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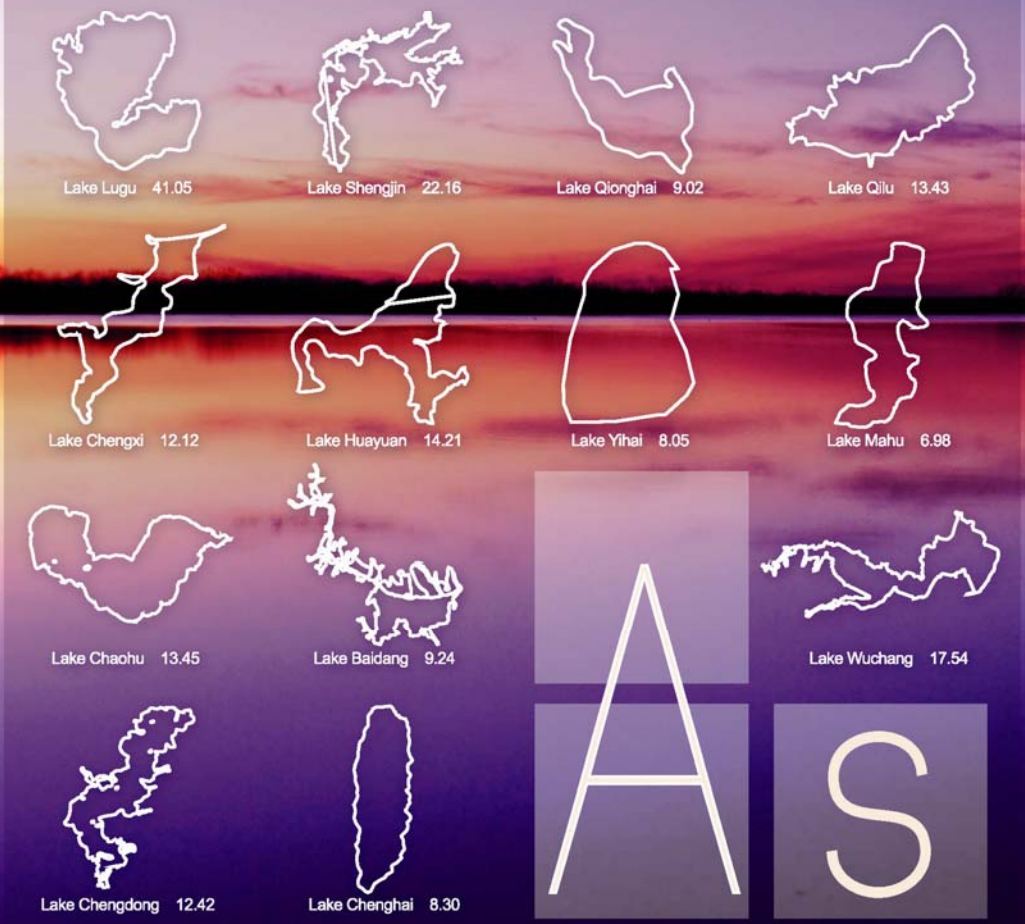

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Mechanism of Cu(II) adsorption inhibition on biochar by its aging process

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ABSTRACT

Biochar exposed in the environment may experience a series of surface changes, which is called biochar aging. In order to study the effects of biochar aging on Cu(II) adsorption, we analyzed the surface properties before and after biochar aging with scanning electron microscopy (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and then explored the influence of the aging process on Cu(II) adsorption by batch experiments. After the aging process, the oxygen concentration, phenolic hydroxyl groups, aromatic ethers and other oxygen-containing functional groups on the biochar surface increased, while carboxyl groups slightly decreased. Thus, over a range of pH, the cation exchange capacity (CEC) and adsorption capacity of Cu(II) on the aged biochar were smaller than those of new biochar, indicating that when biochar is incubated at constant temperature and water holding capacity in the dark, the aging process may inhibit Cu(II) adsorption. Meanwhile, the dissociation characteristics of oxygen-containing functional groups changed through the aging process, which may be the mechanism by which the biochar aging process inhibits the Cu(II) adsorption. Carboxyl groups became more easily dissociated at low pH (3.3–5.0), and the variation of maximum adsorption capability (q_m) of Cu(II) on the old biochar was enlarged. Phenolic hydroxyl groups increased after the aging, making them and carboxyl groups more difficult to dissociate at high pH (5.0–6.8), and the variation of q_m of Cu(II) on the aged biochar was reduced.

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Introduction

Biochar is a pyrolytic product of biomass produced under relatively low temperature (lower than 700°C) and anoxic conditions (Antal and Gronli, 2003; Kwapinski et al., 2010). With its porous structure, large specific surface area and good biological and chemical stability (Zhu et al., 2005), biochar has been widely studied for its potential applications in the fields of environmental and soil improvement, such as soil pH alteration, the sorption of pollutants in soil, the improvement of fertility and water-holding capacity in soil and carbon sequestration in soil (Cao et al., 2009; Chan et al., 2007; Chen and Chen, 2009; Kolodynska et al., 2012; Lehmann and Joseph, 2009; Liang et al., 2006; Liu and Zhang, 2009; Sheng et al., 2005).

Although biochar has stable properties, it still experiences slow changes in the environment. After exposure to the environment, biochar's oxygen concentration, surface acidic functional groups and cation exchange capacity (CEC) are increased while carbon concentration, pH and zero point charge (ZPC) are decreased (Cheng et al., 2006, 2008; Cheng and Lehmann, 2009; Kamegawa et al., 1998, 2002; Liang et al., 2006; Nguyen et al., 2010; Peng et al., 2011). Because the adsorption process of oxygen atoms on biochar surface is an endothermic process, biochar aging is affected by ambient

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temperature: the higher the temperature is, the faster the biochar ages (Cheng et al., 2006, 2008; Cheng and Lehmann, 2009). Previous studies have shown that biochar aging mainly occurs on the surface. After ^{13}C-labeled biochar was incubated in soils, the degradation speed of the biochar was rapid early in the incubation period and then gradually became slow (Bruun et al., 2011; Smith et al., 2010). Bruun et al. (2011) believed that this phenomenon could be caused by rapid surface degradation after the biochar was added into the soil. Through the analysis of synchrotron-based Near-Edge X-ray Fine Structure (NEXAFS), Liang et al. (2008) found that the spectrum of internal non-degraded biochar was the same as that of newly prepared biochar and that the degradation degree of the biochar decreased gradually from the surface to the interior. Liang proposed that the degraded surface biochar protected the internal biochar. A series of surface changes of the biochar may also occur during the aging process (Cheng and Lehmann, 2009). After exposure to the environment, a protective layer is quickly formed on the surface of biochar. Meanwhile its elemental composition and oxygen-containing functional groups are also changed. Surface changes during biochar aging may affect the adsorption of heavy metal ions, since they are adsorbed on the surface of the biochar (Kolodynska et al., 2012).

The biomass material, moisture content, pyrolysis temperature, pyrolysis time and other factors affect the properties of the prepared biochar (Ahmad et al., 2012; Yuan and Xu, 2011; Zhang et al., 2011). In previous studies on the changes of biochar in the environment, the studied biochar samples were extracted from historical charcoal blast furnaces or the soil (Cheng et al., 2008; Kimetu et al., 2008; Liang et al., 2008; Nguyen et al., 2009; Pessenda et al., 2001) and the raw materials and pyrolytic conditions of old and new biochar were not the same. Thus, the previous results are inconclusive. In this study, with biochar prepared under the same conditions, we removed the pyrolytic residues through pretreatment to ensure the same aging starting point, uniform experimental materials and comparable data. Then the prepared biochar was incubated for aging. We studied the variation of Cu(II) adsorption capability after biochar aging. The changes of surface properties of the biochar were also investigated using CEC, SEM and DRIFTS. The results in this study can provide theoretical support for the application of the biochar in environmental remediation of heavy metal pollution as well as in understanding changes in environmental remediation capability.

1. Materials and methods

1.1. Biochar preparation

Rice husk was dried to constant weight at 60 ± 1°C and then loaded in stainless steel containers (18 × 15 × 5 cm). After compaction of rice husk, the stainless steel containers were sealed, put into a muffle furnace (SXL1008, Shanghai Daheng, China), heated to 550°C and maintained for 2 hr under anoxic conditions. The average pyrolysis yield of biochar was 38.4% by mass. Then the stainless steel containers were cooled to room temperature and the samples were taken out. After milling the samples, particles within the diameter range of 0.15–0.25 mm were selected for experiments and hereafter referred to as BC.

1.2. Characterization of biochar

Pyrolysis yields of the biochar were calculated according to the mass loss of rice husk during pyrolysis. The contents of C, H and N were measured using a CHN elemental analyzer (Vario MICRO, Heraeus, Germany). Ash content was analyzed by the loss of weight on combusting the biochar samples at 800°C for 2 hr. The oxygen (O) content was determined by difference. The pH value was measured in 1:20 m/V ratio in H_2O according to the pH determination method for wood-derived activated carbon (GBT 12,496.7–1999). These properties of BC are as follows: C 71.02%; H 3.44%; N 0.03%; O 25.51%; H/C 0.58; (N + O)/C 0.27; pH 10.6; and ash 0.35 g/g.

The specific surface areas were measured using an automatic nitrogen adsorption surface analyzer (JW-004, JWGB, China). The specific surface area of new biochar was 24.73 m^2/g, and that of old biochar was 18.34 m^2/g.

The DRIFTS spectra of biochar samples were obtained using a NEXUS870 spectrometer (Thermo Nicolet, USA) fitted with a diffuse reflectance accessory (Praying Mantis, Harrick Scientific, USA). Potassium bromide (KBr) pellets containing 2.5% of finely ground biochar powder were prepared and scanned. The spectra were obtained at 4 cm^{-1} resolution from 400 to 4000 cm^{-1} with 64 scans. Solid state ^{13}C CPMAS (cross polarization, magic-angle spinning) NMR spectra of biochar samples were obtained using a Bruker Avance-300 NMR spectrometer. Biochar samples were packed into 4 mm-diameter zirconium oxide rotors and spun at 10 kHz. Morphological and chemical properties of biochar samples were examined using a scanning electron microscope (SEM) (S-3400N II, Hitachi, Japan) coupled to an energy-dispersive X-ray spectrometer (EDX) (EX-250, Hitachi, Japan). CEC was determined according to the method proposed by Cheng et al. (2008).

1.3. Pretreatment and aging experiment

1.3.1. Pretreatment

During pyrolysis, some pyrolysis residues (such as bio-oil and carbonates) are firmly adsorbed on biochar and cannot be completely removed through simple soaking with dilute acid and dilute alkali. During biochar aging, an aging layer was formed on the surface and the internal biochar remained unchanged. Therefore, pyrolysis residues and the aging layer were removed by an oxidation method and the biochar surface was restored to the initial state. The restored biochar was defined as new biochar.

The biochar was soaked repeatedly with ethanol until the supernatant was colorless. Then the biochar was soaked with ultrapure water (18.2 MΩ, NJQY, China) until the TOC in the supernatant was below the detection limit. Then it was soaked repeatedly with 0.5 mg/L NaOH and 0.5 mg/L HCl until the TOC in the supernatant was below the detection limit. Then the biochar was washed with ultrapure water to neutral pH before drying. A mixture of 0.4 mg/L 1/6 potassium dichromate and sulfuric acid with 1:2 volume ratio was used as the oxidant (Yang et al., 2013). The biochar was oxidized in 1:500 m/V ratio in the oxidant for 40 min in a boiling water bath. After cooling, the biochar was washed with ultrapure water until no SO_4^{2-} was detected. After drying at 60 ± 1°C, the biochar was sieved to obtain biochar particles within a diameter range from 0.15 to 0.25 mm which were hereafter referred to as NBC.

1.3.2. Aging experiment

NBC (0.15–0.25 mm) and quartz sand (0.38–0.83 mm) were mixed at a ratio of 1:10 by dry weight. Biochar samples were incubated at constant temperature (30 ± 1°C) in the dark at

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60% water holding capacity. After 300 day incubation time, the biochar samples were removed and dried at 60 ± 1°C. Then the biochar samples were defined as old biochar and hereafter referred to as OBC.

1.4. Batch sorption experiments

According to the results of previous studies, the adsorption process of heavy metal ions on biochar is affected by pH, ionic strength, temperature and other factors (Borah et al., 2008; Kolodynska et al., 2012; Wang et al., 2010; Li et al., 2013). Thus all experimental conditions should be controlled. In this study, Cu(II) solution was prepared by dissolving $CuCl_2{\cdot}2H_2O$ in 0.01 mg/L KCl solution. 25 mL of Cu(II) solution with initial concentration ranging from 20 to 250 mg/L was placed in 50 mL plastic centrifuge tubes with a certain dose of biochar samples (0.0500 g) and shaken at a constant speed (200 r/min) for 24 hr. The pH of the adsorption system (including the control) was respectively adjusted to the required pH value (3.3, 5.0 and 6.8) by adding either 0.5 mg/L HCl or 0.5 mg/L KOH solutions. After shaking, the biochar samples were separated by centrifugation at 4000 r/min for 10 min and the concentrations of Cu(II) in the supernatant were measured by inductively coupled plasma atomic emission spectroscopy (ICP) (Optimal 2100DV, Perkin Elmer, USA). The experiments were carried out in triplicate and the average values were obtained.

2. Results and discussion

2.1. Effect of biochar aging processes on the adsorption of Cu(II)

The change of surface properties of the biochar can affect the adsorption process, as Cu(II) adsorption on biochar mainly takes place as surface adsorption (Kolodynska et al., 2012; Wang et al., 2010). The adsorption isotherms of Cu(II) to the BC (original biochar), NBC (new biochar), and OBC (old biochar) are shown in Fig. 1a, and the adsorption data of Cu(II) on biochar samples was analyzed using the Langmuir and Freundlich isotherm models and presented in Table 1.

In this case, the R^2 values of the Langmuir model ranged from 0.978 to 0.994, whereas for the Freundlich model they ranged from 0.727 to 0.972. The data for sorption of Cu(II) on the biochar samples fitted closely to the Langmuir adsorption model. The values of the maximum adsorption capacity, q_m, indicating the maximum value of Cu(II) adsorption on biochar, are also presented in Table 1. Through comparing the Cu(II) adsorption capacity (5.55 mg/g) of original biochar (BC) with that (5.38 mg/g) of new biochar (NBC), we found that q_m was decreased by 3.06%. Comparing the q_m of NBC and old biochar (OBC), it was decreased by 31.60% (which was much more than 3.06%), from 5.38 to 3.68 mg/g, indicating that the change of Cu(II) adsorption was caused by the aging process and that the pretreatment had little influence on Cu(II) adsorption on the biochar.

In consideration of the decrease of specific surface area after biochar aging, this was consistent with the result of adsorption capacity. After the aging process, the specific surface area of biochar showed a decrease of 25.8%, which was smaller than the 31.6% decrease of q_m, so the decrease of the specific surface

Table 1 – Fitting of adsorption of Cu(II) on biochar samples to isotherm equation.

Samples	Isotherm models		pH		
			3.3	5.0	6.8
BC	Langmuir	q_m (mg/g)		5.56	
		K_L (L/mg)		0.161	
		R^2		0.985	
	Freundlich	K_f (mg/g)		2.86	
		n (g/L)		7.68	
		R^2		0.827	
NBC	Langmuir	q_m (mg/g)	4.10	5.38	11.4
		K_L (L/mg)	0.071	0.082	0.524
		R^2	0.988	0.994	0.991
	Freundlich	K_f (mg/g)	0.91	1.78	4.85
		n (g/L)	3.44	4.73	5.38
		R^2	0.972	0.953	0.885
OBC	Langmuir	q_m (mg/g)	2.08	3.68	7.19
		K_L (L/mg)	0.043	0.081	0.436
		R^2	0.993	0.985	0.978
	Freundlich	K_f (mg/g)	0.29	1.23	3.71
		n (g/L)	2.65	4.88	7.35
		R^2	0.948	0.885	0.727

q_m: the maximum amount of Cu(II) adsorbed by biochar, K_L: a constant related to the heat of adsorption, K_f: the maximum adsorption capacity, n: a constant related to adsorption intensity. BC: the original biochar, NBC: the new biochar, OBC: the old biochar.

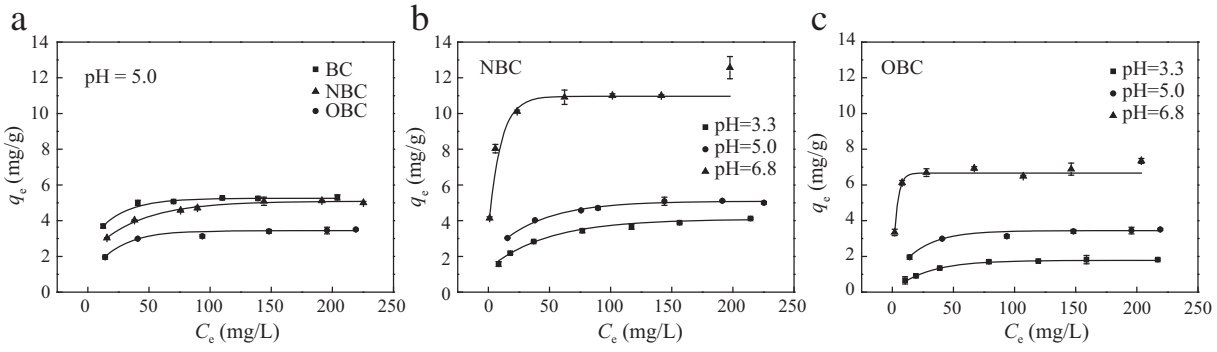

Fig. 1 – Adsorption isotherms of Cu(II) to the BC (original biochar), NBC (new biochar), and OBC (old biochar) at pH 5.0 (a), and effect of pH on the adsorption of Cu(II) to NBC (b) and OBC (c). C_e (mg/L) is equilibrium concentration of Cu(II), and q_e (mg/g) is the equilibrium Cu(II) adsorption capacity.

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area was just one of the reasons for the decline of adsorption capacity. Moreover, since the Langmuir model was a better fit to the data, we consider that chemical adsorption played a major role in Cu(II) adsorption on biochar. Therefore, the effect of the aging process on the adsorption capacity cannot be ignored.

Previous studies have shown that the aging of biochar can increase CEC and enhance the adsorption capability toward heavy metal ions (Cheng and Lehmann, 2009), which was contradictory to the results in this study. This may be interpreted as follows: the aging process changes the composition of the oxygen-containing functional groups on the biochar surface and the degree of dissociation of functional groups affects CEC. Moreover, the degree of dissociation of functional groups is affected by pH. Therefore, Cu(II) adsorption of the biochar was studied at different pH values.

Since Cu(II) in an alkaline environment may form a partial precipitate, the selected pH range was from 3.3 to 6.8. As shown in Fig. 1b and c, Cu(II) adsorption capabilities of new biochar and old biochar were increased with rising pH. Moreover, at three pH values, the Cu(II) adsorption capability of new biochar was greater than that of old biochar.

The Cu(II) adsorption capability of the biochar varied with pH. The variation was related to the dissociation properties of functional groups. When pH rose, the degree of dissociation of surface functional groups, surface electronegativity and number of adsorption sites was increased. Thus, Cu(II) adsorption capability was increased. Through analyzing the change of q_m obtained from Langmuir isotherm model fitting, it was found that when pH rose from 3.3 to 5.0, q_m of new biochar and old biochar were respectively increased by 31.2% and 77.4%, indicating that at low pH (3.3–5.0), more dissociated functional groups were formed on the surface of the biochar and played the main role in Cu(II) adsorption. When pH rose from 5.0 to 6.8, q_m of new biochar and old biochar were respectively increased by 111.2% and 94.9%, indicating that at the high pH (5.0–6.8), the Cu(II) adsorption capability of old biochar was mainly affected by the functional groups that were difficult to dissociate. Moreover, at three pH values, the Cu(II) adsorption capability of old biochar was smaller than that of new biochar, indicating that the aging process may decrease the functional groups serving as Cu(II) adsorption sites.

The degree of dissociation of the surface functional groups of the biochar strongly influenced the Cu(II) adsorption capability. The influences were different for the new and old biochar, indicating that the type or structure of surface functional groups of old biochar was changed and that the change affected the Cu(II) adsorption capability of the biochar.

2.2. Effect of aging process on the surface properties of biochar

2.2.1. Effect of incubation time on the aging layer

During the biochar aging process, a protective layer adapted to the environment (similar to the rust layer on metal surfaces and weathered layer on mineral surfaces) might be formed on the surface. The protective layer was the transition region between the biochar and the surrounding environment and named the aging layer. Because the aging layer was the preliminary pyrolytic product of the biochar, the oxidation resistance of the aging layer was weaker than that of the internal part. Thus, the aging layer that was easier to oxidize could be determined using the oxidation method proposed by Yang et al. (2013). Through analyzing the more easily oxidized substance after different incubation periods, the aging degree of the biochar could be characterized.

As shown in Fig. 2, the aging layer of the biochar was increased with incubation time. The rate of increase of the aging layer was more rapid in the first 200 days. After the 200-day incubation, the rate of increase was stable. While the material of new biochar was obtained through pretreatment, the aging layer was formed during incubation, and the thickness of the aging layer produced was increased with incubation time.

2.2.2. SEM-EDX spectrograms of biochar samples

Since rice husk has an inner surface (concave and smooth surface) and outer surface (convex and rough surface), the two surfaces were selected for analysis for new and old biochar and the O/C ratio is provided in the figure. The EDX measurements were good approximations of the elemental composition of biochar (Brodowski et al., 2005). As shown in Fig. 3, the O/C ratios of the outer surface and inner surface of old biochar were respectively increased from 2.039 and 0.355 to 6.603 and 1.914. This indicated that biochar aging may change the elemental composition on the surface: oxygen content was increased and carbon content was decreased, which was consistent with the results by Cheng et al. (2008). To explore the behavior of oxygen in the aging process, the DRIFTS and ^{13}C CPMAS NMR were carried out.

2.2.3. ^{13}C CPMAS NMR and DRIFTS analysis of biochar samples

In order to determine whether the carbon forms of the biochar changed after aging, ^{13}C CPMAS NMR analysis was carried out. The spectra of new and old biochar shown in Fig. 4a were divided into the following chemical shift regions: alkyl carbon of chain alkenes (0–50 ppm), N-alkyl/O-alkyl carbon (50–100 ppm), aromatic carbon including aromatic bonds of C–C, C–H, C–O and C–N (100–160 ppm), and carboxyl/amide carbon (160–220 ppm) (Hu et al., 2013; Pereira et al., 2011; Zhang et al., 2011).

^{13}C CPMAS NMR spectra of the biochar samples showed no obvious difference after aging, indicating that biochar aging for a short time led only to surface oxidation and that the bulk of the biochar was basically unchanged. DRIFTS analysis can provide information on the types of functional groups on the surface of the biochar. Because the infrared beams are emitted from the surface in a diffuse manner after repeated transmission, refraction and reflection among the carbon

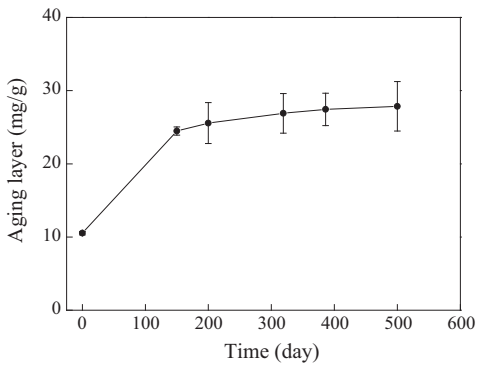

Fig. 2 – Effect of incubation time on the amount of aging layer.

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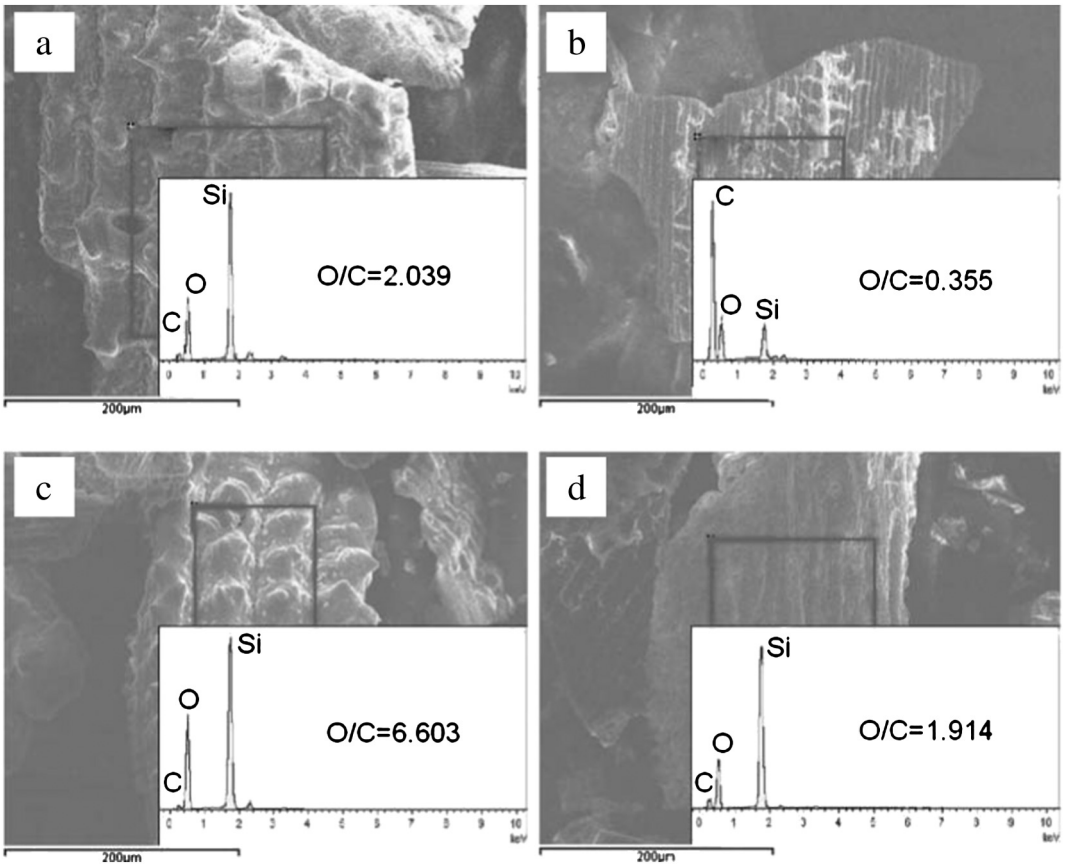

Fig. 3 – Scanning electron micrographs and EDX spectrograms of the outer surface (a) and inner surface (b) of NBC (new biochar), and the outer surface (c) and inner surface (d) of OBC (old biochar).

particles, the diffuse light acts on the biochar particles and carries information of the structure and composition of the biochar, which can be used to characterize the surface properties.

The spectrum shown in Fig. 4b has several adsorption bands. The band around 3450 cm^{-1} was assigned to O–H stretching, and that at 3040 cm^{-1} to C–H stretching of $-CH_2-$. The band centered at 1710 cm^{-1} was assigned to C═O stretching of carboxylic groups, 1600 cm^{-1} to the molecular vibration of ring stretching in C═C, 1200 cm^{-1} to C–O stretching of phenolic and carboxylic groups, and 1050 cm^{-1} to symmetric C–O–C stretching (Cheng et al., 2008; Cheng and Lehmann, 2009; Peng et al., 2011; Uchimiya et al., 2013; Zhang et al., 2011).

Through comparison of DRIFTS spectra of the new and old biochar, we found that the band intensities at 3450 cm^{-1} and 1200 cm^{-1} of the old biochar were greater than those of the

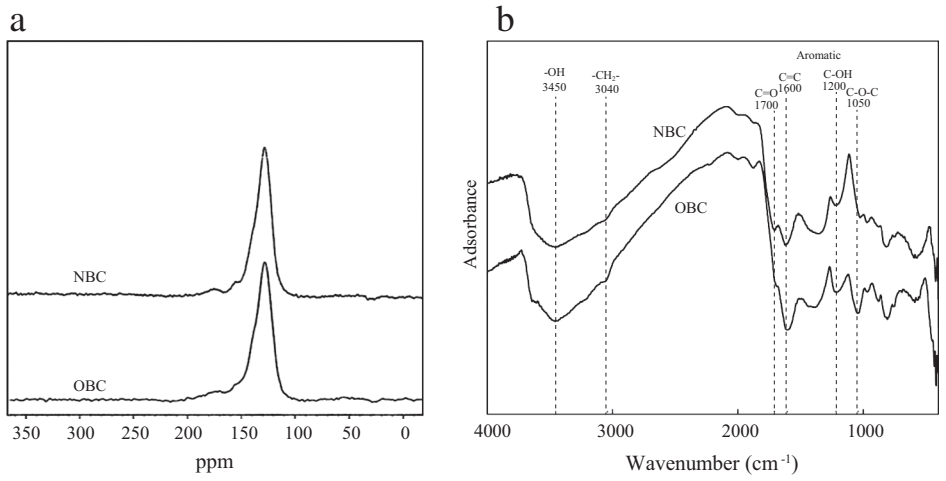

Fig. 4 – ^{13}C CPMAS NMR spectra (a) and DRIFTS (b) of NBC (new biochar) and OBC (old biochar).

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new biochar, indicating that hydroxyl groups were increased on biochar surface after the aging process. The band intensity at 1600 cm^{-1} was increased after aging, indicating that the increased hydroxyl groups on the surface mainly included phenolic hydroxyl groups. In addition, the band intensity at 1050 cm^{-1} was increased, indicating that aromatic ethers were formed after aging. The band intensity at 1710 cm^{-1} assigned to carboxyl groups was decreased. In summary, when biochar was incubated at constant temperature and water holding capacity in the dark, its surface experienced decarboxylation and hydroxylation, and the formed hydroxyl groups and ester groups counteracted the oxygen atom loss during decarboxylation and even increased the total oxygen content on the surface.

Combined with the results of Cu(II) adsorption on the biochar samples at different pH, we found not only that carboxyl groups were slightly decreased after aging, but also that the dissociation characteristics of carboxyl groups were also changed. Compared with new biochar, carboxyl groups of the old biochar were more easily dissociated at low pH (3.3–5.0). Thus, the variation of Cu(II) adsorption capability of old biochar with pH was relatively large in this range. Compared with carboxyl groups, phenolic hydroxyl groups were more difficult to dissociate and they were increased after aging, making the variation of Cu(II) adsorption capability of the biochar after aging relatively small when pH rose from 5.0 to 6.8.

2.2.4. Cation exchange capacity of biochar samples at different pH

In our study, CEC was determined according to the method proposed by Cheng et al. (2008). In the adopted method, the buffering role of the biochar was fully utilized and all the cation adsorption sites were occupied, which made our results more convincing. As shown in Fig. 5, CEC was increased with the rising pH and CEC of new biochar was larger than that of old biochar regardless of pH. The results of CEC were consistent with the results of Cu(II) adsorption capability.

The values of k in Fig. 5 refer to the slopes of each line segment. Comparison of k_1 and k_2, as well as k_1' and k_2' show that the amount of increase of CEC within the pH range from 3.3 to 5.0 was larger than that in the pH range from 5.0 to 6.8. This result indicates that when the process of Cu(II) adsorption on biochar takes place at relatively low pH (3.3–5.0), the functional groups that dissociate easily such as carboxyl play a major role. On the contrary, when adsorption takes place at relatively high pH (5.0–6.8), the hard to dissociate functional groups play a major role.

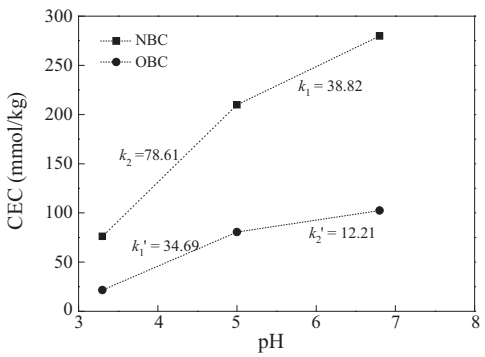

Fig. 5 – Cation exchange capacity of the NBC (new biochar) and OBC (old biochar) at different pH. The values of *k* are slopes of each line segment.

Furthermore, it could be found that k_1 was larger than k_1', and k_2 was larger than k_2', which means the slopes of NBC were larger than slopes of OBC, indicating that the aging process can make it more difficult for functional groups on the biochar surface to dissociate, thus the Cu(II) adsorption capacity was inhibited by biochar aging.

All in all, the surface functional groups of biochar were more easily dissociated at low pH than at high pH, which was more pronounced for the old biochar. This is one of the main factors in Cu(II) adsorption inhibition on biochar by the aging process.

EDX analyses (Fig. 3) showed that oxygen atoms on the surface of old biochar were increased after aging, indicating that oxygen-containing functional groups were increased. However, the CEC of old biochar was decreased after aging because oxygen-containing functional groups that were difficult to dissociate under acidic conditions were formed during the aging. Combined with the results of DRIFTS spectra (Fig. 4b), EDX shows that new biochar contained relatively more carboxyl groups and less phenolic hydroxyl groups. On the contrary, the old biochar contained less carboxyl groups, more phenolic hydroxyl groups and many newly formed ether bonds. Carboxyl groups and phenolic hydroxyl groups were potential Cu(II) adsorption sites and the combination modes between these groups and the biochar determined the dissociation degrees of the groups. Only the dissociated groups can provide Cu(II) adsorption sites.

Combining the results in this paper, we believe that when biochar was incubated at constant temperature and water holding capacity in the dark, both the number and dissociation characteristics of surface functional groups were changed. The Cu(II) adsorption capability of the biochar was mainly realized through the dissociated carboxyl groups and phenolic hydroxyl groups. Carboxyl groups of the old biochar were more easily dissociated and phenolic hydroxyl groups were difficult. Within the pH range from 3.3 to 5.0, carboxyl groups played the major role in Cu(II) adsorption and the increase in q_m of old biochar was larger. Within the pH range from 5.0 to 6.8, phenolic hydroxyl groups played the major role in Cu(II) adsorption and the increase in q_m of old biochar was smaller. Meanwhile, although a large number of phenolic hydroxyl groups and aromatic ethers were formed on the surface of the biochar after the aging process, the number of carboxyl groups was decreased, making the CEC smaller and inhibiting the Cu(II) adsorption on biochar over a range of pH.

3. Conclusions

Based on experimental results, the following conclusions can be drawn.

(1) When biochar was incubated at constant temperature and water holding capacity in the dark, oxygen atoms on the surface were increased. Although carboxyl groups were decreased slightly, phenolic hydroxyl groups and aromatic ether groups were increased. Altogether,

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oxygen-containing functional groups on the surface were increased.

(2) The Cu(II) adsorption capability of the biochar was mainly realized through the dissociated carboxyl groups and phenolic hydroxyl groups. Over a range of pH, the CEC and Cu(II) adsorption capability of old biochar were smaller than those of new biochar. That means the aging process can inhibit Cu(II) adsorption on biochar. One reason is the decrease of specific surface area, and another is changes in the number and dissociation characteristics of surface functional groups on the biochar surface.

(3) Within a relatively low pH range (3.3–5.0), the functional groups that are more easily dissociated such as carboxyl played a major role in Cu(II) adsorption on biochar. On the contrary, within a relatively high pH range (5.0–6.8), functional groups that are more difficult to dissociate played a major role. Furthermore, the aging process could make it more difficult for functional groups on the biochar surface to dissociate. In conclusion, the surface functional groups of biochar were more easily dissociated at low pH than at high pH, and this effect was more pronounced on old biochar, and these were the main mechanisms of Cu(II) adsorption inhibition on biochar by the aging process.

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