The Study on the Fixation Effect of nZVI@BC on Cu

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Abstract. The preparation of biochar composite materials for heavy metal removal is currently a research hotspot. A biochar composite (nZVI@BC) was synthesized from zero-valent iron nanoparticles (nZVI) and rice husk biochar (BC) by ball milling method in this study. SEM and XRD techniques were employed to examine the composite materials' phases and microstructural features. The adsorption capacity of nZVI@BC prepared by ball milling was 1.65 times that of rice husk biochar. The adsorption kinetic studies revealed that the composite material's uptake of Cu^{2+} aligned with a pseudo-second-order kinetic model. This finding suggests that the primary mechanism driving the removal of Cu^{2+} was chemisorption, a process involving chemical interactions between the adsorbent and the metal ions. Soil incubation experiments revealed that introducing the composite material had multiple beneficial effects on acidic soil, decreasing Cu concentration, increasing the pH level, and increasing the electrical conductivity, thereby enhancing the overall physicochemical characteristics of the soil. From a cost-effectiveness standpoint, applying nZVI@BC at 5% concentration proved to be particularly effective in improving the physicochemical properties of acidic soil.

Keywords: biochar, nZVI, Cu, acidic soil

1 Introduction

As mining activities increase, environmental pollution caused by heavy metals has become an increasingly significant concern. Heavy metals are mobile and, once ingested by plants, animals, or humans, they can accumulate in the body over time. The elimination of heavy metals from environmental sources can be effectively accomplished through the process of adsorption [1-4] and biochar (BC) is recognized as a highly efficient adsorbent material. Through the process of high-temperature pyrolysis in oxygen-free conditions, biomass is transformed into biochar, a solid material rich in carbon content. Generally, it possesses an extensive specific surface area, which contributes to decreasing the solubility of organic pollutants and heavy metals within the environment, And biochar also significantly raises the pH of the surrounding area [5,6].

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To improve the efficiency of biochar in treating pollutants, researchers have employed various activation techniques and modification methods to enhance biochar's surface area and functional groups. Zeng Yang et al. [7] investigated phosphorus-enriched biochar (PBC), introducing the precursors used to produce PBC and explaining how phosphorus doping alters the physicochemical properties and adsorption characteristics of biochar. They highlighted the impact of different carbonization processes and parameters on the biochar surface. Additionally, they analyzed various adsorption mechanisms that enable PBC to effectively remove heavy metals from water. Hou Renjie et al. [8] prepared sepiolite-modified biochar under varying conditions. Their results demonstrated that DTPA-extractable Pb in soil decreased by up to 13.55% when treated with sepiolite, and the soluble organic carbon content was reduced by 49.39% compared to the original biochar. The modifications to the biochar resulted in an increase in adsorption sites and oxygen-containing functional groups. These enhancements were responsible for impeding the transformation of heavy metal components. The modified biochar impeded the liberation of activated carbon and decreased the heavy metals' transportability through processes of ion exchange and adsorption complexation. Ma Pengyuan et al.[9] prepared magnetic biochar through impregnation pyrolysis, using iron sulfate or cerium dioxide as magnetic precursors. Under optimal conditions, the magnetic biochar achieved a Pb^{2+} removal efficiency of 91.88%. Even after four adsorption-desorption cycles, the adsorption capacity remained above 70%, demonstrating its potential for biomass resource recovery and environmental protection.

2 Materials and Methods

Rice husk biochar, pyrolyzed at 500°C under vacuum conditions, and carbonyl iron powder were obtained from a local environmental company. Soil samples were collected from a copper mine in Jiangxi Province, China. Before formal experimentation, the soil samples were air-dried and ground to remove large chunks of impurities, and their physicochemical properties were analyzed.

2.1 Material Preparation

In this study, high-energy ball milling was used to synthesize biochar composites [10]. BC and nano-ZVI were mixed evenly at a mass ratio of 10:1. Add 40 g of stainless steel balls and 5 g of the mixture to a 50 ml ball milling jar and perform ball milling using a planetary ball mill. To prevent oxidation of the materials, N_2 was introduced into the milling jar for 60 min. The machine was operated at 300 rpm for 8 h, with the direction of rotation reversed every 30 min. The prepared material is designated as nZVI@BC.

2.2 Experimental Design

2.2.1 Adsorption Kinetics Experiment.

A standard copper solution was diluted to prepare a 30 mg/L Cu-containing solution. The pH is then adjusted to 6.0 ± 0.1 using either 0.1 M HNO_3 or 0.1 M NaOH. For adsorption kinetics studies, 20 mg of BC or nZVI@BC was introduced into 30mL solution. The solution was stirred at 150 rpm in a temperature-controlled water bath set to 25 ± 0.5°C. At specified time points, aliquots were withdrawn, passed through a 0.22 μm syringe filter, and the filtrate was examined to quantify the remaining Cu^{2+} concentration.

2.2.2 Soil Cultivation Experiment.

Weighed and sieved air-dried acidic soil (2 kg) was placed in plastic pots. The experimental variables are listed in Table 1. BC and nZVI@BC were thoroughly mixed into the soil in pots and regularly watered. Cultivation was conducted indoors for 120 days. Following the experiment's completion, soil samples were collected, subjected to drying at 105°C for 6–8 h, and then utilized to analyze the soil's physicochemical properties.

Table 1. Potting experiment variable setting table

	nZVI@BC (w/w)
CK	0
B1	1
B2	2.5
B3	5
B4	10

2.3 Chemical Analysis

The pH of BC and nZVI@BC was evaluated using a 1:20 charcoal-to-water ratio. A pH meter was employed to measure soil pH at a 1:2.5 mass ratio. To assess soil electrical conductivity, a conductivity meter was used with a 1:5 mass ratio. Inductively Coupled Plasma Atomic Emission Spectroscopy (HJ 781-2016) was utilized to determine Cu content in both soil and solution samples.

3 Results and Discussion

3.1 XRD and SEM

3.1.1 XRD.

Figure 1 illustrates the XRD patterns of BC and nZVI@BC. As depicted in Figure 1a, the BC pattern exhibits a broad peak around 22°, characteristic of amorphous graphitic carbon, which is consistent with previous research findings reported in the literature [11]. As depicted in Figure 1b, the modified composite material displayed distinctive peaks at 2θ values of 44.7°, 64.8°, and 82.2°, verifying the existence of Fe^0 [12]. This observation suggests that nZVI was effectively incorporated onto the biochar surface.

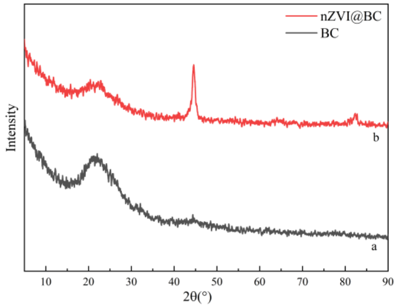

Fig. 1. XRD pattern of (a)BC and (b) nZVI@BC

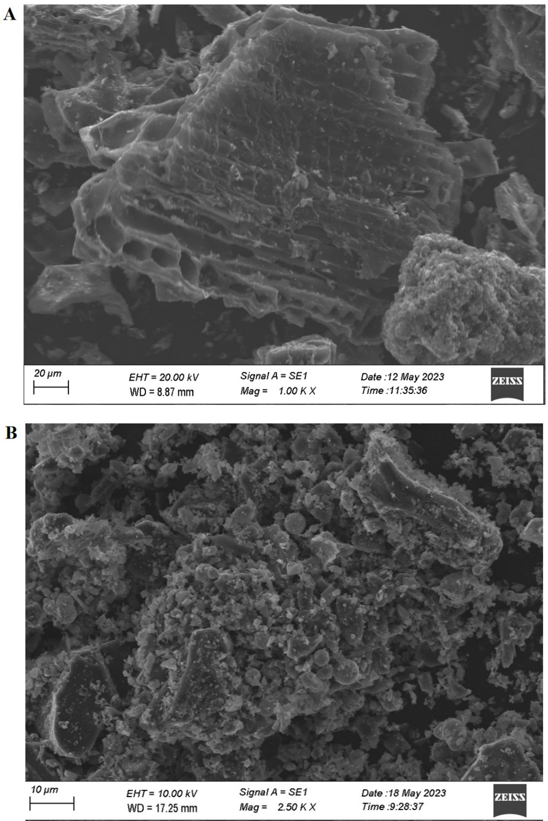

Fig. 2. SEM image of (A)BC and (B) nZVI@BC

3.1.2 SEM.

The surface morphologies of BC and nZVI@BC were examined using scanning electron microscopy. BC exhibited numerous lamellar structures, a diverse pore network, and a substantial specific surface area, making it an excellent loading substrate (Figure 2A). nZVI particles were found to be small in size and prone to spontaneous aggregation. In the case of nZVI@BC, BC acted as a dispersing agent, resulting in nZVI being primarily distributed across the BC structure's surface, significantly reducing the agglomeration effect (Figure 2B).

3.2 Adsorption Kinetics Experiment

Figure 3 shows the adsorption kinetics data and fitting curve. The parameters of the adsorption kinetic model are listed in Table 2. From the fitting results, the quasi-second-order kinetic model generally has a higher R^2 value, good graph fitting, and the predicted maximum adsorption capacity is close to the experimental value. The fitting results demonstrated that the main adsorption mechanism of nZVI@BC for Cu^{2+} in solution involves chemical processes, including ion exchange, electrostatic interactions, surface complexation, and precipitation.

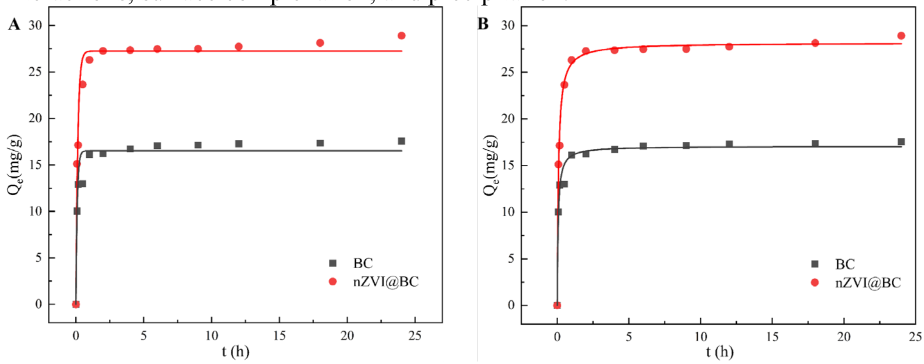

Fig. 3. Adsorption kinetic curves:(A)Quasi-first-order kinetic model fitting curves; (B) Quasi-second kinetic model fitting curves.

Table 2. Adsorption kinetic model parameters

	Q_m/(mg·g-1)	Quasi-first-order kinetic model			Quasi-second-order kinetic model		
		Q_e	k_1	R^2	Q_e	k_2	R^2
BC	17.56	16.521	9.966	0.939	17.074	0.914	0.978
nZVI@BC	28.92	27.254	7.151	0.946	28.153	0.412	0.993

3.3 Impact of nZVI@BC on Heavy Metal Content

The change in Cu content in the acidic soil after the addition of different proportions of composite materials is shown in Figure 4. The composite materials exhibited varying levels of effectiveness in reducing soil Cu content as part of the remediation process. The B4 treatment demonstrated the most significant impact, lowering Cu levels by 34.1%. Following this, the B3 and B2 treatments showed reductions of 26.3% and 20.4%, respectively. The application of nZVI@BC enhanced the soil surface's negative charge, thereby improving its capacity to adsorb heavy metals. Within the soil, nZVI functions as an electron donor, transferring electrons to pollutants and facilitating contaminant removal [13,14].

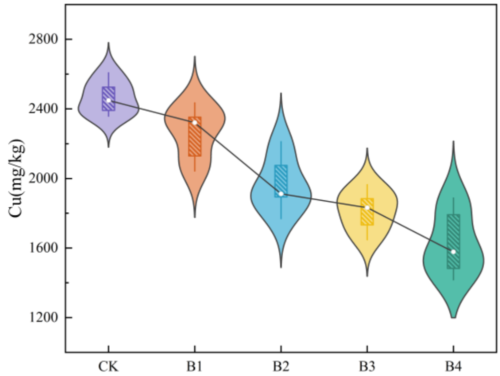

Fig. 4. Changes in Cu content in acidic soils

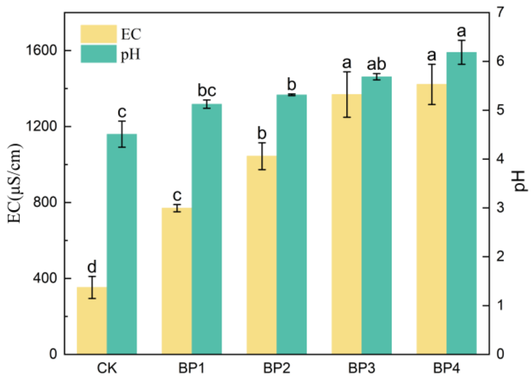

Fig. 5. Changes in soil properties

3.4 ZVI@BC on Soil Physicochemical Properties

As shown in Figure 5, the addition of composite materials improved the acidity of the soil. The soil's pH exhibited a notable rising trend as the quantity of nZVI@BC increased, demonstrating a strong positive relationship between these variables ($R = 0.835$, $P < 0.01$). The pH of the soil in treatment group B4 increased to 6.19, which was 1.81 units higher than that of the untreated group. The pH of nZVI@BC was 10.28. The ash content of biochar was relatively high. When applied to soil, the basic ions in the ash can help neutralize the acidity of the soil through exchange reactions [15].

Applying different nZVI@BC ratios resulted in varying soil electrical conductivity (EC) levels. Compared to the control (CK), adding nZVI@BC significantly increased the EC in acidic soils, with improvements ranging from 118.5% to 288.2%. Specifically, B3 (1368.3 μS/cm) > B2 (1043.9 μS/cm) > B1 (770.1 μS/cm) > CK (352.5 μS/cm). The B4 group exhibited the highest increase in soil EC, reaching 1421.83 μS/cm. The B3 and B4 treatment groups did not vary significantly, indicating that adding 5% nZVI@BC is an economical option for increasing soil EC in acidic environments [16,17].

4 Conclusion

In this study, we developed a modified biochar composite material, nZVI@BC. XRD and SEM characterizations confirmed that nZVI was successfully loaded onto BC, resulting in significant changes in the microstructure of BC in the nZVI@BC composite. Soil cultivation experiments showed that nZVI@BC effectively increased the pH and conductivity of acidic soil and immobilized Cu, a heavy metal, in the soil. In conclusion, nZVI@BC is an effective heavy-metal adsorbent that can improve the properties of acidic soils contaminated by mining activities.

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