Surface Characterization of Aged Biochar Incubated in Different Types of Soil

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The aim of this study was to investigate the changes that occur in the molecular form and surface morphology of aged biochar and to explore the dynamics of aging in various types of soil. For this purpose, the biochar was rice hull heated to 500 °C for 30 min. Approximately 15% of fresh biochar was incubated in either acidic red soil, weak alkaline sandy soil, or alkaline coastal solonchak for 1 and 13 months. Aged biochars incubated without soil were also prepared. The characteristics of fresh biochar and aged biochar were analyzed in terms of elemental composition, specific surface area, and pore size, together with scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The results for aged biochar relative to fresh biochar included: (1) decreased carbon and nitrogen contents; (2) reduced pH values which tended to be neutral; (3) reduced porosity and specific surface area (Brunauer-Emmett-Teller, BET), depending on incubation environment; and (4) increased oxygen-containing functional groups on the surface. In general, the surface characteristics of the aged biochar were changed and varied with soil type.

Keywords: Biochar; Aging; Structure; Surface character; Soil types

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INTRODUCTION

Biochar is referred to as plant-derived biomass produced through pyrolysis at low temperatures (< 700 °C) under limited oxygen conditions (Joseph *et al.* 2010; Freddo *et al.* 2012). Some agricultural and forestry by-products can be used to produce biochar. Biochar has attracted widespread interest globally because of its applications as soil amendment, pollution treatment, carbon sequestration, *etc.* (Lehmann *et al.* 2006; Woolf *et al.* 2010; Beesley and Marmiroli 2011; Zhang *et al.* 2013; Muter *et al.* 2014). These applications of biochar can be attributed, in part, to its developed pore structure, large specific surface area, abundant surface functional groups, and stable carbon skeleton (Lehmann and Joseph 2009; Guo *et al.* 2014; Ścisłowska *et al.* 2015).

Nevertheless, biochar's high stability does not mean that it remains unchanged. Biochar's physical-chemical properties, soil types, tillage management, soil meso- and microorganisms have an influence on biochar stability (Ameloot *et al.* 2013; Rechberger *et al.* 2017). Once biochar is exposed to the environment, the number of surface acidic functional groups and oxygen-containing functional groups can increase, and the pH value and carbon content have been reported to decrease (Cheng *et al.* 2006, 2008, 2009). Moreover, the responses of aged biochar under various environments were also reported. High temperature (Puri 1961; Cheng *et al.* 2006) and moisture (Billinge and Evans 1984) can accelerate the oxidation of biochar. Incubation at 30 °C only enhances the oxidation reaction on biochar surfaces, while the oxidation process extends into the interior of biochar during incubation at 70 °C (Cheng *et al*. 2006). Cheng *et al.* (2008) explained the characteristics of eleven historical charcoals in different furnace sites. It is of practical importance to study the difference between aged biochar under various climatic and soil regimes. Besides, there has been little research on the effect of soil pH on the process and the mechanism of biochar aging, and the differences between aged biochars in soil or in the air are also unclear. Thus, the objectives of this study are: (1) to investigate the characteristics of aged biochar incubated in different types of soil, and (2) to study the dynamics of the biochar aging with or without soil.

EXPERIMENTAL

Materials

The biochar (OBC) was produced by pyrolyzing the rice hull at 500 °C and 30 min under oxygen-limited conditions. Three types of surface soils (0 cm to 20 cm) were collected from red soil (23°6′ E, 114°25′ N) in the district of Huizhou, Guangdong (China), sandy soil (121°53′ E, 42°42′ N) in Zhangwu, Liaoning (China), and coastal solonchak (122°03′ E, 41°22′ N) in Panjin, Liaoning (China). The determination of soil texture was referred by USDA. The characteristics of these three soils are provided in Table 1. The soils were air-dried at average room temperature and passed through a 2-mm sieve. For each soil type, 30 g of biochar was mixed with or without 200 g air-dried soil in a column that was made of polyvinyl chloride (PVC) measuring 22-cm in height and 4-cm in diameter. 200 mL of double-distilled water was introduced through the top of each column, and the columns were incubated at a constant room temperature (32 °C) and 80% relative humidity for the desired duration of the study. To simulate long-term aging, the column was leached every 15 days, for a total of 27 leaching times. The samples were collected at 1 and 13 months of incubation periods. After the biochar-soil mixtures were air-dried, the extraction of aged biochar was achieved using static electricity generated from nylon mesh.

Table 1. Characteristics of Soils and OBC

Parameter	Red Soil	Sandy Soil	Coastal Solonchak	OBC
C (%)	1.0	0.5	1.1	48.54
N (%)	0.1	0.1	0.1	0.68
pH	4.7	7.6	8.8	9.30
Organic Matter (%)	1.7	1.9	1.8	ND
Sand (%)	60.39	80.07	31.08	ND
Silt (%)	23.30	18.81	40.56	ND
Clay (%)	16.31	1.12	28.36	ND
*Note: All data are means (n=3); "ND" represents not determined.				

Methods

Elemental C, N, and O contents were analyzed using an elemental analyzer (Vario MACRO cube, Elementar, Hanau, Germany), and the H content was calculated *via* the difference method. The ash content was determined by weight loss after combustion at 750 °C for 6 h with no cover in a muffle furnace (Zhongxing Laboratory Equipment Inc., Beijing, China) and the ash (in percentage) was calculated from: Ash (%) = (weight of ash) / (weight of biochar) × 100. The volatile matter content was determined at 950 °C for 11 min in a muffle furnace and the volatile matter content (in percentage) was calculated from:

volatile matter (%) = (weight of biochar - weight of residue) / (weight of biochar) × 100 (ASTM International, 2007). The pH values of all samples were measured at a ratio of 1:25 (w/v) in water after being shaken for 30 min at 130 rpm with a calibration check pH meter (HI2221, Hanna Instruments, Romania). The BET specific surface area and porosity were determined using specific surface area and pore size analyzers (3H-2000PS2, Beijing, China), and the surface functional groups of the biochar samples were determined by a Fourier transform infrared spectrometer (FTIR) (Nicolet 380, Thermo Fisher Scientific, Waltham, USA). FTIR spectroscopy was performed using the potassium bromide (KBr) pellet method. All analyses were run in triplicate.

Statistical analysis

A statistical analysis was performed using SPSS 16.0 (SPSS Inc., Chicago, IL, USA) and Graph Pad Prism 5 software (Graph-Pad Software, San Diego, CA, USA). The data were recorded for each parameter in triplicates, and the mean and standard deviations (mean ± SD) were calculated. The T-test was conducted to compare the treatment effects. The least significant difference (LSD) test, with significance at 0.05 level probability, was applied to assess the differences between the mean values.

RESULTS AND DISCUSSION

Physicochemical Analysis

The OBC used in this study contained high amounts of carbon (48.54%) and nitrogen (0.68%), while all of the aged biochar samples showed a higher reduction in those elemental compositions.

Table 2. Physicochemical Characteristics and Elemental Composition of Biochar Samples

Sample	Atomic Ratio			Ash (%)	Volatile Matter (%)
	H/C	O/C	(O+N)/C		
OBC	0.45±0.07d	0.20±0.04d	0.08±0.01d	36.48±1.40c	32.33±1.96ab
BC1	0.26±0.03d	0.23±0.02d	0.09±0.01d	34.69±0.62c	30.88±1.96ab
BC13	1.05±0.05cd	0.26±0.07d	0.10±0.03d	33.60±1.40c	37.19±12.83ab
R1	0.28±0.00d	0.32±0.05c	0.13±0.02c	50.25±3.89b	18.18±2.03c
R13	1.09±0.22cd	0.41±0.03b	0.16±0.01b	46.76±1.61b	33.18±1.92a
S1	1.60±0.02cd	0.24±0.05d	0.10±0.02d	47.09±4.06b	27.19±2.42b
S13	8.03±2.12a	0.52±0.00a	0.20±0.00a	67.96±8.80a	27.94±3.9ab
C1	2.08±0.38c	0.36±0.05bc	0.14±0.02bc	61.48±3.60a	27.26±6.16b
C13	4.34±0.24b	0.51±0.05a	0.20±0.02a	64.51±3.26a	30.26±1.64ab

*Note: BC represents aged biochar incubated without soil; R, S, and C represent red soil, aeolian sandy soil, and coastal solonchak, respectively; 1,and 13 in the sample column represent months of incubation; a, b, c, and d represent significant differences (P < 0.05) between different biochars, respectively

The elemental composition of aged biochar varied clearly with incubation environment (Fig. 1A, B, C). C and N contents of aged biochar incubated without soil were significantly higher than aged biochar incubated in three types of soil in two incubation times ($P < 0.05$). The results implied that biological and abiotic factors of soil contributed to the aging of biochar. Incubation time had no effect on BC, R, and C for C and N contents, and the contents of S1 were significantly greater than S13. This might have been due to the good permeability of sandy soil, leading to more C and N being leached or the good ventilation conditions speeding up the mineralization of organic carbon and nitrogen in sandy soil, thus resulting in further leaching. The C and N contents of BC were higher than R, and R higher than S and C. It has been suggested that carbon loss is dominantly driven by microbial colonization and utilization of the biochars or the mineralization of soluble organic carbon (Nguyen *et al.* 2010; Bird *et al.* 2015). The results were consistent with previous studies (Yao *et al.* 2010; Hale *et al.* 2011). While a significant decrease in carbon was found after one year of moist aging of oak biochars at temperatures ranging from -22 °C to 70 °C (Cheng and Lehmann 2009), carbon content of aged biochar was reduced in freeze-thaw cycles (Miao *et al.* 2016). Thus, in the present study, the effect was mainly due to moderate incubation environment leading to a low aging degree. With the aging of OBC, an increase in O content was observed; R13 was significantly higher than R1 ($P < 0.01$) and C13 was significantly higher than C1 ($P < 0.05$) (Fig. 1C), the result was consistent with previous research that the chemisorption of oxygen onto biochar surfaces through the formation of surface functional groups or the formation of hydroxyl and ether bonds not only offset the losses oxygen atoms caused by decarboxylation, but they even can lead to an overall increase oxygen content in surface during the process of decarboxylation and hydroxylation in aged biochar surface (Puri 1970; Cheng *et al.* 2006; Guo *et al*. 2014). The O contents of R were significantly higher than S and C; the result revealed that O contents of aging biochar could be increased by increasing soil acidity.

Marked declines in pH were observed for all aged biochars and were more pronounced for aged biochar incubated in soils than BC (Fig. 1D). Decreases in pH of aged biochar has been observed previously (Cheng and Lehmann, 2009), and it was due to dissolution of basic species (Yao *et al*. 2010). Mukherjee *et al.* (2014) suggested that the pH decrease can be attributed to enhanced surface acidity generated through extensive oxidation. The surface acidity may be produced by a strong oxidation reaction that its increase promotes abiotic chemisorption for water and oxygen on the surface of biochar. Furthermore, the pH of R was lower than S and C during the same incubation time, the results revealed that acid soil had a stronger effect on the reduction of aged biochar pH. S1 and C1 were significantly higher than S13 and C13 for pH ($P < 0.01$, $P < 0.05$), which showed that incubation time promotes further reduction of aged biochar pH (Rechberger *et al.* 2017).

Moreover, the atomic ratios of H/C, O/C, and (O+N)/C were calculated to estimate the aromaticity, oxidation, and polarity of the aged biochars. In general, the processes of aging resulted in an increase of H/C, O/C, and (O+N)/C ratios, which was attributed mainly to the labile carbon leaching for aged biochar during the oxidation (Table 2 and Fig. 1A). The higher H/C in 13 months aged biochar compared to OBC might be due to the following three possible reasons: (i) decrease of total C due to leaching, (ii) the inclusion of aliphatic organic C due to sorption, (iii) introduction of H and/or O during aging with surface functional groups leading to a relative decrease in total C (Mia *et al.* 2017). The rise in the O/C from one month aged biochar to 13 months aged biochar is reflective of the increase of their surface hydrophilicity, which consequently enhances their affinity for water molecules (Fang *et al.* 2014). The (O+N)/C ratios of aged biochar incubated in 13 months were higher than that of biochar incubated for 1 month, which suggested that the polar functional group contents had increased on the surface of aged biochars. Cheng *et al.* (2008) also reported similar results. These results indicated that the aged biochars would have strong bonding affinity to weak hydrated anion (Fang *et al.* 2014). In general, these three ratios of R, S, and C were significantly higher than for BC ($P < 0.05$), which indicated that the aging intensity of soil was higher than that without soil.

Ash contents of R, S, and C were significantly higher than OBC because of the surface of aged biochars being attached to some soil particles (Fig. 2). In contrast, the ash contents of the air oxidized biochars decreased, which was attributed to the leaching of the parts of ash during the incubation. Volatile matter contents of most aged biochars showed no significant differences ($P > 0.05$) with the OBC. The results implied that soil types and incubation time had no significant influence on ash contents and volatile matters of aged biochar.

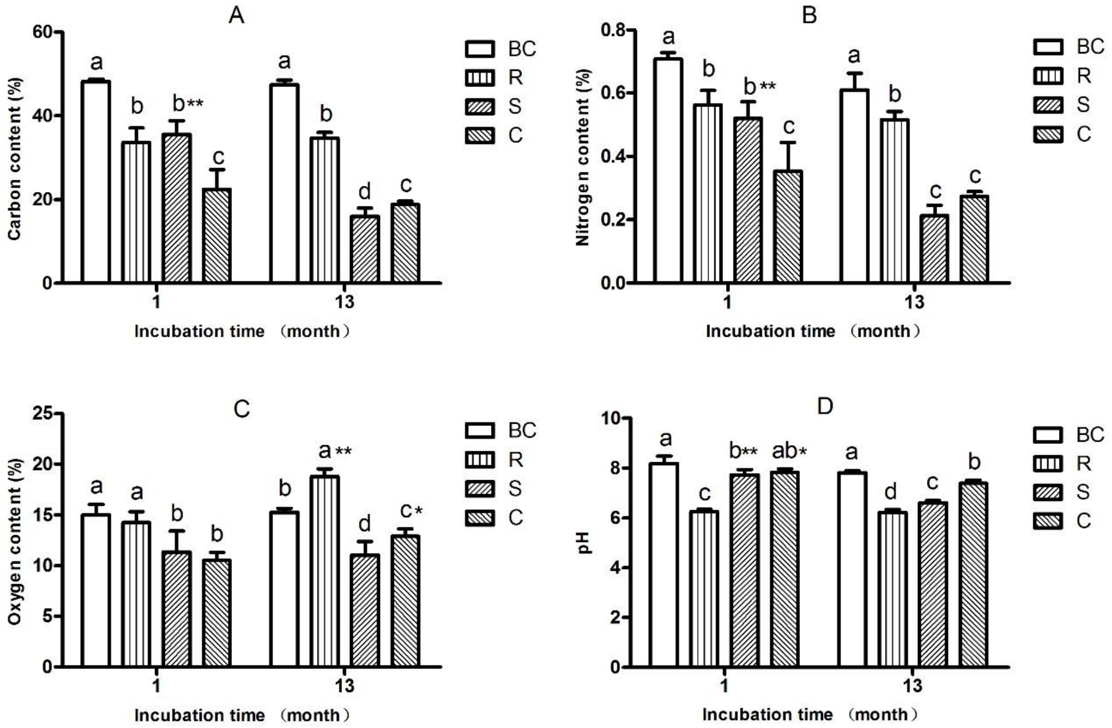

Fig. 1. Elemental composition and pH of aged biochar. A, B, C, and D represent carbon contents, nitrogen contents, oxygen contents, and pH of different biochars; a, b, c, and d represent significant difference between treatments in equal incubation times ($p < 0.05$); * and ** indicate the significant difference between treatments in same incubation environment (level of significance: $p < 0.05$ and $p < 0.01$) and the data represent averages of three replicates and error bars are standard deviation, respectively.

Surface Characteristics and Porosity

In the SEM images, the surfaces of OBC and aged biochars incubated in air were relatively clean and they had no substantial changes in appearance with prolonged incubation time. The unaged biochars exhibited a cellulosic structure (Fig. 2). In contrast, all aged biochars incubated in soil were no longer smooth and were coated with many soil particles. Moreover, there were more soil particles that covered the surface of the aged biochars incubated in coastal solonchak, which might be due to the texture of the soil with a different viscosity. Then, the soil particles attached to the surface of the aged biochar incubated in soils blocked some of the biochar pores, as indicated by the biochar BET specific surface area, total pore volume, and average pore diameter (Fig. 3). These results were consistent with the previous study by Mukherjee *et al.* (2014). Aged biochar that was incubated in the soils for 13 months were generally lower than that of one month old samples for the above three indexes. Biochar undergoes a series of physical changes after its application in soil, including infilling by minerals, soil organic matter, microorganisms, and physical breakage. All of these changes can lead to the change of biochar porosity (Mia *et al.* 2017). Cracks and fractures (physical disintegration) are induced by biochar surfaces being exposed to water and soil, which increased pore connectivity. Similarly, the particles in suspension carried by flowing water could fill or block biochar pores (Joseph *et al.* 2010). Previous studies have shown that soil particles fill the biochar pores (Spokas 2013; Spokas *et al.* 2014). The images in Fig. 2 support the idea that soil minerals change the physical properties of biochar, and microorganisms influence the physical properties of biochar.

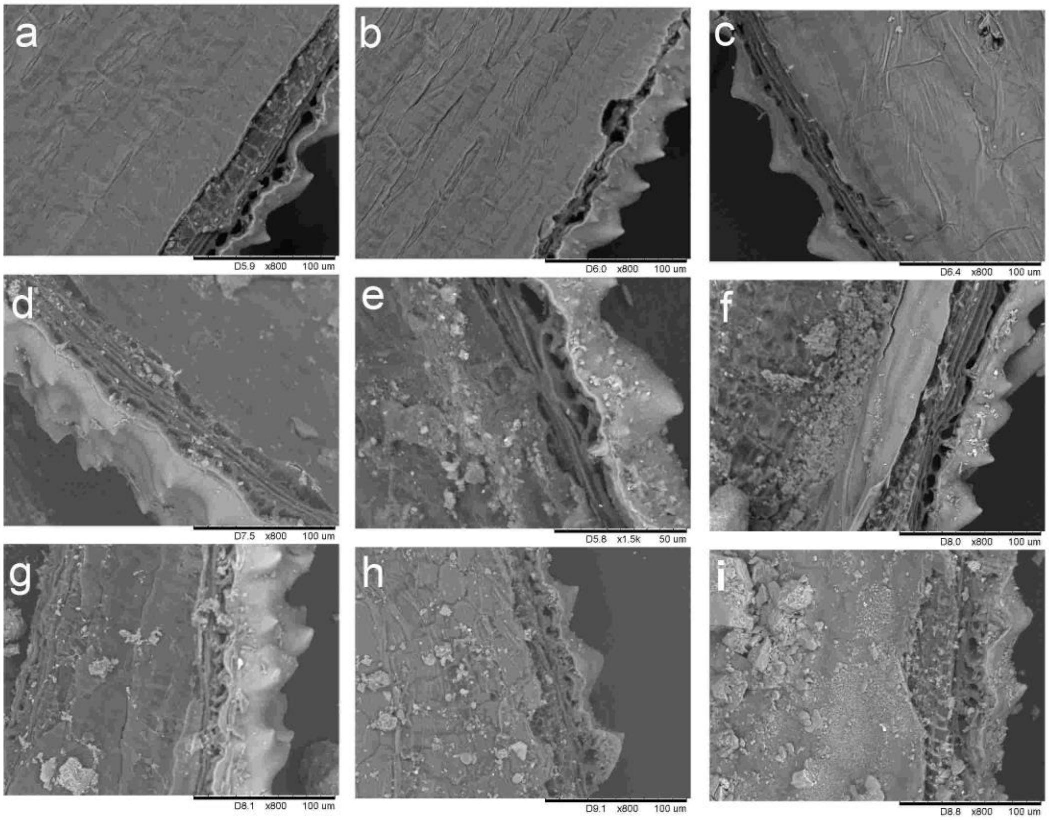

Fig. 2. SEM images of biochar samples; a) original biochar; b) aged biochar incubated without soil for one month; c) aged biochar incubated without soil for 13 months; d) aged biochar incubated in red soil for one month; e) aged biochar incubated in red soil for 13 months; f) aged biochar incubated in aeolian sandy soil for one month; g) aged biochar incubated in aeolian sandy soil for 13 months; h) aged biochar incubated in coastal solonchak for one month; and i) aged biochar incubated incoastal solonchak for 13 months

The BET specific surface area and porosity of BC increased, which was mainly caused by the leaching of ash and mineral phases during incubation. Studies have shown that the micro- and nanostructures of biochar are important for determining biochar stability and the composition of biochar surfaces (Qureshi *et al.* 2003; Nguyen *et al.* 2008). Thus, the porosities of aged biochar were reduced with prolonged incubation time, which certainly affected the adsorption capacity of aged biochars. Many previous studies have concluded that biochar not only has the ability to adsorb organic pollutants, but also has the ability to improve the physical and chemical properties of soil. For instance, the capacity of soil to hold water and nutrients is due to the high surface area and porosity of biochar (Glaser *et al.* 2002; Cohen-Ofri *et al.* 2006). Thus, the adsorption capacity of BC might be better than that of aged biochar in soil.

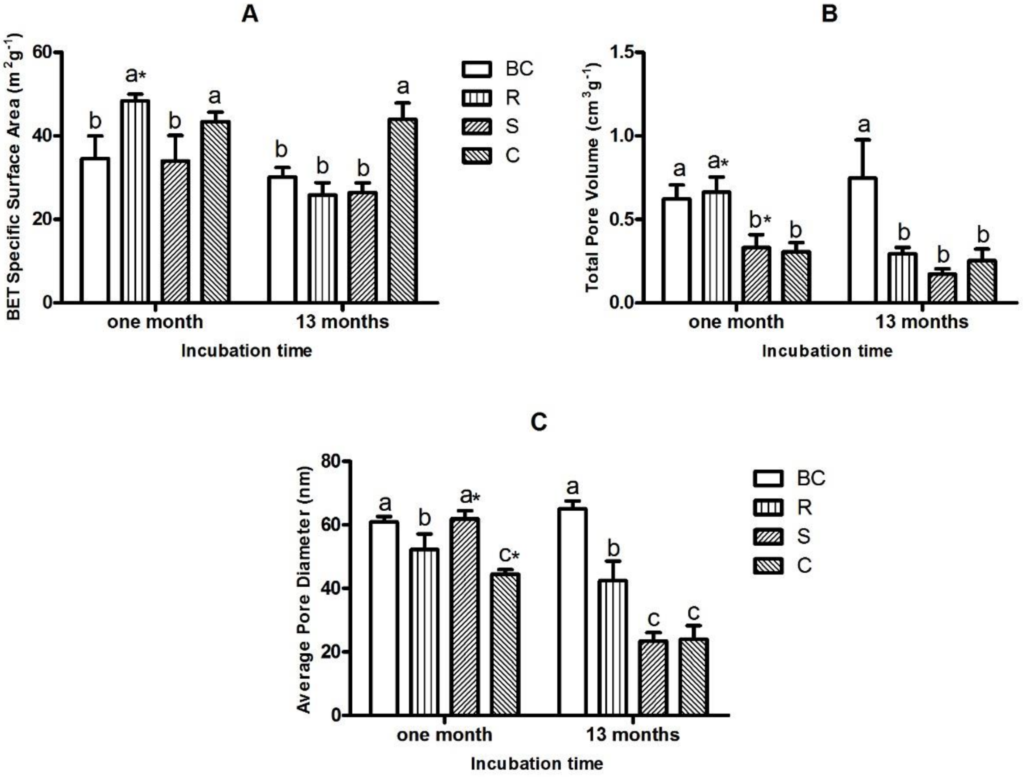

Fig. 3. Surface characteristics and porosities of biochar samples; A: BET specific surface area; B: total pore volume; and C: average pore diameter; a, b, c, and d represent significant difference between treatments in equal incubation times ($p < 0.05$);
* indicates a significant difference between treatments in same incubation environment (level of significance: $p < 0.05$ and $p < 0.01$) and the data represent averages of three replicates and error bars are standard deviation, respectively

FTIR Spectroscopy

To understand the involvement of the functional groups on the biochar surface, original biochar and biochar specimens after aging in three types of soil under the condition of leaching were examined by FTIR spectroscopy (Fig. 4). The adsorption bands and peaks provided the evidence for the presence of some surface functional groups. The wave numbers of the major bands for all aged biochars were 3440 cm^{-1}, 1637 cm^{-1}, 1388 cm^{-1}, 1100 cm^{-1}, and 1038 cm^{-1}. The band at 3440 cm^{-1} was assigned to the −OH bond, 1637 cm^{-1} to aromatic C=C and C=O bonds, 1388 cm^{-1} to the -C-N, 1107 cm^{-1} and 1038 cm^{-1}

to the C-O (Vergnoux *et al.* 2011; Zhang *et al.* 2015; Yavari *et al.* 2016). In fact, the distribution of bands for various groups of aged biochar could not be well distinguished, even though the aged biochars were incubated in different types of soil, and little differences between diverse incubation times were noticed. Compared with OBC, the stretching vibration of C-O at 1107 cm^{-1} began to appear in R, S, and C, while it was not observed in BC, which suggested that the interaction of soil promoted the formation of C-O, regardless of soil type, and incubation time. These results indicated that the oxygen content increase was not merely due to the sorption of oxygen to the aged biochar surfaces, but due to the formation of oxygen-containing functional groups during the aging process (Puri 1970; Boehm 1994; Cheng *et al.* 2008). It was shown that the presence of oxidized functional groups on the surface of biochar improve soil fertility by increasing cation exchange capacity (Liang *et al*. 2006; Liu *et al.* 2013). The functional groups on the surface of biochar did not change significantly. Therefore, the ability of biochar to retain soil nutrients, to decrease migration of heavy metals, and to adsorb organic pollutants was retained. Furthermore, the similar functional groups observed on aged biochar may have been the direct reason for similar pH values. Hardy *et al.* (2017) suggested that carboxylic acids, as well as phenolic acids of aged biochar decreased gradually with cultivation time. It implied that the decreased functional groups might lead to aged biochar pH increase. Besides, the similarity of surface functional groups of R, S, and C can be regarded as the main reason that their pH values were approximately the same.

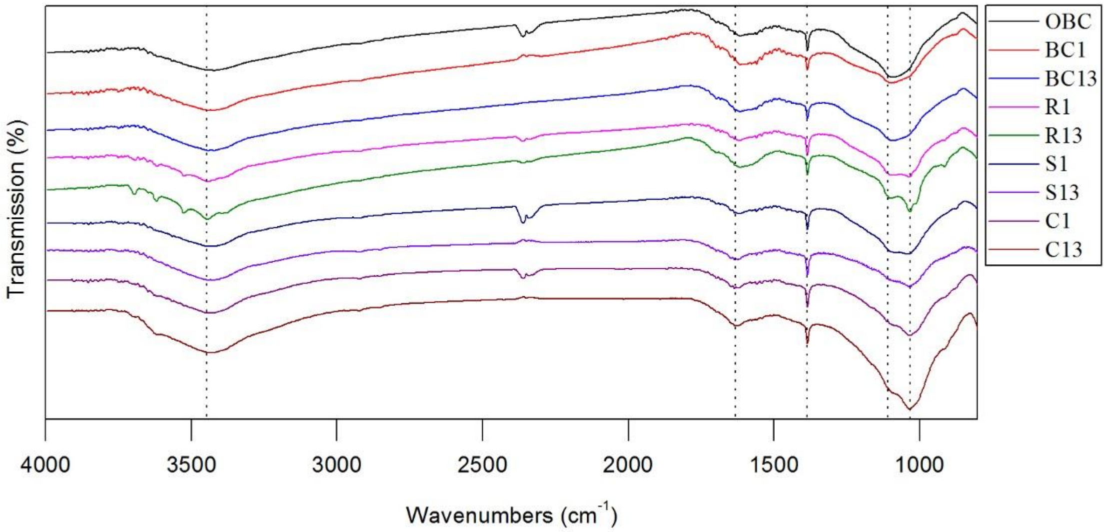

Fig. 4. FTIR spectra of OBC and aged biochars incubated in red soil

CONCLUSIONS

1. The aged biochars, whether incubated with soil or not, showed decreases of carbon and nitrogen contents, while they showed increases of oxygen contents, H/C, O/C, and (O+N)/C. The contents of carbon, nitrogen, and oxygen in R were generally higher than that of S and C. The ash contents of biochar incubated without soil were decreased, while the ash contents of aged biochar incubated in soil were increased.

2. Soil pH and incubation time affected pH of aged biochar, and lower soil pH and longer incubation time increased the acidity of aged biochar. The low pH of biochar incubated without soil was mainly due to the reduction of the ash content, while the low pH of aged biochar incubated in soils depended on the ash content and surface functional groups.
3. The BET specific surface area, total volume, and average pore diameter of aged biochar were varied with increases in incubation time. Aging promoted the formation of oxygen-containing functional groups, and the acceleration of C was stronger than R and S. The adsorption properties of aged biochar must be changed compared with OBC; thus, the effects of aged biochar on adsorption and desorption of soil nutrient or pollutants need further research.

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