RESEARCH ARTICLE

Insights into influence of aging processes on zero-valent iron modified biochar in copper(II) immobilization: from batch solution to pilot-scale investigation

Huabin Wang^{1,2}, Dingxiang Chen^{1,2}, Yi Wen^{1,2}, Ting Cui^{1,2}, Ying Liu^{1,2}, Yong Zhang^{1,2}, Rui Xu (🖂)^{1,2}

1 School of Energy and Environment Science, Yunnan Normal University, Kunming 650500, China 2 Yunnan Key Laboratory of Rural Energy Engineering, Kunming 650500, China

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Abstract The zero-valent iron modified biochar materials are widely employed for heavy metals immobilization. However, these materials would be inevitably aged by natural forces after entering into the environment, while there are seldom studies reported the aging effects of zerovalent iron modified biochar. In this work, the hydrogen peroxide and hydrochloric acid solution were applied to simulate aging conditions of zero-valent iron modified biochar. According to the results, the adsorption capacity of copper(II) contaminants on biochar, zero-valent iron modified biochar-1, and zero-valent iron modified biochar-2 after aging was decreased by 15.36%, 22.65% and 23.26%, respectively. The surface interactions were assigned with chemisorption occurred on multi-molecular layers, which were proved by the pseudo-second-order and Langmuir models. After aging, the decreasing of capacity could be mainly attributed to the inhibition of ionexchange and zero-valent iron oxidation. Moreover, the plant growth and soil leaching experiments also proved the effects of aging treatment, the zero-valent iron modified biochar reduced the inhibition of copper(II) bioavailability and increased the mobility of copper(II) after aging. All these results bridged the gaps between bio-adsorbents customization and their environmental behaviors during practical agro-industrial application.

Keywords zero-valent iron modified biochar, aging processes, copper removal, adsorption, pilot-scale experiments

1 Introduction

With the development of urbanization and Received August 22, 2022; accepted November 8, 2022

E-mail: ecowatch_xr@163.com

industrialization, the problem of environmental pollution by heavy metals is becoming increasingly prominent with high toxicity to biological organisms and ecosystems [1]. Among various metal contaminants, Copper (Cu) is a typical heavy metal (with a density of 8.96 g \cdot cm⁻³) and as the rapid development of electroplating, chemical and mineral industries, Cu pollution is becoming more and more serious and the content has exceeded the background value in the environment by dozens of times. Although Cu is an essential element for human body, the intake of excessive Cu(II) can endanger human health, such as potential detrimental effects for kidney failure and gastrointestinal diseases [2]. Recently, the removal methods of Cu(II) mainly include chemical precipitation, membrane filtration, phytoremediation, and adsorption [3-6].

Among these Cu decontamination approaches, adsorption was considered as a promising method with the advantages of the lower cost, higher efficiency, less energy consumption, and neglectable second pollution [7]. Furthermore, zero-valent iron (ZVI) modified biochar (BC) as an efficient adsorbent has attracted much attention, due to this functional material combines the high chemical reactivity of ZVI and the large surface area as well as the rich functional groups of BC [8,9]. ZVI modified BC (ZVI/BC) can reduce contaminants to a less toxic states and then form complexations or co-precipitants on the BC surface [10]. Our group applied ZVI/BC for chromium (VI) removal, with the mechanisms of reduction and adsorption [11]; while Yang et al. [12] derived ZVI/BC and employed for the remediation of Cu(II)-polluted wastewater, finding the mechanisms of adsorption, precipitation, reduction, and complexation. These results provide possibilities for the Cu pollution control by ZVI/BC.

One of the shortcomings of ZVI/BC species was easy to be oxidized, as facing to the inevitable aging processes due to the natural forces after entering into the environment. During this process, the elemental components, surface functional groups, specific surface area, and other physicochemical properties could be changed [13]. Hou et al. [14] investigated the aging effects of BC, and freeze-thaw cycle were applied to simulate the aging process, while the results indicated that the specific surface area and oxygen-containing functional groups of the BC were decreased dramatically. Luo et al. [15] analyzed the aging of ZVI species with hydrochloric acid and hydrogen peroxide, which formed excess iron oxide passivation layer and FeO-depleted hollow spheres. But the current research on aging normally focused on the aging of BC, as for the ZVI/BC the changes on physicochemical properties as well as mechanisms variations before and after aging are seldom studied. Moreover, the investigation of aged ZVI/BC on soil leaching toxicity and plant growth are also urgently demand for evaluating the environmental feasibility of this functional material. Addressing these issues are very important for the removal of Cu(II) in soil by ZVI/BC.

To address this knowledge gap, in this work, we applied pinewood sawdust and iron salts to prepare ZVI/BC by a facile one-pot carbothermal reduction, and HCI and H_2O_2 were employed to simulate acidification and oxidative aging processes. This study has three objectives: (1) exploring the aging effects of ZVI/BC on physicochemical properties and Cu(II) adsorption performance changes; (2) illuminating the absorption mechanisms transformation of ZVI/BC for Cu(II) after aging; (3) evaluating the practical influence of fresh and aged ZVI/BC by pilot-scale plant growth experiments.

2 Experimental

2.1 Materials and reagents

The pinewood sawdust was obtained from rural areas in Kunming city, Yunnan province, China. The copper sulfate pentahydrate (CuSO₄·5H₂O), ferric chloride hexahydrate (FeCl₃·6H₂O), H₂O₂, NaOH, and HCl were all purchased from Sinopharm Co., Ltd. All reagents were obtained as purchased without further purification.

2.2 ZVI/BC preparation and aging treatment

The obtained sawdust was smashed and filtered through 70 mesh sieves, then washed with deionized water for three times, subsequently dried under 80 °C for overnight. The 8.0 or 16.0 g FeCl₃·6H₂O was dissolved in 60 mL deionized water and 8.0 g biomass was added into iron solution to form slurry, and then this mixture was ultra-sounded for 30 min. After that, 20 mL NaOH $(0.1 \text{ mol} \cdot \text{L}^{-1})$ solution was added into the solution, and the mixture was stirred for another 2 h by a magnetic

agitator under room temperature (25 °C). Then the mixture was poured into an autoclave for hydrothermal treatment for 10 h, at 120 °C. After cooling down to room temperature, the slurry was vacuum filtered, and resulted solid products was the hydrochar [16], then washed three times with deionized water and finally dried in an oven at 60 °C. After drying, the obtained solid was pyrolysis at 800 °C for 2 h with temperature increasing rate of 5 °C·min⁻¹ under protection of nitrogen. The resulting products were washed for three times with deionized water, while iron salts of 8.0 and 16.0 g were denoted as ZVI/BC-1, ZVI/BC-2, respectively, while the controlled one without adding of iron slats was labeled as BC.

When the adsorbent material enters the environment, it will be oxidized and acidified by various natural forces. The simulated acidification and oxidation of aging processes were referred to former research [17]. Briefly, 4.0 g pristine ZVI/BC and 50 mL deionized water were mixed and HCl solution (0.1 mol·L⁻¹) was employed to adjust the pH to 3 and maintained for 4 h. After acidification, 10 mL H_2O_2 (10% v/v) solution was poured into the solution and stirred for 1 h, then filtered and washed with deionized water for three times. After that, the obtained solid was dried in an oven at 80 °C for further analysis. The aged BC, ZVI/BC-1, and ZVI/BC-2, respectively.

2.3 Batch adsorption experiment

The 20 mL CuSO₄ solution (200 mg·L⁻¹) was prepared for batch experiments, the initial solution pH was varied from 4 to 7 via adding of NaOH or HCl solution (0.1 mol·L⁻¹), and 20 mg different adsorbents were added into 20 mL solution for adsorption performance evaluation. The concentration of Cu(II) was determined by the sodium diethyl dithiocarbonate method, and each sample was tested for three times for the integrity of experimental date.

The adsorption amount of Cu(II) in the solution can be calculated by the following formula:

$$q_{\rm e} = \frac{(C_0 - C_t)V}{m},\tag{1}$$

where $q_e(\text{mg} \cdot \text{g}^{-1})$ is the adsorption capacity; $C_0 \text{ (mg} \cdot \text{L}^{-1})$ and $C_t \text{ (mg} \cdot \text{L}^{-1})$ are the mass concentration of Cu(II) in the solution at the initial time and time *t* respectively; *V* (L) is the volume of the solution, and *m* (g) is the amount of adsorbent.

2.4 Kinetics and isothermal adsorption experiments

Each 20 mg sample was added into 200 mg·L⁻¹ Cu(II) solution, and then the solution pH was adjusted to 7 with NaOH and HCl. The samples were stirred for 12 h with the speed of 200 r·min⁻¹ at room temperature, and taken

liquid supernatant at different time intervals (5, 10, 30, 60, 80, 120, 180, 220, 315, 450, 560, 680 and 720 min, respectively). The 0.45 μ m filter paper was employed for filtering Cu(II) solution and then the concentration was measured. The data obtained through kinetics have been depicted with pseudo-first-order models and pseudo-second-order models, as follows:

Pseudo-first-order model:
$$q_t = q_e (1 - e^{-k_1 t}),$$
 (2)

Pseudo-second-order model:
$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$
, (3)

where $q_e (\text{mg} \cdot \text{g}^{-1})$ is the equilibrium adsorption capacity; $q_t (\text{mg} \cdot \text{g}^{-1})$ is the adsorption capacity at *t* time; k_1 is the pseudo-first-order model adsorption rate constant, and k_2 is the pseudo-second-order model adsorption rate constant.

For the isothermal adsorption experiment, 20 mg samples of tested materials were added to centrifuge tubes, and 20 mL solutions of different Cu(II) concentrations (100, 150, 200, 250, 350 and 500 mg·L⁻¹) were then added to the centrifuge tubes. Centrifuge tubes were sealed in constant temperature oscillation chambers (25, 35 and 45 °C) and oscillated at 220 r·min⁻¹ for 12 h. Langmuir and Freundlich models were applied to fit the isothermal adsorption experiment data. Their equations are as follows:

Langmuir model:
$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$$
, (4)

Freundlich model:
$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n}$$
, (5)

where $q_{\rm m} \,({\rm mg} \cdot {\rm g}^{-1})$ is the maximum adsorption capacity, $q_{\rm e} \,({\rm mg} \cdot {\rm g}^{-1})$ is the equilibrium quantity, $K_{\rm L}$ is the adsorption equilibrium constant, $C_{\rm e} \,({\rm mg} \cdot {\rm L}^{-1})$ is the concentration of Cu(II) in the solution, $K_{\rm F}$ is the affinity coefficient, and *n* is the constant that represents the adsorption intensity.

2.5 Plant growth trials

The bok choy planting experiment was conducted to further evaluate the effect of aging on ZVI/BC. Eight groups of 5.00 kg soils were established using soil samples obtained from the University campus, Kunming, China. Then, 5.86 g CuSO₄·5H₂O was melted into 1000 mL distilled water and the solution was evenly poured into seven groups of uncontaminated soil to bring the soil copper pollution content to 300 mg·kg⁻¹. Uncontaminated soil and the seven groups of contaminated soil were cultured together under room temperature for 25 days. Bok choy seeds were purchased and added to the soil, and different bio-sorbents (fresh and aged BC, ZVI/BC-1, and ZVI/BC-2) were mixed into six groups of contaminated soil and cultivated under natural conditions for 21 days. After the growth of plants, the length of roots was compared, and the leaching of Cu(II) in the soil samples was analyzed according to the national standard methods (GB/T-17138). Simultaneously, the root, stem and leaf of bok choy were selected and the Cu(II) concentration of these three parts was determined by flame atomic spectrophotometry after the digestion. All data were replicated three times to ensure the integrity of the experimental date.

2.6 Regeneration experiment

In this study, elution experiment was performed with HCl solution. Briefly, ZVI/BC-1 adsorbent and Cu(II) solution were mixed and shaken for 12 h. After adsorption, ZVI/BC-1-loaded-Cu(II) was washed several times with HCl solution and deionized water under a vacuum filter and then dried in an oven at 60 °C. This adsorption–desorption cycle experiment was to be repeated five times to evaluate the reusability of ZVI/BC-1.

2.7 Characterization of materials

Elemental analyzer (EA, Elementar Vario EL cube, Germany) was used to determine the contents of C, H, O, and N of materials. Scanning electron microscopy (SEM, Zeiss Supra 55, Germany) was employed for observing the surface microstructures before and after aging. The specific surface area and pore size of functional materials were measured with nitrogen adsorption and desorption methods (BET, Mike 2240, USA). X-ray diffraction (XRD, Rigaku Ultima IV, Japan) was applied to analyze the crystal structure and composition of obtained materials, while X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha. USA) was used to analyze the element composition and chemical valence of the material surface. The functional groups of the material were observed by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS50, USA) with conventional KBr methods.

3 Results and discussion

3.1 Material characterization and structural analysis

The composition analysis of C, H, O, and N elements of fresh and aged bio-adsorbents was shown in Table 1.

Table 1 Element content of adsorbent materials

Adsorbent	C/(wt %)	H/(wt %)	O/(wt %)	N/(wt %)	H/C	O/C
BC	39.15	1.84	12.52	0.42	0.56	0.24
A-BC	47.85	2.20	13.49	0.55	0.60	0.21
ZVI/BC-1	26.56	1.71	15.72	0.43	0.77	0.44
A-ZVI/BC-1	38.86	1.92	14.77	0.49	0.59	0.29
ZVI/BC-2	12.32	0.83	5.35	0.11	0.81	0.33
A-ZVI/BC-2	17.84	0.89	4.01	0.18	0.59	0.17

According to the results that the carbon content of BC (39.15 wt %) was significantly higher than that of modified BC, that could be related to the loss of organic components and transformation of iron species during pyrolysis. The atomic ratio of H/C indicates the aromaticity of adsorbents, where the lower H/C ratio was corresponded to the stronger aromaticity [18]. The H/C ratios of BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2 were 0.56, 0.60, 0.77, 0.59, 0.81, and 0.59, respectively. Demonstrating the aromaticity of BC did not change significantly, while the aromaticity of ZVI/BC was enhanced after aging [19]. Meanwhile, atomic ratios of O/C were applied to evaluate the polarity of adsorbents [20], O/C ratios of BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2 was 0.24, 0.21, 0.44, 0.29, 0.33, and 0.17, respectively. The O/C ratios of the original materials were higher than those of the aged materials, suggesting that the aging processes of acidification and oxidation enhanced the polarity of materials, which could enhance the electron transformation between contaminants and metals [20]. The O content of aging materials was lower than that of original materials, but the C content was higher than that of original materials. This might be attributed to the leaching and dissolution of unstable components or minerals, which was in accordance with former reports [21].

The surface morphology and elemental distribution of material before and after aging were observed using SEM-EDX. As shown in Fig. S1 and Fig. S2 (cf. Electronic Supplementary Material, ESM), the surface of BC was porous and smooth, while in the case of ZVI/BC-1, the porous layer was covered with many small particles, for ZVI/BC-2, the main component was iron and there was no obvious pore structure, indicating the equally distribution of ZVI materials. After aging treatment, the plane structure of fresh BC was destroyed, as A-BC, A-ZVI/BC and ZVI/BC-2 exhibited many fragments of carbon structure. From mapping picture of ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2 and A-ZVI/BC-2 (Fig. S2), it can be observed that the uniformly distribution of iron species. The EDX

elemental analysis of ZVI/BC-1 and ZVI/BC-2 (Fig. S2), which also verifies that Fe⁰ has been successfully loaded onto BC [22]; The EDS element picture results of A-ZVI/BC-1 and A-ZVI/BC-2, which can be seen from the picture that Fe content decreased after aging.

The N₂ adsorption-desorption isotherms of the prepared samples were shown in Fig. 1. All materials have obvious hysteresis returns, which belong to type IV isotherms, indicating that the prepared materials belong to mesoporous structures of containing micropores and mesopores. The specific surface area and pore size structure parameters of the materials were shown in Table 2. After modification, the specific surface area of ZVI/BC-1 (209.47 $m^2 \cdot g^{-1}$) was smaller than that of BC (262.35 $m^2 \cdot g^{-1}$), which is because ZVI and other iron oxides fill the pore channels during the modification process of iron salts, resulting in a reduced specific surface area. The results of the specific surface area of ZVI/BC-2 (68.63 $m^2 \cdot g^{-1}$) shown that too much iron salt has a large negative impact on the specific surface area. Simultaneously, it can be seen that the specific surface area of all the modified BC increased after aging, which may be formed by irregular superposition and dispersion of iron oxides during the aging process [23]. In general, an excessive specific surface area will provide more adsorption sites, which is favorable for the adsorption of Cu(II) of heavy metals, which will be carried out in batch adsorption experiments. The aging treatment destroyed the pore structure of the BC and increased the pore volume of BC and ZVI/BC-1, while excess iron particles filled the pore channels of A-ZVI/BC-2 resulting in a decrease in pore volume [24]. Moreover, the decrease in the average pore size of A-ZVI/BC-1 and A-ZVI/BC-2 may be related to the blockage of pore channels by iron particles [25].

The adsorbed materials were further analyzed by XRD and FTIR characterization techniques, and the characterization results were shown in Fig. 2. The crystal structure of the materials were studied by XRD spectra as shown in the Figs. 2(a, b). In the XRD spectrogram of BC there



Fig. 1 N₂ adsorption-desorption isotherm of (a) before and (b) after aging materials.

was an obvious peak at 2θ of 29.56° , which corresponds to SiO₂ (PDF#01-8083-1833). For A-BC, two new peaks were found at 2θ of 26.86° and 35.34° , both peaks corresponded to SiO₂. This was associated with more crystals and metal oxide structures of BC were exposed after aging [26]. For ZVI/BC-1, a peak can be seen at 2θ of 44.04° , which correspond to Fe⁰ and indicating that ZVI has been successfully loaded onto the BC by the carbothermal onestep reduction method, the familiar peaks were observed at 2θ of 45.02° and 2θ of 65.34° for ZVI/BC-2 (PDF#03-065-4899). The peaks intensity of Fe⁰ in A-ZVI/BC-1 and A-ZVI/BC-2 decreased, new peaks were generated which related to other iron oxides (Fe₂O₃, Fe₃O₄), indicating that Fe⁰ was oxidized to other iron oxides after aging.

The surface functional groups of the materials were studied by FTIR spectroscopy as shown in Figs. 2(c, d). The peak near 3413 cm⁻¹ was associated with stretching vibration of -OH [27], the peak near 3230 cm⁻¹ was the

 Table 2
 Pore structure parameters of adsorbent materials

Adsorbent	Surface area/ $(m^2 \cdot g^{-1})$	Pore volume/(cm ³ ·g ⁻¹)	Average pore diameter/Å
BC	262.35	0.18	26.51
A-BC	234.49	0.19	31.01
ZVI/BC-1	209.47	0.17	33.12
A-ZVI/BC-1	261.89	0.22	32.89
ZVI/BC-2	68.63	0.11	64.33
A-ZVI/BC-2	132.18	0.10	32.21

stretching vibration of -NH₂ [28] and the peak near 2924, 1614, 1048, and 874 cm^{-1} was the stretching vibration of -CH₂, C=O, C-O, C-H, respectively [29]. It was noteworthy that, as for ZVI/BC-1, the weak signal of Fe-O was detected at wavelength 560 cm⁻¹, which confirmed that Fe was successfully loaded onto BC [30], while this peak was detected at wavelength 600 cm⁻¹ for ZVI/BC-2. The vibration peaks of aromatic and heterocyclic compounds were obvious between 500 and 1000 cm⁻¹ for BC and ZVI/BC-1, indicating the highly aromatic and heterocyclic structure, which was in accordance with the results of elementary analysis. Meanwhile, the slight decrease of -OH and C=O intensity for A-ZVI/BC-1 could be explained by the lower O content of BC after aging treatment, thus reducing the strength of oxygen-containing functional groups.

To further elucidate the chemical states of surface elements, the XPS spectra were tested as shown in Fig. 3. As in the Figs. 3(a, b), the C 1s signal peak was divided into C–C peak at 284.78 eV, C–O peak at 285.95 eV, and O–C=O/C=O peak at 288.68 eV [31]. After aging, as for BC, the ratio of C–C increased from 52.72% to 70.16%, while that of C–O decreased from 32.56% to 22.66%, with the ratio of O–C=O/C=O decreased from 14.72% to 8.18%. The decrease of C–O and O–C=O/C=O could be explained by the dissolution of unstable components and the hydrolysis of O–C=O/C=O during aging process [17]. According to O 1s fine spectra (Figs. 3(c,d)), C–O



Fig. 2 (a, b) The XRD and (c, d) FTIR spectra picture of adsorb materials.



Fig. 3 C 1s spectra of (a) BC and (b) A-BC, O 1s spectra of (c) BC and (d) A-BC, Fe 2p spectra of (e) ZVI/BC-1, (f) A-ZVI/BC-1, (g) ZVI/BC-2, and (h) A-ZVI/BC-2.

(532.78 eV) increased from 55.70% to 73.52% while C=O (531.48 eV) decreased from 37.60% to 26.48% after aging of BC, which may be related to the hydrolysis of C=O structure.

The fine Fe spectra of ZVI/BC-1, A-ZVI/BC-1, ZVI/ BC-2, and A-ZVI/BC-2 XPS were also demonstrated (Figs. 3(e–h)). According to the fitting results, the peaks at binding energy of 706.48 eV were corresponded to the existence of Fe⁰ [32], further proved the successfully loading of ZVI species onto BC substrates. The peak of Fe²⁺ at 710.88 eV and the peak of Fe³⁺ at 713.68 eV were all observed, indicating the partially oxidation of iron species during reaction. After aging, the peak area of Fe⁰ and Fe²⁺ decreased (from 22.54% to 8.23%, from 40.46% to 29.58%), while the peak area of Fe³⁺ increased (from 27% to 62.19%), indicating that both Fe⁰ and Fe²⁺ were oxidized to Fe³⁺, which was consistent with the XRD analysis. This phenomenon was attributed to the oxidation and acidification of aging processes.

Hence, according to the various techniques on the physicochemical characteristics of ZVI/BC, it could be concluded that after aging treatment, the carbon contents increased and the surface of bio-adsorbent could be more porous, and chemical states of iron species varied with existence of Fe^0 species. All these changes could influence the interactions with pollutant species, which need to be further investigated by batch and soil experiments.

3.2 Batch experiments

3.2.1 Effects of pH

(a)

Removal efficiency/%

The Cu(II) adsorption capacities of the six adsorption materials were shown in Fig. S3 (cf. ESM). The adsorption capacities of BC, ZVI/BC-1 and ZVI/BC-2 on Cu(II) decreased after aging, with the values of 114.14 to 96.47 mg \cdot g⁻¹ (15.36%), 181.25 to 140.07 mg \cdot g⁻¹ (22.65%), and 172.91 to 132.14 mg \cdot g⁻¹ (23.26%), respectively. This phenomenon could be attributed to the changes of physicochemical properties as analyzed before. Figure 4 exhibited the Cu(II) removal efficiency at different pH and zeta potential of adsorption materials, as shown in Fig. 4(a), at pH 3-9, the removal efficiency increased with the increasing of pH, which indicated that Cu(II) removal was favorable under alkaline conditions. When at lower pH, the presence of a large amount of H⁺ in solution will compete with Cu(II) for adsorption sites [33], which greatly reduces the removal of Cu(II). The zeta potentials of the six adsorption materials were shown in Fig. 4(b), the zero potentials (pH_{ZPC}) of BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2 and A-ZVI/BC-2 were 3.97, 4.13, 5.18, 5.87, 7.86, and 8.09, respectively. When the pH is less than pH_{ZPC} , the material surface was protonated and positively charged, and Cu(II) ions could generate electrostatic repulsion. On the contrary, the surface of the material was deprotonated and negatively charged, which generated electrostatic attraction with Cu(II) ions [34]. With the rise of pH, the electronegativity of the material surface increased with it, which enhanced the electrostatic attraction with Cu(II). In addition, in alkaline solutions, OH⁻ in the solution forms precipitates with Cu(II), which was a reason for the increase of Cu(II) removal under alkaline conditions.

3.2.2 Effect of co-existing ions

In general, the coexistence of heavy metals and multiple cations (e.g., K⁺, Na⁺, Ca²⁺, Mg²⁺) in a real environment may affect the adsorption of heavy metals by adsorbent since these cations have the same charge as the heavy metals. To evaluate the effect of cation coexistence on ZVI/BC-1 on the removal of Cu(II), Cu(II) and K⁺, Na⁺, Ca²⁺, Mg²⁺ cations were selected for coexistence and their adsorption effects on Cu(II) was shown in Fig. S4 (cf. ESM). The adsorption of Cu(II) by ZVI/BC-1 decreases with increasing ion concentration due to the competition between these cations and Cu(II) at the adsorption sites. It was noteworthy that although the adsorption of Cu(II) by ZVI/BC-1 decreased, this decrease was not significant and the removal of Cu(II) in the coexistence of various cations concentration was above 70%. The same phenomenon was found in A-ZVI/BC-1, which indicated the potential of ZVI/BC-1 for promising applications in real environments.

3.2.3 Adsorption kinetics



Fig. 4 Cu(II) removal efficiency of at different (a) pH and (b) zeta potential of adsorption materials.

The Cu(II) adsorption kinetics on the bio-adsorbents in solution were analyzed and demonstrated in Fig. 5. Based on the results, the adsorption rates increased rapidly at



Fig. 5 The kinetic fitting of the pseudo-first-order model and pseudo-second-order model (a) before and (b) after aging and the intra-particle diffusion model of (c) before, (d) after aging on Cu(II).

first stage and then tended to reach the equilibrium at nearly 450 min. The saturated adsorption capacities of BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2 were 114.23, 96.27, 182.28, 138.94, 160.61, and 131.29 mg·g⁻¹, respectively, which indicated that the influence of aging on adsorption capacity.

The fitting parameters results of kinetics data via pseudo-first-order kinetic and pseudo-second-order kinetic were listed in Table S1 (cf. ESM). The R^2 values of pseudo-first-order kinetic fitting parameters of BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, A-ZVI/BC-2 were 0.911, 0.903, 0.886, 0.902, 0.872, and 0.876, respectively, and the R^2 values of pseudo-second-order kinetic fitting parameters were 0.971, 0.929, 0.969, 0.921, 0.969, and 0.917, respectively. The R^2 values of the pseudo-secondorder kinetic fitting parameters of the six adsorption materials were higher, indicating that the adsorption of Cu(II) by BC, A-BC, ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2 and A-ZVI/BC-2 were dominated by chemical adsorption [9]. To further understand the surface interactions, the intra particle diffusion model was used to investigate the relationship between adsorption quantity q_t and time t. As shown in Figs. 5(c, d), the adsorption of Cu(II) by the six adsorbent materials mainly included boundary diffusion and internal diffusion. The first stage was boundary

diffusion, and indicating Cu(II) was adsorbed on the surface of the adsorbent material. The second stage was corresponded to the internal diffusion, while Cu(II) species entered the internal pores and then reached adsorption equilibrium [26]. Meanwhile, fitting line was not passing through the origin point, demonstrating that internal diffusion was not the only determinant steps of Cu(II) adsorption, and other mechanisms were involved.

3.2.4 Adsorption isotherms

The variation of adsorption capacity with solution concentration was analyzed by adsorption isotherms to study the type of interactions between adsorbent and adsorbate, as shown in Fig. 6. It can be seen that the adsorption capacity was enhanced with the increasing of Cu(II) concentration, and the adsorption capacity reached equilibrium with the initial solution of 500 ppm. The fitting results of isothermal adsorption via Langmuir and Freundlich models were listed in Table S2 (cf. ESM) it can be found that the adsorption process of Cu(II) on BC, A-BC, were more consistent with Langmuir model, while ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2 were more consistent with Freundlich model [35]. This result indicated that the adsorption processes of Cu(II) on



Fig. 6 Isothermal adsorption of adsorbent materials for Cu(II).

BC and A-BC were monolayer adsorption, while those of Cu(II) on ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2 were multi-molecular layer adsorption, this could be explained by the existence of ZVI/BC species on the surface of ZVI/BC-1, A-ZVI/BC-1, ZVI/BC-2, and A-ZVI/BC-2, resulting in the uneven surface distribution of contaminants [36]. In addition, for ZVI/BC-2, R^2 was reduced after aging, indicating that more mechanisms and reactions may be involved on Cu(II) adsorption. According to Fig. 6, the adsorption capacity increased with the increase of temperature, indicating that the

adsorption of Cu(II) was endothermic [37]. The larger the $K_{\rm F}$ value in the Freundlich isothermal adsorption model, the greater the adsorption ability [38]. The $K_{\rm F}$ of ZVI/BC-1 has the highest adsorption capacity with the value of 20.140 mg·g⁻¹. In addition, it could be concluded that the $K_{\rm F}$ of the aged material decreased (Table S2), indicating that the adsorption capacity for Cu(II) was also decreased. Meanwhile, the parameter 1/n represents the adsorption strength, when 1/n is equal to 1, it is a linear model; when 1/n is less than 1, it is a nonlinear model. Further, the 1/n values of materials were all less than 1, indicating that the

adsorption of Cu(II) was nonlinear adsorption contained different mechanisms, which needed further investigations [38].

3.3 Removal mechanisms and effects of aging processes

Many techniques were employed to reveal the surface interactions between Cu(II) species and BC. The XRD of biochar materials and ZVI modified ones after adsorption were depicted (Fig. S5, cf. ESM). According to those results, there were no newly formed Cu related peaks, indicating the less involvement of co-precipitation during the adsorption of Cu(II) [39]. Moreover, the intensity of OH⁻ peaks in FTIR was weakened after the adsorption (Fig. S6, cf. ESM), indicating that OH⁻ groups were involved in the adsorption Cu(II) and Cu(OH)₂ complexations generated after the reaction [40]. In terms of ion-exchange, Table S3 (cf. ESM) listed the concentration of Ca(II) and Mg(II) ions before and after adsorption of the bio-materials with Cu(II) solution. It can be found that the concentration of Ca(II) and Mg(II) obviously increased after the reaction (from 37.85 to 50.07 mg·L⁻¹ for Ca and 0.18 to 4.21 mg·L⁻¹ for Mg), indicating that the occurrence of ion-exchange, between Cu(II) ions in the solution and Ca^{2+} and Mg^{2+} ions of BC occurred [41]. The full spectra of XPS after adsorption showed that Cu peak appeared (Fig. S7, cf. ESM), which also confirmed the successful adsorption of Cu(II) by ZVI/BC, for ZVI modified BC materials. As for ZVI/ BC, ZVI has strong reduction ability to adsorb Cu(II) directly [42]. In the ZVI/BC-1, the contribution of ion exchange to Cu(II) adsorption was quantified by calculating the difference of ion release before and after adsorption, the contribution of ion exchange to Cu(II) adsorption was 51.86 mg \cdot g⁻¹, accounting for 28.45% of the total adsorption capacity [43]. By comparing the XPS spectra

of Fe before and after adsorption, it can be estimated that chemical reduction contributed 73.33 $\text{mg}\cdot\text{g}^{-1}$, accounting for 40.23% of the total adsorption capacity. While the rest could be the contribution of complexation and electrostatic. But the decreasing of capacity after aging treatment was definitely associated with the transformation of these mechanism as mentioned before [44]. The mechanisms of ZVI/BC were shown in Fig. 7.

3.4 Performance assessment of adsorbent by bok choy experiment

To further evaluate the Cu(II) toxicity and immobilizing effects on Cu(II) via various adsorbent in soil, bok choy seeds were planted in copper-contaminated soil to observe the growth and root system. The growth of bok choy in soil at different days were shown Fig. S8 (cf. ESM). Bok choy exhibited the lower budding rate when grown in soil treated with aged adsorbent at 15 days of cultivation. After 32 days of cultivation, it was observed that the growth and plant height of bok choy in ZVI/BC-1 treated soil was almost the same as those in uncontaminated soil, which indicated that ZVI/BC-1 can effectively inhibit the bioavailability of Cu(II) [45]. Meanwhile, the root growth of bok choy in the soil treated with aging adsorbent materials was shorter and then that of the fresh ones, indicating that the inhibition effects of Cu(II) bioavailability was reduced after aging, this could be explained by the transformation of removal mechanisms before and after aging. The root length of bok choy grown for 32 days was shown Fig. S8, it can be tested that the growth of bok choy in the soil treated with the aging adsorbent was inhibited compared with the fresh one, which again indicated that the inhibition effects of aging adsorbent on Cu(II) bioavailability was reduced. Further, the concentration of Cu(II) in the leaching solu-



Fig. 7 Adsorption mechanisms of modified biochar.

tion after plant growth was determined (Fig. 8), the Cu(II) concentration of ZVI/BC-1 treated soil was the lowest, indicating that ZVI/BC-1 could effectively inhibit the migration of Cu(II) by BC and plants. After aging, Cu(II) concentration in ZVI/BC-1, BC, and ZVI/BC-2 treated soil increased to 0.16, 0.17 and 0.19 mg·L⁻¹, respectively.

To further study the effects of aging on Cu(II) accumulation in bok choy, Cu(II) content in the roots, stems and leaves of bok choy was examined. As shown in Fig. 9, the Cu(II) content in the roots, stems, and leaves of the aged material-treated bok choy were higher than that of the unaged material, which again indicated that the inhibitory effect of the aged material on the bioavailability of Cu(II) was diminished. In conclusion, ZVI/BC reduced the inhibition of Cu(II) bioavailability and increased the mobility of Cu(II) after aging, which was assigned with solution experimental data and mechanisms variation, this pilot-scale further provided evidence for the practical application of this environmental functional materials.

3.5 Regeneration of ZVI/BC biosorbent

The regenerative capacity of the adsorbent material was an important factor in environmental applications, which determined the possibility of application in the environment. The regenerability of ZVI/BC-1 was evaluated by performing five adsorption–desorption experiments, and as shown in Fig. S9 (cf. ESM), the removal rate of Cu(II) by ZVI/BC-1 decreased from 91.08% to 70.36% and the adsorption capacity decreased from 182.56 to 140.72 mg·g⁻¹ after five cycles. Despite five adsorption–desorption, ZVI/BC maintained over 70% removal capacity of Cu(II), which again demonstrated the potential of ZVI/BC-1 for environmental applications.



Fig. 8 Cu(II) leaching and root growth of bok choy.



Fig. 9 Cu(II) in roots (a), steams (b), and leafs (c) of varouis treaments bok choy.

4 Conclusions

Based on the characterizations of ZVI/BC before and after aging and the batch experimental results, the main adsorption mechanisms of ZVI/BC were elucidated, while the capacity decreased was associated with mechanisms varied after aging treatment. The adsorption capacity for Cu(II) was decreased after aging and main reasons were reduction of ion-exchange and oxidation of ZVI. Through investigated by pilot-scale experiment, ZVI/BC could immobilize Cu(II) in soil and improve the growth of plants, while these functionalities were weakened after aging treatment. All these results can provide detailed understanding for the ZVI/BC as well as its practical environmental application.

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