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Removal Efficiency and Performance Optimization of Organic Pollutants in Wastewater Using New Biochar Composites

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Abstract: The purpose is to optimize the catalytic performance of biochar (BC), improve the removal effect of BC composites on organic pollutants in wastewater, and promote the recycling and sustainable utilization of water resources. Firstly, the various characteristics and preparation principles of new BC are discussed. Secondly, the types of organic pollutants in wastewater and their removal principles are discussed. Finally, based on the principle of removing organic pollutants, BC/zero valent iron (BC/ZVI) composite is designed, among which BC is mainly used for catalysis. The effect of BC/ZVI in removing tetracycline (TC) is comprehensively evaluated. The research results reveal that the TC removal effect of pure BC is not ideal, and that of ZVI is general. The BC/ZVI composite prepared by combining the two has a better removal effect on TC, with a removal amount of about 275 mg/g. Different TC concentrations, ethylene diamine tetraacetic acid (EDTA), pH environment, tert-butanol, and calcium ions will affect the TC removal effect of BC composites. The overall effect is the improvement of the TC removal amount of BC composites. It reveals that BC has a very suitable catalytic effect on ZVI, and the performance of BC composite material integrating BC catalyst and ZVI has been effectively improved, which can play a very suitable role in wastewater treatment. This exploration provides a technical reference for the effective removal of organic pollutants in wastewater and contributes to the development of water resource recycling.

Keywords: new biochar; compound material; organic pollutants; tetracycline; biochar/zero valent iron

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1. Introduction

With the progress of society, the use of various new products has caused a serious impact on the environment. In particular, trace persistent organic pollutants in water bodies pose a serious threat to the normal life activities of human beings and organisms, and the effective removal of these pollutants has become a top priority [1]. General water treatment technology is difficult to work with. As a pyrolysis product of biomass waste, biochar (BC) is gradually applied to treat polluted water bodies. It can effectively improve the removal of organic pollutants in wastewater and improve the comprehensive utilization efficiency of water resources [2]. Although the current treatment technology of organic pollutants in wastewater is not advanced enough, many studies have provided technical support for it.

Pan and Tang (2021) [3] pointed out that water environment pollution and water resource shortage are two major problems of global freshwater resources. Water consumption has increased sharply due to the rapid progress of the social economy, the increase in population, the gradual improvement of people's living standards, and the acceleration of industrialization and urbanization. Sewage discharge has also increased accordingly, aggravating the shortage of freshwater resources and the pollution of the water environment. The current backward sewage treatment facilities and low sewage treatment rate are the main reasons for water environment pollution [3]. Lu et al. (2021) [4] pointed out that water consumption has increased sharply with the development of industrial and agricultural production and improved people's living standards. Moreover, the vast majority of huge amounts of untreated industrial wastewater and urban sewage are discharged into water bodies, causing serious pollution to limited water resources [4]. Xiao et al. (2021) [5], through an in-depth investigation of contemporary urban planning practices and combining with the latest research results of environmental theories, made an empirical analysis of the corresponding problems and proposed that environmental protection countermeasures should be adopted in urban planning was a very important measure [5]. Grosso et al. (2022) [6] pointed out that BC can remain in the soil for hundreds to thousands of years to achieve carbon sequestration and fixation. BC can also improve soil physical and chemical properties and microbial activity, cultivate soil fertility, reduce the loss of fertilizer and soil nutrients, delay the release of fertilizer nutrients, and reduce soil pollution [6]. Hota and Diaz (2021) [7] prepared magnetic hydroxyapatite/BC composites and studied the adsorption kinetics and thermodynamic properties of Pb2+ and solid-liquid separation and recovery properties. Scanning electron microscopy, X-ray diffraction, and Fourier infrared spectrometer were used to characterize and analyze the microstructure of materials before and after composite [7]. Wang et al. (2021) [8] loaded magnetic media such as iron oxide onto the surface of BC to achieve simple solid-liquid separation under the action of the external magnetic field, which is a new hotspot in the development of BC materials in recent years [8]. McKenna et al. (2021) [9] argued that there were potential threats to the human body and ecological environment caused by refractory organic matter in water, and it was of great significance to develop an efficient, environmentally friendly, and low-cost catalytic system for the restoration of such wastewater [9]. Industrial and agricultural discharge, leachate leakage of municipal garbage, and environmental accidents all lead to excessive heavy metals in water bodies. It is difficult to remove heavy metal-polluted wastewater, which has a serious impact on water plants and animals, human production and life, and endangers human health. Therefore, it is necessary to remove pollutants in the environment to a great extent through various means so as to provide a guarantee for sustainable social development [10]. Based on these, firstly, the preparation principle and application concept of novel BC composites are discussed. Secondly, the organic pollutants in wastewater and their treatment ideas are expounded. Finally, the BC/ZVI organic pollutant removal material is designed, and its performance is evaluated comprehensively. On account of the novel BC composites, this exploration studied the removal effect and performance optimization effect of organic pollutants in wastewater, thereby improving the removal effect of organic pollutants in wastewater, comprehensively advancing the protection of water resources, and promoting the sustainable utilization of water resources in society. This exploration provides a reference for enhancing the removal effect of organic pollutants and also makes a contribution to promoting the rational utilization of social resources.

BC has been widely used. In recent years, BC has not only been used to improve soil quality but also for soil pollution control and water pollution control. Therefore, BC has become a kind of functional material [11]. The chemical properties of BC mainly refer to the basic chemical properties of different BC. Among them, the main constituent elements of BC include carbon, hydrogen, oxygen, and nitrogen, while the secondary elements cover potassium, calcium, sodium, and magnesium [12]. The chemical properties that determine the properties of BC also involve the structure of functional groups between diverse elements, such as -OH, -(C=O) OH, -OR, and others. At the same time, with the increase in pyrolysis temperature, the acidic group of BC decreases, and the basic group increases. Thus, BC is mostly alkaline [13]. To prepare the new bio-composite, BC composites, namely, BC/zero valent iron (BC/ZVI), can be made by co-heating by adding hematite and pine powder under the main condition of nitrogen. ZVI, with a particle size of less than 100 nm, is usually prepared by wet or dry methods. ZVI has a high specific surface area and strong reducibility, showing excellent reactivity in the removal of water pollutants [14]. However, due to its small size, it is prone to self-aggregation, and its surface is also prone to oxidation to form surface passivation, reducing the reactivity and availability. The best way to solve this problem is to disperse ZVI on the surface of the carbon material so that more reactive sites are activated, thus improving its adsorption. Meanwhile, BC is the best medium for the fixation and dispersion of ZVI due to its complex pore structure and large surface area [15]. To develop an efficient S-type heterojunction photocatalyst to remove harmful pollutants, Li et al. (2022) designed and developed a novel S-type $TaON/Bi_2WO_6$ heterojunction nanofibers by in situ growing Bi_2WO_6 nanosheets with oxygen vacancies on TaON nanofibers [16]. In order to treat wastewater containing heavy metals and microorganisms, 1-naphthylamine (-NA, chromophore group) was grafted onto the $-NH_2$ group in a portion of NH_2-MIL-125(Ti) by photocatalysis, NA/NH_2-MIL-125(Ti) homologous coalescence was prepared, and the optical and structural changes were further studied [17]. S-type heterostructures were prepared by coupling Cd0.5Zn0.5S nanoparticles and $Bi2MoO_6$ microspheres as effective photocatalysts for antibiotic oxidation [18]. Based on the above theories, the two materials are designed to prepare new BC composites, which can be employed to remove organic pollutants from wastewater and optimize water quality.

2. Results and Discussion

2.1. Specific Surface Area Analysis of BC Composites

The specific surface area of the composites is analyzed and compared with BC composites obtained by other methods, such as precipitation. The results are exhibited in Table 1.

Table 1. The specific surface area of BC composites.

Performance Testing	BC/ZVI	BC	ZVI
The specific surface area (m^2/g)	52.05	-	33.11
The specific surface area of other methods (m^2/g)	39.75	-	-

Table 1 describes that compared with BC and ZVI, BC/ZVI composites have a larger specific surface area. Compared with other methods, the specific surface area of this method is larger, and the effect is more obvious.

2.2. Diffraction Results and Morphological Structure of New Biocarbon Composites

Three BC materials are designed and prepared: pure BC, ZVI, and BC/ZVI. First, the basic properties of the three materials can be analyzed by X-ray diffraction results. The diffraction results of three BC composites are expressed in Figure 1.

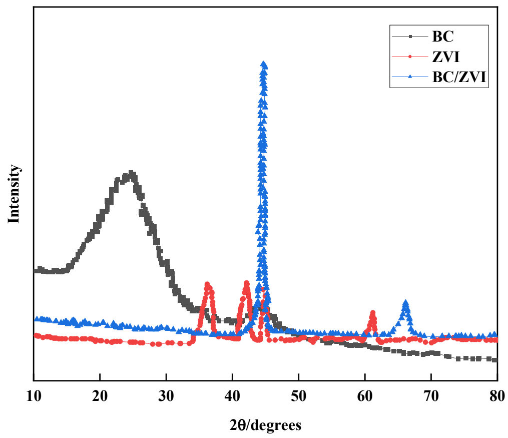
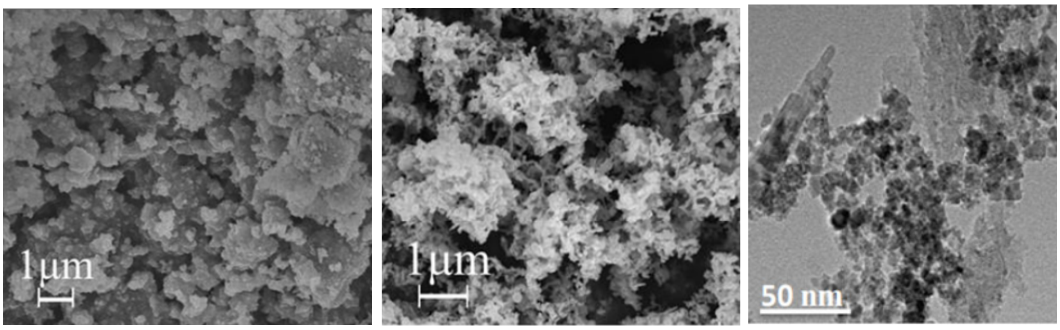


Figure 1. Diffraction results of three BC composites.

Figure 1 shows that when the 2θ value is 24.5° and 44.7°, the characteristic derivative peak of graphite carbon appears, indicating that the graphitization temperature of biomass is higher, and hematite can be calcined by nitrogen at 800 °C. Then, when the 2θ values are 35.8°, 44.3°, and 44.8°, respectively, there are three characteristic peaks, namely FeO, Fe_3O_4, and Fe^0, and there are also very small iron carbide peaks. BC mainly plays a catalytic role in BC composites, so BC mainly acts as a catalyst.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) detection techniques are used to further observe the surface morphology and microstructure of BC composites, as denoted in Figure 2.



(a) (b) (c)

Figure 2. Diffraction results of three BC composites ((**a**): SEM characterization result of ZVI; (**b**): SEM characterization result of BC Composites; (**c**): TEM representation results of BC composites).

In Figure 2, it can be observed that the distribution of black spots in the TEM image represents the presence of iron elements. It can be seen from the SEM image that BC composites show irregular massive morphology, and the formed pore structure is conducive to the adsorption process.

2.3. Evaluation of TC Removal Effect of BC Composite

TC is one of the main organic pollutants that pollute water resources and has an important impact on the protection of water resources. First, BC composites are designed to study the removal effect of TC. At present, ozone and carbon monoxide (CO) are usually used as the main catalysts for the catalytic process in wastewater treatment. Therefore, this exploration designs to compare the performance of the BC catalyst with the above two catalysts. The TC removal effect of three BC composites is displayed in Figure 3.

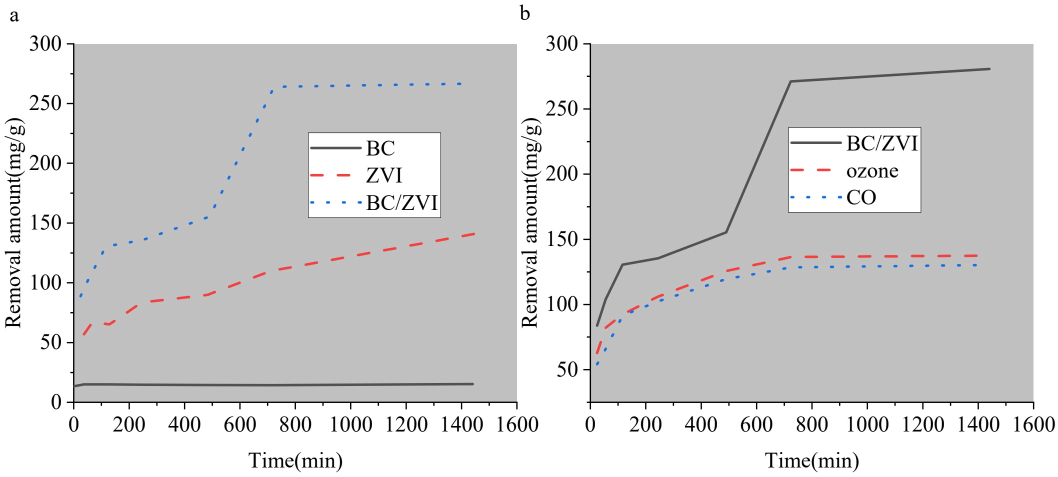


Figure 3. Performance evaluation of BC composite ((**a**) is the TC removal effect of BC composite, and (**b**) is the comparison of TC removal effect under the use of different catalysts).

Figure 3 signifies that the removal effect of pure BC on TC is not ideal, the removal curve is always very stable, and the removal amount is generally maintained at about 20 mg/g. Compared with pure BC, ZVI has improved the removal effect of TC. During the recording process, the removal amount of TC by ZVI always increases steadily, and the final removal amount is about 140 mg/g. The removal effect of BC/ZVI composite is the best, and it is significantly different from the other two materials. Before 800 min, the TC removal amount of composite materials rose rapidly, and after 800 min, it remained stable, with the maximum removal amount of about 275 mg/g. Moreover, when using different catalysts, the composite material using the BC catalyst has a better pollutant removal effect than the other two catalysts.

2.4. Effect of TC Concentration on Properties of BC Composites

In the process of studying the TC removal effect, the TC removal effect of BC composites is evaluated through the use of different concentrations of TC to study the effect of different concentrations on the properties of BC composites. Figure 4 portrays the TC removal effect of pure BC at diverse concentrations.

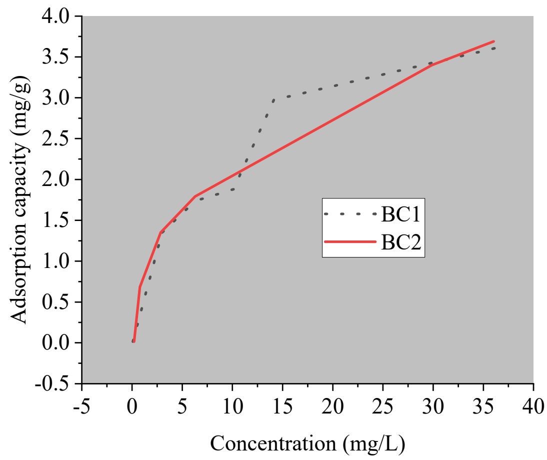


Figure 4. TC removal effect of pure BC at different TC concentrations.

Figure 4 suggests that under different concentrations, the TC removal effect of pure BC is poor, and the removal amount is very low, up to about 3.7 mg/g. It means that the TC removal effect of pure BC is generally poor, and its comprehensive performance can be improved only through optimization. Figure 5 plots the TC removal effect of ZVI and BC/ZVI composites at different concentrations.

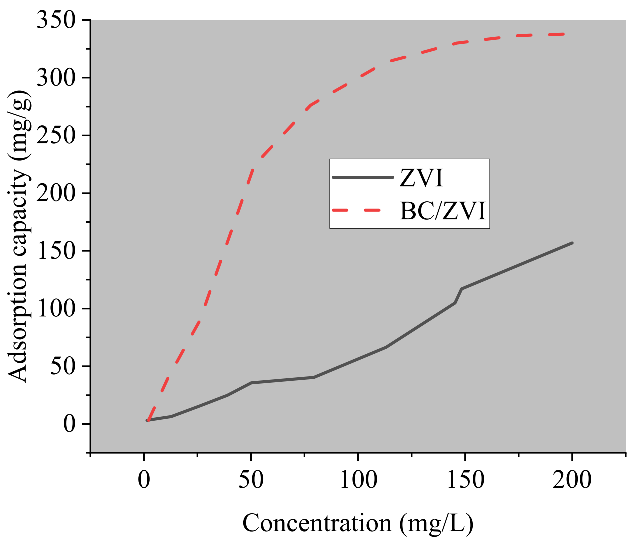


Figure 5. TC removal effect of ZVI and BC/ZVI composites at different concentrations.

Figure 5 details that when the concentration of TC continues to increase, the removal amount of TC by ZVI also continues to increase, showing a rising trend. When the TC concentration is 200 mg/L, the adsorption capacity of ZVI for TC is about 150 mg/g. BC/ZVI composite has a better removal effect on TC. With the increase in TC concentration, the TC adsorption capacity of BC/ZVI composites increases significantly. When the concentration of TC is 200 mg/L, the adsorption capacity of BC/ZVI composite for TC is about 346 mg/g.

2.5. Effects of Different pH Environments on the Properties of BC Composites

pH value has a significant effect on different materials. With the increase in pH value, different BC materials will present diverse adsorption conditions. Thereupon, it is important to study the adsorption effect of BC materials on TC through the change of pH value. Figure 6 demonstrates the adsorption effect of BC material on TC at different pH values.

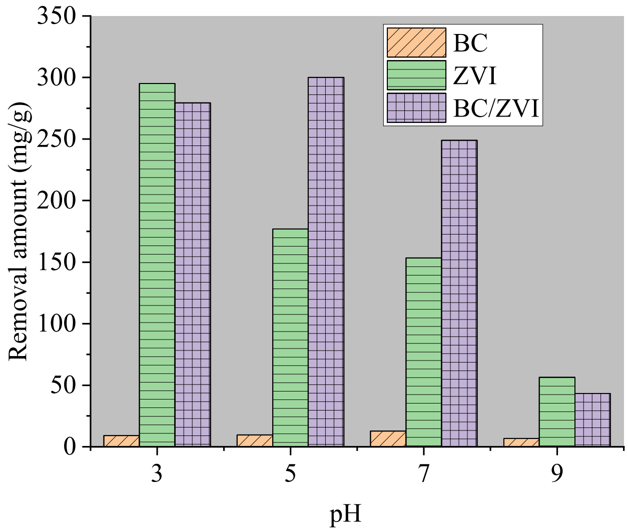


Figure 6. Adsorption effect of BC material on TC at different pH values.

Figure 6 indicates that the TC removal amount of pure BC in different pH environments does not change much, and it is generally stable, with the highest removal amount of about 20 mg/g. The removal amount of TC by ZVI shows a downward trend with the continuous increase in pH value. When pH is 3, its removal of TC is the highest, about 300 mg/g. The removal amount of TC by BC/ZVI composites changes continuously with the increase in pH. At pH 5, the removal amount is the highest, about 300 mg/g, but at pH 9, the removal amount decreases significantly, about 50 mg/g.

2.6. TC Removal Mechanism of BC Composites

The mechanism of TC removal by BC composites designed is mainly that ZVI reacts with oxygen in the solution to generate divalent iron ions and hydroxyl groups, and oxhydryl promotes the degradation of TC. If EDTA is added to the solution, the TC removal effect of the three materials may be affected. The effect of EDTA on the TC removal effect of BC composites is portrayed in Figure 7.

Figure 7 reveals that EDTA has little effect on the TC removal effect of pure BC. Among them, when the EDTA concentration is 1 mM, the TC removal amount of pure BC is the highest, about 10 mg/g. The concentration of EDTA significantly affects the TC removal effect of ZVI and BC/ZVI composites. The maximum removal amount of ZVI is about 210 mg/g when the concentration of EDTA is 5 mM. However, when the TC removal amount of BC/ZVI composite is the highest, the EDTA concentration is 1 mM, and the removal amount is 290 mg/g when the EDTA concentration is 5 mM.

In addition, tert-butanol and calcium ions will greatly impact the TC removal effect of these three materials. Figures 8 and 9 present the effect of tert-butanol and calcium ions on the TC removal effect of the three materials.

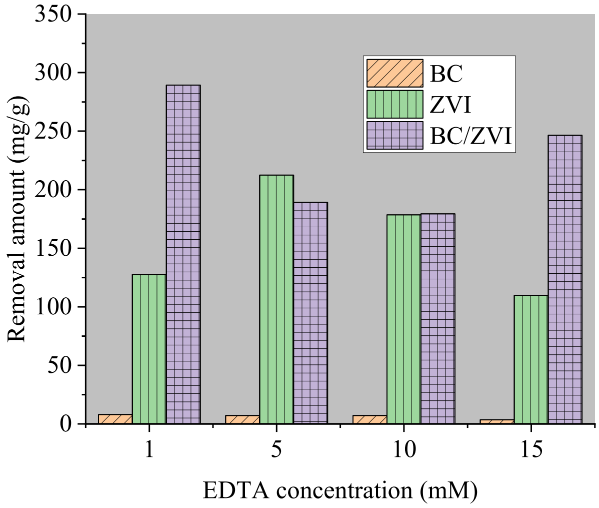


Figure 7. Effect of EDTA on TC removal effect of BC composites.

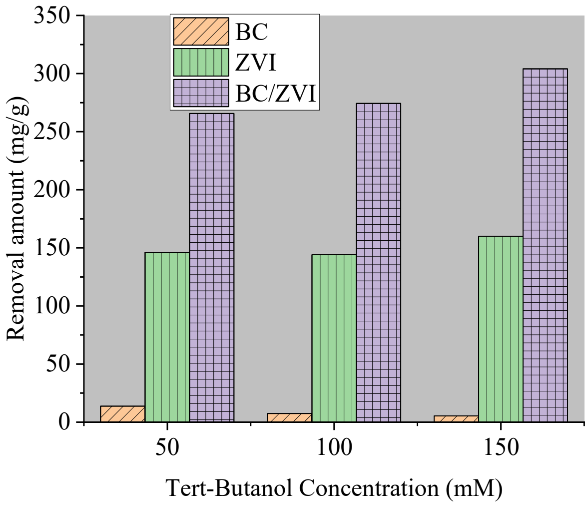


Figure 8. Effect of tert-butanol on TC removal efficiency of three materials.

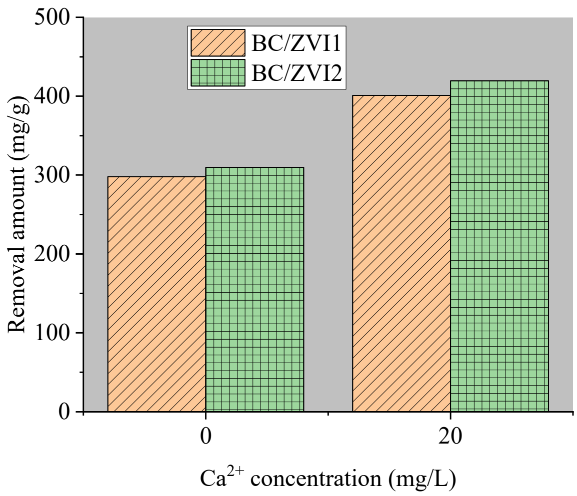


Figure 9. Effect of calcium ion on TC removal efficiency of three materials.

Figure 8 suggests that the tert-butanol has a relatively significant effect on the TC removal effect of the BC/ZVI composites. With the increase in tert-butanol concentration, TC removal of BC/ZVI composites is also increasing.

Figure 9 suggests that adding calcium ions to BC/ZVI composites can significantly improve the TC removal ability of BC/ZVI composites.

2.7. Comparison of Cu(II) Adsorption Capacity of BC Composites

Under the condition of pH = 5 and Cu(II) concentration of 60 mg/L, the adsorption capacity of BC composites on Cu(II) is compared, and the performance is compared with that of BC composites obtained by coprecipitation method, as outlined in Table 2.

Table 2. Comparison of Cu(II) adsorption capacity of BC composites prepared by different methods.

Carbonization Temperature (°C)	Heating Rate (°C/min)	Retention Time (h)	Q_e (mg/g)
A: 500	10	4	16.82
A: 600	10	4	17.71
A: 700	10	4	19.79
A: 700	10	3	19.59
A: 700	10	2	18.82
A: 700	20	4	18.03
A: 700	5	4	18.52
B: 700	10	4	19.02

In Table 2, A represents the experimental method, and B represents the coprecipitation method. It can be seen that under the conditions of 700 °C, 10 °C/min, and 4 h residence time, the adsorption capacity of Cu(II) is the highest, which is 19.79 mg/g. The reason may be that the BC prepared at high temperatures has a larger specific surface area and more aromatic rings to form a π-conjugated bond with Cu(II). The proposed method has a better adsorption capacity of Cu(II) than other methods, and the adsorption capacity is higher.

The isothermal thermodynamic parameters of Cu(II) adsorption on BC composites is revealed in Table 3.

Table 3. The isothermal thermodynamic parameters of Cu(II) adsorption on BC composites.

Sample	Langmuir			Freundlich		
	q_m (mg/g)	P_L (L/mg)	R^2	1/n	P_F (mg/g)	R^2
ZVI	19.28	2.0145	0.9999	0.0159	17.7281	0.9708
BC/ZVI	33.45	0.0997	0.9995	0.1172	17.0025	0.9812

In Table 3, the correlation coefficients of the Langmuir model of BC/ZVI and ZVI are 0.9999 and 0.9995, respectively, which are both higher than those of the Freundlich model of 0.9708 and 0.9812, illustrating that Cu(II) adsorption by materials is monolayer adsorption. The saturated adsorption capacity of BC/ZVI and ZVI of the Langmuir model is 33.45 mg/g and 19.28 mg/g, respectively. BC composites have a higher adsorption capacity.

3. Materials and Methods

3.1. Preparation Process of BC

It is necessary to clarify the raw materials for BC preparation. The commonly used BC raw materials include agricultural waste, and the biomass raw materials mainly cover cellulose, lignin, inorganic ash, hemicellulose, and many other woody fiber substances. In the process of preparing BC, firstly, appropriate biomass raw materials should be selected according to the characteristics of these organisms; secondly, the production process of BC should be controlled [19]. In this process, biomass is mainly used as the control object. By controlling the heating rate of biomass during the process of BC, the biomass raw materials are generated into different substances after pyrolysis. By controlling the pyrolysis process of biomass, the preparation process of BC can be divided into fast decomposition, flash carbonization, pyrolytic gasification, as well as slow pyrolysis. Moreover, slow pyrolysis is the commonly used preparation method of BC. Additionally, preparation conditions are also an important factor affecting the preparation process of BC [20]. Figure 10 displays the main preparation process of BC.

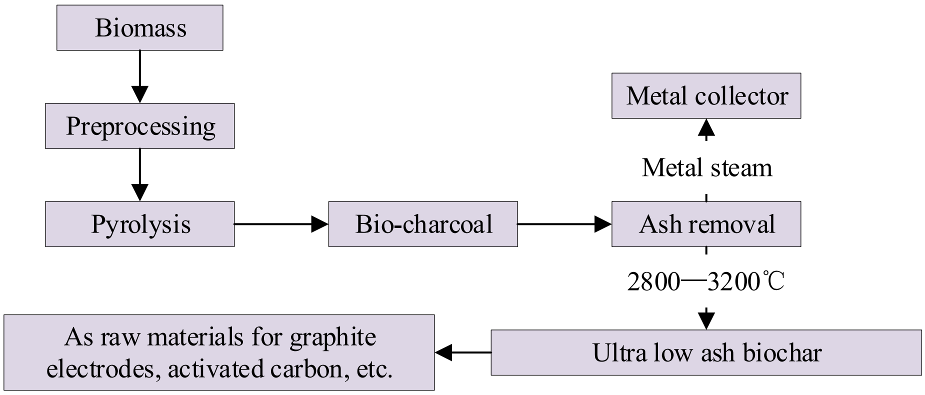


Figure 10. Main preparation process of BC.

Figure 10 shows that the preparation conditions of BC mainly include the holding time at the maximum pyrolysis temperature, the maximum pyrolysis temperature, and the pretreatment of raw materials and carrier gas, among which the effect of the maximum pyrolysis temperature is the most obvious. The pyrolysis process of biomass can be divided into three stages: dehydration, thermal decomposition, and carbonization [21]. BC has a variety of uses, among which the strong adsorption makes BC become the current main material of organic pollutant removal. By controlling the preparation process of BC, the comprehensive performance of BC can be controlled, and the removal effect of BC on organic pollutants can be improved. The preparation process requires little energy and does not require activation. BC has a relatively high yield and suitable pore structure and is widely used due to its easy operation and control [22].

3.2. Experimental Design

(1) Experimental Reagent

It includes TC, hydrochloric acid, sodium hydroxide, running water, ferric chloride, tert-butanol, hematite, EDTA, pine biomass, and deionized water with a resistance of 182 Ω.

(2) Preparation of BC Composites

The designed BC preparation process was to weigh 1.0 g hematite and 5.0 g biomass, place them in a beaker in a ratio of 1:5, and add 50 mL of deionized water. After sufficient stirring, the solution was sonicated for 30 min. Then, the solution was heated at 60 °C, and then the mixture was pyrolyzed in a tubular furnace for 1 h. During this period, the temperature was maintained at 800 °C, and 400 mL/min nitrogen was used for protection. Finally, the BC/ZVI composite was taken out and washed three times with ethanol and deionized water. Then, it is put into the oven and dried at 60 °C for 12 h. Next, pure BC was prepared by the same method, and ZVI was prepared by reducing ferric chloride with sodium borohydride as the experimental control material.

(3) Removal Experiment

0.01 g of the test material (BC, BC/ZVI, and ZVI) was weighed and placed in a centrifuge tube. Then, 10 mL TC solution with a concentration of 400 mg/L was added and vibrated for 24 h. Samples were taken at 30, 60, 120, 240, 480, 720, and 1400 min, respectively, and the results were recorded for analysis. Next, different concentrations of TC solution (25, 50, 100, 150, 200, 250, and 300) and different pH (3, 5, 7, and 9) were used for intervention to comprehensively study the removal effect of BC composites on organic pollutants in wastewater.

3.3. Adsorption Kinetic Analysis

(1) Adsorption Kinetics

The dynamic adsorption behavior of Cu(II), Pb(II), and Co(II) on BC composites is studied by fitting dynamic adsorption data, and the quasi-first-order and quasi-second-order kinetic models have been used to fit the data [23], as illustrated in Equations (1) and (2).

$$\lg(q_e - q_t) = \lg q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

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

q_t (mg/g) and q_e (mg/g) represent the adsorption capacity at time t and equilibrium, respectively; k_1 (min^{-1}) and k_2 (g mg^{-1}·min^{-1}) refer to the rate constant of the quasi-first-order kinetic equation and quasi-second-order kinetic equation, respectively, and t (min) stands for the adsorption time.

(2) Adsorption Isotherm

In the isothermal thermodynamic adsorption experiment, Langmuir and Freundlich models are adopted to fit the data [24], whose equations are written as Equations (3) and (4):

$$\frac{c_e}{q_e} = \frac{1}{P_L q_m} + \frac{c_e}{q_m} \quad (3)$$

$$\lg q_e = \lg P_F + \frac{1}{n}\lg C_e \quad (4)$$

q_e (mg/g) expresses the equilibrium adsorption capacity; q_m (mg/g) indicates the saturated adsorption capacity; c_e (mg/L) means the solution concentration after adsorption equilibrium; P_L (L·mg^{-1}) implies a parameter used by Langmuir to characterize the affinity between adsorbent and adsorbate; P_F (mg/g) stands for the parameter of Freundlich adsorption capacity, and n describes the trend of isotherm change.

4. Conclusions

With society's progress, industrial construction and agricultural development have become society's main tasks, and many problems have occurred in the construction process of these tasks, which seriously impact the environment. In particular, the pollution of water resources has been very serious. Thereupon, this exploration aims to solve the pollution of water resources and promote the recycling and sustainable utilization of water resources. Firstly, the basic concept of BC and the preparation procedure of BC composites are expounded. Secondly, the main organic pollutants that pollute water resources are discussed. Finally, the preparation method of BC composites with BC as the catalyst is designed, and the pollutant removal effect of the prepared BC composites is comprehensively evaluated. Meanwhile, the performance of the BC catalyst is compared with that of other catalysts. The results manifest that the TC removal effect of pure BC is not ideal, while the TC removal effect of ZVI is general. The BC/ZVI composite prepared by combining the two has a better removal effect on TC, and the removal amount is about 275 mg/g. Different TC concentrations, EDTA, pH environment, tert-butanol, and calcium ions will affect the TC removal effect of BC composites. Although a relatively new BC composite material is designed and comprehensively evaluated here, too few indicators are used in the evaluation process, which is not comprehensive enough. Therefore, future research will use more indicators to comprehensively study the removal effect of organic pollutants of new BC composites.

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Data Availability Statement: The data used to support the findings of this study are included within the article.

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

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