.6°, 57.1°, 62.7°, and 74.1° were observed on MB400, indicating that Fe<sub>3</sub>O<sub>4</sub> and/or γ-Fe<sub>2</sub>O<sub>3</sub> [21] were generated during the pyrolysis of banana pseudostem with K<sub>2</sub>FeO<sub>4</sub>. A weak diffraction peak of ZVI at 44.8° was also detected on MB400 [22], likely resulting from reduction by reactive intermediates enhanced by basic K<sub>2</sub>FeO<sub>4</sub> [17]. The characteristic peaks corresponding to crystalline cellulose and carbon were only weakly detected, indicating the complete conversion of biomass into amorphous carbon. Similar diffraction peaks were also observed on MMB400, but much stronger intensities were recorded. The diffraction peaks of Fe<sup>0</sup> (44.8°, 65.1°, and 82.5°) were notably increased and exceeded those of Fe<sub>3</sub>O<sub>4</sub> and/or γ-Fe<sub>2</sub>O<sub>3</sub> (30.2°, 35.7°, 43.1°, 53.6°, 57.1°, 62.7°, and 74.1°). This indicated that NaOH further facilitated the reduction of Fe<sup>6+</sup> into nZVI during pyrolysis at a relatively low temperature (400 °C), which is in contrast to previous works in which high temperatures (>600 °C) were usually required to efficiently reduce iron salts into Fe<sup>0</sup> [8]. This might be because reductants such as CO, H<sub>2</sub>, CH<sub>4</sub>, and other small organic molecules were generated in large quantities, which allowed for FeO<sub>4</sub><sup>2-</sup> to be efficiently reduced into Fe<sup>0</sup>, with co-promotion of NaOH. In this process, the formation of Fe<sup>0</sup> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles that are uniformly dispersed and fixed on the carbon matrix endows the biochar with magnetic properties, providing the basis for easy separation and recovery. This was also proven by the fact that alkali could accelerate the gasification of biomass, leading to an increase in the generation of reductive molecules including H<sub>2</sub> [17] and CO [23]. It can be deduced that NaOH promoted the gasification of biomass and produced reductants [6], facilitating the efficient transformation of FeO<sub>4</sub><sup>2-</sup> into Fe<sup>0</sup> through synergy with K<sub>2</sub>FeO<sub>4</sub>, even at a relatively low temperature.

The magnetic hysteresis curves revealed that MMB400 exhibited significantly higher saturation magnetization than MB400 (Figure 1d), further confirming the substantial gener-

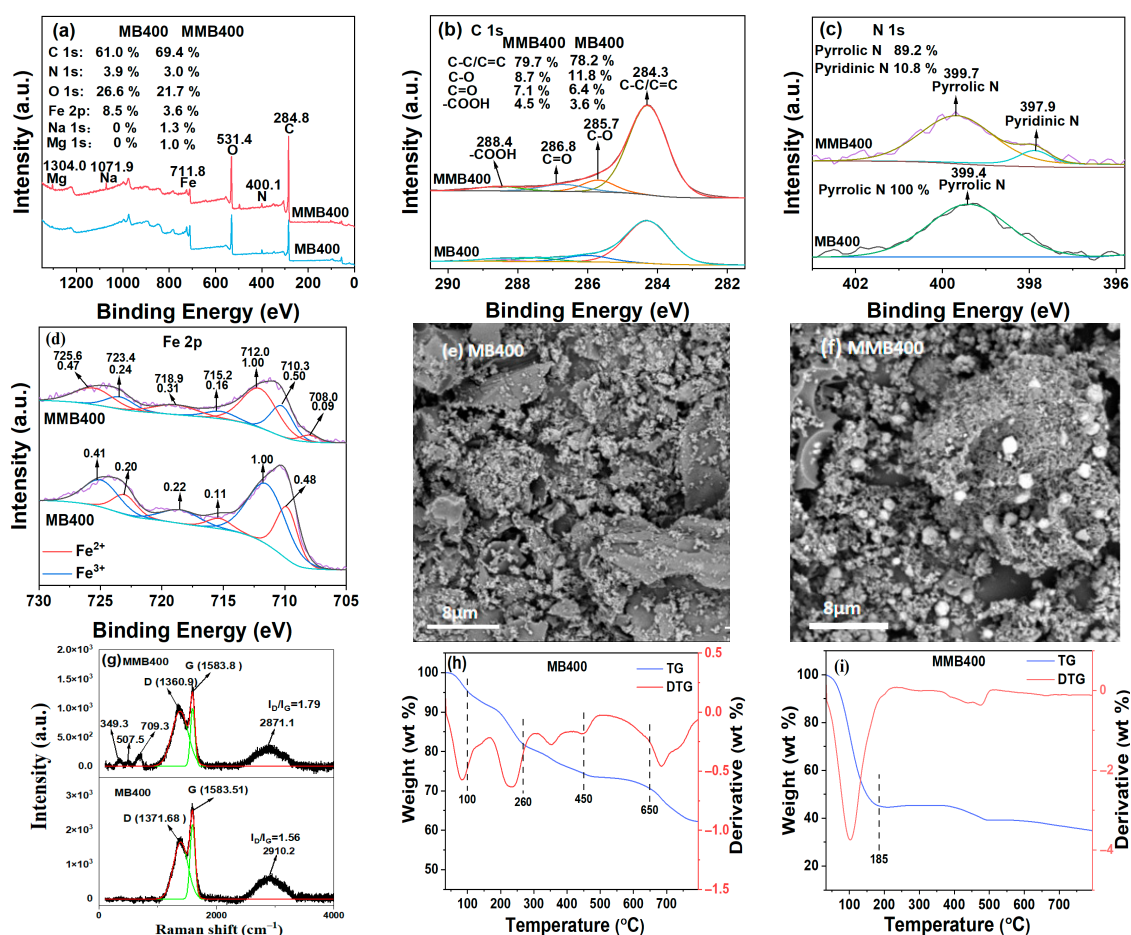
ation of magnetic iron species, including ZVI and  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ , due to the co-promotion effect of NaOH. Notably,  $\text{FeO}_4^{2-}$  was efficiently transformed into ZVI during pyrolysis with NaOH, underscoring the indispensability of NaOH for enhancing saturation magnetization. Additionally, extensive decomposition of banana pseudostem also led to a highly carbonized matrix, resulting in a reduction in carbon content and an increase in the number of magnetic irons on MMB400. Overall, the combination of  $\text{K}_2\text{FeO}_4$  and NaOH efficiently accelerated biomass pyrolysis, providing an effective method for preparing biochar with high magnetic performance at a relatively low temperature.

### 3.1.3. Functional Groups

The FTIR spectra of MBs and MMBs (Figure 1e) exhibited primary peaks at approximately 3401, 1570, 1350, and 573  $\text{cm}^{-1}$ , which were assigned to the -OH, C=O/C=C, -OH, and Fe-O groups [24,25], respectively. From these spectra, it can be observed that MMB300 had a stronger -OH peak intensity than MB300, whereas the MMB pyrolyzed at higher temperatures possessed weaker intensity than the corresponding MB. Therefore, NaOH-promoted pyrolysis could generate -OH at 300 °C but caused intensive dehydroxylation at higher temperatures. The Fe-O peak significantly decreased for MMB when the temperature was elevated from 300 to 500 °C, while it remained almost unchanged for MB prepared within this temperature range. Moreover, the peak intensity for Fe-O was obviously reduced on MMB compared to the corresponding MB pyrolyzed at the same temperature. This is probably largely because of the reduction of iron oxides into  $\text{Fe}^0$  with promotion of NaOH, particularly at temperatures exceeding 400 °C, where the reduction process became more pronounced. The XRD spectra of MMB400 supported this observation, displaying prominent diffraction peaks for  $\text{Fe}^0$ , in contrast to the significantly weaker peaks attributed to  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$  (Figure 1c). According to previous work [17,18], alkaline conditions could enhance the decomposition of biomass into reductive molecules, which subsequently facilitates the reduction of iron salts to ZVI. Thus, the NaOH/ $\text{FeO}_4^{2-}$  combination facilitated the decomposition of biomass into reductive molecules during pyrolysis, facilitating efficient reduction of  $\text{FeO}_4^{2-}$  into  $\text{Fe}^0$  at a relatively low temperature. Additionally, MMB400 exhibited a significantly higher negative charge than MB400 across a pH range of 4.0–9.0, probably due to the introduction of -OH and -COOH. Overall, this process enabled multilevel optimization of the physicochemical properties, allowing the preparation of high-performance magnetic biochar.

The surface characteristics of the magnetic biochars were analyzed via XPS (Figure 2). MB400 primarily consisted of C, O, N, and Fe (Figure 2a). Significantly, MMB400 exhibited not only C, O, N, and Fe, but also detectable amounts of Mg and Na, which likely existed as -OMg and -ONa. This suggested that NaOH modification promoted the formation of additional carboxylate and aloxylate groups, leading to increased negative charge on MMB400 (Figure 1f). It is worth noting that the Mg detected in MMB400 originates from the biomass feedstock, and its retention is facilitated by NaOH-assisted pyrolysis, which promotes the conversion and stabilization of Mg species (e.g.,  $\text{Mg}(\text{OH})_2$ , -OMg, and  $\text{MgFe}_2\text{O}_4$ ) within the biochar matrix, thereby preventing the volatilization losses observed in MB400. Meanwhile, the surface Fe/C ratio measured using XPS is lower for MMB400 than MB400, likely due to the surface enrichment of Mg and Na, which affects the Fe distribution on the outermost layers. This explains the apparent discrepancy with bulk elemental analysis (Table 1), as XPS probes only the top ~5–10 nm of the material. Consistent with the elemental analysis, the O content on MMB400 was significantly lower than that on MB400 due to reduction of iron oxides into ZVI. The C 1s spectra revealed that both magnetic biochars contained similar oxygen-containing functional groups, including C-O, C=O, and -COOH, in addition to C-C/C=C groups (Figure 2b). Compared to MB400,

MMB400 exhibited increased abundances of C=O (7.1% vs. 6.4%) and -COOH (4.5% vs. 3.6%) functional groups, likely resulting from NaOH-induced oxidation during pyrolysis. These functional groups are expected to anchor iron oxides through complexation or hydrogen bonding, while also facilitating the adsorption of TC and CIP via hydrogen bonding interactions. The N 1s spectra showed that a pyrrolyl peak around 399.4 eV [26,27] was observed on MB400, whereas two peaks at about 397.9 and 399.7 eV, attributed to pyridinyl and pyrrolyl, respectively, were detected on MMB400 (Figure 2c). Therefore, the NaOH engineering facilitated the formation of pyridine rings during pyrolysis.



**Figure 2.** The XPS spectra (a–d), SEM images (e,f), Raman spectra (g), and thermogravimetric analysis (h,i) of the magnetic biochars.

The Fe 2p spectra showed that the magnetic biochars possessed Fe<sup>2+</sup> signatures (710.3 and 723.4 eV) and Fe<sup>3+</sup> peaks (712.3 and 725.6 eV), with their satellite features at 715.2 and 718.9 eV (Figure 2d). The peak intensity ratios of Fe<sup>2+</sup> to Fe<sup>3+</sup> were all approximately 1/2, indicating that magnetic Fe<sub>3</sub>O<sub>4</sub> was the dominant iron species on the surface. Additionally, a weak peak corresponding to ZVI at 708.0 eV was detected on MMB400, suggesting that a small amount of ZVI was also present, likely coated with iron oxides [28]. In contrast, ZVI was scarcely detected on the surface of MB400. These findings suggest that ZVI might act as a support for dispersing Fe<sub>3</sub>O<sub>4</sub>, in addition to the carbon matrix [29], thereby reducing Fe<sub>3</sub>O<sub>4</sub> aggregation and enhancing its contribution to pollutant adsorption. Overall, the ZVI-dispersed Fe<sub>3</sub>O<sub>4</sub> and abundant oxygen-containing groups on the surface are expected to synergistically enhance the adsorption of TC and CIP by ZVI. It should be noted that the magnetic iron species on the magnetic biochars were primarily composed of Fe<sub>3</sub>O<sub>4</sub> and Fe<sup>0</sup> rather than γ-Fe<sub>2</sub>O<sub>3</sub>.

### 3.1.4. Morphology and Carbon Structure

SEM characterization of MB400 revealed the formation of irregularly shaped micro-particles with a range of sizes (Figure 2e). Additionally, nano-iron oxides were observed to be dispersed on the biochar matrix, though some degree of aggregation occurred due to excessive doping of iron oxides. Furthermore, porous structures were formed on both the carbon matrix and iron oxides, providing pathways for the transfer of the adsorbate into MB400. Size-variable micro-particles were also observed for MMB400, with iron nanoparticles being heavily doped (Figure 2f). Sphere-like iron micro-particles with varying sizes were well distributed on the biochar matrix. Porous honeycomb structures were formed on MMB400, a process facilitated by the addition of NaOH even at relatively low temperatures. These abundant porous structures should provide internal active adsorption sites for the adsorption of pollutants. The SEM image of regenerated MMB400 (Figure S3) shows that the morphology and porous structure remain largely unchanged, indicating good structural stability after repeated adsorption–desorption cycles.

Raman spectroscopy was used to analyze the molecular structure of the magnetic biochars, as illustrated in Figure 2g. Distinct D bands ( $1360.9$  or  $1371.7\text{ cm}^{-1}$ ) and G bands ( $1583.8$  or  $1583.5\text{ cm}^{-1}$ ) [24] were observed in both magnetic biochars. The D band represents  $\text{sp}^3$  hybridized carbon as well as disordered  $\text{sp}^2$  carbon structures, while the G band is associated with graphitic carbon. Additionally, a 2D band, typically observed around  $2871.7$  or  $2910.2\text{ cm}^{-1}$ , was also detected, further confirming the presence of a highly crystalline graphite structure. These findings indicated the successful formation of graphitic domains within the biochar matrix, highlighting the effectiveness of the synthesis process in promoting graphitization even at a relatively low temperature. The  $\text{Fe}_3\text{O}_4$  bands around  $349.3$ ,  $507.5$ , and  $709.3\text{ cm}^{-1}$  can clearly be observed on MMB400 [30], whereas they are hardly detectable on MB400. Therefore, the NaOH modification significantly enhanced the transformation of  $\text{FeO}_4^{2-}$  into highly crystalline  $\text{Fe}_3\text{O}_4$  as well as nZVI, which aligns well with the XRD characterization results.

### 3.1.5. Thermogravimetric Analysis of Pyrolysis

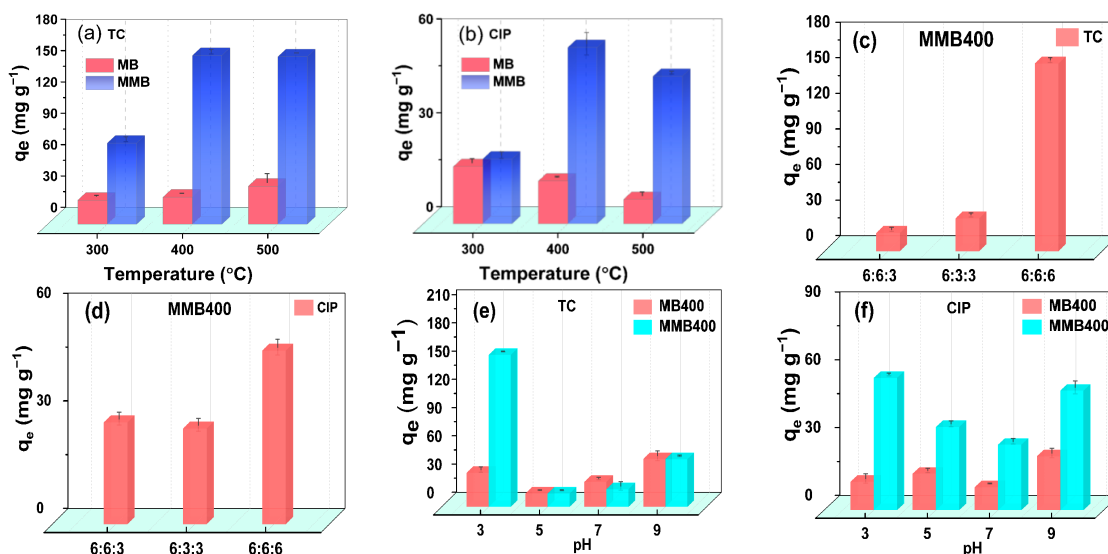
Thermogravimetric analysis was used to assess the pyrolysis process of the blended precursors [31]. Distinctly differentiated degradation processes were observed for the banana/ $\text{K}_2\text{FeO}_4$  and banana pseudostem/ $\text{K}_2\text{FeO}_4$ /NaOH systems. Five degradation stages were identified for the banana pseudostem/ $\text{K}_2\text{FeO}_4$ :  $<100\text{ }^\circ\text{C}$ ,  $100\text{--}260\text{ }^\circ\text{C}$ ,  $260\text{--}450\text{ }^\circ\text{C}$ ,  $450\text{--}650\text{ }^\circ\text{C}$ , and  $650\text{--}800\text{ }^\circ\text{C}$  (Figure 2h). These stages could correspond to crystalline water evaporation, hemicellulose degradation, cellulose decomposition, and carbonization, respectively [32]. In particular, a smooth degradation state was observed at  $450\text{--}650\text{ }^\circ\text{C}$ , likely due to the formation of a carbon structure through the reconstruction of small versatile molecules. The decomposition of the banana pseudostem/ $\text{K}_2\text{FeO}_4$ /NaOH consisted of only two stages, which occurred below and above  $185\text{ }^\circ\text{C}$  (Figure 2i), which could correspond to biomass (hemicellulose, cellulose, lignin) decomposition and carbonization, respectively. Notably, a rapid weight loss to 45.2% occurred at  $180\text{ }^\circ\text{C}$ , followed by a gradual decrease to 34.9% at  $800\text{ }^\circ\text{C}$ . This indicated that the decomposition of biomass and the transformation of  $\text{FeO}_4^{2-}$  into iron species were efficiently accelerated by NaOH even at low temperatures. This phenomenon could be attributed to NaOH's dual function in promoting dehydration and decarboxylation, while simultaneously generating reductive molecules [18] and enabling efficient  $\text{K}_2\text{FeO}_4$  reduction. As demonstrated above, a significant amount of ZVI was generated alongside  $\text{Fe}_3\text{O}_4$  in the pyrolysis system with NaOH and  $\text{K}_2\text{FeO}_4$  at  $400\text{ }^\circ\text{C}$ . These results demonstrate that  $\text{K}_2\text{FeO}_4$  and NaOH synergistically facilitate the rapid decomposition of banana pseudostem into small reductive molecules,

enabling the efficient reduction of  $K_2FeO_4$  into ZVI for synthesizing magnetic biochar via low-temperature pyrolysis.

### 3.2. TC and CIP Adsorption

#### 3.2.1. Pyrolysis Temperature Effect on Adsorption Performance

The pyrolysis temperature fundamentally controlled the biomass reaction with  $K_2FeO_4$  and NaOH, markedly affecting the magnetic biochar's properties and adsorption capacity. To achieve optimal adsorption and magnetic performance, a temperature range of 300–500 °C was investigated. The adsorption capacity of MB for TC showed a gradual increase, rising from 22.55 to 36.49 mg/g with increasing pyrolysis temperature (Figure 3a). In comparison, the adsorption capacity of MMB for TC exhibited a significant increase from 77.69 to 161.22 mg/g as the temperature was raised from 300 to 400 °C, but remained nearly constant with a further temperature increase to 500 °C. The improved adsorption performance likely resulted from enhanced impregnation of  $Fe^0$ -dispersed  $Fe_3O_4$  at relatively high temperatures (400–500 °C). A rise in temperature from 300 to 500 °C led to a reduction in the adsorption capacity of MB for CIP (Figure 3b). In contrast, the adsorption capacity of MMB for CIP increased from 20.67 to 55.29 mg/g when the temperature was increased from 300 to 400 °C, followed by a slight decline to 47.05 mg/g at 500 °C. Clearly, MMB shows consistently superior adsorption for TC and CIP compared to MB, with 400 °C yielding the highest adsorption capacity. This evidently demonstrates that the addition of NaOH during pyrolysis enhances adsorption due to the formation of nZVI, -Omg, and -ONa. Consequently, the synthesized magnetic biochars produced at 400 °C (MB400 and MMB400) were selected for further investigation of adsorption behavior in subsequent experiments.



**Figure 3.** Effects of biomass treatment conditions and adsorption parameters on the adsorption capacity of TC and CIP. (a,b) Pyrolysis temperature and composition of biomass/NaOH/ $K_2FeO_4$  (6/6/6 g/g/g). (c,d) Effects of NaOH and  $K_2FeO_4$  dosages (100  $mg\ L^{-1}$  contaminant, pH 3.0, 0.5  $g\ L^{-1}$  adsorbent, 24 h, 25 °C). (e,f) Influence of solution pH (100  $mg\ L^{-1}$  contaminant, 0.5  $g\ L^{-1}$  adsorbent, 24 h, 25 °C).

#### 3.2.2. Effect of $K_2FeO_4$ and NaOH Dosages on Adsorption Capability

As NaOH and  $K_2FeO_4$  could simultaneously accelerate the decomposition of biomass during pyrolysis, their dosages were evaluated. The TC adsorption capacity significantly dropped from 161.22 to 14.04  $mg\ g^{-1}$  when the ratio of NaOH to banana pseudostem and  $K_2FeO_4$  reduced from 6/6/6 to 6/6/3 g/g/g (Figure 3c). When the ratio of  $K_2FeO_4$  to banana pseudostem and NaOH was reduced from 6/6/3 to 3/6/3 g/g/g, the adsorp-

tion of TC increased to 26.35 mg/g. Consistent with this trend, the adsorption performance for CIP showed a reduction from 55.29 to 28.35 mg/g when the NaOH/banana pseudostem/ $K_2FeO_4$  ratio was adjusted to 3/6/6. When the ratio of  $K_2FeO_4$  to banana pseudostem and NaOH was reduced from 6/6/3 to 3/6/3, the adsorption capacity for CIP remained nearly constant. Therefore, the optimal ratio of  $K_2FeO_4$  to banana pseudostem and NaOH was identified as 6/6/6 g/g/g, which not only maximized the adsorption of TC and CIP but also resulted in high saturation magnetization (56.3 emu/g). These results demonstrate that NaOH and  $K_2FeO_4$  play pivotal synergistic roles in enhancing magnetic biochar's adsorption performance for TC and CIP by collectively optimizing its physicochemical characteristics.

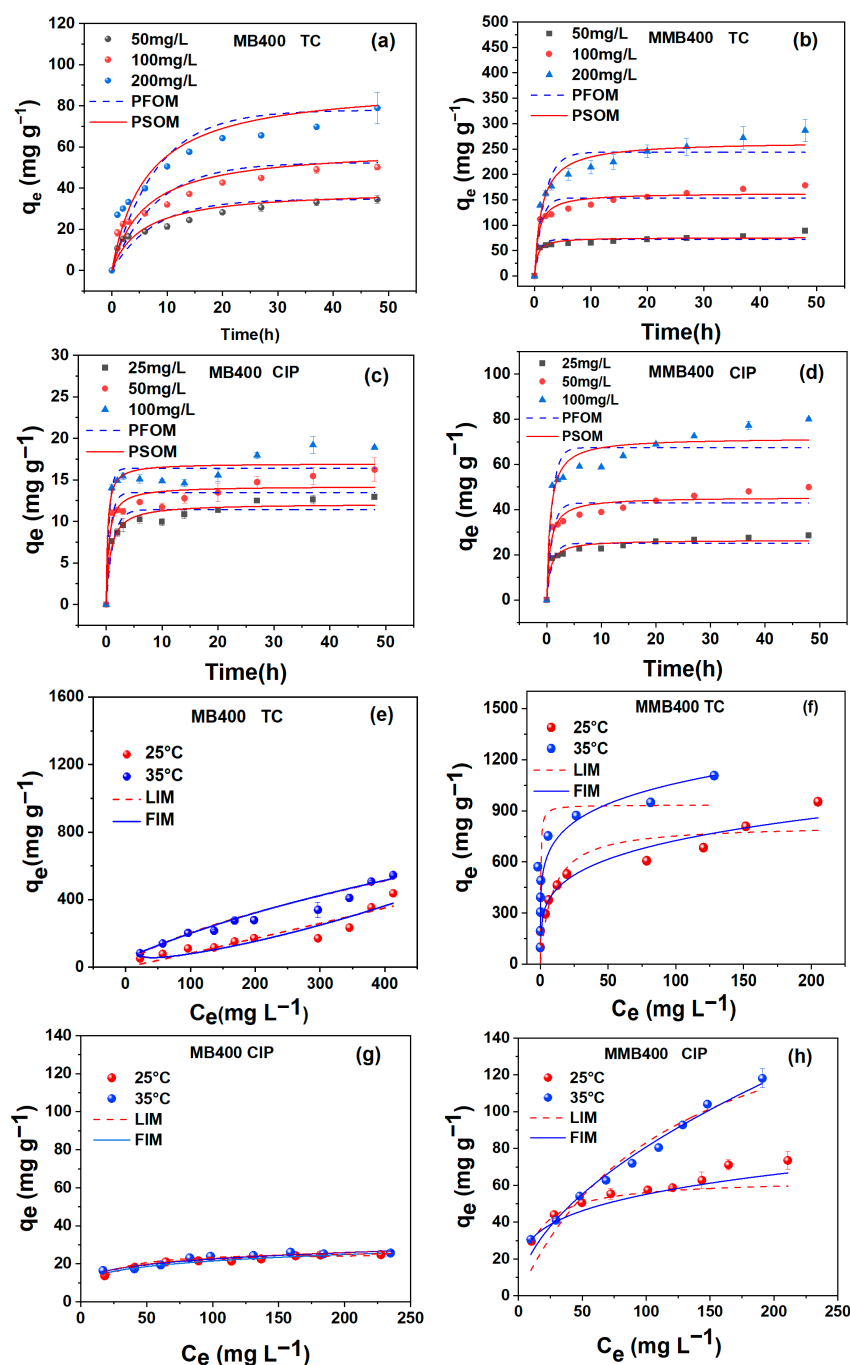
### 3.2.3. Influence of Solution pH on Adsorption Performance

Since the characteristics of pollutant and magnetic biochar were simultaneously influenced by pH, their interaction during adsorption in aqueous solutions could also be affected by pH. The adsorption of TC and CIP was investigated under conditions ranging from acidic (pH 3.0) to alkaline (pH 9.0) environments. The adsorption of TC by MMB400 exhibited a significant decrease from 161.22 to 14.12 mg/g when the pH was increased from 3.0 to 5.0, but then increased as the pH was further raised to 7.0–9.0 (Figure 3e). These results indicate that strongly acidic conditions favored the adsorption process,  $H^+$  bridging magnetic biochar and TC through hydrogen bonding. Similarly, the adsorption of TC onto MB400 declined as the pH was increased from 3.0 to 5.0, followed by a gradual increase as the pH was further increased. The adsorption of CIP onto MMB400 gradually strengthened as the pH increased from 3.0 to 7.0, reaching optimal capacity at pH 9.0 (Figure 3f). In contrast, the adsorption of CIP onto MB400 remained almost unchanged across the pH range 3.0–7.0 but strengthened at pH 9.0. Overall, the optimal pH for the adsorption of TC and CIP by MMB400 was 3.0, and MMB400 showed significantly higher adsorption capability than MB400. Therefore, subsequent adsorption kinetics and isotherm experiments were conducted at the optimal pH of 3.0.

### 3.2.4. Adsorption Kinetics

The adsorption behaviors were studied using concentration ranges of 50–200 mg/L (TC) and 25–100 mg/L (CIP) (Figure 4a–d). MMB400 achieved rapid TC removal (61.23%) within the first hour at 50 mg/L, owing to its abundant binding sites, and approached a plateau after 6 h (Figure 4b). Similar adsorption trends were observed at higher concentrations, although a longer duration was required to achieve equilibrium. Notably, the equilibrium adsorption increased with rising initial concentrations, which can be attributed to stronger adsorption driving forces and higher equilibrium concentrations. In contrast, the adsorption of TC by MB400 showed a gradual increase over time within the concentration range of 50–200 mg/L, eventually reaching equilibrium after 48 h (Figure 4a). Notably, MMB400 exhibited significantly higher equilibrium adsorption capacities than MB400 at the same initial concentration. For CIP, MMB400 demonstrated enhanced adsorption kinetics and superior equilibrium capability relative to MB400 across the tested concentration range (Figure 4c,d). The adsorption kinetics of TC and CIP were quantitatively analyzed through nonlinear regression fitting with pseudo-first-order (PFO) and pseudo-second-order (PSO) models, enabling determination of rate-controlling steps and adsorption phase dominance [33]. As shown in Table S1, the PSO model demonstrated superior fitting performance compared to the PFO model, suggesting chemisorption as the dominant mechanism. Evidently, MMB400 consistently exhibited significantly higher equilibrium adsorption capacities compared to MB400, while requiring either shorter or comparable

adsorption times to reach equilibrium. This highlighted the significant advantage of NaOH modification in enhancing the adsorption rates of TC and CIP on MB400.



**Figure 4.** Adsorption kinetics and isotherms of MB400 and MMB400. (a) TC kinetics of MB400 (biomass/K<sub>2</sub>FeO<sub>4</sub>, 6/6 g/g; 50–200 mg L<sup>-1</sup>, pH 3.0, 0.5 g L<sup>-1</sup>, 25 °C, 84 h); (b) TC kinetics of MMB400 (biomass/NaOH/K<sub>2</sub>FeO<sub>4</sub>, 6/6/6 g/g/g; 50–200 mg L<sup>-1</sup>, pH 3.0, 0.5 g L<sup>-1</sup>, 25 °C, 84 h); (c) CIP kinetics of MB400 (biomass/K<sub>2</sub>FeO<sub>4</sub>, 6/6 g/g; 25–100 mg L<sup>-1</sup>, pH 3.0, 0.5 g L<sup>-1</sup>, 25 °C, 72 h); (d) CIP kinetics of MMB400 (biomass/NaOH/K<sub>2</sub>FeO<sub>4</sub>, 6/6/6 g/g/g; 25–100 mg L<sup>-1</sup>, pH 3.0, 0.5 g L<sup>-1</sup>, 25 °C, 72 h); (e) TC isotherms of MB400 (biomass/K<sub>2</sub>FeO<sub>4</sub>, 6/6 g/g; pH 3.0, 0.5 g L<sup>-1</sup>, 25 & 35 °C, 84 h); (f) TC isotherms of MMB400 (biomass/NaOH/K<sub>2</sub>FeO<sub>4</sub>, 6/6/6 g/g/g; pH 3.0, 0.5 g L<sup>-1</sup>, 25 & 35 °C, 84 h); (g) CIP isotherms of MB400 (biomass/K<sub>2</sub>FeO<sub>4</sub>, 6/6 g/g; pH 3.0, 0.5 g L<sup>-1</sup>, 25 & 35 °C, 72 h); (h) CIP isotherms of MMB400 (biomass/NaOH/K<sub>2</sub>FeO<sub>4</sub>, 6/6/6 g/g/g; pH 3.0, 0.5 g L<sup>-1</sup>, 25 & 35 °C, 72 h).

### 3.2.5. Adsorption Isotherms

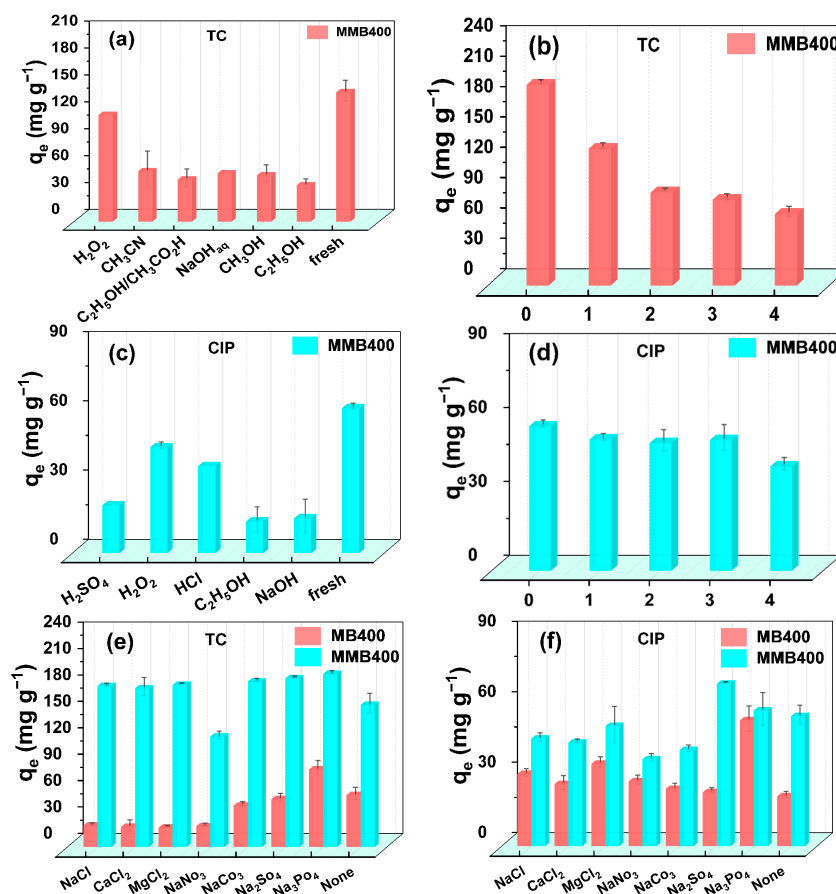
The adsorption performance of magnetic biochar was systematically evaluated through isotherm studies conducted at 25 and 35 °C (Figure 4e–h). The adsorption of TC on MMB400 showed a steep initial increase at low concentrations (<400 mg/L), then slowed at higher concentrations until the maximum value was reached. This phenomenon could be due, in part, to the abundance of available active sites at low concentrations; these sites gradually became saturated as concentration increased, leading to site-limitation effects. In contrast, TC adsorption by MB400 gradually increased with rising initial concentrations until the maximum adsorption capacity was attained. For the adsorption of CIP, MMB400 exhibited a gradually increasing trend with rising initial concentration but did not reach a clear maximum adsorption capacity. The adsorption by MB400 exhibited a gradual increase with rising initial concentrations until an adsorption plateau was reached. A positive temperature effect was observed for MMB400, with its adsorption performance with TC and CIP significantly improving when the temperature increased from 25 to 35 °C. This result demonstrated that the adsorption of TC and CIP onto MMB400 was endothermic. For MB400, the adsorption capability for TC was notably enhanced by an increase in temperature; however, temperature had little effect on the adsorption of CIP. It was evident that MMB400 possessed significantly higher maximum adsorption capacities for both TC and CIP compared to MB400, indicating that additional adsorption sites were generated through the co-pyrolysis process with NaOH. This can be attributed to the formation of a significant amount of ZVI, which exhibited strong affinity toward TC and CIP [34], as well as nano-Fe<sub>3</sub>O<sub>4</sub> [35] dispersed by ZVI.

The adsorption isotherms were analyzed using both the Langmuir (homogeneous monolayer adsorption) and the Freundlich (heterogeneous multilayer adsorption) models [36], with the fitting parameters summarized in Table S2. The Freundlich model provided higher correlation coefficients ( $R^2$ ) for the adsorption of TC onto both MB400 and MMB400, with  $1/n$  values ranging from 0 to 1, confirming favorable adsorptions. This suggests that the magnetic biochars possess active adsorption sites on heterogeneous surfaces, and that the processes by which TC was adsorbed onto them were multilayered. However, the Langmuir model gave slightly higher  $R^2$  values for the adsorption of CIP by the magnetic biochars, indicating a monolayer adsorption. MMB400 outperformed MB400 in adsorption performance, achieving an experimental TC maximum capacity of 1106.25 mg/g and a calculated CIP maximum capacity of 182.03 mg/g at 35 °C (Table S2). Notably, these adsorption capacities were considerably higher than those reported for other magnetic biochars in previous studies (Table S3). This demonstrates that MMB400 exhibits excellent potential as an effective adsorbent for TC and CIP removal from wastewater.

### 3.2.6. Regeneration of MMB400

The reusability of MMB400 was evaluated to evaluate its cost-effectiveness. A TC desorption study was conducted using NaOH<sub>aq</sub> (0.1 M), C<sub>2</sub>H<sub>5</sub>OH/CH<sub>3</sub>CO<sub>2</sub>H (9/1 mL/mL), 0.03% H<sub>2</sub>O<sub>2</sub><sub>aq</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, and CH<sub>3</sub>CN as regenerants to recover MMB400. As depicted in Figure 5a, the initial concentration of both TC and CIP was 100mg/L. Aqueous H<sub>2</sub>O<sub>2</sub> exhibited the best efficiency and was selected for the regeneration of MMB400. MMB400 showed an adsorption efficiency of 134.71 mg/g toward TC in the first cycle, remaining at 70.22 mg/g after four cycles (Figure 5b). The observed decrease in adsorption efficiency likely resulted from competitive occupation of active sites by residual TC molecules and their degradation intermediates [37]. Additionally, iron oxides may be released from MMB400 into acidic aqueous solutions (pH 3.0), leading to a reduction in the adsorption sites for TC. FTIR characterization revealed that the functional groups remained

largely unchanged after adsorption (Figure S1), demonstrating the stability of MMB400 under adsorption conditions.



**Figure 5.** Recycling and the mineral effect on the adsorption of MMB400 (100 mg L<sup>-1</sup>, 0.5 g L<sup>-1</sup>, pH 3.0, 25 °C, 24 h). (a) TC desorption with different regenerants (NaOH, C<sub>2</sub>H<sub>5</sub>OH/CH<sub>3</sub>COOH, H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, CH<sub>3</sub>CN); (b) TC regeneration cycles (initial 134.7 mg g<sup>-1</sup>, 70.2 mg g<sup>-1</sup> after 4 cycles); (c) CIP desorption with different regenerants (H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, HCl, C<sub>2</sub>H<sub>5</sub>OH, NaOH); (d) CIP regeneration cycles (28.8% capacity loss after 4 cycles); (e) Mineral effect on TC adsorption (pH 3, 25 °C, 24 h); (f) Mineral effect on CIP adsorption (pH 3, 25 °C, 24 h).

The desorption of CIP was investigated using various regenerants, including 0.05 mol/L H<sub>2</sub>SO<sub>4</sub>aq, 0.03% H<sub>2</sub>O<sub>2</sub>aq, 0.05 mol/L HClaq, C<sub>2</sub>H<sub>5</sub>OH, and NaOHaq (0.1 M). As before, aqueous H<sub>2</sub>O<sub>2</sub> (0.03%) proved to be the most effective and was used for recycling MMB400 (Figure 5c). This indicated that the magnetic biochar exhibited good catalytic activity for Fenton-like oxidation, enabling the degradation and desorption of pollutants without a significant loss of adsorption capacity. The amount of adsorption slightly decreased with the number recycling cycles, with a 28.8% reduction observed after four cycles (Figure 5d). This might be because of CIP residues and degradation intermediates remaining on the MMB400. FTIR spectra showed that the main peaks remained largely unchanged after four regeneration cycles, demonstrating that MMB400 maintained superior stability and reusability for CIP adsorption. Thus, MMB400 exhibited excellent recyclability, i.e., retained its adsorption capacity, further confirming its strong potential for industrial applications.

### 3.2.7. Mineral Interference Effect on Adsorption Capability

The impact of co-existing minerals on the adsorption TC and CIP by MMB400 was assessed at a concentration of 10 mM. The presence of typical minerals (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>,

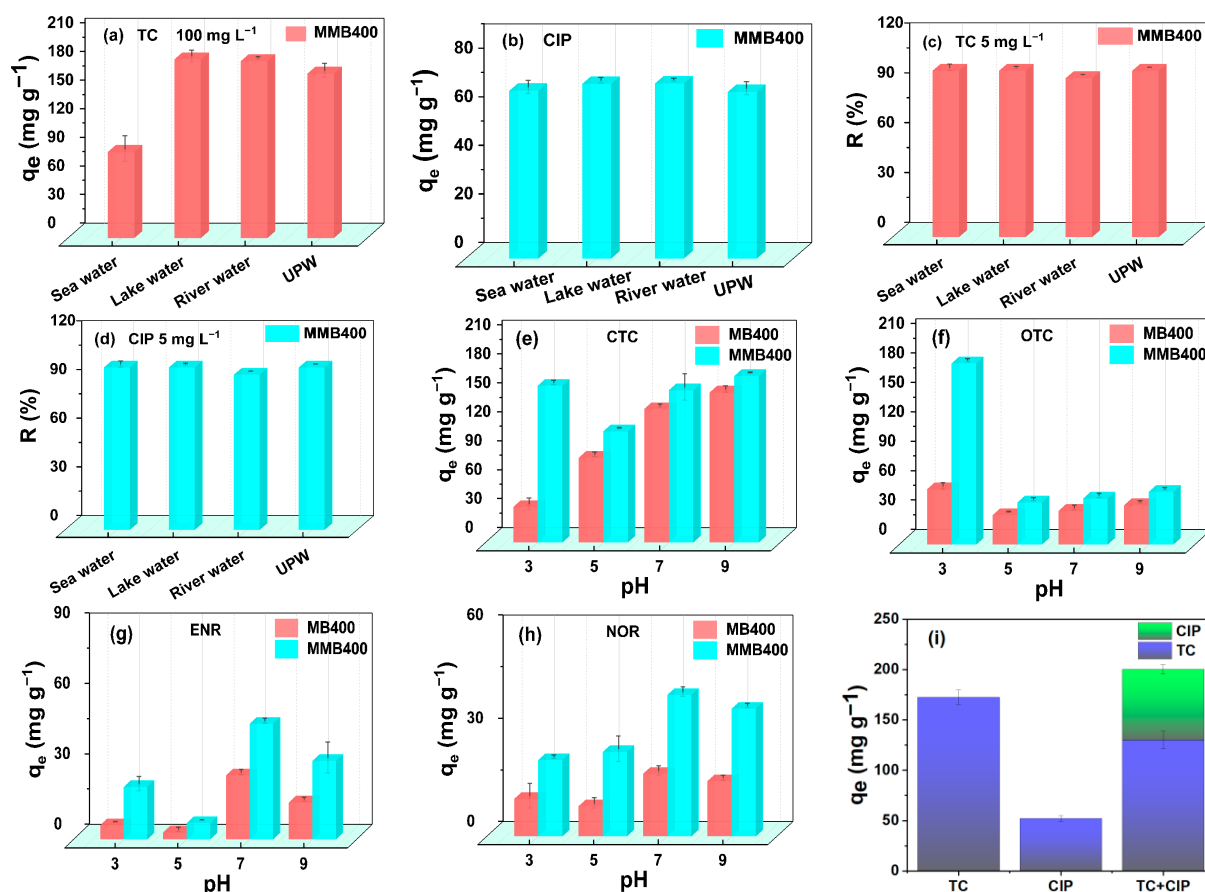
$\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_3\text{PO}_4$ ) caused an obvious increase in the adsorption of TC by MMB400; adsorption capacities of around 170.00 mg/g were achieved (Figure 5e). However,  $\text{NaNO}_3$  showed a somewhat negligible effect on adsorption, with the capacity decreasing from 161.22 to 125.27 mg/g. Conversely, MB400 exhibited a significantly diminished TC adsorption capacity in the presence of these co-existing minerals, except for  $\text{Na}_3\text{PO}_4$ . The adsorption of CIP onto MMB400 was generally inhibited by co-existing minerals, apart from  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ , which had no significant effect (Figure 5f). In contrast, all tested minerals enhanced CIP adsorption onto MB400, suggesting strengthened interfacial interactions. Overall, these results clearly demonstrated that MMB400 was suitable for real-world applications, as it exhibited outstanding adsorption performance for TC and CIP that was not significantly affected by co-existing minerals.

### 3.2.8. Adsorption of MMB400 in Natural Water Matrices

To further evaluate the applicability of MMB400 for wastewater treatment in industrial settings, its adsorption capabilities were tested using three types of water matrices—lake water, river water, and seawater—each containing varying concentrations of minerals and organic matter. The adsorption of TC onto MMB400 slightly increased in water from Hongcheng Lake and Nandu River compared to that in ultrapure water, but decreased to 90.30 mg/g in seawater due to strong competition from salts for TC active sites (Figure 6a). In contrast, the adsorption of CIP onto MMB400 remained unchanged in sea, Hongcheng Lake, and Nandu River water matrices compared to ultrapure water (Figure 6b). Moreover, TC and CIP were effectively removed in these natural water matrices, as well as in ultrapure water (UPW), at low concentrations (5 mg/L) (Figure 6c,d). These results reveal that MMB400 maintains high adsorption performance with minimal interference from minerals and organic matter in natural water matrices, highlighting its outstanding practical applicability for the treatment of TC- and CIP-polluted wastewater in industrial settings.

### 3.2.9. Application of MMB400 to the Adsorption of Other TC and CIP Derivatives

The general adsorption of MMB400 was investigated using four structurally related antibiotics: CTC and OTC (TC derivatives), and ENR and NOR (CIP derivatives). The adsorption of these molecules was influenced by the initial pH of the aqueous solution (Figure 6e–h). For CTC, high adsorption capacity was achieved across a broad pH range (3.0–9.0), with MMB400 consistently exhibiting a greater adsorption capacity than MB400 (Figure 6e). In the case of OTC, optimal performance was obtained at pH 3.0, with MMB400 exhibiting a significantly higher capability (184.93 mg/g) compared to MB400 (55.29 mg/g) (Figure 6f). Although a reduced adsorption capacity was observed in the pH range 5.0–9.0, MMB400 maintained a superior adsorption capacity compared to MB400. These results clearly confirm the superior versatility of MMB400 for the adsorption of TC derivatives. MMB400 exhibited lower adsorption efficiencies for ENR and NOR across the pH range 3.0–9.0 compared to OTC adsorption, reaching a maximum at pH 7.0 (Figure 6g,h). Nevertheless, MMB400 consistently exhibited significantly higher adsorption capacities for these CIP derivatives compared to MB400, suggesting that NaOH modification also enhanced the adsorption efficiency and suitability of magnetic biochar for TC- and CIP-type antibiotics. The enhanced adsorption capacity for TC and CIP derivatives was primarily attributed to the introduced -OH groups and well-dispersed nano- $\text{Fe}_3\text{O}_4$  on ZVI. Evidently, the adsorption capacity for CIP derivatives remained significantly lower than that for TC derivatives, primarily due to the fewer available functional groups in CIP derivatives. Nevertheless, MMB400 consistently displayed significantly higher adsorption capabilities for TC and CIP derivatives compared to MB400, demonstrating the significant promise of NaOH modification in antibiotic remediation.



**Figure 6.** Adsorption in different water matrices at high (a,b) and low (c,d) concentrations (0.5 g L<sup>-1</sup>, pH 3.0, 25 °C, 2 h). The adsorption capabilities of TC and CIP derivatives ((e–h): 100 mg L<sup>-1</sup>, 0.5 g L<sup>-1</sup>, pH 5.0, 24 h). Adsorption in a binary aqueous system ((i): 100 + 100 mg L<sup>-1</sup>, 0.5 g L<sup>-1</sup>, pH 3.0, 25 °C, 24 h).

### 3.2.10. Synergistic Adsorption in TC-CIP Binary System

The competitive adsorption behavior of TC and CIP was evaluated in a binary aqueous solution (Figure 6i). The adsorption capabilities of MMB400 were 0.29 mmol/g (TC) and 0.21 mmol/g (CIP) (Figure 6i), further demonstrating its significantly higher affinity for TC than for CIP. The enhanced adsorption affinity for TC over CIP likely stems from more favorable interactions between TC's functional groups and MMB400's active sites. These adsorption values also demonstrate that high adsorption capacities are still achieved when TC and CIP are concurrently eliminated. The total adsorption capability in the binary system was comparable to the sum of their individual capacities in single-solute systems. This indicated that most active adsorption sites were simultaneously accessible for both TC and CIP, demonstrating that simultaneous elimination of TC and CIP was feasible with minimal mutual interference. Importantly, the adsorption capability of CIP was greater in the binary system than in the single-solute system, likely due to interactions such as hydrogen bonding and acid–base interactions between TC and CIP. It can be concluded that multilayer adsorption is likely involved in the binary system.

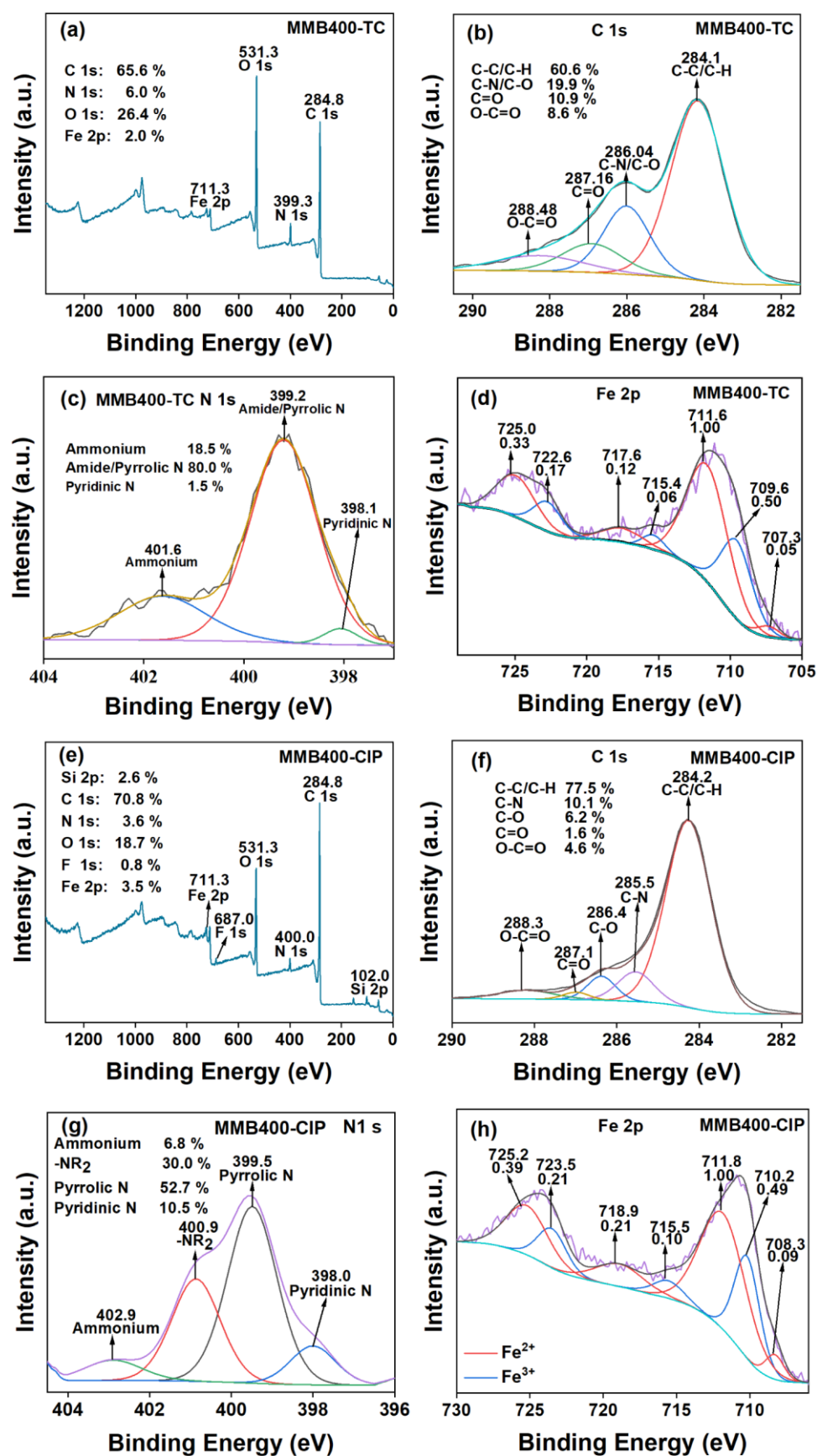
### 3.2.11. MMB400 Adsorption Mechanism

The average molecular sizes of TC and CIP are approximately  $1.2 \times 0.8 \times 0.6$  nm and  $1.0 \times 0.7 \times 0.5$  nm, respectively, indicating that adsorption mainly occurs in the mesopores of MMB400, while micropores contribute less due to size exclusion. To elucidate the adsorption mechanism of MMB400, XPS characterization was performed after adsorption. As depicted in Figure 7a, the N content significantly increased from 3.0% to 6.0% on the

surface after the adsorption of TC. The C 1s analysis indicated that the content of C-N/C-O and C=O increased from 11.15% to 20.47% (Figure 7b). These results demonstrate that TC was adsorbed on the surface of the carbon matrix of MMB400. As the carbon matrix of MMB400 and TC are both rich in O- and N-containing groups, these groups could interact through hydrogen bonding. For example, the carboxyl, hydroxyl, and amido groups of TC could interact with the hydroxyl and carboxyl groups of MMB400 via hydrogen bonding. The abundant graphite structures in MMB400 could adsorb TC through  $\pi$ - $\pi$  electron staking. The deconvolution of the N 1s peak revealed the presence of ammonium (401.6 eV) and amide (399.2 eV) peaks [38] (Figure 7c), while the signals for Mg and Na disappeared. These results suggest that cation exchange between  $\text{Mg}^{2+}/\text{Na}^{+}$  and  $\text{TC}^{+}$  [39] occurred at pH 3.0. At pH 3.0, TC and CIP predominantly exist as the cations  $\text{TC}^{+}$  and  $\text{CIP}^{+}$ , respectively, while MMB400 carries a positive surface charge, excluding significant electrostatic attraction but allowing hydrogen bonding,  $\pi$ - $\pi$  stacking, and cation exchange interactions (Figure 1f). The Fe content sharply decreased from 3.6% to 2.0%, suggesting TC was adsorbed around iron species (Figure 7a). Moreover, the Fe 2p binding energy showed a 0.5 eV negative shift from 711.8 to 711.3 eV, likely due to its coordination bonding and hydrogen bonding with TC's functional moieties [35]. Surface  $\text{Fe}^0$  also likely participates in TC adsorption by complexation [34], as its binding energy shifted from 708.0 to 707.3 eV after adsorption (Figure 7d). Pore diffusion could also have occurred in the mesopores of MMB400, where active internal adsorption sites facilitated the uptake of TC.

F was detected on the surface of MMB400 after adsorption (Figure 7e), demonstrating successful adsorption of CIP onto MMB400. The C 1s XPS spectrum indicated that the -COOH groups increased from 4.5% to 6.3% (Figure 7f), suggesting that CIP was loaded on the surface of the carbon matrix via hydrogen-bonding and  $\pi$ - $\pi$  staking. Ammonium at 402.9 eV and tertiary amino (-NR<sub>2</sub>) at 400.86 eV [40] were observed on MMB400, as well as pyrrole (399.5 eV) and pyridine (398.0 eV) (Figure 7g), while  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$  disappeared. These results indicated that cation exchange involving  $\text{CIP}^{+}$  and MMB400 took place at pH 3.0 [39]. Additionally, the Fe content slightly reduced even with release of Mg and Na (Figure 7e), proving that CIP was coated with Fe species. The binding energy of Fe also changed from 711.8 to 711.3 eV (Figure 7h), evidencing the interaction between Fe species and CIP via hydrogen bonding and complexation [41]. These findings explain the lower adsorption capacity observed for CIP compared to TC, which was primarily due to the relatively weaker hydrogen bonding and complexation that resulted from the fewer functional groups on CIP. Diffusion of CIP into the mesopores of MMB400 also likely occurs in this type of adsorption. Similarly, electrostatic interactions are unlikely to be involved in the adsorption of CIP, since both CIP and MMB400 carry positive charges at pH 3.0 [39].

In brief,  $\text{Fe}^0$ ,  $\text{Fe}_3\text{O}_4$ , and the carbon matrix cooperatively facilitated the adsorption of TC and CIP. In particular, nano- $\text{Fe}_3\text{O}_4$  is likely dispersed on both the ZVI and carbon matrix, serving as crucial active adsorption sites. Additionally, surface oxygen groups were critical for CIP and TC adsorption, while also facilitating the dispersion and stabilization of iron species.



**Figure 7.** XPS spectra of MMB400 after adsorption. (a) Survey spectrum (TC); (b) C 1s (TC); (c) N 1s (TC); (d) Fe 2p (TC); (e) Survey spectrum (CIP); (f) C 1s (CIP); (g) N 1s (CIP); (h) Fe 2p (CIP).

## 4. Conclusions

The  $K_2FeO_4/NaOH$  co-promoted pyrolysis strategy enabled successful synthesis of ZVI-doped magnetic biochar at a relatively low temperature (400 °C), achieving efficient removal of tetracycline (TC) and ciprofloxacin (CIP) from aqueous solutions. Abundant ZVI was embedded within the biochar matrix, imparting high-saturation magnetization, while  $Fe_3O_4$  particles, dispersed by ZVI, were accompanied by hydroxyl groups (–OH) introduced during pyrolysis. These features synergistically enhanced TC and CIP adsorption through hydrogen bonding and complexation. The magnetic biochar maintained high adsorption capacity in the presence of common minerals and in natural water matrices, underscoring its robustness for practical applications. Moreover, it exhibited strong adsorption performance for amoxicillin (AM) and oxytetracycline (OTC) and a notable capacity for enrofloxacin (ENR) and norfloxacin (NOR) adsorption. This work demonstrates the potential of  $K_2FeO_4/NaOH$  co-promoted oxidative pyrolysis as a versatile route for producing ZVI-doped biochar via carbothermal reduction at low temperatures.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr13092806/s1>, Figure S1: The FTIR spectra of fresh and recycled MMB400; Figure S2: Prepare flow charts; Figure S3: SEM image after regeneration; Table S1: The fitted parameters of adsorption kinetics for TC; Table S2: The fitted parameters of adsorption isotherms for TC; Table S3: Comparison of magnetic biochar for TC and CIP adsorption in the literature. Refs. [37,39,42–49] are cited in Table S3.

**Author Contributions:** Y.J.: Investigation, Data Analysis, Writing—Original Draft, Methodology. C.Z.: Investigation, Visualization. A.S.: Investigation. H.J.: Project administration. Y.X.: Visualization. J.L. (Jinying Li): Resources. S.L.: Resources. Z.B.: Formal analysis, Resources, Project administration, Supervision. X.-F.M.: Project administration. J.L. (Jihui Li): Conceptualization, Methodology, Writing—Reviewing and Editing, Funding acquisition, Project administration, Supervision. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Data will be made available upon request.

**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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