Research Article

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Effects of ageing on the surface characteristics and Cu(II) adsorption behaviour of rice husk biochar in soil

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Abstract: The properties of rice husk biochar during the ageing process in soil and the resulting impacts on sorption capacity with respect to Cu(II) were assessed. Rice husk-derived biochar was placed in fabric bags and buried in a plastic incubator filled with soil for 0–240 d. The aged biochar was then characterised and its sorption capacity compared with control (unaged) biochar in batch sorption experiments. The structural composition and morphology of the biochar before and after ageing were analysed based on element composition, scanning electron microscopy (SEM) coupled with energy X-ray dispersive spectroscopy (EDS), diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS), and X-ray photoelectron spectroscopy (XPS). The concentration of O, atomic O/C ratios, and carboxyl and hydroxyl functional groups increased at the surface of the biochar during ageing, which together indicated oxidation. Within the biochar particles, O/C ratios progressively increased towards their outer surfaces. Furthermore, ageing for more than 120 d facilitated Cu(II) sorption as oxygen-containing groups were able to develop. The maximum adsorption capacity ($q_m$) of biochar increased by 1.24 ~ 1.32 times after ageing in the soil for 240 d. It is suggested that biochar surface properties were gradually altered during environmental exposure and the aged rice husk biochar showed increased performance in Cu(II) adsorption. However, the performance of aged biochar as a soil remediator or conditioner will be affected by the ageing process and interactions among different soil components. As such, further research is required to evaluate these complex effects.

Keywords: biochar, ageing, surface properties, adsorption, Cu(II)

1 Introduction

Biochar is a carbon-rich solid by-product produced from biomass pyrolysis and has remarkable environmental properties (e.g., porous structure, large surface area, high aromaticity) [1–3]. Biochar has received much attention owing to its ability to improve soil fertility, adsorb environmental pollutants, and reduce greenhouse gas emissions [1,4–7]. Even though biochar appears to be relatively recalcitrant, it ultimately mineralises to CO$_2$ [8]. Biochar may be altered by a variety of time-dependent environmental processes, which is referred to as “ageing” [9,10]. It is likely that ageing alters the biogeochemical properties of biochar and affects its sorption behaviour [11,12]. It is difficult to collect aged biochar from the environment and so ageing experiments over environmentally relevant timescales can be very challenging. To overcome this, physical, biological and chemical methods have been used to artificially age biochar. This includes using physical wetting/drying and freezing/thawing cycles, which can modify the stability of biochar after field exposure [13,14]. Different chemical oxidants such as oxygen, hydrogen peroxide, nitric acid, acidified potassium dichromate, ozone and even air alone have also been used as ageing reagents in biochar experiments [15–19]. Biological mineralisation of biochar has also been investigated by incubating biochar with sand, soil, inoculum solution and specific nutrients [20–23].
Previous studies have shown that the characteristics of biochar often change over time, with ageing resulting in more carboxylic surface functional groups, more acidic conditions with a greater cation exchangeable capacity (CEC) and higher oxygen content but a lower point of zero charge, pH and carbon content [24–27]. Naisse et al. [28] suggested that physical weathering induced a 10–40% loss of the total C mass of biochar and the formation of carbonyl and carboxylic functional groups. Ghaffar et al. [29] found that biochar aged with HNO₃/H₂SO₄ experienced a surface area reduction but increased oxygen content and enhanced phthalates sorption on the oxidised biochar surfaces. As such, ageing may change the functional groups on the surfaces of biochar, which, in turn, can affect its adsorption capacity with respect to heavy metals and organic pollutants.

Most existing biochar ageing experiments have been performed using artificial methods, while incubation experiments in soil are rare. To improve the knowledge of the long-term behavior of biochar for the change in biochar adsorption capacity over time on the remediation of soil, the effect of ageing processes on biochar should be elucidated, especially when it is exposed to actual environmental conditions. The objectives of this study were, therefore, to assess changes in the properties of biochar when exposed in a soil environment and the resulting effects on the sorption of typical organic contaminants over time. For this, rice husk biochar was produced at two temperatures and incubated in soil contaminated with heavy metals and organic pollutants. Biochar elemental C, H and N contents were determined before and after the ageing experiments using a CHN elemental analyser (Vario MICRO, Heraeus, Germany). The ash content was determined by loss on ignition at 800°C for 2 h. The oxygen (O) content of the samples was estimated by subtraction as follows: O = 100 – (C + H + N) (wt%). Scanning electron microscopy (SEM) (S-3400N II, Hitachi, Japan) coupled to an energy-dispersive X-ray spectrometer (EDS) (EX-250, Hitachi) was used to examine the morphological and chemical properties of the biochar. A NEXUS870 spectrometer (Thermo Nicolet, USA) fitted with a diffuse reflectance accessory (Praying Mantis, Harrick Scientific, USA) was used to obtain the diffuse reflectance infrared Fourier transform spectroscopy.

## 2 Materials and methods

### 2.1 Biochar preparation and pre-treatment

Rice husk was obtained from cropland near to Nanjing Agricultural University, Jiangsu, China. This was then oven-dried to a constant weight at 60 ± 1°C, loaded into sealed metal containers (18 × 15 × 5 cm) and pyrolyzed in a muffle furnace (SXL1008, Shanghai Daheng, China) under oxygen-limited conditions. The furnace was set to a heating rate of approximately 20°C/min, held for 2 h at 350°C and 550°C respectively, and then cooled to room temperature. To remove pyrolysis residues from the biochar samples, particles were leached repeatedly with ethanol (1:10 w/v), ultrapure water (1:10 w/v), 0.5 mg/L NaOH (1:10 w/v) and 0.5 mg/L HCl (1:10 w/v) as previously described [30]. Before drying, the obtained particles were washed with ultrapure water to obtain a neutral pH and dried at 60 ± 1°C. After the samples were ground and sieved, particles with a diameter of 0.15–0.25 mm were collected for the ageing experiments, marked as R350 and R550 to reflect the respective carbonisation temperatures.

### 2.2 Ageing experiments

Ageing experiments were conducted using soil collected from the surface (0–25 cm) of a field in Liyang, Jiangsu, China. The soil was characterised as a clay loam with 18.8% sand, 29.2% silt and 52% clay, a pH of 5.34 and a soil organic matter content of 14.40 g kg⁻¹.

Ageing was carried out using incubation experiments. For each treatment, 2 g of biochar was placed into a fabric bag (10 × 5 cm) in a thin layer (approximately 2 mm). The fabric bags were buried in a plastic incubator (60 × 30 × 30 cm) filled with the field soil before incubation. The ageing experiments were conducted in triplicate. During the incubation period, the soil was kept at room temperature with a constant water holding capacity (60%) as determined gravimetrically. After 0, 120 and 240 d, the biochar samples were collected and dried (60 ± 1°C) and labelled R350-0 and R550-0, R350-120 and R550-120, and R350-240 and R550-240, respectively.

### 2.3 Analysis methods

Biochar elemental C, H and N contents were determined before and after the ageing experiments using a CHN elemental analyser (Vario MICRO, Heraeus, Germany). The ash content was determined by loss on ignition at 800°C for 2 h. The oxygen (O) content of the samples was estimated by subtraction as follows: O = 100 – (C + H + N) (wt%). Scanning electron microscopy (SEM) (S-3400N II, Hitachi, Japan) coupled to an energy-dispersive X-ray spectrometer (EDS) (EX-250, Hitachi) was used to examine the morphological and chemical properties of the biochar. A NEXUS870 spectrometer (Thermo Nicolet, USA) fitted with a diffuse reflectance accessory (Praying Mantis, Harrick Scientific, USA) was used to obtain the diffuse reflectance infrared Fourier transform spectroscopy.
(DRIFTS) spectra of the biochar samples. For this, biochar particles (2.5%) were prepared in KBr pellets and recorded with a DRIFTS accessory between 400 and 4,000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). The biochar particles were also analysed using X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, Uivac-Phi, Japan) to determine the C and O 1s spectra using a monochromatic Al-K\(\alpha\) X-ray source and a spot size diameter of \(\sim\)1 mm. The binding energies were determined in reference to the C 1s component (284.8 eV) and the background was linearly subtracted. All data were evaluated using XPSPEAK Version 4.0 and Origin 7.0 software.

### 2.4 Adsorption experiment

Batch adsorption experiments were subsequently conducted in aqueous Cu(II) solutions prepared using Cu(NO\(_3\))\(_2\)·2H\(_2\)O in 0.01 mol L\(^{-1}\) KCl solutions. Biochar samples (0.0500 g) and 25 mL of the Cu(II) solution at concentrations ranging from 0 mg L\(^{-1}\) to 250 mg L\(^{-1}\) were placed in 50 mL plastic centrifuge tubes. The suspensions were then shaken at a constant speed (200 rpm\(^{-1}\)) for 24 h. The pH of the adsorption system (including the control) was respectively adjusted up or down to 5.0 using either 0.5 mg L\(^{-1}\) HCl or 0.5 mg L\(^{-1}\) KOH solutions, respectively. After shaking, the biochar samples were separated by centrifugation at 4,000 rpm\(^{-1}\) for 10 min. In each case, the supernatant was then passed through a 0.45 \(\mu\)m organic membrane to remove the biochar particles. The concentrations of Cu(II) in the supernatant were measured using inductively coupled plasma atomic emission spectroscopy (Optima 2100DV, Perkin Elmer, USA). All experiments were carried out in triplicate.

Adsorption isotherms were expressed as the amount of Cu(II) adsorbed by the rice husk biochar before and after ageing in soil, at the equilibrium concentration, and fitted according to the Langmuir and Freundlich equations. The Langmuir model was applied as follows:

\[
q_e/\:q_m = C_e/q_{max} + 1/(b: \: q_{max})
\]

where \(q_e\) is the amount of adsorbate adsorbed per unit mass of biochar sample at equilibrium (mg g\(^{-1}\)); \(C_e\) is the equilibrium solution concentration (mg L\(^{-1}\)); \(b\) is the adsorption equilibrium constant; and \(q_{max}\) is the maximum adsorption amount (mg g\(^{-1}\)).

The Freundlich equation was applied as follows:

\[
\ln q_e = \ln K_f + 1/n(\ln C_e)
\]

where \(K_f\) and \(n\) are the Freundlich constants.

**Ethical approval:** The conducted research is not related to either human or animal use.

### 3 Results

#### 3.1 Elemental and chemical analyses

The rice husk biochar had a relatively high concentration of C and a low concentration of O (Table 1). After ageing in the soil for 120 and 240 d, the C content decreased while the O content increased in both cases. The O/C molar ratios consequently increased, implying an increase in oxygen-containing functional groups after ageing in soil. It is noteworthy that the content of C and O was relatively more variable during the first 0–120 d than during the 120–240 d period, which may reflect the formation of an ageing layer during the initial stages of the experiment that can prevent further oxidation [31].

The H/C and (N + O)/C molar ratios were used to estimate the carbonisation degree and polarity of the biochar produced at the two different temperatures [32]. Both of these ratios increased after incubation in soil for 120 and 240 d, indicating an increase in the saturation and hydrophilicity of the surface polar functional groups of both types of biochar.

**Table 1:** Elemental compositions and chemical characteristics of R350 and R550 biochar during ageing in soil for 0–240 d

| Sample  | Ash/g g\(^{-1}\) | C/%  | H/%  | N/%  | O/%  | H/C | O/C | (N + O)/C |
|---------|-----------------|------|------|------|------|-----|-----|-----------|
| R350-0  | 0.0118          | 64.61| 3.88 | 0.06 | 31.44| 0.72| 0.37| 0.37      |
| R350-120| 0.0601          | 62.17| 3.91 | 0.08 | 33.78| 0.75| 0.41| 0.41      |
| R350-240| 0.045           | 62.89| 4.07 | 0.08 | 32.91| 0.78| 0.39| 0.39      |
| R550-0  | 0.0383          | 71.88| 2.78 | 0.10 | 25.20| 0.46| 0.26| 0.26      |
| R550-120| 0.0937          | 67.52| 2.84 | 0.10 | 29.44| 0.50| 0.33| 0.33      |
| R550-240| 0.0704          | 67.73| 2.59 | 0.10 | 29.40| 0.48| 0.33| 0.33      |
3.2 SEM-EDS analysis

Based on the SEM observations, biochar prepared from rice husk had an inner concave surface and an outer convex surface. The outer surface is nodular convex structure, while the inner surface arranged in order longitudinally with clear structure. The surface morphologies and the O/C ratios of the biochar during the ageing process are shown in Figure 1, demonstrating similar patterns between the samples obtained at the two different temperatures. Specifically, the O/C ratios of the outer surfaces were higher than those of the inner surfaces (Table 2).

These results imply that the oxygen and carbon content of the inner and outer surfaces of biochar became relatively increased and decreased, respectively, during the ageing process. This is further supported by the elemental and chemical analyses. As such, biochar oxidation occurred during the ageing process and started at the surfaces of the biochar particles.

Table 2: O/C of the R350 and R550 biochar samples during ageing in soil for 0–240 d

| Sample   | O/C (atomic percentage) |
|----------|-------------------------|
|          | Inner       | Outer       |
| R350-0   | 0.260       | 0.340       |
| R350-120 | 0.264       | 0.365       |
| R350-240 | 0.329       | 0.538       |
| R550-0   | 0.240       | 0.380       |
| R550-120 | 0.265       | 0.408       |
| R550-240 | 0.260       | 0.388       |

Figure 1: SEM-EDS analysis of the aged biochar samples. (a) c1 (c1’), c2 (c2’), and c3 (c3’) show the SEM-EDS images of the inner (outer) R350 after 0, 120, and 240 d incubation; (b) d1 (d1’), d2 (d2’), and d3 (d3’) show the SEM-EDS images of the inner (outer) R550 after 0, 120, and 240 d incubation.
3.3 DRIFTS

The functional groups of the biochar during ageing in the soil were estimated using DRIFTS (Figure 2). DRIFTS spectra showed the presence of alkyl, hydroxyl, carbonyl, carboxylic acid, carboxylate and ester groups in both the high- and low-temperature biochar. The band at approximately 3,450 cm\(^{-1}\) represented O–H stretching vibration; the band at 2,970 cm\(^{-1}\) was attributed to the C–H stretching of –CH\(_2\)–; the bands centred at 1,710 cm\(^{-1}\) were assigned to carboxylic (COOH) groups; the peaks at 1,620 cm\(^{-1}\) were probably due to ring stretching in C\(=\)C and C\(=\)O; the band at 1,250 cm\(^{-1}\) indicated the occurrence of phenolic (C–O) and COOH groups; and a peak at 1,050 cm\(^{-1}\) corresponded to the symmetric stretching vibration of C–O–C or polysaccharide [33,34].

As shown in Table 2, the relative proportions (%) of each functional group were determined from their corresponding spectrum intensities (as a semi-qualitative measure), which indicated that biochar ageing for different periods resulted in variable peak intensities. The ratios of the main characteristic peaks at the surfaces of the biochar could be analysed in comparison with a set intensity of 1,620 cm\(^{-1}\) (Table 2) and other semi-qualitative wavenumbers on the biochar surfaces could be analysed in comparison with 1,620 cm\(^{-1}\).

For the two types of biochar, the changes in peak intensity during ageing were mainly caused by oxygen-containing functional groups. Specifically, biochar ageing reduced the relative intensity of the C–O–C or polysaccharide functional moieties at approximately 1,050 cm\(^{-1}\). The hydroxyl groups (O–H) at 3,450 cm\(^{-1}\) and C–H at 2,970 cm\(^{-1}\) and the carbonyl groups (C–O) at 1,710 cm\(^{-1}\) increased, while the relative proportions of phenolic (C–O) and COOH groups at 1,250 cm\(^{-1}\) and C–O–C at 1,050 cm\(^{-1}\) decreased. Thus, the characteristic ratios 3,450/1,620; 2,970/1,620; and 1,710/1,620 increased, while the ratios 1,250/1,620 and 1,050/1,620 decreased during ageing (Table 3). This indicated oxidation and the formation of carbonyl and aliphatic hydroxyl functional groups during ageing in the soil, while at the same time, ether groups decreased.

3.4 XPS analysis

XPS is effective at providing information on surface chemical composition; it can reveal the atomic content of elements and their chemical binding states on the outer surfaces of biochar. As the DRIFTS analysis revealed an increase in oxygen-containing functional groups during the ageing process, XPS was used to

![Figure 2: DRIFTS spectra of the biochar samples during the ageing process in soil.](image)

| Sample  | Wavenumber (cm\(^{-1}\)) | 3450/1620 | 2970/1620 | 1710/1620 | 1250/1620 | 1050/1620 |
|---------|--------------------------|-----------|-----------|-----------|-----------|-----------|
| R350-0  | 1.77                     | 1.31      | 0.96      | 0.77      | 0.42      |
| R350-120| 2.05                     | 1.45      | 1.05      | 0.75      | 0.375     |
| R350-240| 2.42                     | 1.55      | 0.99      | 0.52      | 0.065     |
| R550-0  | 1.25                     | 0.19      | 0.78      | 0.81      | 0.31      |
| R550-120| 1.29                     | 0.21      | 0.89      | 0.77      | 0.62      |
| R550-240| 2.25                     | 0.50      | 0.81      | 0.50      | 0.00      |
characterise the concentration of carbon and oxygen and their chemical bonding states for the biochar aged for 0, 120 and 240 d (Figures 3 and 4). The C 1s and O 1s peaks were split, such that the C 1s binding energy of C–C/C–H/C= was assigned at 284.8 eV. The binding energies 286.2 eV, 287.9 eV and 289.0 eV were defined as C–(O, N) (i.e. alcohols and amides or amines), C=O/O–C–O (i.e. acetals, hemiacetals, amides and carboxylates) and O–C==O (i.e. ester or carboxyl functionalities) binding states, respectively. The O 1s binding energies 531.2, 532.6, 531.8 and 533.4 eV were assigned as O=C (i.e. amides, esters and carboxyl moieties), C–O/C–OH (i.e. alcohols and ethers) and O==C–O–(C,H) (i.e. ester and carboxyl), respectively. Further details are given in Table 4.

After exposure to soil, the atomic percentage of the samples notably varied. For the biochar produced at both temperatures, the relative occurrence of the surface oxygen bonding state O=C (531.2 eV) and oxygen bonding state O–C==O (289.0 eV) significantly increased during the ageing process, which indicated that the carboxyl groups increased as a result of oxidation.

Figure 3: XPS C 1s scan and peak fitting for the R350 and R550 biochar samples during ageing in soil for 0, 120 and 240 d. Notes: The scan and peak fitting for biochar samples ageing for 0 d originated from Huang et al. [35].
reactions on their surfaces [36]. Moreover, the occurrence of the oxygen bonding states C–O–C and C–OH at 532.6 eV decreased, especially for R550, mirroring the DRIFTS result that the carbonyl groups and aliphatic hydroxyl functional groups increased while the ether groups decreased. Together, this indicated that the ether groups on the surfaces of the biochar were destroyed whilst carboxyl and aliphatic hydroxyl groups were formed during the ageing process. This resulted in the polarity of the biochar and the increased oxygen content after ageing in the soil.

Cheng et al. [20] incubated biocahr and biocahr-soil mixtures with and without microbial inoculation, additional nutrients and manure amendment for four months and found that abiotic processes were more important for the oxidation of biocahr than biotic processes during short-term incubation. In our study, the biochar samples were placed into fabric bags and as
such could interact with all substances in the soil, such as organic substances and minerals. Although the samples were prepared under different temperatures and possessed different properties, after being placed in the soil, both types of biochar exhibited similar changes, possibly due to the adsorption of soil organic matter.

3.5 Effect of biochar ageing in soil on adsorption

As the surface properties of biochar substantially affect sorption properties, the changes produced during ageing may profoundly affect adsorption properties. Cu(II) was

Table 4: C 1s and O 1s bonding states and relative atomic percentages on the biochar surfaces

| Line   | Binding Energy (eV) | Structure     | R350 0 d | 120 d | 240 d | R550 0 d | 120 d | 240 d |
|--------|---------------------|---------------|----------|-------|-------|----------|-------|-------|
| C 1s   | 284.8               | C=-(C,H), C=O | 66.04    | 86.64 | 74.04 | 67.90    | 73.52 | 88.89 |
|        | 286.2               | C=-(O, N)     | 19.65    | 8.24  | 18.21 | 19.32    | 21.08 | 0.00  |
|        | 287.9               | C=O; O–C–O    | 11.83    | 0.21  | 0.00  | 8.51     | 0.00  | 5.65  |
|        | 289.0               | O=O–O         | 2.48     | 4.90  | 7.75  | 4.27     | 5.37  | 5.46  |
| O 1s   | 531.2               | O=O           | 15.23    | 31.59 | 21.44 | 18.77    | 18.26 | 51.93 |
|        | 531.8               | O=O–O–(C,H)   | 22.28    | 21.88 | 22.33 | 21.37    | 21.95 | 17.48 |
|        | 532.6               | C=O=O; C–OH   | 24.04    | 19.32 | 23.01 | 23.85    | 23.41 | 12.97 |
|        | 533.4               | O=O–O–(C,H)   | 38.44    | 27.22 | 31.22 | 36.00    | 36.38 | 17.63 |

Notes: The data of relative atomic percentages on the biochar surface for 0 d originated from Huang et al. [35].

Figure 5: Cu(II) adsorption isotherms of rice husk biochars after different aging time in the soil.
consistent with an increase in the Cu(ii) sorption capacity of aged biochar produced from different biomass sources [41–43]. The formation of surface O-containing functional groups on the surfaces of aged biochar increases the availability of complexation sites for Cu(ii) and directly enhances the surface negative charge that allows biochar to be more electrostatically attractive with respect to heavy metal ions and, in this case, Cu(ii) sorption [42,44]. Moreover, in comparison to the control samples, the maximum adsorption capacity ($q_m$) of biochar was higher after 240 d than after 120 d. Thus, the effects of biochar ageing on the Cu(ii) sorption capacity was notably dependent on ageing time.

### 4 Discussion

Our results indicate that the exposure of rice husk biochar in soil affects both its physiochemical structure and sorption properties. Ageing in the soil environment led to an increase in the elemental O and a decrease in the elemental C content of the biochar. An increase in the H/C and (N + O)/C molar ratios at the surface of the biochar after ageing also demonstrated that the degree of carbonisation and the polarity of the biochar increased. Beyond laboratory ageing, biochar that has been previously exposed in the environment also shows higher O and lower C concentrations [21,34].

The increase in the O/C ratio of the outer (inner) surfaces of the biochar after ageing, as identified using EDS, corresponded with the observed variations in elemental composition and implies that oxidation occurred during the soil ageing. With respect to the fate of the oxygen and the oxidation products, the DRIFTS spectra showed that carbonyl and aliphatic hydroxyl functional groups were formed during the ageing process, while the occurrence of ether groups decreased. Similarly, the XPS analysis confirmed that the aged biochar was functionalised with carboxyl and hydroxyl groups. Oxygen-containing functional groups on the surfaces of biochar can form complexes with heavy metal cations, whereby the increase in oxygenated functional groups enhances the potential to adsorb heavy metals [45–47].

For the aged biochar, an increase in the Cu(ii) adsorption capacity was evident and can be explained by the formation of surface O-containing functional groups (e.g. carboxyl and hydroxyl groups) when exposed to the soil environment. Carboxyl groups and hydroxyl groups are potential Cu(ii) adsorption sites.
which play a vital role in the environmental application of biochar as a soil amendment, and the combination modes between these groups and the biochar would have determined their dissociation degrees. The presence of these polar groups can further facilitate the interaction between positively charged Cu(II) and other cations. Such interactions can lead to a series of reactions between surface carboxyl and hydroxyl functional groups and metal ions, which can and stabilise metal ions as a result [44,46]. Xu and Zhao [48] presented that biochar mainly increased Cu(II) adsorption through a non-electrostatic mechanism, possibly via oxygen-containing functional groups on the surfaces of biochars can form surface complexes with Cu(II) and other metal cations or surface precipitation of Cu(II). These ageing effects are also in agreement with the findings of Wang et al. [43] who found that sludge-derived biochar favoured Pb(II) and As(III) sorption after atmospheric ageing as a result of higher densities of available oxygen-containing groups. They also studied how various oxidising agents (e.g. chemical oxidants, O₃ and thermal oxidation) enhances cation uptake. The long-term natural oxidation of biochar can produce a similar range of maximum Cu(II) sorption capacities as other biomass chars that have been artificially oxidised using chemical reagents [41,42].

Our results indicate that exposure of biochar in soils has effects on both its physiochemical structure and sorption properties. The higher sorption capacities for Cu(II) on aged biochar correspond well with the formation of surface O-containing functional groups during the natural oxidation of biochar. It is worth noting that the time of exposure affected the degree and quality of ageing in our experiments. Furthermore, ageing effects are expected to continue beyond the maximum examined time (240 d), as biochar samples recovered after 130 years in soils showed much greater levels of oxidation [34]. After the addition of biochar to soil, the performance of biochar would be affected by oxidation as well as its effects on soil fertility and biogeochemistry. Adding biochar to Zn-contaminated soil after 180-days were found immobilize excess Zn, reduce its uptake by the plant and promote plant biomass growth [41]. Long-term atmospheric ageing suppresses the Cr(VI) sorption capacity [43]. The Cd binding to oxidized biochar was significantly affected by the coexistence of Al via acidification and competition [49]. These indicates that ageing process may have distinct effects on different heavy metal sorption and the long-term effect should be paid more attention.

5 Conclusions

The present study evaluate the effects of ageing on rice husk-derived biochar and its sorption capacity with respect to Cu(II). The observed increase in the O content and decrease in the C content of the aged biochar, and increase in atomic O/C ratios, indicated that the biochar surfaces became more oxidised during the ageing process. The development of surface O-containing functional groups during ageing—especially carboxyl and hydroxyl structures—enhanced Cu(II) sorption and also increased the polarity of the biochar. As such, our laboratory experiments have demonstrated that rice husk biochar becomes increasingly oxidised over time when exposed to the soil environment. It implies that the potential for rice husk biochar to remediate contaminated soils is not short lived but, rather, becomes enhanced over time through surface oxidation processes. The performance of biochar in soil is, however, expected to be affected by the complex interactions between a range of factors including the type of biochar and the components of the soil (e.g. microbes, nutrients and contaminants). Further research is now required to better understand the nature of these interactions as well as their effects on biochar performance over time.

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