Enhanced Removal of Heavy Metals from Water by Hydrous Ferric Oxide-Modified Biochar

Yan Li, Liangmin Gao,* Zhongxiang Lu, Yuchen Wang, Yan Wang, and Shunli Wan*

ABSTRACT: Biochar has become an attractive adsorbent for heavy metal removal, but its application potential is very limited because of the relatively low adsorption capacity and poor selectivity. In the present study, we decorated the biochar (BC) by impregnating hydrous ferric oxide (HFO) within the pore of biochar and consequently obtained a new hybrid adsorbent denoted as HFO-BC. The results show HFO-BC exhibited excellent performance to two representative heavy metals, i.e., Cd(II) and Cu(II), with maximal experimental sorption capacities of 29.9 mg/g for Cd(II) and 34.1 mg/g for Cu(II)). HFO-BC showed satisfactory anti-interference ability for Cd(II) and Cu(II) removal in the presence of high levels of Ca(II) and Mg(II) owing to the specific inner-sphere complexation between the immobilized HFO and Cd(II) and Cu(II), which was probed by XPS analysis. Cd(II) and Cu(II) removal onto HFO-BC experienced two distinct stages prior to be adsorbed, i.e., migration from solution to the outside surface of adsorbent and pore diffusion and approached equilibrium within 100 min. In the laboratory-scale small column adsorption experiment, HFO-BC can generate ∼129 and 300 BV effluents for Cd(II) and Cu(II), equivalent to 774- and 1854-fold of its own weight, to meet their treatment standards. Moreover, the exhausted HFO-BC can be effectively regenerated using HCl−CaCl2 binary solution with a desorption rate more than 95%. All results validate that impregnating HFO inside the pores of BC is a promising approach to promote the practical applicability of BC for removing heavy metals from the polluted water.

1. INTRODUCTION

Heavy metals such as cadmium, copper, and lead in various waters pose a huge threat to the water quality security, and its contamination has been a global environmental issue. Owing to the high toxicity and strong bioaccumulation, the trace level of heavy metal can even cause irreversible damage to a living organism. To reduce the harmfulness of heavy metals, more rigid discharge standards were established to restrict their maximum residual concentration in various effluents. For instance, the maximum discharge levels of cadmium and copper were recommended to be 0.1 and 1.0 mg/L, respectively, for integrated wastewater by Chinese government and the maximum acceptable value of the two metals in drinking water were set to be 0.003 and 2 mg/L by WHO. Consequently, it is of high urgency to develop technically and economically feasible approaches to decontaminate the toxic metal polluted water.

To date, numerous of traditional techniques such as chemical precipitation, coagulation, membrane filtration, ion exchange, and adsorption have been used for cleanup of heavy metals from water. Among these available methods, adsorption has been accepted as one of the most attractive techniques and widely used in field application as a result of its uncomplicated operation and good treatment effect. Various adsorbents have been developed for heavy metal sequestration such as activated carbon, ion exchangers, and numerous low-cost sorbents. Recently, biochar, a carbon-rich material generated from the thermal decomposition of biomass in an oxygen-free atmosphere such as agricultural wastes, animal wastes, and sludge, has aroused wide concern as adsorbents for heavy metals. Compared to the traditional adsorbents, biochar has several remarkable advantages such as stable framework, wide availability, and excellent hydraulic characteristic as well as the additional carbon sequestration effect. Biochar was proven to be an effective adsorbent for lots of heavy metal (e.g., Pb, Cd, Cu, As, and Ni) removal. Nevertheless, there are still several crucial technical barriers, i.e., relatively low adsorption capacity and dissatisfaction adsorption selectivity toward targeted heavy metal, restricting its large-scale application. For example, the sorption capacity of the...
cadmium onto pine wood-based biochar is only 5.4 mg/g, and that for copper onto manure-based biochar is 6.5 mg/g, respectively, as well as the coexisting cations can paralyze its sorption to target metals. Thus, it is of great necessity to improve the adsorption performance of biochar for practical application of heavy metal capture.

Metallic oxides such as Fe(III), Mn(IV), Zr(IV), and Ti(IV) oxides are always recognized as the promising adsorbents for heavy metal sequestration regardless of the sorption capacity or selectivity owing to their great reactive activity and strong and specific affinity to metal ions. Compared to other metallic oxides, hydrous ferric oxides (HFO) possess the advantages of low cost and excellent environmental friendliness, and thus it is widely studied in the field of heavy metal cleanup from water. Moreover, similar to other metal oxides, the spent HFO can be effectively regenerated using dilute acidic solution as a result of its protonation or deprotonation at different solution pH’s caused by its relatively low isoelectric point (4.0−7.3). Unfortunately, HFO is far from the field application for wastewater decontamination due to its fine or ultrafine particles (micrometer scale), which can generate unacceptable pressure drop applied in a fixed-bed setting and unthorough solid−liquid separation applied in an adsorption tank. Immobilizing HFO within porous carriers of large size such as activated carbon, polymers, and biomass is a feasible approach to improve the applicability of fine HFO. Though various HFO-based composite adsorbents have been exploited for water treatment, development of new carriers is still a hot issue because the optional carriers have some inherent disadvantages from technical and economical viewpoints. For example, the preparation of the host polymers is complicated and expensive, however, using biomass as a carrier probably trigger the secondary pollution as a result of the unavailable release of organic matter from biomass.

The main objective of the current study is to prepare a hydrous ferric oxide-modified biochar (HFO-BC) and investigate its performance for effective removal of heavy metals from water. A widely used inorganic adsorbent HFO was employed as the active component for improving the sorption ability of biochar to heavy metal. The surface and structural properties of the as-obtained HFO-BC particles were systematically characterized. The sorption properties of two typical heavy metals (e.g., cadmium and copper) by HFO-BC were evaluated as the function of pH effect, isotherm, kinetics, and competing effect. The underlying sorption mechanism was probed by means of the X-ray photoelectron spectroscopy (XPS). Additionally, the feasibility of practical application of HFO-BC for decontaminating Cd(II)- and Cu(II)-polluted wastewater was also evaluated in laboratory-scale fixed-bed column test.

2. MATERIALS AND METHODS

2.1. Materials. All chemicals of analytical grade (AR) used in this study were purchased from Aladdin Industrial, and they can be directly applied without special treatment. All solution was prepared using ultrapure water with a resistivity of >18.25 MΩ/cm. Cadmium and copper solutions were acquired from the dilution of 1 g/L stock solution prepared from dissolving their corresponding chloride salts. The precursor of biochar, i.e., peanut shell (PS), was collected from the local farmer’s market of Huangshan, China. The fresh PS was subjected to repeated washing and then was naturally dried. Then, PSs were simply crushed for further use.

2.2. Preparation of HFO-BC. The supporter BC was fabricated on the basis of the classic pyrolysis technique reported in previous references. In this regard, first, the PS (2 g) was put into the quartz cell and then placed into a muffle furnace. Then, the temperature of the muffle furnace was elevated from room temperature to 600 °C with a rate of 15 °C/min and subsequently held for 1 h, followed by a natural cooling process. The oxygen-free atmosphere of the entire process was guaranteed by the constantly injected Ar (200 mL/min). Finally, the black solids were rinsed with pure water until neutral pH and dried at 100 °C for 20 h.

HFO-BC was synthesized by employing BC as the host according to the following procedures. First, 5.0 g BC was added into 1 mol/L FeCl₃ solution and then constantly agitated for 24 h at 298 K. Second, the Fe(III)-laden BC was separated from the solution and then dispersed into 5% NaOH solution. After that, the solution was stirred for another 24 h to generate ferric oxide precipitate in situ. Finally, the obtained solids were washed with deionized water until neutral pH and then desiccated at 60 °C until reaching the constant weight. The HFO-BC with a size of 0.15−0.25 mm was chosen and sealed for later use. The ferric oxide precipitate was produced in situ through the pathway as follows:

\[
\begin{align*}
3\text{BC} + \text{CO}_2 \text{H}^+ (s) + 3\text{Fe}^{3+} (aq) & \rightleftharpoons [3(\text{BC} - \text{COO}^-)\text{Fe}^{3+}(s) + 3\text{H}^+] \\
3\text{BC} + \text{CO}_2 \text{H}^+ (s) + 3\text{NaOH} (aq) & \rightleftharpoons 3(\text{BC} - \text{COO}^-)\text{Na}^+ (s) + \text{Fe(OH)}_3 (s)
\end{align*}
\]

2.3. Batch Adsorption Experiments. Batch sorption experiments were carried out in 100 mL flasks. HFO-BC or BC (0.01 g) was dispersed into 50 mL aqueous solution with preset concentration of target pollutants. HCl or NaOH solution (1.0 mol/L) was employed to adjust the solution pH, and CaCl₂ and MgCl₂ were served as the background cations, as necessary. The prepared flasks were shaken for 24 h at 180 rpm and 298 K in a thermostatic orbit incubator equipped with the water bath. Based on the preliminary kinetic experiments, it is very sufficient for 24 h to reach sorption equilibrium. As for the kinetic experiment, a certain amount of solution was taken out from the flask and analyzed at preset time intervals. On the basis of mass balance, the sorption capacities and removal of Cd(II) and Cu(II) were acquired.

2.4. Column Sorption and Desorption. Three milliliters of wet HFO-BC or BC (dry weight ~ 0.5 g) was encased into a polyethylene column, with a length and inner diameter 230 and 12 mm, respectively. The simulated Cd(II)- and Cu(II)-contaminated wastewater passed through the column at a desired flow controlled by a peristaltic pump (BT100-2 J, China). An automatic partial collector was employed to sample the effluent at preset time intervals. The collected solution was analyzed to produce breakthrough curves. The used adsorption setting is sketched in Figure S1. Afterward, the spent HFO-BC in a fixed-bed column was eluted in situ with HCl−CaCl₂ binary solution as regenerator. Several crucial operation parameters, e.g., superficial liquid velocity (SLV) and empty bed contact time (EBCT), are shown in the caption of the related figure.

2.5. Analyses. The concentrations of Cd(II) and Cu(II) in solution were analyzed using a flame atom adsorption spectrophotometer of TAS-990 (Persee inc., China) when
higher than 0.5 mg/L and an atom fluorescence spectrophotometer of AFS-230E (Haiguang Co., Ltd) when lower than 0.5 mg/L. The Fe amount in HFO-BC was measured by the HNO$_3$−HClO$_4$ digestion method. In detail, 0.1 g HFO-BC was added into 20 mL HNO$_3$−HClO$_4$ binary solution and then subjected to continuous heating until the solids completely disappear. After that, Fe concentration in this solution was analyzed to calculate the loading amount of HFO. The morphology of HFO-BC and the framework was detected using a scanning electron microscope (S-3400 N, Japan) and transmission electron microscopy (Tecnai G2 F30 S-Twin, Holland). The crystallinity of the immobilized HFO was analyzed through X-ray diffraction (X'Pert PRO, Holland).

The surface functional groups of HFO-BC were revealed using Fourier transform infrared spectroscopy (Nicolet 6700, USA) in a range of 400−4000 cm$^{-1}$. The interaction between Cd(II) or Cu(II) and HFO-BC was probed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan) equipped with the excitation source of an Al Kα anode radiation. The XPS data were predicted by a curve-fitting program (XPS-peak4.1).

3. RESULTS AND DISCUSSION

3.1. Characterization of the As-Obtained HFO-BC. According to the SEM images of BC and HFO-BC (Figure 1a,b), there are a few large pores (micrometer level) in the rough surface of BC, while the pores become small after HFO impregnation owing to the blocking effect. Compared to the BC surface, some apparent particles scattered in the HFO-BC surface, which were confirmed to be HFO through EDS analysis (Figure S2). The TEM image in Figure 1c shows that the size of HFO particles is in the range of 10−50 nm. The FTIR spectrum of BC and HFO-BC is shown in Figure 1d. As illustrated, there are three obvious adsorption peaks located at 3419, 1575, and 1383 cm$^{-1}$ assigned to −OH, −C=O, and −C−H groups, respectively, in the FTIR spectra of BC. But for that of HFO-BC, another band placed in 580 cm$^{-1}$ representing the Fe−O group is also observed except the aforementioned three peaks, further indicating the successful loading of HFO. The HFO amount in HFO-BC was determined to be 9.19 mg/g in the Fe content through digestion. Of note, there is no Fe detected in the host BC. Figure 1e shows two weak and broad peaks located at 25.8 and 44.7 in the XRD pattern of HFO-BC, which are similar to those of Fe$_2$O$_3$ (JCPDS #39-1346) and Fe$_3$O$_4$ (JCPDS #26-1136). It implies that most of the immobilized HFO is amorphous in nature.

3.2. pH Effect on Adsorption. As a crucial index of solution chemistry, solution pH can usually influence the chemical state of adsorbate and surface chemical characteristics of the given adsorbent, and thus dominates the sorption process. Herein, the pH effect on Cd(II) and Cu(II) adsorption onto the resultant HFO-BC was performed, and the results are depicted in Figure 2. As shown, both Cd(II) and Cu(II) retention onto HFO-BC increases with the lifted solution pH. The pH effect curves are similar to that of Cd(II) and Cu(II) removal onto other conventional biochar-based composites, and can be ascribed to the combined action of the supporting BC and immobilized HFO adsorption to targeted ions. For BC, Cd(II), and Cu(II), retention is through the H$^+$ exchange of the carboxyl and hydroxyl groups covalently bound on BC to cationic metal ions, as shown in following reactions,

$$\text{HFO} + \text{BC} + \text{H}^+ \rightarrow \text{HFO-BC}$$

Figure 1. SEM images of (a) BC and (b) resultant HFO-BC, (c) TEM image of HFO-BC, (d) FTIR spectrum of BC and HFO-BC, and (e) XRD pattern of the as-obtained HFO-BC.
where \( S \) represents the surface of BC. Obviously, increasing solution pH promotes the H\(^+\) exchange process and further enhances targeted metal ion adsorption. As for the loaded HFO, it removes Cd(II) and Cu(II) by forming an inner-sphere complex with metal ions as follows:

\[
2\text{SO}^-(s) + M^{2+} (aq) \rightleftharpoons [\text{SO}^2M]_2M^{2+} (s) + 2H^+ (aq)
\]

(3)

Higher solution pH, that is, more OH\(^-\), is favorable for Cd(II) and Cu(II) adsorption by the impregnated HFO. Consequently, the pH effect of BC and HFO jointly led to the pH-dependent curves of HFO-BC. The sharp decrease of Cd(II) and Cu(II) uptake in the low pH region indicates the great possibility to regenerate the saturated HFO-BC with a dilute acid solution. In addition, we also investigated the stability of HFO-BC toward solution pH. As shown in Figure 2, a relatively low Fe dissolution of 1.1–15.6% was observed when solution pH decreased from 4.0 to 2.0, suggesting its satisfactory acidic stability.

### 3.3. Adsorption Isotherm

Sorption isotherm tests of Cd(II) and Cu(II) onto BC and HFO-BC at 25, 45, and 60 °C were carried out, and the results are recorded in Figure 3. As shown, for both BC and HFO-BC, Cd(II) and Cu(II) sorption on them increases with the elevated temperature, suggesting that the sorption processes are endothermic. Two widely used sorption isothermal models (the Langmuir and Freundlich equations) were employed to predict the experimental data.

\[
\log Q_e = \log K_t + \frac{1}{n} \log C_e
\]

(7)

\[
\frac{1}{Q_e} = \frac{1}{Q_m} + \left( \frac{1}{Q_mK_L} \right) \frac{1}{C_e}
\]

(8)

In which \( Q_e \) (mg/g) and \( Q_m \) (mg/g) represent the equilibrium and maximum sorption capacities of Cd(II) and Cu(II), respectively. \( C_e \) (mg/L) denotes adsorbate concentration in solution, \( K_t \) (L/g) denotes the relative adsorption capacity, \( 1/n \) denotes the heterogeneity factor (adsorption intensity), and \( K_L \) (L/mg) denotes the Langmuir adsorption constant. The specific fitting parameters are shown in Table S1.

Overall, the Freundlich model can better fit two-metal adsorption onto BC and HFO-BC than the Langmuir one, and the related coefficients are higher than 0.94, indicating that the processes are heterogeneous chemisorption. The experimental adsorption capacities of Cd(II) and Cu(II) for HFO-BC (11.2 mg/g for Cd(II) and 16.8 mg/g for Cu(II) at 25 °C, 20.2 mg/g for Cd(II) and 24.8 mg/g for Cu(II) at 45 °C) are much greater than those of BC (2.8 mg/g for Cd(II) and 6.8 mg/g for Cu(II) at 25 °C, 3.4 mg/g for Cd(II) and 11.2 mg/g for Cu(II) at 45 °C) at two temperatures. It clearly suggests that the immobilization of HFO within BC has achieved the anticipated goal, i.e., increasing the sorption capacity of BC to heavy metals. Moreover, the maximum experimental adsorption capacities of Cd(II) and Cu(II) onto HFO-BC (29.9 mg/g for Cd(II) and 34.1 mg/g for Cu(II)) were also generally higher than their maximum sorption capacity on other BC-based adsorbents (Table 1). Another noteworthy is that the molar adsorption capacities of Cu(II) on two adsorbents are higher those of Cd(II), implying the greater affinity of Cu(II) with HFO-BC and BC. In addition, the effect of adsorbent dose and initial concentration of adsorbate on Cd(II) and Cu(II) adsorption by HFO-BC was also investigated, and the results are recorded in Figure S3a,b. As illustrated, with the increase of adsorbent dose, the adsorption capacities of Cd(II) and Cu(II) gradually decreases. But with the elevation of initial concentration of adsorbate, the adsorption capacities of Cd(II)
Table 1. The Comparison of Maximum Adsorption Capacities of Cd(II) and Cu(II) onto HFO-BC and Other Biochar-Based Adsorbents

| adsorbent           | Cd(II) (mg/g) | Cu(II) (mg/g) | references |
|---------------------|---------------|---------------|------------|
| oak bark char       | 5.40          | NA            | 17         |
| carbon F-400        | 8.00          | NA            | 17         |
| earthworm manure biochar | 8.64   | 12.81         | 36         |
| pine sawdust biochar| 2.0           | 5.5           | 28         |
| sulfonated resin biochar | NA     | 12.7          | 37         |
| spruce sawdust biochar | 13.4   | 8.89          | 38         |
| rice husk biochar   | 7.81          | 4.16          | 39         |
| acacia biochar      | NA            | 9.7           | 17         |
| eucalyptus biochar  | NA            | 3.48          | 40         |
| corn cob biochar    | NA            | 2.7           | 40         |
| buffalo weed biochar| 11.63         | NA            | 41         |
| HFO-BC              | >29.9<sup>a</sup> | >34.1<sup>a</sup> | present study |

<sup>a</sup>The maximum sorption capacity obtained from sorption experiments in bold.

and Cu(II) gradually increased. Of note, no ferric loss was detected for HFO-BC when immersed in solutions at 25, 45, 60, and 80 °C for five days, indicating its high thermal stability, which is very beneficial for its practical application.

The thermodynamic characteristic for HFO-BC adsorption toward these two metals was further quantified through calculating the free energy change (ΔG), enthalpy change (ΔH), and standard entropy change (ΔS) by means of the van’t Hoff equation as follows:

\[
\Delta G = -nRT
\]

\[
\frac{d(\ln C_e)}{dT} = \frac{\Delta H}{R}
\]

\[
\Delta G = \Delta H - T\Delta S
\]

Where \( T \) is the absolute temperature (K), and \( R \) is the gas constant (8.314 J/(mol·K)). The calculated parameters are listed in Table S2. As illustrated, the negative \( \Delta G \) and positive \( \Delta H \) manifest that this sorption system is essentially spontaneous and endothermic. The positive \( \Delta S \) implies that the randomness is increased at the solid–liquid interface during two metal adsorptions onto HFO-BC.

3.4. Adsorption Kinetics. The equilibrium time of target pollutants adsorption onto the given adsorbents can determine the volume of sorption devices in practical application and further influence the initial investment. Herein, we investigated the effect of contact time on Cd(II) and Cu(II) sorption by HFO-BC, and the obtained kinetics curves are shown in Figure 4. It can be seen that Cd(II) and Cu(II) adsorption onto HFO-BC can approach equilibrium within 100 min and can be roughly divided into two stages, i.e., a quick sorption step in initial 30 min followed by a relatively slow sorption process in 30–100 min. The pseudo-first- and second-order kinetics models listed below were first applied to fit the experimental data, and the pseudo-second-order can better simulate two metal sorptions by HFO-BC with related coefficients more than 0.96 (Figure 4a).

### Equation as follows:

\[
\ln(Q_e - Q_t) = \ln Q_e - \frac{K_1}{2.303} t
\]

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}
\]

Where \( Q_e \) is the equilibrium sorption of Cd(II) and Cu(II) (mg/g). \( Q_t \) indicates the adsorption capacity at time \( t \) (min), and \( k_1 \) and \( k_2 \) are the pseudo-first- and pseudo-second-order kinetic adsorption rate constants, respectively. The predicted \( Q_e \) values based on the pseudo-second-order are 9.3 and 15.9 mg/g for Cd(II) and Cu(II), respectively, which are close to the experimental values (8.6 mg/g for Cd(II) and 15.3 mg/g for Cu(II)). To clarify the microprocess of two pollutant adsorptions onto HFO-BC, we also employed the classic intraparticle diffusion model to predict the sorption kinetics.

\[
\frac{Q_t}{e} = K_f t^{1/2} + C
\]

Where \( K_f \) is the diffusion rate constant of Cd(II) and Cu(II), and \( C \) is the intercept of the model. As shown in Figure 4b, the divided two stages well represent the migration of Cd(II) and Cu(II) from solution to the outside surface of HFO-BC and their diffusion inside the pore region of adsorbent, according to the widely accepted sorption diffusion theory. Of note, the quicker diffusion of Cu(II) than Cd(II) for two stages is put down to its lower hydrated ionic radius (0.073 vs 0.095 nm), which is subjected to less diffusion resistance.

3.5. Competing Effect of Coexisting Cations. In various waters, there are high levels of eco-friendly cations coexisting with heavy metals, which usually impact the adsorption...
performance of given adsorbents because of their similar chemistry to targeted metals. Among these cations, Ca(II) and Mg(II) have lower hydration energy and thus possess greater ion exchange ability.33 In this study, the effect of Ca(II) and Mg(II) on Cd(II) and Cu(II) uptake by HFO-BC was investigated with the carrier BC as reference adsorbent, and the results are illustrated in Figure 5. As depicted, Cd(II) and Cu(II) retention onto HFO-BC and BC was affected by the introduced coexisting cations to varying degrees. More specifically, increasing the molar ratio of Ca(II) and Mg(II) to target metals from 0 to 50 only causes 60 and 35% drop for Cd(II) and 30 and 23% drop for Cu(II) in removal by HFO-BC, respectively. As for BC, the corresponding drop values for Cd(II) and Cu(II) are 73, 53, and 70, 56%, respectively. Clearly, the presence of HFO has greatly enhanced the sorption preference of HFO-BC to two metals in the coexistence of high levels of Ca(II) and Mg(II). Furthermore, the greater interference of Ca(II) toward Cd(II) and Cu(II) sorption onto HFO-BC compared to Mg(II) was also put down to its higher hydration energy (−1656 vs −2049 kJ/mol).44 It can be ascribed to the specific inner-sphere complexation (two atoms share a couple of electrons, one atom affords the empty orbit, and the other one provides the lone electron pair) between HFO and Cd(II) and Cu(II), which was elaborated in elsewhere by means of EXAFS.45 We also preliminarily revealed this interaction through XPS analysis in the subsequent section. Of note, Ca(II) and Mg(II) adsorption on either HFO or the host BC was through the nonspecific Coulomb attraction.

Further, the distribution coefficient $K_d$ was also employed to quantify the adsorption selectivity of Cd(II) and Cu(II) by HFO-BC and BC, and the calculated results are shown in Table 2.

$$K_d = \frac{C_0 - C}{m} \times \frac{V}{C_0}$$  \hspace{1cm} (15)

Where $C_0$ (mg/L) indicates the initial concentrations of heavy metals, $V$ (mL) represents the volume of the solution, and $m$ (g) represents the mass of BC or HFO-BC. Obviously, the $K_d$ values of Cd(II) and Cu(II) adsorption onto HFO-BC are ~1 order of magnitude greater than those for BC, confirming the greater sorption preference of HFO-BC to Cd(II) and Cu(II).

Another noteworthy phenomenon is that Cd(II) adsorption onto HFO-BC suffers more significant impact by the added Ca(II) and Mg(II) compared to Cu(II), indicating the stronger binding of Cu(II) with two adsorbents. It is attributed to the higher covalent index of Cu(II) than Cd(II) (6.41 vs 5.51).45,46 In other words, Cu(II) with higher covalent index is easier to form covalent bonds with HFO, and thus result in a stronger adsorption on HFO-BC. The excellent sorption selectivity of HFO-BC to Cd(II) and Cu(II) manifests that it is of great promise for the decontamination of the practical heavy metal-polluted wastewater.

### Table 2. The $K_d$ Values of Cd(II) and Cu(II) Adsorption onto BC and HFO-BC

| coexisting cations | adsorbate | adsorbents | 0  | 10  | 20  | 30  | 40  | 50  |
|--------------------|-----------|------------|----|-----|-----|-----|-----|-----|
| Ca(II)             | Cd(II)    | HFO-BC     | 508| 421 | 352 | 271 | 213 | 202 |
|                    |           | BC         | 96 | 76  | 57  | 38  | 38  | 25  |
| Cu(II)             | HFO-BC    | 1748       | 1386| 1265| 1247| 1229| 1216|
| Mg(II)             | Cd(II)    | HFO-BC     | 498| 272 | 264 | 236 | 177 | 149 |
|                    |           | BC         | 96 | 89  | 70  | 51  | 57  | 44  |
| Cu(II)             | HFO-BC    | 1748       | 1588| 1497| 1474| 1420| 1337|
|                    |           | BC         | 498| 372 | 329 | 285 | 236 | 218 |
spectra of Cd\textsubscript{3d5/2} in Figure 6a shows that the binding energy of the Cd\textsubscript{3d5/2} peak for Cd(II)-adsorbed HFO-BC is around 405.1 eV, which is about 0.6 eV lower than that of the pure CdCl\textsubscript{2}. For Cu(II)-loaded HFO-BC, the binding energy of the Cu\textsubscript{2p3/2} peak is centered at 934.3 eV and a negative 0.8 eV shift compared to that of CuCl\textsubscript{2} in Figure 6b. The lower XPS binding energies of two metals for the spent HFO-BC compared to those for their corresponding chlorides suggest that the interaction of the targeted metal and HFO-BC is stronger than the electrostatic attraction. It is put down to the specific and strong affinity of the impregnated HFO to Cd(II) and Cu(II), that is, the inner-sphere complexation.\textsuperscript{21}

To further support the aforementioned mechanism, we also performed the XPS analysis of the high-resolution O\textsubscript{1s} spectra for the fresh and spent HFO-BC (Figure 6c). The O\textsubscript{1s} peak was first divided into four peaks corresponding to Fe–O–Fe, Fe–OH/carbonyl/quinone, H–O–H/ethers/hydroxyl, and anhydride/lactone/carboxylic acids according to the earlier studies,\textsuperscript{34} and the detailed results are listed in Table S4. It can be found that although the proportion of four oxygen forms is relatively fixed for HFO-BC before and after Cd(II) and Cu(II) adsorption, the binding energies of Fe–O–Fe and Fe–OH groups for Cd(II)- and Cu(II)-adsorbed HFO-BC were higher than the corresponding values of the fresh HFO-BC. It further validates that the inner-sphere complexation between the embedded HFO and targeted metals and also indicates that this specific interaction was formed through the binding of the Fe–O–Fe and Fe–OH groups to Cd(II) and Cu(II), consistent with the results of eqs 3 and 4. On the basis of EXAFS analysis, Cd(II) and Cu(II) were adsorbed through forming the edge-linked complexes with Fe(O,OH)\textsubscript{6} octahedra of the impregnated HFO, which involved to Fe–O and –OH groups.\textsuperscript{47,48} According to the aforementioned results for XPS
analysis, the schematic diagram for Cd(II) and Cu(II) adsorption mechanism onto HFO-BC is presented in Figure 7.

Figure 7. The schematic graph of the adsorption mechanism of Cd(II) and Cu(II) onto HFO-BC.

3.7. Column Adsorption Test. The laboratory-scale small column adsorption experiments were preformed to evaluate the practical application feasibility of HFO-BC for decontaminating Cd(II)- and Cu(II)-polluted wastewater through using the synthetic wastewater as feeding solutions, and the breakthrough curves are recorded in Figure 8a. As shown, HFO-BC can treat 129 and 300 BV of Cd(II)- and Cu(II)-contaminated wastewater, respectively, to meet their corresponding discharge limits recommended by the integrated wastewater discharge standard of China (0.1 mg/L for Cd(II) and 1 mg/L for Cu(II)), equivalent to 774- and 1854-fold of its own weight. But for the reference BC, it can only generate 15 and 18 BV effluents for Cd(II) and Cu(II), respectively, with the same breakthrough points. The maximum removal efficiencies of Cd(II) and Cu(II) by HFO-BC column are up to 99.9 and 99.8%, respectively (Figure S5). The excellent treatment ability of HFO-BC toward Cd(II)- and Cu(II)-laden wastewater can be ascribed to the strong and specific interaction of the impregnated HFO to the targeted metals. More importantly, the spent HFO-BC can be in situ-desorbed using the acid–salt binary solution. More than 95% of the adsorbed Cd(II) can be eluted by the 0.01 mol/L HCl and 4 wt % CaCl₂ binary solution (pH around 1). A 10 times more acidic regenerant was used to elute the Cu(II)-sorbed HFO-BC due to the stronger binding of HFO and Cu(II), and a desorption rate of ~98% was obtained (Figure 8b). Furthermore, the majority of the loaded Cu(II) and Cd(II) was desorbed in the initial 5 BV as shown in Figure S6. Furthermore, after three adsorption–desorption cycles, the removal of Cu(II) and Cd(II) by HFO-BC has no noticeable decline (Figure S7). The outstanding performance of HFO-BC in column adsorption experiments indicates it has great potential for practical application.

4. CONCLUSIONS

In this study, to promote the adsorption capacity and selectivity of BC to heavy metals, a new composite adsorbent named HFO-BC was prepared through immobilizing HFO within the pore region of BC. The as-obtained hybrid material showed excellent sorption performance to Cd(II) and Cu(II). The removal of Cd(II) and Cu(II) onto HFO-BC can be facilitated by the increased solution pH and was limitedly influenced by high concentrations of Ca(II) and Mg(II) as a result of the specific inner-sphere complexation between HFO and target metal. The sorption of Cd(II) and Cu(II) by HFO-BC approached equilibrium within 100 min and accorded to the intraparticle diffusion model. The satisfactory performance of HFO-BC in column adsorption and desorption tests implied that it has great possibility to be applied in practical engineering to capture heavy metals from wastewater. All results show that loading HFO is a feasible measure to broaden the application space of biochar.

ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03893.

The fitting parameters for adsorption isotherms and kinetics, thermodynamic parameters of Cd(II) and Cu(II) adsorption, and the details of the divided four oxygen forms for O1s XPS spectra of the fresh and spent HFO-BC. The schematic diagram of the column adsorption setting, EDS analysis of HFO-BC, the influence of the HFO-BC dosage and initial concentration on Cd(II) and Cu(II) adsorption in solution, the full scan XPS spectra of HFO-BC before and after Cd(II) and Cu(II) adsorption, the removal efficiency of Cd(II) and Cu(II) by HFO-BC in column adsorption test, regeneration of the exhausted HFO-BC for each BV, and the adsorption–desorption cycles of Cd(II) and Cu(II) on HFO-BC (PDF).
AUTHOR INFORMATION

Corresponding Authors
Liangmin Gao — School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China; Phone: +86-554-6631015; Email: lmgao@aust.edu.cn; Fax: +86-554-6631015
Shunli Wan — College of Life & Environmental Sciences, Huangshan University, Huangshan 245041, China; orcid.org/0000-0001-5662-1373; Phone: +86-559-2546852; Email: wsl@hsu.edu.cn

Authors
Yan Li — School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China; College of Life & Environmental Sciences, Huangshan University, Huangshan 245041, China
Zhongxiang Lu — College of Life & Environmental Sciences, Huangshan University, Huangshan 245041, China; orcid.org/0000-0002-1786-4994
Yuchen Wang — College of Life & Environmental Sciences, Huangshan University, Huangshan 245041, China
Yan Wang — College of Life & Environmental Sciences, Huangshan University, Huangshan 245041, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03893

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The majority of this work was supported by the Natural Science Foundation of China (no. 22006047), the Natural Science Foundation of Anhui province (no. 1908085QB86), the Open Fund of State Key Laboratory of Pollution Control and Resource Reuse (no. PCRRF19028), the Fund of the Quality Engineering of Education Department for Anhui Province (no. 2018JXTD149), the Innovative Training Foundation of College Students of Huangshan University (2019069), the Talent Startup Fund of Huangshan University (2019xjqt007), and the Fund of Research Platform of Huangshan university (kypt201802).

REFERENCES

(1) Fu, F.; Wang, Q. Removal of heavy metal ions from waters: a review. J. Environ. Manage. 2011, 92, 407−418.
(2) Khanam, R.; Kumar, A.; Nayak, A. K.; Shahid, M.; Tripathi, R.; Vijayakumar, S.; Bhaduri, D.; Kumar, U.; Mohanty, S.; Panneerselvam, P.; Chatterjee, D.; Satapathy, B. S.; Pathak, H. Metalloid(s) (As, Hg, Se, Pb and Cd) in paddy soil: Bioavailability and potential risk to human health. Sci. Total Environ. 2020, 699, 134330.
(3) Wadhwana, S.; Jain, A.; Nayar, J.; Mehta, S. K. Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: a review. J. Water Process Eng. 2020, 33, 101038.
(4) China EPA, Emission standard of pollutants for electroplating (GB21900−2008); EPA China, 2008.
(5) WHO. Guidelines for drinking-water quality; World Health Organization 2006.
(6) Zhang, Y.; Duan, X. Chemical precipitation of heavy metals from wastewater by using the synthetic magnesium hydroxy carbonate. Water Sci. Technol. 2019, 81, 1130−1136.
(7) al Aji, B.; Yavuz, Y.; Koparal, A. S. Electrococagulation of heavy metals containing model wastewater using monopolar iron electrodes. Sep. Purif. Technol. 2012, 86, 248−254.
(8) Khulbe, K. C.; Matsura, T. Removal of heavy metals and pollutants by membrane adsorption techniques. Applied Water Science 2018, 8, 19.
(9) Moosavirad, S. M.; Sarikhani, R.; Shahsavani, E.; Mohammadi, S. Z. Removal of some heavy metals from inorganic industrial wastewaters by ion exchange method. J. Water Chem. Technol. 2015, 37, 191−199.
(10) Sdiri, A. T.; Higashi, T.; Jamoussi, F. Adsorption of copper and zinc onto natural clay in single and binary systems. Int. J. Environ. Sci. Technol. 2013, 11, 1081−1092.
(11) Atkowska, K.; Lisichkov, K.; Ruseksa, G.; Dimitrov, A. T.; Grozdanov, A. Removal of heavy metal ions from wastewater using conventional and nanosorbents: a review. J. Chem. Technol. Metal. 2018, 53, 202−219.
(12) Zhu, Y.; Fan, W.; Zhou, T.; Li, X. Removal of chelated heavy metals from aqueous solution: A review of current methods and mechanisms. Sci. Total Environ. 2019, 678, 253−266.
(13) Afroze, S.; Sen, T. K. A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. Water Air Soil Poll. 2018, 229, 225.
(14) Mohan, D.; Sarswat, A.; Ok, Y. S.; Pittman, C. U., Jr. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent — A critical review. Bioresour. Technol. 2014, 160, 191−202.
(15) Ahmad, M.; Rajapaksha, A. U.; Lim, J. E.; Zhang, M.; Bolan, N.; Mohan, D.; Vithanage, M.; Lee, S. S.; Ok, Y. S. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere 2014, 99, 19−33.
(16) Doumer, M. E.; Rigol, A.; Vidal, M.; Mangrich, A. S. Removal of Cd, Cu, Pb, and Zn from aqueous solutions by biochars. Environ. Sci. Pollut. R. 2016, 23, 2684−2692.
(17) Mohan, D.; Pittman, C. U., Jr.; Bricka, M.; Smith, F.; Yancey, B.; Mohammad, J.; Steele, P. H.; Alexandre-Franco, M. F.; Gómez-Serrano, V.; Gong, H. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J. Colloid. Interface Sci. 2007, 310, 57−73.
(18) Kolodyńska, D.; Wnętrzak, R.; Leahy, J. J.; Hayes, M. H. B.; Kwapiński, W.; Hubicki, Z. Kinetic and adsorptive characterization of biochar in metal ions removal. Chem. Eng. J. 2012, 197, 295−305.
(19) Su, Q.; Pan, B.; Wan, S.; Zhang, W.; Lv, L. Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water. J. Colloid Interface Sci. 2010, 349, 607−612.
(20) Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q. Heavy metal removal from water/wastewater by nanosized metal oxides: a review. J. Hazard. Mater. 2012, 211−212, 317−331.
(21) Kinniburgh, D. G.; Syers, J. K.; Jackson, M. L. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminum. Soil Sci. Soc. Am. J. 1975, 39, 464−470.
(22) Liu, R.; Liu, F.; Hu, C.; He, Z.; Liu, H.; Qu, J. Simultaneous removal of Cd(II) and Sb(V) by Fe-Mn binary oxide: positive effects of Cd(II) on Sb(V) adsorption. J. Hazard. Mater. 2015, 300, 847−854.
(23) O’Reilly, S. E.; Hochella, M. F., Jr. Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. Geochim. Cosmochim. Acta 2003, 67, 4471−4487.
(24) Hu, J. L.; Yang, X. S.; Liu, T.; Shao, L. N.; Zhang, W. Dynamic desorption of arsenic from polymer-supported hydrated iron(III) oxide in a wastewater treatment plant. Water Sci. Technol. 2017, 76, 2380−2388.
(25) Wan, S.; Liu, G.; He, H.; Qu, N.; Ma, Z.; Xue, Y. Hydrated ferric oxide (HFO)-encapsulated tea waste for enhanced lead(II), cadmium(II), and copper(II) removal from waters. Desalin. Water Treat. 2015, 57, 19456−19465.
(26) Gupta, V. K.; Nayak, A. Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe3O4 nanoparticles. Chem. Eng. J. 2012, 180, 81−90.
(27) Wang, J.; Wang, S. Preparation, modification and environmental application of biochar: A review. J. Clean. Prod. 2019, 227, 1002–1022.

(28) Peng, H.; Gao, P.; Chu, G.; Pan, B.; Peng, J.; Xing, B. Enhanced adsorption of Cu(II) and Cd(II) by phosphoric acid-modified biochars. Environ. Pollut. 2017, 229, 846–853.

(29) Karaozmanolu, F.; Işığığır-Ergüdenler, A.; Sever, A. Biochar from the straw-stalk of rapeseed plant. Energy Fuel 2000, 14, 336–339.

(30) Zaitsev, V. S.; Filimonov, D. S.; Presnyakov, I. A.; Gambino, R. J.; Chu, B. Physical and chemical properties of magnetite and magnetite-polymer nanoparticles and their colloidal dispersions. J. Colloid Interface Sci. 1999, 212, 49–57.

(31) Cao, X.; Huang, Y.; Tang, C.; Wang, J.; Jonson, D.; Fang, Y. Preliminary study on the electrocatalytic performance of an iron biochar catalyst prepared from iron-enriched plants. J. Environ. Sci. China 2020, 88, 81–89.

(32) Ahmad, Z.; Gao, B.; Mosa, A.; Yu, H.; Yin, X.; Bashir, A.; Ghoveis, H.; Wang, S. Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. J. Cleaner Prod. 2018, 180, 437–449.

(33) Wan, S.; Wu, J.; Zhou, S.; Wang, R.; Gao, B.; He, F. Enhanced lead and cadmium removal using biochar-supported hydrated manganese oxide (HMO) nanoparticles: Behavior and mechanism. Sci. Total Environ. 2018, 616-617, 1298–1306.

(34) Dong, X.; Ma, L.; Q.; Zhu, Y.; Li, Y.; Gu, B. Mechanistic investigation ofmercury sorption by Brazilian pepper biochars of different pyrolytic temperatures based on X-ray photoelectron spectroscopy and flow calorimetry. Environ. Sci. Technol. 2013, 47, 12156–12164.

(35) Amin, M. T.; Alazba, A. A.; Shafoq, M. Removal of Copper and Lead using Banana Biochar in Batch Adsorption Systems: Isotherms and Kinetic Studies. Arabian J. Sci. Eng. 2017, 43, 5711–5722.

(36) Wang, Z.; Shen, F.; Shen, D.; Jiang, Y.; Xiao, R. Immobilization of Cu(II) and Cd(II) by earthworm manure derived biochar in acidic circumstance. J. Environ. Sci. China 2017, 53, 293–300.

(37) Elabbas, S.; Ouazzani, N.; Mandi, L.; Berrekhis, F.; Perdicakis, M.; Pontvianne, S.; Pons, M. N.; Lapicque, F.; Leclerc, J. P. Treatment of highly concentrated tannery wastewater using electrocoagulation: Influence of the quality of aluminium used for the electrode. J. Hazard. Mater. 2016, 319, 69–77.

(38) Štefešová, J.; Zelenka, T.; Slovak, V. Biosorption (removing) of Cd(II), Cu(II) and methylene blue using biochar produced by different pyrolysis conditions of beech and spruce sawdust. Wood Sci. Technol. 2017, 51, 1321–1338.

(39) Xu, X.; Cao, X.; Zhao, L. Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: role of mineral components in biochars. Chemosphere 2013, 92, 955–961.

(40) Arán, D.; Antelo, J.; Fiol, S.; Macías, F. Influence of feedstock on the copper removal capacity of waste-derived biochars. Bioresour. Technol. 2016, 212, 199–206.

(41) Yalkala, K.; Yu, M. R.; Roh, H.; Yang, J. K.; Chang, Y. Y. Buffalo weed (Ambrosia trifida L. var. trifida) biochar for cadmium (II) and lead (II) adsorption in single and mixed system. Desalin. Water Treat. 2013, 51, 7732–7745.

(42) Liu, X.; Gao, M.; Qiu, W.; Khan, Z. H.; Liu, N.; Lin, L.; Song, Z. Fe-Mn-Ce oxide-modified biochar composites as efficient adsorbents for removing As(III) from water: adsorption performance and mechanisms. Environ. Sci. Pollut. Res. 2019, 26, 17373–17382.

(43) Singh, D. B.; Prasad, G.; Rupainwar, D. C. Adsorption technique for the treatment of As(V)-rich effluents. Colloids Surf. A. 1996, 111, 49–56.

(44) Marcus, Y. Thermodynamics of solvation of ions. part 5-gibbs free energy of hydration at 298.15 K. J. Chem. Soc., Faraday Trans. 1991, 87, 2995–2999.

(45) Nieboer, E.; Mcbryde, W. A. E. Free-energy relationships in coordination chemistry. III. a comprehensive index to complex stability. Can. J. Chem. 1973, 51, 2512–2524.