Article

Preparation of Iron Salt-Modified Sludge Biochar and Its Uptake Behavior for Phosphate

Guoxin Lan 1,†, Xixi Yan 1,†, Peiyao Deng 2, Tingzhen Li 1, Yaping Xia 1, Zhihao Zhu 1, Yan Wu 1,3,*, and Chuan Fu 1,*

1 Chongqing Key Laboratory of Water Environment Evolution and Pollution Control in Three Gorges Reservoir, Chongqing Three Gorges University, Chongqing 404100, China
2 Chongqing Green Karbon Environmental Protection Technology Co., Ltd., Chongqing 400050, China
3 College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China
* Correspondence: wuyan19850827@hotmail.com (Y.W.); casual20050163.com (C.F.);
Tel.: +86-189-0559-1879 (Y.W.); +86-139-0826-9439 (C.F.)
† These authors contributed equally to this work.

Abstract: Residual sludge is a significant waste resource, and the preparation of biochar achieves sludge disposal. Biochar has a high uptake capacity for phosphate. To prepare a sludge biochar adsorbent for phosphate, sludge was chemically and anaerobically treated in the presence of iron salts and pyrolyzed. We investigated the effects of the pyrolysis temperature and iron salt on the phosphate uptake capacity, finding that the pretreatment of the sludge with iron salts removed intrinsic phosphate, thus improving the uptake ability. The optimal adsorbent, denoted SB-B-Fe, was prepared by pyrolysis at 700 °C and subsequently modified with a 20 g/L iron-containing solution, yielding a phosphate uptake capacity of 0.5 mg/g. Further, the performance of SB-B-Fe remains high at pH 5–9 and is less affected by interfering anions. The sorption kinetics are consistent with the pseudo-second-order kinetic model, suggesting uptake by chemisorption, and the Langmuir model has a saturation capacity of 0.85 mg/g for uptake and prefers monolayer molecular uptake. The characterization showed that the adsorbent surface provided many uptake sites for phosphate and a high specific surface area. We hope that these findings will encourage the development of other value-added waste-based materials for environmental remediation.

Keywords: excess sludge; sludge biochar; phosphate removal; modification

1. Introduction

Increasing urbanization has resulted in an increase in the output of municipal sludge. For example, the annual sludge output in China in 2019 exceeded $6 \times 10^7$ tons (the moisture content was 80%), and the annual sludge output in China is expected to exceed $9 \times 10^7$ tons in 2025 [1]. Sludge contains a variety of pollutants, including heavy metals, drug residues, persistent organic pollutants (POPs), pathogens, and microplastics (MPs) [2]. Moreover, the moisture content of sludge is high (>90%) [3], meaning that sludge takes up significant storage space.

However, sludge rich in biomass can be pyrolyzed to obtain sludge biochar, which has a high uptake capacity for phosphorus-containing compounds and compared with other phosphorus removal agents, the raw material cost of sludge biochar phosphorus removal agent is much lower [4]. In particular, the preparation of biochar-based phosphate adsorbents can help reduce the eutrophication of water bodies and the disposal of sludge simultaneously, thus “treating waste with waste”. Hou et al. [5] conducted an uptake experiment on phosphorus after drying the sludge, and the maximum uptake capacity was 6.06 mg/g; Yang et al. found that the phosphorus uptake capacity of the sludge biochar modified by FeCl$_3$ was as high as 111 mg/g [6]; Saadat et al. [7] modified sludge biochar with metal cations, and the maximum phosphorus uptake capacity of sludge-based biochar
after modification was 153.85 mg/g. It can be seen that the sludge-based adsorbent has a better removal effect on phosphorus in sewage.

However, existing studies of this method have often ignored the phosphate intrinsically present in the sludge, and the direct preparation of biochar-based phosphate adsorbents without removing the phosphate naturally present in the sludge risks phosphate release and reduced phosphate removal. In fact, although untreated sludge biochar adsorbs phosphate, phosphate release also occurs [8].

FeCl₃ and K₂FeO₄ are two commonly used sludge conditioners, and anaerobic fermentation (AF) is the most common process for the biological treatment of excess sludge [9]. The sludge was first pretreated with FeCl₃ or K₂FeO₄ and then subjected to anaerobic treatment. The sludges treated with FeCl₃ (dosage of 10 mg/L, AF 28 h) and K₂FeO₄ (dosage of 50 mg/L, AF 18 h), denoted SB-AN-FC and SB-AN-KF, respectively, showed better phosphate release. In addition, we found that sludge biochar has a negatively charged surface, which is not conducive to the uptake of phosphate [10]. Therefore, to improve the phosphate uptake capacity of the biochar, further modification with Fe³⁺ salts was carried out, and optimal modification conditions were obtained. The uptake experiments were conducted by varying the sorbent dosage, initial phosphate concentration, pH, and interfering anions to investigate their effects on the phosphate uptake ability. The uptake mechanism of the modified sludge biological phosphorus removal agent was explored through the classical uptake isotherm model of Freundlich and Langmuir, as well as the fitted uptake kinetics of the pseudo-first-order and pseudo-second-order uptake kinetic models. Finally, the surface micromorphology, pore size, surface functional groups and surface elemental composition of the biochar materials were analyzed by specific surface area and pore size analyzer, FTIR spectrometer, scanning electron microscope and X-ray energy spectrum to elucidate the efficient phosphorus removal mechanism of modified sludge biochar.

2. Materials and Methods

2.1. Materials

The sludge samples were collected from the sludge return pump room of Xintian Town Sewage Treatment Plant, Wanzhou District, Chongqing City. The sludge had a solid content of 10.93 g/L, a moisture content of 98%, an organic content of 51.3%, a mixed liquor sludge concentration of 9781.67 mg/L, and a pH ranging from 7.12 to 7.67. Two different sludge-treatment processes were used: treatment with FeCl₃ (dosage of 10 mg/L, AF 28 h) and treatment with K₂FeO₄ (dosage of 50 mg/L, AF 18 h), and these samples were used for subsequent sludge biochar preparation experiments. The biochar was prepared by pyrolysis at 300, 500, or 700 °C, respectively, and the temperature was increased at a rate of 10 °C/min and maintained at the target temperature for 120 min. To improve the phosphate uptake performance, subsequent modification with FeCl₃·6H₂O was carried out. The concentration of the modification solutions was 10, 15, or 20 g/L, and these were added to the sludge biochar in a solid-to-liquid ratio of 1:30.

2.2. Determination of Optimal Uptake Conditions

To determine the optimal conditions for the preparation of sludge biochar, phosphate release and uptake tests were conducted. For this, 1 ± 0.0005 g of sludge biochar was mixed with 100 mL of deionized water or 10 mg/L phosphate solution and shaken at 25 °C and 120 rpm for 24 h. The mixed solution was then filtered through a 0.45-µm aqueous microporous membrane, and the phosphate concentration in the filtrate was determined according to the molybdenum-blue ascorbic acid method [11].

Meanwhile, the uptake performance of the adsorbents was investigated under different dosage and pH conditions, as well as in the presence of other anions (Cl⁻, NO₃⁻, SO₄²⁻, and CO₃²⁻). The adsorbent dosages used were 0.5, 1, 2, 4, 6, 8, 10, 12, and 16 g/L, the pH values were 3, 5, 7, 9, and 11, and the salts were 10 mg of NaCl (calculated as Cl⁻), NaNO₃
(calculated as NO$_3^-$), Na$_2$SO$_4$ (calculated as SO$_4^{2-}$), and Na$_2$CO$_3$ (calculated as CO$_3^{2-}$). Each group of experiments was repeated three times, and the average value was taken.

2.3. Sample Characterization

The changes in the specific surface area, pore volume, and pore size distribution of the adsorbent were observed by an automatic specific surface area and porosity analyzer (ASAP 2460, Micromeritics). The functional groups were characterized using Fourier transform infrared spectrometry (Thermo Scientific Nicolet iS20, Waltham, MA, USA). The morphological structure of the adsorbent was observed and analyzed using a scanning electron microscope (ZEISS Gemini 300), while the elemental distribution on the surface of the sludge biochar was observed by energy spectral point scanning.

2.4. Kinetic and Isothermal Experiments

Using different reaction times (0.5–24 h), we placed the optimum dose of sludge biochar (see later) in 100 mL of 10 mg/L phosphate solution for uptake tests at 25 °C with 120 rpm agitation. The isothermal uptake tests were carried out at different phosphate concentrations (1–100 mg/L). Each experiment was repeated thrice and the average value was taken.

2.5. Data Analysis

The phosphate uptake capacity of the sludge biochar was calculated using Equation (1).

$$q_e = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (1)

Here, $q_e$ (mg/g) is the amount of phosphate adsorbed by the biochar at uptake equilibrium; $C_0$ and $C_e$ (mg/L) are the phosphate concentrations initially and at equilibrium, respectively; $V$ (L) is the volume of the uptake solution, and $m$ (g) is the dosage of sludge biochar.

The phosphate uptake rate of the sludge biochar was calculated using Equation (2) with the same definitions as above.

$$\text{Adsorption rate} = \frac{C_e - C_0}{C_0}$$  \hspace{1cm} (2)

The amount of released phosphate was calculated using Equation (3).

$$q_e = \frac{(C_e - C_0)V}{m}$$  \hspace{1cm} (3)

The phosphate uptake of the adsorbents was assessed by fitting the uptake data to the Langmuir (Equation (4)) and Freundlich (Equation (5)) isotherms.

$$q_e = \frac{Q_{\text{max}}bC_e}{1 + bC_e}$$  \hspace{1cm} (4)

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

Here, in addition to the previously defined variables, $Q_{\text{max}}$ (mg/g) is the maximum uptake capacity, $b$ (L/mg) is the Langmuir constant correlated with uptake energy, $K_f$ [(mg/g)·(L/mg)$^{1/n}$] is the Freundlich constant related to uptake intensity, and $n$ is the element of heterogeneity.

The kinetic data were fitted to the pseudo-first-(Equation (6)) and pseudo-second-order (Equation (7)) models.

$$\ln(q_e - q_t) = \ln q_e - k_1t$$  \hspace{1cm} (6)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (7)
Here, $k_1$ (min$^{-1}$) and $k_2$ (g/(mg·min)) are the pseudo-first- and pseudo-second-order rate constants, $q_e$ (mg/g) is as before, and $q_t$ (mg/g) is the amount of phosphate adsorbed on the adsorbent at time $t$.

3. Results and Discussion

3.1. Effect of Pyrolysis Temperature on Uptake and Release of Phosphate by Sludge Biochar

The phosphate release and uptake were assessed for the raw sludge biochar (denoted SB-CK), anaerobically treated sludge biochar (denoted SB-AN-CK), and anaerobically treated sludge biochar treated with FeCl$_3$ or K$_2$FeO$_4$ (denoted SB-AN-FC and SB-AN-KF, respectively).

At each pyrolysis temperature, the biochar treated to remove phosphate showed higher phosphate uptake than SB-CK (Figure 1a), demonstrating the necessity of this step. In addition, the use of an iron-based treatment agent provided iron-containing active sites for uptake, thus improving the phosphate uptake capacity. SB-AN-KF showed better phosphate uptake than SB-AN-KC at all pyrolysis temperatures, probably because SB-AN-KF released more phosphate during pretreatment (Figure 1b). SB-AN-KF contains more iron-containing agents than SB-AN-FC, so it also contains more iron-containing uptake sites. Thus, among the investigated samples, SB-AN-KF is the best phosphate adsorbent.

![Figure 1](image.png)

**Figure 1.** Phosphate uptake (a) and release (b) of sludge biochar pyrolyzed at 300, 500, and 700 °C.

As shown in Figure 1a, the phosphate uptake capacity of the biochar increased with an increase in pyrolysis temperature, probably because of the increasing loss of C, H, O, and N from the biochar and, consequently, the relative increase in Fe, Al, and Ca contents. The increase in the concentration of these elements on the surface of the biochar provides more active sites for phosphate uptake [12]. However, it has been shown that when the pyrolysis temperature exceeds 700 °C, the uptake efficiency begins to decline because such high temperatures result in structural collapse and loss in uptake capacity [13].

The phosphate release first increased with an increase in pyrolysis temperature and then decreased, as shown in Figure 1b. At each pyrolysis temperature, the phosphate release from the biochar treated with an iron salt was lower than those of the non-treated samples because the iron salt resulted in the removal of existing phosphate, thus decreasing the amount available for release. Further, the amount of released phosphate was lowest in the samples pyrolyzed at 700 °C, probably because the high temperature caused the phosphate in the sludge to decompose and volatilize. In summary, SB-AN-KF pyrolyzed at 700 °C showed the best phosphate release and uptake and was used for subsequent experiments.
3.2. Effect of Modification Solution Concentration on Phosphate Uptake and Release

To improve the phosphate uptake capacity of SB-AN-KF, a further modification step with iron salts was carried out, and the effect of the concentration of this solution on the uptake and release of phosphate was investigated, as shown in Figure 2. With the increase in iron salt concentration, the phosphate uptake capacity increased. When the concentration of the iron salt solution was 20 g/L, the highest phosphate uptake capacity was achieved: 0.5 mg/g. Crucially, the modification step introduced a large number of positively charged Fe$^{3+}$ sites to the biochar, which enabled electrostatic uptake and precipitation by reaction with PO$_4^{3-}$, thus improving the uptake capacity of the biochar [8]. Further, none of the modified biochar samples showed phosphate release, mainly because the Fe$^{3+}$ reacted with phosphate in the biochar, thus immobilizing it.

![Figure 2. Effect of different concentrations of FeCl$_3$·6H$_2$O on phosphate uptake and release.](image)

On the basis of these results, the optimal modified biochar (denoted SB-B-Fe) was SB-AN-KF modified with an FeCl$_3$·6H$_2$O solution of 20 g/L, and this adsorbent was selected for subsequent experiments.

3.3. Phosphate Uptake by Modified Sludge Biochar

3.3.1. Effect of Biochar Dose

The effect of the biochar dose on phosphate uptake was investigated using the raw biochar (denoted as SB-B-CK) as a control and the optimal SB-B-Fe adsorbent as the experimental group. As shown in Figure 3, with an increase in adsorbent dosage, the phosphate uptake capacity of SB-B-CK first decreased and then increased, whereas that of SB-B-Fe decreased continuously. The highest phosphate uptake capacities for SB-B-CK and SB-B-Fe were obtained at 0.5 g/L dosage: 0.47 and 0.73 mg/g, respectively. With regard to the phosphate uptake rate, both SB-B-CK and SB-B-Fe showed an increasing pattern, and the highest values for SB-B-CK and SB-B-Fe were 34.80% and 79.90%; that is, the latter was 2.29-times higher.

These results can be explained as follows: As the biochar dose increases, there are more uptake sites for phosphate; thus, the removal efficiency increases continuously, but at the same time, the amount of phosphate adsorbed decreases as the amount of phosphate per unit mass of biochar is exposed to less phosphate. In the decreasing process of SB-B-Fe phosphorus uptake, the uptake capacity remained stable from 2 g/L to 8 g/L, while the
uptake rate of phosphate was increased. Therefore, the dosage of 8 g/L was chosen for the subsequent uptake experiments.

![Figure 3](image-url)  
**Figure 3.** Effect of adsorbent dosage on phosphate uptake (left-hand axis) and uptake rate (right-hand axis).

### 3.3.2. Effect of pH

The pH affects the speciation of phosphate salts. Theoretically, phosphate in an aqueous solution is present as H$_3$PO$_4$ at pH < 2.15, H$_2$PO$_4^-$ from pH 2.15 to 7.2, and HPO$_4^{2-}$ from pH 7.2 to 12.33 [14]. At pH 3, the uptake capacity of SB-B-CK and SB-B-Fe decreased greatly compared to other pH values, and the phosphate uptake capacity of SB-B-Fe was only 0.11 mg/g, and phosphorus from SB-B-CK was released. Further, the amount of released phosphate was 0.23 mg/g. However, the uptake capacity of SB-B-Fe was maintained at 0.54-0.57 mg/g at pH 5 to 9, subsequently decreasing at pH 11 (Figure 4). In contrast, SB-B-CK maintained a suitable uptake capacity at pH 3–11.

Under acidic conditions, phosphate exists in the form of H$_3$PO$_4$, which reduces electrostatic repulsion in the solution, resulting in a lower phosphate uptake capacity [15]. On the basis of these results, the phosphate in SB-B-CK is not completely immobilized, and the negatively charged phosphate is more easily leached into the solution, resulting in phosphate release from the biochar in an acidic environment. With pH increase, the electric potential in the solution decreases, whereas the electrostatic repulsion between phosphate in the sludge biochar and solution increases [16]. Under alkaline conditions, phosphate mostly exists as HPO$_4^{2-}$ and negatively charged OH-competes with HPO$_4^{2-}$ for uptake sites, leading to a decrease in phosphate uptake capacity [17].

### 3.3.3. Effect of Coexisting Anions

In real water samples, a range of anions is present, and these can affect the uptake efficiency. Therefore, four common anions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$) were added to the phosphate solution to explore their effect on phosphate uptake (Figure 5). As shown, chloride had a strong effect on SB-B-CK, reducing the phosphate uptake by 6.97%; this could be because chloride competes for uptake sites with phosphate. The other anions had little effect on phosphate uptake. Unlike SB-B-CK, SB-B-Fe was not affected by chloride or the other anions, possibly because of the specific uptake of phosphate by the iron-containing
active sites in SB-B-Fe [6]; the phosphate-selective uptake increases the potential of SB-B-Fe for practical application.

Figure 4. Effect of pH on phosphate uptake.

3.3.3. Effect of Coexisting Anions

In real water samples, a range of anions is present, and these can affect the uptake efficiency. Therefore, four common anions (Cl\(^{-}\), NO\(_3\)^{-}, SO\(_4\)^{2-}, and CO\(_3\)^{2-}) were added to the phosphate solution to explore their effect on phosphate uptake (Figure 5). As shown, chloride had a strong effect on SB-B-CK, reducing the phosphate uptake by 6.97%; this could be because chloride competes for uptake sites with phosphate. The other anions had little effect on phosphate uptake. Unlike SB-B-CK, SB-B-Fe was not affected by chloride or the other anions, possibly because of the specific uptake of phosphate by the iron-containing active sites in SB-B-Fe [6]; the phosphate-selective uptake increases the potential of SB-B-Fe for practical application.

Figure 5. Effect of coexisting anions on phosphate uptake.

3.3.4. Isothermal Adsorption and Adsorption Kinetics

The mechanism of phosphate uptake by SB-B-CK and SB-B-Fe was investigated by fitting the adsorption isotherms to two classical models: the Freundlich and Langmuir isotherms. The fitted data and parameters are shown in Figure 6a,b and listed in Table 1, respectively. As discussed, with an increasing concentration of phosphate in solution, the uptake of phosphate by both SB-B-CK and SB-B-Fe increased, mainly because of the increase in the probability of contact between the uptake sites and phosphate in solution. On fitting,
it was found that the Langmuir model provided a better fit, suggesting that uptake is dominated by monolayer uptake [18]. This result suggests that the uptake of the modified biochar is a result of the surface uptake sites created during the modification process. Using the fitted model, the theoretical saturated uptake values \( q_m \) of SB-B-CK and SB-B-Fe were calculated to be 0.25 and 0.85 mg/g, respectively. Thus, the uptake capacity of the modified biochar was improved by 3.4 times compared to that of the unmodified biochar.

Using an initial phosphate concentration of 10 mg/L, uptake experiments were carried out, and the uptake data were fitted to the pseudo-first-order and pseudo-second-order kinetic models, as shown in Figure 6c,d; the results are listed in Table 2. After 4 h of uptake with SB-B-CK, the uptake sites continued to bind to phosphate, and the number of free uptake sites gradually decreased; thus, the contact between phosphate and uptake sites in solution gradually weakened, and a slow uptake phase started [19] until uptake equilibrium was reached. However, SB-B-Fe only entered the slow uptake stage after 12 h of uptake, subsequently reaching uptake equilibrium. The shorter time for SB-B-CK to reach uptake equilibrium indicates that there are fewer uptake sites compared to SB-B-Fe and the internal resistance is lower [20].

**Figure 6.** Isotherm and kinetic models of SB-B-CK (a,c), isotherm and kinetic models of SB-B-Fe (b,d).

**Table 1.** Results of fitting the experimental data to the Langmuir and Freundlich models.

|          | Langmuir | Freundlich |
|----------|----------|------------|
|          | \( q_m \) | \( R^2 \) | \( K_L \) | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) |
| SB-B-CK  | 0.2498   | 0.5662     | 0.0682   | -0.3286   | 0.4230   |
| SB-B-F   | 0.8496   | 0.9356     | 0.3950   | -0.2289   | 0.8621   |
Table 2. Results of fitting the experimental data to the pseudo-first-order and pseudo-second-order kinetic models.

|                      | Pseudo-First-Order Model | Pseudo-Second Order Model |
|----------------------|--------------------------|---------------------------|
|                      | $q_e$ | $K_1$   | $R^2$ | $q_e$ | $K_2$   | $R^2$ |
| SB-B-CK              | 0.1823 | 3.1138 | 0.7929 | 0.1869 | 40.4046 | 0.9927 |
| SB-B-Fe              | 0.5820 | 2.3698 | 0.6850 | 0.6019 | 7.5323  | 0.9331 |

The adsorption kinetics of SB-B-CK and SB-B-Fe are consistent with the pseudo-second-order kinetic model, indicating that the uptake of phosphate by the biochar mainly involves chemisorption [21]. The amounts of adsorbed phosphate were calculated using these fitted data: 0.18 and 0.58 mg/g for SB-B-CK and SB-B-Fe for pseudo-first-order kinetics and 0.19 and 0.6 mg/g for pseudo-second-order kinetics, respectively. Therefore, the modification increased the uptake capacity of the sludge biochar for phosphate by 3.16 times.

3.4. Mechanistic Analysis

3.4.1. Analysis of Specific Surface Area, Pore Size Distribution, and Pore Volume of Materials

The specific surface area, pore size distribution, and pore volume parameters of the adsorbent material can reflect the distribution of uptake sites on the adsorbent surface to a certain extent. To explore the distribution of uptake sites on the surface of the adsorbent, Brunauer–Emmett–Teller (BET) analysis of the raw sludge biochar (SB-Raw) and optimal SB-AN-KF and SB-B-Fe adsorbents, which had been pyrolyzed at 700 °C, was carried out (Table 3). SB-Raw has a large specific surface area and uptake capacity. The specific surface area of SB-AN-KF increased significantly after phosphorus release by the cracking agent, indicating that the addition of the cracking agent released the phosphate contained on the surface of sludge biochar and increased the specific surface area of the material. At the same time, the pore size of phosphorus-releasing sludge biochar increased compared to SB-Raw, which is due to the cracking agent addition and anaerobic both have a certain cracking effect, resulting in more surface gaps in the sludge, which improves the phosphorus uptake capacity of phosphorus-releasing sludge biochar to some extent. The modification of the adsorbent with further iron salts yielding SB-B-Fe resulted in an enhanced specific surface area and pore volume [22].

Table 3. BET analysis of surface area, pore size, and pore volume.

|                  | Surface Area (m²/g) | Average Pore Size (nm) | Pore Volume (cm³/g) |
|------------------|---------------------|------------------------|---------------------|
| SB-Raw           | 43.4658             | 7.0739                 | 0.0289              |
| SB-AN-KF         | 70.0682             | 8.8821                 | 0.0148              |
| SB-B-Fe          | 71.0794             | 8.3436                 | 1.0277              |

3.4.2. Analysis of Surface Functional Groups of Materials

As shown in Figure 7, the Fourier transform infrared (FTIR) spectra contain bands at 3406 and 1658 cm⁻¹, indicating the presence of -OH and -C = O groups, respectively. This is consistent with the presence of organic matter in the four biochar samples [23,24]. In addition, the bands at 460 and 1028 cm⁻¹ correspond to hematite and Fe-OH [25,26]. There are bands corresponding to iron-bound functional groups in the spectra of several of the biochar samples; in particular, at 1028 cm⁻¹, the spectrum of SB-B-Fe is wider than those of the others, indicating the presence of more iron-containing functional groups, consistent with the observation of iron-based crystallites in the SEM images. The crystals of iron salts were successfully attached to the sludge biochar surface. The bands in the spectrum of SB-B-Fe-P are more intense compared to those of the others, suggesting the presence of more oxygen- and iron-containing functional groups, which likely play an important role in the uptake of phosphate.
Figure 7. FTIR spectra of the biochar samples.

3.4.3. Surface Micromorphological Analysis of Materials

The roughness of the adsorbent surface is an important indicator in evaluating its uptake performance, the morphologies of the SB-Raw, SB-AN-KF, SB-B-Fe, and spent SB-B-Fe (denoted SB-Fe-P) samples were observed by scanning electron microscopy (SEM). As shown in Figure 8a, the SB-Raw is rough, which is favorable for the uptake of phosphate. In contrast, as shown in Figure 8b, SB-AN KF has a well-developed pore structure because of the effect of K$_2$FeO$_4$, and this is also favorable for the uptake of phosphate. Figure 8c shows that some crystallites have formed on the surface of SB-B-Fe, suggesting the precipitation of the iron salt on the surface and a large number of uptake sites for phosphate, which should also increase the uptake capacity. The SEM image of SB-Fe-P is shown in Figure 8d; as shown, rough particles are close to the surface crystallites, suggesting that the crystals provide sites for the uptake of phosphate and deposition of phosphate salts.

3.4.4. Surface Element Analysis of Materials

To investigate the changes in surface elements of SB-Raw, SB-AN-KF, SB-B-Fe, and SB-Fe-P and to elucidate the promotion mechanism of surface elements on phosphorus removal by sludge biochar, the four sludge biochars were analyzed by EDS, and the results are listed in Table 4. SB-AN-KF contains 0.5% more Fe compared with SB-Raw, further confirming the introduction of the modification agent in the adsorbent. The amount of iron in SB-B-Fe increased by 0.69% and 1.19% compared with those of SB-AN-KF and SB-Raw, respectively. In addition, Al, Ca, and Mg were also detected, and these metals can also adsorb phosphate [7]; however, as the amount of iron salts added increased, the proportion of these elements on the surface of sludge biochar decreased slightly.

Interestingly, the amount of P in SB-AN-KF was reduced by 0.31% compared to that of SB-Raw. Further, the addition of a modifier has a fixing effect on phosphorus, which makes the P element in the sludge further reduced. The amount of P in SB-B-Fe was reduced by 0.23% and 0.54% compared with those of SB-AN-KF and SB-Raw, respectively. The low amount of P in SB-B-Fe explains the low phosphate release. Finally, the amount of P in the SB-B-Fe-P increased by 0.55%, and the amount of O increased by 7.24%, confirming the uptake of phosphate by SB-B-Fe.
shown in Figure 8d; as shown, rough particles are close to the surface crystallites, suggesting that the crystals provide sites for the uptake of phosphate and deposition of phosphate salts.

3.4.4. Surface Element Analysis of Materials
To investigate the changes in surface elements of SB-Raw, SB-AN-KF, SB-B-Fe, and SB-B-Fe-P and to elucidate the promotion mechanism of surface elements on phosphorus removal by sludge biochar, the four sludge biochars were analyzed by EDS, and the results are listed in Table 4. SB-AN-KF contains 0.5% more Fe compared with SB-Raw, further confirming the introduction of the modification agent in the adsorbent. The amount of iron in SB-B-Fe increased by 0.69% and 1.19% compared with those of SB-AN-KF and SB-Raw, respectively. In addition, Al, Ca, and Mg were also detected, and these metals can also adsorb phosphate [7]; however, as the amount of iron salts added increased, the proportion of these elements on the surface of sludge biochar decreased slightly. Interestingly, the amount of P in SB-AN-KF was reduced by 0.31% compared to that of SB-Raw. Further, the addition of a modifier has a fixing effect on phosphorus, which makes the P element in the sludge further reduced. The amount of P in SB-B-Fe was reduced by 0.23% and 0.54% compared with those of SB-AN-KF and SB-Raw, respectively. The low amount of P in SB-B-Fe explains the low phosphate release. Finally, the amount of P in the SB-B-Fe-P increased by 0.55%, and the amount of O increased by 7.24%, confirming the uptake of phosphate by SB-B-Fe.

| Element | SB-Raw(%) | SB-AN-KF(%) | SB-B-Fe(%) | SB-B-Fe-P(%) |
|---------|-----------|-------------|------------|--------------|
| C       | 51.74     | 59.06       | 64.84      | 54.4         |
| O       | 33.00     | 27.71       | 22.81      | 30.57        |
| Al      | 2.66      | 2.57        | 2.03       | 2.36         |
| Si      | 7.62      | 6.49        | 6.82       | 6.74         |
| Ca      | 0.75      | 0.47        | 0.20       | 0.59         |
| P       | 0.73      | 0.42        | 0.19       | 0.74         |
| Fe      | 1.37      | 1.87        | 2.56       | 2.09         |
| Mg      | 0.60      | 0.41        | 0.25       | 0.43         |
| Mn      | 0.05      | 0.96        | 0.01       | 0.02         |
| Cl      | 0.02      | 0.02        | 0.11       | 0.11         |
| N       | 1.45      | 0.03        | 0.17       | 1.95         |

4. Conclusions
An optimized phosphate adsorbent (SB-B-Fe) having a high phosphate-adsorbing capacity was prepared from waste sludge by pretreatment with K$_2$FeO$_4$, pyrolysis at 700 °C, and post treatment with 20 mg/L of FeCl$_3$·6H$_2$O solution. The uptake capacity of the optimal adsorbent was 1.16-times higher than that of the unmodified one. In addition, for SB-B-Fe, with an increase in the biochar dose, the phosphate uptake capacity decreased continuously. However, when the dosage was 2 to 8 g/L, the uptake capacity was stable. In contrast, the uptake rate increased continuously, so 8 g/L was determined to be the optimal dosage. Further, a high phosphate uptake was maintained at pH 5–9, and the presence of other anions had little effect on phosphate uptake, indicating that SB-B-Fe showed phosphate-specific uptake. The suitable fit of the isothermal uptake data to the Langmuir isotherm indicates monolayer molecular uptake, and the uptake kinetics matched the pseudo-second-order kinetic model, indicating that uptake was dominated by chemisorption. The FTIR spectra of SB-B-Fe confirm the presence of iron-based functional
groups in the biochar. Finally, SEM images showed that the pretreatment of the sludge resulted in more pores on the SB-AN-KF surface, and a lower phosphorus content was also determined by EDS. The SEM images also show small crystallites on the SB-B-Fe surface, and further crystals were observed on the surface of the spent adsorbent (SB-B-Fe-P), along with an increased percentage of phosphorus, suggesting that the adsorbed crystallites could be iron salts that react and immobilize phosphate. Overall, our findings show that pretreatment to remove phosphate from sludge improves the uptake performance of the final product. In addition, the produced modified biochar showed suitable performance that was stable under a range of conditions. Therefore, we hope that our findings will encourage the development of adsorbents for environmental remediation from waste materials.

Author Contributions: Conceptualization, Y.X.; Data curation, P.D.; Methodology, Z.Z.; Supervision, C.F.; Visualization, T.L.; Writing—original draft, G.L. and X.Y.; Writing—review and editing, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (grant numbers 51808089), the Science and Technology Innovation Project of Wan Zhou (grant numbers wzstc20210308 and 201503050).

Data Availability Statement: Not applicable.

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

References

1. Deng, W.; Yin, A.; Ma, J.; Su, Y. Investigation of NO conversion by different types of sewage sludge chars under low temperature. J. Environ. Manag. 2018, 209, 236–244. [CrossRef] [PubMed]
2. Smith, S.R. Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling. Philos. Trans. R. Soc. Math. Phys. Eng. Sci. 2009, 367, 4005–4041. [CrossRef] [PubMed]
3. Lin, Y.F.; Jing, S.R.; Lee, D.Y. Recycling of wood chips and wheat dregs for sludge processing. Bioresour. Technol. 2001, 76, 161–163. [CrossRef]
4. Blaney, L.M.; Cinar, S.; SenGupta, A.K. Hybrid anion exchanger for trace phosphate removal from water and wastewater. Water Res. 2007, 41, 1603–1613. [CrossRef]
5. Hou, Q.; Meng, P.; Pei, H.; Hu, W.; Chen, Y. Phosphorus adsorption characteristics of alum sludge: Adsorption capacity and the forms of phosphorus retained in alum sludge. Mater. Lett. 2018, 229, 31–35. [CrossRef]
6. Yang, Q.; Wang, X.; Luo, W.; Sun, J.; Xu, Q.; Chen, F.; Zhao, J.; Wang, S.; Yao, F.; Wang, D.; et al. Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. Bioresour. Technol. 2018, 247, 537–544. [CrossRef]
7. Saadat, S.; Raei, E.; Talebbeydokhti, N. Enhanced removal of phosphate from aqueous solutions using a modified sludge derived biochar: Comparative study of various modifying cations and RSM based optimization of pyrolysis parameters. J. Environ. Manag. 2018, 225, 75–83. [CrossRef]
8. Wang, H.; Xiao, K.; Yang, J.; Yu, Z.; Yu, W.; Xu, Q.; Wu, Q.; Liang, S.; Hu, J.; Hou, H.; et al. Phosphorus recovery from the liquid phase of anaerobic digestate using biochar derived from iron-rich sludge: A potential phosphorus fertilizer. Water Res. 2020, 174, 115629. [CrossRef]
9. Swierczek, L.; Cieslik, B.M.; Koniczka, P. The potential of raw sewage sludge in construction industry—A review. J. Clean. Prod. 2018, 200, 342–356. [CrossRef]
10. Yao, H.; Lu, J.; Wu, J.; Lu, Z.; Wilson, P.C.; Shen, Y. Upt Adsorption ake of Fluoroquinolone Antibiotics by Wastewater Sludge Biochar: Role of the Sludge Source. Water Air Soil Pollut. 2013, 224, 1370. [CrossRef]
11. Murphy, J.; Riley, J.P. Citation-Classic—A Modified Single Solution Method for the Determination of Phosphate in Natural-Waters. Curr. Contents/Agric. Biol. Environ. Sci. 1986, 12, 16.
12. Agrafioti, E.; Bouras, G.; Kalderis, D.; Diamadopoulos, E. Biochar production by sewage sludge pyrolysis. J. Anal. Appl. Pyrolysis 2013, 101, 72–78. [CrossRef]
13. Fu, P.; Hu, S.; Xiang, J.; Sun, L.; Yang, T.; Zhang, A.; Wang, Y.; Chen, G. Effects of Pyrolysis Temperature on Characteristics of Porosity in Biomass Chars. In Proceedings of the 2009 International Conference on Energy and Environment Technology, Guilin, China, 16–18 October 2009; pp. 109–112. [CrossRef]
14. Li, X.; Xie, Y.; Jiang, F.; Wang, B.; Hu, Q.; Tang, Y.; Luo, T.; Wu, T. Enhanced phosphate removal from aqueous solution using resourceable nano-CaO2/BC composite: Behaviors and mechanisms. Sci. Total Environ. 2020, 709, 136123. [CrossRef] [PubMed]
15. Wang, Z.; Miao, R.; Ning, P.; He, L.; Guan, Q. From wastes to functions: A paper mill sludge-based calcium-containing porous biochar adsorbent for phosphorus removal. J. Colloid Interface Sci. 2021, 593, 434–446. [CrossRef] [PubMed]
16. Liu, X.; Wang, Y.; Smith, R.L.; Fu, J.; Qi, X. High-capacity structured MgO-Co adsorbent for removal of phosphorus from aqueous solutions. *Chem. Eng. J.* 2021, 426, 131381. [CrossRef]

17. Wan, J.; Zhu, C.; Hu, J.; Zhang, T.C.; Richter-Egger, D.; Feng, X.; Zhou, A.; Tao, T. Zirconium-loaded magnetic interpenetrating network chitosan/poly(vinyl alcohol) hydrogels for phosphorus recovery from the aquatic environment. *Appl. Surf. Sci.* 2017, 423, 484–491. [CrossRef]

18. Veni, D.K.; Kannan, P.; Edison, T.N.J.I.; Senthilkumar, A. Biochar from green waste for phosphate removal with subsequent disposal. *Waste Manag.* 2017, 68, 752–759. [CrossRef]

19. Wu, J.; Cheng, X.; Li, Y.; Yang, G. Constructing biodegradable nanochitin-contained chitosan hydrogel beads for fast and efficient removal of Cu(II) from aqueous solution. *Carbohydr. Polym.* 2019, 211, 152–160. [CrossRef]

20. Li, Y.; Gao, B.; Wu, T.; Sun, D.; Li, X.; Wang, B.; Lu, F. Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide. *Water Res.* 2009, 43, 3067–3075. [CrossRef]

21. Mohammed, N.A.S.; Abu-Zurayk, R.A.; Hamadneh, I.; Al-Dujaili, A.H. Phenol adsorption on biochar prepared from the pine fruit shells: Equilibrium, kinetic and thermodynamics studies. *J. Environ. Manag.* 2018, 226, 377–385. [CrossRef]

22. Song, Z.; Lian, F.; Yu, Z.; Zhu, L.; Xing, B.; Qiu, W. Synthesis and characterization of a novel MnOx-loaded biochar and its adsorption properties for Cu^{2+} in aqueous solution. *Chem. Eng. J.* 2014, 242, 36–42. [CrossRef]

23. Yin, Q.; Liu, M.; Ren, H. Biochar produced from the co-pyrolysis of sewage sludge and walnut shell for ammonium and phosphate adsorption from water. *J. Environ. Manag.* 2019, 249, 109410. [CrossRef]

24. Yan, L.-G.; Yang, K.; Shan, R.-R.; Yan, T.; Wei, J.; Yu, S.-J.; Yu, H.-Q.; Du, B. Kinetic, isotherm and thermodynamic investigations of phosphate adsorption onto core-shell Fe3O4@LDHs composites with easy magnetic separation assistance. *J. Colloid Interface Sci.* 2015, 448, 508–516. [CrossRef] [PubMed]

25. Krishnan, K.A.; Haridas, A. Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. *J. Hazard. Mater.* 2008, 152, 527–535. [CrossRef] [PubMed]

26. Ruan, H.D.; Frost, R.L.; Kloprogge, J.T.; Duong, L. Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. *Spectrochim. Acta Part A-Mol. Biomol. Spectrosc.* 2002, 58, 967–981. [CrossRef]