Synthesis of zero-valent iron/biochar by carbothermal reduction from wood waste and iron mud for removing rhodamine B

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GRAPHICAL ABSTRACT

ABSTRACT

This study proposes a new process to synthesize zero-valent iron/biochar (Fe⁰-BC) by carbothermal reduction using wood waste and iron mud as raw materials under different temperature. The characterization results showed that the Fe⁰-BC synthesized at 1200°C (Fe⁰-BC-1200) possessed favorable adsorption capacity with the specific surface area of 103.18 m²/g, and that the zero-valent iron (Fe⁰) particles were uniformly dispersed on the biochar surface. The removal efficiency of rhodamine B (RB) was determined to evaluate the performance of the prepared Fe⁰-BC. Fe⁰-BC-1200 presented the best performance on RB removal, which mainly ascribe to that more Fe⁰ particles generated at higher temperature. The equilibrium adsorption capacity reached 49.93 mg/g when the initial RB concentration and the Fe⁰-BC-1200 dosage were 100 mg/L and 2g/L, respectively, and the pseudo-second-order model was suitable to fit the removal experimental data. LCMC and XRD analyses revealed that the removal mechanism included the physical adsorption of biochar and the redox reaction of Fe⁰. Moreover, copper existed in the iron mud was also reduced to Cu⁰, which was beneficial to catalyze the oxidation of iron, the degradation of RB was promoted at the same time.

Keywords: Wood waste; Iron mud; Carbothermal reduction; zero-valent iron/biochar; Rhodamine B.
In recent years, with the rapid growth in the living standard in China, the life cycle of many furniture is becoming shorter and shorter, and frequent housing rental activities increase the probability of wood waste being abandoned. According to statistics, about 85 million m³ of bulky wood waste are produced every year in China. The main component of wood waste is wood, and the carbon content is between 40% and 50% (Emandi et al., 2011; Tsoumis, 2013; Demirbaş, 2005). Thus, preparing biochar by pyrolysis of wood waste is one of the effective recycling methods. Biochar shows outstanding potential for removing organic contaminants from the environment by possessing abundant oxygen-containing functional groups and large surface area (Liu et al., 2015; Zhang et al., 2019; Huang et al., 2018; Wang et al., 2018). However, the application of biochar in wastewater has some problems, such as difficult separation and incomplete removal (Chen et al., 2011; Du et al., 2020). To overcome these shortcomings, many researchers loaded zero-valent iron (Fe⁰) on biochar surface to synthesize zero-valent iron/biochar (Fe⁰-BC). Fe⁰, especially nano size Fe⁰ is also an excellent environmental remediation material has been widely used in wastewater and contaminated soil treatment due to its high reducibility for heavy metals and organic matter (Pourrezaei et al., 2014; Reddy et al., 2016; Calderon and Fullana, 2015; Ghariani et al., 2019). As a combination, Fe⁰-BC has the advantages of both biochar and Fe⁰, thereby it provides higher reduction or degradation efficiency and other benefits including easiness to recycle, non-aggregation (Bakshi et al., 2018; Li et al., 2020; Dong et al., 2017; Li et al., 2019). More and more studies proved that Fe⁰-BC show better performance in removing different contaminants through reduction, adsorption, precipitation and other mechanisms (Frick et al., 2016; Oh et al., 2016; Oleszczuk and Kołtowski, 2017; Mitzia et al., 2020).

In order to obtained the more valuable Fe⁰-BC, the other solid waste, iron mud could be used as an iron resource for collaborative utilization with wood waste. Iron mud refers to the waste slag with high iron content produced in chemical industrial production, such as dyeing and printing enterprises (Pani et al., 2019; Liu et al., 2018). The iron mud mainly contains iron oxide and organic compounds that can be recovered (Zhu et al., 2018). At present, iron mud is usually disposed by stacking, landfilling, or sending to steel plants as a raw material of iron-making in China (Liu et al., 2014). The stacking and landfilling of iron mud take up massive land, and the existing hazardous substances permeate into the underground, causing secondary pollution to the environment. For sending to steel plant, iron mud can easily block the furnace because of its fine particle size, thereby seriously reducing the product quality and complicating the recycling process.

At present, the most used widely synthesis method is the two-step method (Devi et al., 2014; Liu et al., 2015; Zhao et al., 2020; Han et al., 2019; Sun et al., 2019; Dewage et al., 2018), which refer to that the biomass is pyrolyzed to obtain biochar firstly, then strongly impregnated in the high valent iron salts, and then reduced through liquid-
phase or gas-phase reductant. Devi et al. (2014) synthesized Fe\textsuperscript{0}/BC composites from the paper mill sludge through the following process: paper mill sludge was pyrolyzed to biochar at 700 °C, mixed with FeSO\textsubscript{4}·H\textsubscript{2}O, and then added NaBH\textsubscript{4} as a reducing agent for the reduction of Fe\textsuperscript{3+} to Fe\textsuperscript{0} at the same time. Liu et al. (2015) obtained Fe\textsuperscript{0}/BC by the reduction of natural limonite and pine biomass using H\textsubscript{2} at 550°C. The above synthesis process needs a large number of reducing reagents, with high raw material cost and complex operation, thus, it can only be applied to laboratory research.

Carbothermal reduction is another synthesis method (Lawrinenko et al., 2017; Mandal et al., 2017; Hussain et al., 2017), in which iron compounds and biomass are mixed to pyrolysis at a high temperature, the iron compounds are reduced by the reducing substances generated during biomass pyrolysis, and then Fe\textsuperscript{0}/BC is prepared by one step. Lawrinenko et al. (2017) successfully prepared Fe\textsuperscript{0}/BC through the slow pyrolysis of lignin and magnetite mixtures in a muffle furnace and heated at 900 °C for 4 h. By contrast, carbothermal reduction has the advantages of low raw material cost, simple process, easy scaling, continuous production (Shang et al., 2017).

Rhodamine B (RB), C\textsubscript{28}H\textsubscript{31}N\textsubscript{2}O\textsubscript{3}Cl, a highly water-soluble and bright red fluorescent xanthene dye, is widely used as colorant for textiles and food industry (Long et al., 2014). However, it has been proven that RB has toxic effects on animals and humans, including carcinogenicity, reproductive toxicity and neurotoxicity (Dong et al., 2010). RB is a ubiquitous organic pollutant in printing and dyeing wastewater due to the wide application in the textile industry (Lops et al., 2019; Huang et al., 2017). Therefore, it has great significance to find a suitable process or material to remove the RB in wastewater.

The massive production and stacking of wood waste and iron mud engenders a serious environmental pollution and waste of resources. To overcome these problems, in this study, a novel process, wood waste and iron mud were used as raw materials, to synthetize Fe\textsuperscript{0}-BC through carbothermal reduction, was proposed. At the same time, the removal efficiency of RB was conducted to evaluate the performance of synthetic Fe\textsuperscript{0}-BC. The structural composition and micromorphology of synthetic Fe\textsuperscript{0}-BC was investigated. Moreover, the interaction process between the Fe\textsuperscript{0}-BC and RB was also studied.

### Materials and Methods

#### Materials

The iron mud used in this study was obtained from a printing and dyeing factory in Shanghai, China. The chemical compositions of iron mud measured by X-ray fluorescence spectrometry (XRF) is shown in Table 1, and the X-ray diffraction (XRD) pattern of the iron mud is presented in Figure 1. The results show that the iron mud contain 41.71% Fe\textsubscript{2}O\textsubscript{3}, 15.23% CuO, and 10.12% C, and the main phases are magnetite (Fe\textsubscript{3}O\textsubscript{4}), Tenorite (CuO), organic iron (Fe\textsubscript{2}C\textsubscript{6}H\textsubscript{10}O\textsubscript{4}) and calcium aluminosilicate. Wood
waste used in this study was abandoned wooden chair from the laboratory. The chair is made of pine wood board and is not painted. The carbon content of the chair is 43.14%, which was measured by Elemental Analyzer (FlashSmart, Thermo, American).

All chemical reagents are analytically pure, and ultrapure water was used throughout this study.

Table 1 Chemical compositions of the iron mud

| Component | Fe$_2$O$_3$ | CuO  | C    | CaO  | Al$_2$O$_3$ | SiO$_2$ | MgO  | TiO$_2$ | P$_2$O$_5$ | Na$_2$O |
|-----------|-------------|------|------|------|-------------|---------|------|---------|-----------|---------|
| Content(%) | 41.71       | 15.23| 10.12| 5.24 | 4.43        | 4.31    | 1.37 | 0.65    | 0.12      | 0.08    |

Figure 1. XRD patterns of the iron mud

Synthesis of Fe$^0$-BC

According to our previous related works (Geng et al., 2020; Chen et al., 2019), Fe$^0$-BC was prepared as shown in Figure 2. Firstly, the wooden chair and iron mud were dried in an oven for 2 h at 110 °C after cleaning, and then the wood flour was prepared by crushing in a crusher and passing through a 40-mesh sieve. Additionally, the wood flour and dried iron mud with a mass ratio of 1:2 were homogeneously mixed using a 150r/min roller mill for 5 min, and then a 40 g mixture was placed into a corundum crucible. Subsequently, carbothermal reduction of the mixture was conducted by heating under nitrogen in a sealed furnace at 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, respectively. The furnace temperature was increased at an average of 15 °C/min, and a 180 min holding time was applied when the temperature reached the target temperature. After roasting, the reduced product was taken out when self-cooled down to laboratory temperature. Finally, Fe$^0$-BC was prepared by grinding in a 200r/min rod mill for 10 min and passing through a 200-mesh sieve, named as Fe$^0$-BC-T, where T indicates the carbothermal reduction temperature. The synthesis process was repeated three times at each temperature. The subsequent experimental data used for plotting graphs is the average value of three experimental data.

After synthesis of Fe$^0$-BC-T, some samples were cleaned repeatedly using 2 mol/L HCl until no change in weight after drying. And then the biochar without Fe was obtained, named as BC-T.
Characterizations

The pore-structure parameters were measured by specific surface area and porosity analyzer (ASAP2010, Micromeritics, American) using N₂ adsorption method. The phase composition present in the samples was detected by XRD (D/max-2550, Rigaku, Japan) with Cu Kα radiation over a 2θ collection range of 10°~90°. Micromorphology was analyzed by scanning electron microscope (SEM), and energy dispersive spectrometry (EDS) ((JSM-6460LV, JEOL, Japan).

Removal experiments

The removal efficiency of RB on different materials was investigated, including the Fe⁰-BC-T, BC-T and the purchased Fe⁰ powder. 1.6 g of each material (2g/L) was added into a 1000 mL conical flask with 800 mL RB solution with an initial concentration of 100 mg/L and an initial pH ranging from 1.5 to 6. The pH of the prepared 100mol/L RB solution is 4.02. The target initial pH value of solution was adjusted by diluted HCl or NaOH. The conical flasks were placed in a 60 r/min shaker at 25 ℃, and 5ml of suspension extracted from flask was filtered with a 0.45 μm microporous filtration membrane at predetermined time intervals. Meanwhile, the solution pH value was recorded during the whole removal process. The residual RB concentrations were evaluated by ultraviolet and visible spectrophotometry (UV-Vis) (5B-3B, Lian-hua, China). RB removal capacity and removal efficiency can be obtained by Eq. (1) and Eq. (2), respectively.

\[ q_e = \frac{C_0 - C_e}{m} V \]  
\[ R = \frac{C_0 - C_t}{C_0} \times 100 \]
Where $q_e$, $R$, $m$, $V$ stand for the RB removal capacity (mg/g), removal efficiency (%), RB solution volume (L), and the dose (g) of materials. $c_0$, $c_e$, $c_t$ stand for initial concentration (mg/L), equilibrium concentration (mg/L) and residual concentration (mg/L) at time $t$ (min).

Adsorption kinetic of removal process was evaluated by pseudo-first order and pseudo-second-order models, as shown in Eq. (5) and Eq. (6) respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $k_1$ (min$^{-1}$) and $k_2$ (g/(mg min)) stand for the sorption rate constants of quasi-first order and quasi-second order, respectively; $q_e$ (mg/g) represent the removal capacities at the equilibrium; $q_t$ (mg/g) represent the removal capacities at the time $t$ (min).

Reaction products at different times were measured by LCMS (1290II-6460, Agilent, American) under the following conditions: chromatographic column of XDB-C8 4.6*150mm, 5μm, column temperature of 50℃, mobile phase of methanol-water (70:30), test time of 30min, and flow rate of 0.8mL/min.

**Results and discussion**

**Characterization of Fe$^0$-BC**

The XRD analysis results of Fe$^0$-BC prepared at different temperature are shown in Figure 3. The main phases of Fe$^0$-BC-800 and Fe$^0$-BC-900 are both Fe$_3$O$_4$ and CuO. This finding indicated that the organic iron in the mixture were pyrolyzed to Fe$_3$O$_4$, whereas the iron oxide was not reduced under 900 ℃. The diffraction peaks of CuO disappeared and the diffraction peaks of zero valent copper (Cu$^0$) were observed in the XRD pattern of Fe$^0$-BC-1000, which confirmed that CuO was reduced by the reducibility of pyrolysis products such as C, CO, H$_2$, as shown in Eq. (3). When the reduced temperature reached 1100 ℃, the diffraction peaks of zero valent iron (Fe$^0$) appeared and the diffraction peaks of Fe$_3$O$_4$ weakened, proving that part of Fe$_3$O$_4$ was reduced via Eq. (4) at this temperature (Chen et al., 2017). The main phases of Fe$^0$-BC-1200 are Fe$^0$ and Cu$^0$, and the iron oxide in the mixture completely reduced to Fe$^0$ at 1200 ℃.

$$\text{CuO} + \text{C}/\text{CO}/\text{H}_2 \rightarrow \text{Cu} + \text{CO}/\text{CO}_2/\text{H}_2\text{O} \quad (5)$$

$$\text{Fe}_3\text{O}_4 + 4\text{C}/\text{CO}/\text{H}_2 \rightarrow 3\text{Fe} + 4\text{CO}/\text{CO}_2/\text{H}_2\text{O} \quad (6)$$
Figure 3. XRD patterns of Fe<sup>0</sup>-BC

Table 2 shows the main element composition of different Fe<sup>0</sup>-BC materials. As shown in Table 2, the content of C was higher than those of Fe and Cu, and the content of Fe and Cu increased with the increase of temperature. This result can be ascribed to the fact that the increase of temperature is conducive to the reduction of iron and copper compounds. Thus, the carbon reductant was consumed at a high temperature. The surface area and pore size of Fe<sup>0</sup>-BC are shown in Table 3. It can be seen that the Fe<sup>0</sup>-BC have similar properties in pore structure with the specific surface area is about 100 m<sup>2</sup>/g and a pore size between 3 and 4 nm, indicating favorable adsorption performance to some extent.

Table 2 Main element contents of Fe<sup>0</sup>-BC

| Element   | Fe  | C     | Cu   |
|-----------|-----|-------|------|
| Fe<sup>0</sup>-BC-800 | 23.8 | 44.2  | 16.6 |
| Fe<sup>0</sup>-BC-900  | 23.6 | 43.3  | 16.9 |
| Fe<sup>0</sup>-BC-1000 | 26.7 | 40.7  | 17.8 |
| Fe<sup>0</sup>-BC-1100 | 27.2 | 37.4  | 17.6 |
| Fe<sup>0</sup>-BC-1200 | 31.2 | 34.3  | 20.4 |

Table 3 The pore-structure parameters of Fe-C

| Sample   | specific surface area (m<sup>2</sup>/g) | pore Diameter (nm) |
|----------|---------------------------------------|--------------------|
| Fe<sup>0</sup>-BC-800 | 151.8 | 4.19 |
| Fe<sup>0</sup>-BC-900  | 143.6 | 3.32 |
| Fe<sup>0</sup>-BC-1000 | 116.7 | 3.35 |
| Fe<sup>0</sup>-BC-1100 | 97.2  | 4.21 |
| Fe<sup>0</sup>-BC-1200 | 103.18| 3.69 |

Consistent with previous studies (Kong et al., 2018; Geng et al., 2019; Shen et al.,
200 2019), the above results proved that the temperature of carbothermal reduction
202 considerably influenced the phase of Fe, and only Fe\textsuperscript{0}-BC-1200 existed no other iron-
203 containing phases aside from Fe\textsuperscript{0}. SEM and EDS analyses were performed on Fe\textsuperscript{0}-BC-
204 1200, and the results are shown in Figure 4. As shown in Figure 4(a), the gray part of
205 the picture was detected as biochar and the brighter dots were detected as Fe\textsuperscript{0}. In
206 addition, the Fe\textsuperscript{0} particles were appropriately dispersed on the granular biochar surface.
207 Moreover, no aggregation of iron occurred, the size Fe\textsuperscript{0} particles of was Fe\textsuperscript{0} particle
208 very small, basically approached nanometer level. A random section of biochar surface
209 was selected for EDS analysis, and the result is presented in Figure 4(b). It illustrates
210 that the Cu\textsuperscript{0} migrated to the biochar surface at the same time. In general, according to
211 the previous study, the presence of Cu can form bimetals with Fe\textsuperscript{0}, that is favor to
212 accelerate the degradation of organic pollutants by catalyzing the corrosion of iron.

![SEM image and EDS results of Fe\textsuperscript{0}-BC-1200](image)

**Figure 4.** SEM image and EDS results of Fe\textsuperscript{0}-BC-1200

### Removal performance

#### Removal efficiency

Figure 5 shows the removal efficiency of RB on Fe\textsuperscript{0}-BC prepared at different
216 temperatures. It is obvious to see that Fe\textsuperscript{0}-BC-1200 showed the best removal ability on
217 RB, with the removal efficiency reaching more than 99% after 30 min, followed by Fe\textsuperscript{0}-
218 BC-1100, with the removal efficiency of 86%. However, the three other materials
219 exhibited relatively low removal ability, with the removal efficiency was under 60%.
220 Compared with the XRD results in Figure 3, the presence of Fe\textsuperscript{0} was the main difference
221 between these materials, demonstrating that the reduction of Fe played a key role in the
222 removal process of RB. In addition, the order of removal efficiency of the three
223 materials without Fe\textsuperscript{0} was Fe\textsuperscript{0}-BC-800 > Fe\textsuperscript{0}-BC-900 > Fe\textsuperscript{0}-BC-1000, which was
224 consistent to that of their specific surface areas (shown in Table 3). This result can be
225 ascribed to the fact that smaller specific surface area implies the lower adsorption sites
226 and worse absorption performance.
Figure 5. Removal efficiency on RB using various Fe$^0$-BC materials ($C_0=100\text{mg/L}, \text{pH}=4.02$, dosage=2g/L, $T=25\, ^\circ\text{C}$).

For in-depth understanding of the effects of Fe$^0$ and BC on the removal of RB, the removal efficiency of RB on BC-T and Fe$^0$ powder was investigated. As shown in Figure 6, it is clear that the removal efficiency decreased with the increase of temperature. In general, a high temperature can accelerate carbon graphitization, causing worse adsorption capacity (Yu et al., 2019). Besides, compared the results in Figure 5, the removal efficiency using BC-1000, BC-900 and BC-800 was higher than that of Fe$^0$-BC-1000, Fe$^0$-BC-900 and Fe$^0$-BC-800, respectively. This is because of BC-T contained more biochar at the same dosage, and other compositions in Fe$^0$-BC-1000, Fe$^0$-BC-900 and Fe$^0$-BC-800 had no positive effect on RB removal. Moreover, the ultimate removal efficiency of RB on BC-1200 was only 48%, which was much lower than that of Fe$^0$-BC-1200, whereas the Fe$^0$ powder had no removal ability on RB, with the removal efficiency of 0%. The result suggested that the favorable removal efficiency of RB on Fe$^0$-BC-1200 was attributed to the interaction of various multiple components. As a reducing active site, the presence of Fe$^0$ on biochar surface could effectively degrade RB, and the removal efficiency improved simultaneously.
Figure 6. Removal efficiency on RB using BC and Fe⁰ powder ($C_0=100\text{mg/L}$, pH=4.02, dosage=2g/L, T=25 ℃).

From the above results, it can be indicated that the main factors affecting removal efficiency of RB on Fe⁰-BC were the amount of Fe⁰ particles and the specific surface area, while the Fe⁰ particles had dominant influence. Consequently, a high temperature is necessary to obtain Fe⁰-BC with better performance on RB removal due to more Fe⁰ particles generated.

**Adsorption kinetic**

The removal capacities of RB on Fe⁰-BC-1200 and the linear transformed models of the pseudo-first-order and pseudo-second-order models are presented in Figure 7. As shown in Figure 7(a), RB was removed rapidly in the first 10 min and tends to balance after 20 min. The structure of Fe⁰-BC-1200 with high specific surface area accelerated the mass transfer process, which is benefit to improve the removal rate of RB. Table 4 shows the fitting kinetics parameters in Figure 7(a) and Figure 7(b). Clearly, the goodness of fit ($R^2$) of the pseudo-second-order model was 0.9998, which is much higher than that of the pseudo-first-order model of 0.8256. Moreover, the $q_e$ calculated by pseudo-second-order was 49.93 mg/g, that was in good agreement with the experimental data compared with the pseudo-first-order model of 7.46 mg/g. Therefore, the pseudo-second-order model fits well to the experiment data, indicated that the removal process of RB by Fe⁰-BC-1200 resulted from the synergetic effect including physical and chemical adsorption.
Figure 7. Removal capacities of RB on Fe$_0$-BC-1200 with time (a), kinetic liner plots of pseudo-first-order model (b) and pseudo-second-order model (c) ($C_0$=100mg/L, pH=4.02, dosage=2g/L, T=25 ℃).

Table 4 Kinetics parameters for sorption of RB on Fe-C-1200

| Pseudo-first-order model | Pseudo-second-order model |
|--------------------------|---------------------------|
| $q_e$ (mg/g)             | $k_1$ (min$^{-1}$)        | $R^2$ | $q_e$ (mg/g) | $k_2$ (g/(mg·min)) | $R^2$ |
| 7.46                     | 0.014                     | 0.8256| 49.93        | 0.0062                 | 0.9998 |

Effect of pH on RB removal

Usually, rhodamine B wastewater has acidic property. Thus, the effect of various initial pH values on RB removal by Fe$_0$-BC-1200 was investigated under acidic conditions, and the results are shown in Figure 8. Within 1 min, the removal efficiencies were 99%, 90%, 77%, and 82% at initial pH values of 1.5, 2.5, 4.02, and 6, respectively. This trend showed that the removal rate significantly increased with the decrease of pH. The reasons of this fact are presented as follows: On the one hand, Fe$_0$ is more easily oxidized to Fe$^{2+}$ under acidic conditions as presented in Eq. (7) (Peng et al., 2017; Li et al., 2017), and the reaction with RB was promoted at the same time; on the other hand, some polar groups were generated on the biochar surface during the adsorption process, and these polar groups displayed the ability of polarized adsorption under acidic conditions (Zhang et al., 2018; Qian et al., 2017). Thus, the adsorption capacity of biochar was enhanced. Moreover, above 99% removal efficiency was obtained within 30 min at all tested initial pH values. It revealed that the prepared Fe$_0$-BC-1200 could exhibit outstanding removal capacity in practical situation.

$$\text{Fe}_0 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (7)$$
Figure 8. Effects of initial solution pH on removal efficiency by Fe⁰-BC-1200 ($C_0=100\text{mg/L}$, dosage=$2\text{g/L}$, $T=25$ °C).

In order to further investigate the effect of pH on the removal of RB, the solution pH values were determined at different selected reaction time, and the results are shown in Figure 9. From the picture, the curves of pH value with time presented the same trend as follows: a rapid increase at first, followed by decrease, and then a slow increase again, and eventually stabilized at about 9. This finding could be explained as follows. The reaction between Fe⁰ and H₂O (Eq. (7)) was conducted rapidly when Fe⁰-BC-1200 was added to the RB solution. Slight oxidation occurred on the surface and a large amount of H₂ was produced in a short time. Therefore, the pH value increased rapidly at first. Then, due to the severe oxidation or corrosion on the surface of Fe⁰ and the accumulation of Fe²⁺ and H₂, the reaction rate of Eq. (7) was less than that of Eq. (8), so Fe²⁺ was reduced and pH value decreased at the same time. At last, the pH value increased again, which may be ascribed to the formation of a coupling pair between Fe⁰ and Cu⁰. Because of the high standard electrode potentials difference between Fe⁰ (-0.44V) and Cu⁰ (0.34V) (Bratsch and Steven, 1989), the electrical current flowed from relatively active Fe⁰ to Cu⁰ and the active atom hydrogen (H⁺) was simultaneously generated with H⁺ adsorbed on the copper surface (Eq. (9)) (Wang et al., 2017) and the presence of H⁺ reinforced the reduced process of RB (Xiong et al., 2016). Due to the consumption of H⁺, the pH value increased again, and finally reached the equilibrium state. As one of the most important physical and chemical parameters in this reaction system, the change of pH value demonstrated that Cu⁰ may play a catalytic role in RB removal by Fe⁰-BC-1200.

\[
\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}^0
\]  
(8)

\[
\text{FeCu} + \text{H}^+ + e^- \rightarrow \text{FeCuH}^+
\]  
(9)
Mechanisms analysis

The residual products at different reaction time during the process of RB removal by FeO-BC-1200 were detected by LCMC, and the results are shown in Figure 10. Figure 10(a) presents the mass spectra of RB solution without adding FeO-BC-1200, m/z 443 and 444 were molecular ion peaks of RB ions or its isotopes. The molecular iron peaks of RB were strong and its molecular fragment peaks were small and weak. Thus, the RB molecular structure was possibly not destroyed under ESI MS. As shown in Figure 10(b), the result of MS at 1 min was basically consistent with that of Figure 10(a), indicating that RB was not degraded in the first 1 min. However, compared with the result in Figure 5, the concentration of RB decreased by 77% within 1 min, this finding proved that the RB removal is mainly reached by physical adsorption in the early stage. As shown in Figure 10(c), new molecular ion peaks were observed in the MS result at 15 min, among which m/z 331 was the molecular ion peak of RB with four ethyl groups removed (Horikoshi et al., 2002), and m/z 107, 143 and 201 were the molecular iron peaks of small molecule products after the benzene rings in RB were opened (Jun et al., 2020). The molecular ion peak of RB disappeared and the molecular iron peak of small molecules strengthened in the result of mass spectrometry at 30 min, as shown in Figure 10(d), indicating that RB was completely degraded. The above results confirm that RB was degraded in the removal process.

To further understand the mechanisms of FeO-BC-1200 for RB removal, the XRD of FeO-BC-1200 before and after RB removal were analyzed, and the results were shown in Figure 11. After reacting with the RB solution, the diffraction peaks of FeO located at 44.2°, 65.0° and 82.3° weakened and the diffraction peaks of Fe2O3 and Fe3O4 located at 64.1° and 35.4° were detected, illustrating that the redox reaction occurred
between Fe$^0$ and RB and Fe$^0$ was oxidized to Fe$^{2+}$ and Fe$^{3+}$. Therefore, Fe$^0$-BC-1200 is considered an efficient reductant to remove RB. In addition, the phase of Cu showed no difference, indicating that Cu$^0$ only play a catalytic role and did not participate directly in the degradation of RB.

**Figure 10.** Mass spectra of RB at different reaction time: (a) 0min, (b) 1min, (c) 15min, (d) 30min.

**Figure 11.** XRD patterns of Fe$^0$-BC-1200 before and after removal of RB

Based on the above results, it can be concluded that the removal mechanism of Rb by Fe$^0$-BC-1200 mainly includes the following: 1) In the initial stage of reaction, RB was adsorbed on the surface of biochar mainly through physical adsorption; 2) Subsequently, abundant microscopic primary cells formed between the Fe$^0$ particles located on the biochar surface and biochar itself. The presence of Cu catalyzed this process, and the electrons flowed to Cu$^0$ with low potential, thereby promoting the corrosion of Fe$^0$, accelerating the electron transfer with RB. This redox action destroyed
the C-N bond of the RB molecular branched chain and removed ethyl. Then the deethylated products underwent ring-opening reaction and generated many organic compounds with small mass charge ratio, followed by complete degradation. The mechanism diagram of RB removal by Fe$^0$-BC-1200 is presented in Figure 12.

![Figure 12. Mechanism diagram of RB removal by Fe$^0$-BC-1200.](image)

**Conclusions**

In this study, wood waste and iron sludge were used as carbon and iron sources, respectively, and a new process was proposed to synthesize the zero-valent iron/biochar (Fe$^0$-BC) by carbothermal reduction under the condition of oxygen isolation. Characterization results showed that Fe$^0$-BC-1200 prepared at 1200 °C has the advantages of large specific surface area, small granularity of Fe$^0$ particles and high Fe$^0$ loading on the biochar surface. Besides, Fe$^0$-BC-1200 showed excellent performance on removal of RB, and the equilibrium adsorption capacity reached 49.93 mg/g when the initial concentration of RB and the dosage of Fe$^0$-BC-1200 were 100 mg/L and 2 g/L, respectively. The pseudo-second-order model was suitable to fit the removal experimental data. Meanwhile, the removal mechanism included the physical adsorption of biochar and the redox reaction of Fe$^0$. The presence of Cu$^0$ was conducive to catalyze the oxidation of iron, thus enhancing the degradation effect. Therefore, the carbon supported by the zero-valent iron material prepared by carbothermal reduction process with low cost of raw materials, no additional reductant, simple operation, and significant detoxification effect, has the potential of industrial production.
Declarations

Ethics approval and consent to participate Not applicable
Consent for publication Not applicable
Availability of data and materials The datasets used and analysed during the current study are available from the corresponding author on reasonable request.
Competing Interests The authors declare that they have no conflict of interest.
Authors Contributions Jianguo Liu contributed to the conception of the study; Chao Chen, Chao Gen and Wenzhi Qi performed the experiment; Chao Chen performed the data analyses and wrote the manuscript; Qin Liu, Xuetao Zhu and Fang Wang helped perform the analysis with constructive discussions. All authors commented on previous versions of the manuscript and approved the final manuscript.
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