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DOI: 10.2478/ahr-2022-0015
Acta hort regiotec, 25, 2022(2): 115–120

Research Article

Content of adsorbed film water and density of oxygen-containing functional groups on surface of ageing biochar in sandy spodosol

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Article Details: Received: 2022-05-06 | Accepted: 2022-10-13 | Available online: 2022-11-30

Application of different types of feedstocks and conditions of their pyrolysis can result in different properties and sustainability of biochar during changes (aging) of its properties in soils. The aim of the studies was to assess the consequences of aging of biochar in soil for a content of adsorbed film water and a density of oxygen-containing functional groups on its surface. Sampling of soil and biochar was conducted in May and July of 2021 in a plot experiment with an applied rate of biochar of 20 $t.ha^{-1}$ in 2016. WP4-T dew point potentiometer was used for measurements of relationships of potentials of adsorbed film water and its content in soil and biochar. Infrared Fourier FSM 2201/2202 spectrometer was applied for determination of densities of oxygen-containing functional groups on surface of biochar in a mid-infrared spectrum. Results showed that retention capacity of adsorbed film water by soil increased from May to July, possibly because of increasing content of hydrophilic organic compounds of plant origin. Aging of biochar in soil also resulted in an increase of retention capacity of adsorbed film water on its surface. The results of infrared Fourier spectroscopy confirmed that densities of oxygen-containing functional groups on the surface of biochar increased from May to July at spectra of wavenumbers of 1,600–1,400 cm^{-1} and 1,400–1,100 cm^{-1}.

Keywords: soil, biochar, aging, film water, oxygen-containing functional groups

1 Introduction

Application of biochar in agriculture is one of useful ways of sequestration of atmospheric carbon into soils and further accumulation in soils (Kamali et al., 2022; Lehmann et al., 2011; Verheijen, Montanarella & Bastos, 2012).

Biochar is a product of fast or slow pyrolysis of different feedstocks (wood, plant residues etc.) under a lack of oxygen and at high temperatures of 300–900 °C (Das, Ghosh & Avasthe, 2021; Lehmann et al., 2011). Biochar consists of a high amount (>80%) of aromatic organic matter which is resistant to effects of biotic and abiotic factors in soils (Keiluweit et al., 2010). However, this stable nature of biochar does not mean that its structure, composition, and surface properties do not change during an aging of biochar in soils. Different technological conditions (temperatures, oxygen concentrations) of pyrolysis and types of feedstock result in different biochar properties which can induce a lower and higher intensity of changes in biochar stability in soils (Banik et al., 2018; Guo et al., 2021; Kloss et al., 2012).

Incorporation of biochar into soils leads to favorable and unfavorable changes in soil properties. Application of biochar in arable soils contributes to an increase in their water holding capacity (Basso et al., 2013; Haider et al., 2017; Mukherjee & Lal, R., 2013), water-stable aggregation (Islam et al., 2021), soil porosity (Baiamonte et al., 2019), organic carbon accumulation (El-Naggar et al., 2019), pH (Horák, 2015), cation exchange capacity (Laghari et al., 2015), crop productivity (Kuppusamy et al., 2016) and to a decrease in N_2O emission (Balashov et al., 2021; Hangs, Ahmed & Schoenau, 2015; Horák et al., 2021) and CO_2 emission from soils (Kotuš & Horák, 2021). However, the incorporation of biochar into soils can lead to an unfavorable immobilization of nitrogen (Yao et al., 2010), nutrients (Kookana et al., 2011), no changes in N_2O emissions (Clough et al., 2010), no improvement of crop productivity and nitrogen efficiency (Güereña et al.,

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2013), decreasing microbial biomass content (Dempster et al., 2012).

Biochar is a habitat of soil microorganisms and participates in hydrophysical, biochemical and physicochemical interactions in soils. These interactions lead to an oxidation of surface of biochar and to its so-called aging (de la Rosa et al., 2018). Aging of biochar demonstrates more or less pronounced changes in the activity of its surface. The intensity of aging of biochar depends on technological conditions of pyrolysis of different feedstocks.

The quantification of direction and intensity of changes in the surface properties of different biochars while aging in soils is an important objective of current research. An oxidation of biochar in soils results in an increase of density of oxygen-containing functional groups (OFGs) on its surface (Singh et al., 2014). A higher density of polar OFGs (carboxyl, carbonyl, phenolic, hydroxyl) on the biochar surface leads to its higher adsorption of water molecules, nutrients and labile organic substances (Liu et al., 2017; Pastor-Villegas et al., 2010; Singh et al., 2014). Interaction of water with carboxyl groups is two orders of magnitude stronger than that of water with carbonyl or hydroxyl groups (Nguyen et al., 2014).

Current hydro-physical studies of biochar are usually focused on measurements of their water retention curves and available water contents at high matric potentials (>-15 MPa) using pressure plate chambers (Marshall et al., 2019; Nelissen et al., 2015). Less attention was focused on the assessment of water vapor adsorption-desorption characteristics of biochar surface while aging in soils. More information on these processes is necessary for better understanding of changes in an affinity of surface of aged biochar to its interactions with soil mineral and organic phases.

The objective of this study was to assess the differences in water vapor desorption characteristics and density of OFGs on surface of non-aged (control) and aging biochar in sandy Spodosol.

2 Material and methods

The study was conducted at the experimental station of the Agrophysical Research Institute in the St. Petersburg region of Russia (59° 34′ N, 30° 08′ E) in 2021. The studied soil was a sandy Spodosol and contained 91.7 $g.kg^{-1}$ of sand, 5.2% $g.kg^{-1}$ of silt, and 3.1 $g.kg^{-1}$ of clay particles. In 2016, a small-scale field experiment was established on 3 plots (16 m^2) without biochar and on 3 plots (16 m^2) amended with a rate of biochar of 20 $t.ha^{-1}$. A slow pyrolysis biochar was produced from small birch logs and branches in a controlled kiln at temperature of the pyrolysis of 600 °C. The produced biochar (control biochar) was oxidated in air conditions during one year. Afterwards, the biochar was mixed with topsoil layers (0–10 cm) at the beginning of the experiment. The particle size of the incorporated biochar was >5 mm. Chemical and physical properties of the control biochar were: total carbon content – 825.5 $g.C.kg^{-1}$, total N content – 5.7 $g.N.kg^{-1}$, C : N ratio – 145, pH_{H2O} – 7.0, moisture content –1.92% and ash content – 0.23%. All the soil chemical and physical analyses were conducted by standard and traditional methods used in Russian soil science laboratories (Rastvorova et al., 1995).

In May and July of 2021, bulk soil samples and biochar particles were collected from a depth of 0–10 cm on the experimental plot with the only biochar treatment. Air-dried soil samples were sieved through sieves of 2–3 mm to receive corresponding soil fractions. Soil samples were also removed carefully from a surface of biochar particles (>1 cm in a diameter) by a soft brush. Particles of control biochar were stored for 5 years in hermetically sealed plastic vessels without access of oxygen at temperature of 4 °C. It was assumed that these storage conditions could not result in any significant changes in the surface and physicochemical properties of the biochar samples. The 2–3 mm size fractions of bulk soil samples and the size fractions (<1 mm) of soil samples from the surface of biochar were used in the studies. The fractions of biochars of >1 cm were crushed and sieved through sieves with diameters of openings of 5 and 2 mm to obtain the size fractions of biochar of 2–5 mm.

Before the beginning of water vapor adsorption-desorption measurements all the plastic vessels were opened and all biochar samples, apart from all the soil samples, were kept at a room temperature and an ambient laboratory atmosphere for one day to achieve an initial equilibrium content of hygroscopic water in the samples.

A dewpoint potentiometer (WP4-T, Decagon Devices, Inc., Pullman, WA, USA) was used to measure water potentials of the biochar and soil samples. Weight of biochar and soil samples was equal to 0.5 g and 3 g, respectively. One cycle of water vapor adsorption-desorption process was carried out for the biochar and soil samples. During the 24-hr adsorption process the biochar and soil samples were saturated by water vapor in plastic vapor-tight vessels (100 cm^3) over distilled water at 95–98% of relative air humidity. The measurements of water potentials and weights of biochar and soil samples were carried out immediately after the end of the adsorption process.

The measurements of equilibrium water potentials and weights of biochar and soil samples were recorded seven times: after 30 s, 1 min, 3 min, 10 min, and three times for 20 min of water vapor desorption at temperature of 23.5 °C. After the end of the cycle of adsorption-desorption process biochar and soil samples were dried at 105 °C and their moisture content was calculated. These data were presented as relationships between water potentials and content of adsorbed film water in soil and biochars.

Infrared Fourier spectrometer FSM 2201/2202 (Infraspek, Russia) was used to quantify a distribution of adsorption bands and peaks provided the evidence for the presence of oxygen-containing functional groups on the surface of biochar. These infrared spectroscopic measurements were carried out at a mid-infrared range of wavenumbers of 4,000–500 cm^{-1}. The wavenumbers of the major adsorption bands for the studied biochars were assigned to carboxylic, phenolic, hydroxylic functional groups.

The results were subjected to an analysis of variance (one-way ANOVA) at $p \leq 0.05$.

3 Results and discussion

As mentioned above, only one cycle of water vapor adsorption-desorption process was carried out for the biochar and soil samples. Initial samples of soil and biochar had different initial contents of hygroscopic water at the beginning of adsorption-desorption process and, therefore, different water retention curves. Therefore, means, standard deviations and significance of differences between water retention curves were not calculated.

Results of studies of water vapor adsorption-desorption on a soil surface showed that its retention capacity of adsorbed film water had insignificantly ($p < 0.26$) increased from May to July (Fig. 1).

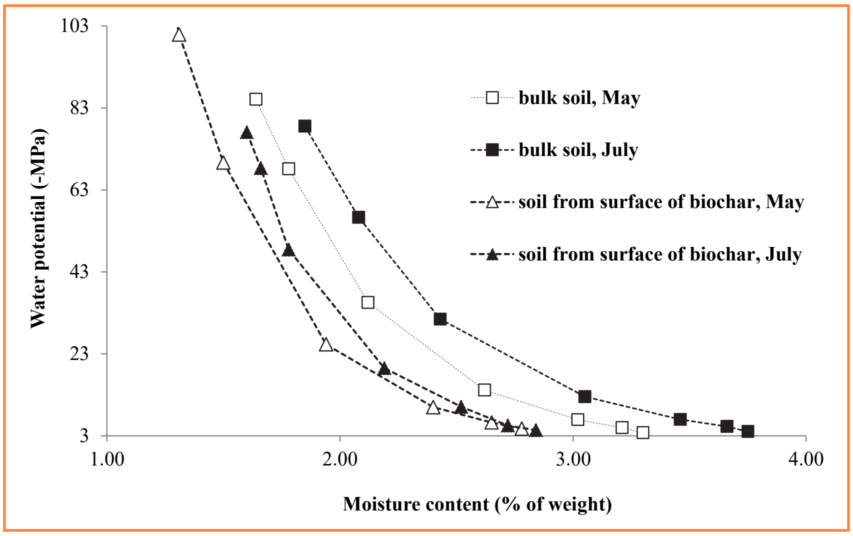

Figure 1 Water retention curves of bulk soil and soil from surface of biochar in May and July

The increase in retention capacity of adsorbed film water by the bulk soil was probably induced by increasing content of hydrophilic organic substances (carbohydrates, fatty acids) of plant origin. The retention capacity of adsorbed film water by the soil from the biochar surface was insignificantly less than that of the bulk soil in May ($p < 0.23$) and in July ($p < 0.06$).

It is possible that the soil from the biochar surface had a lower content of available hydrophilic organic substances which were more subjected to microbial mineralization than the same substances in the bulk soil. Nevertheless, there was still a trend of temporal slight increasing retention capacity of adsorbed film water by the soil from the biochar surface.

Fresh biochar is usually hydrophobic but if its surface was oxidized by air or water molecules this biochar becomes more hydrophilic and accessible

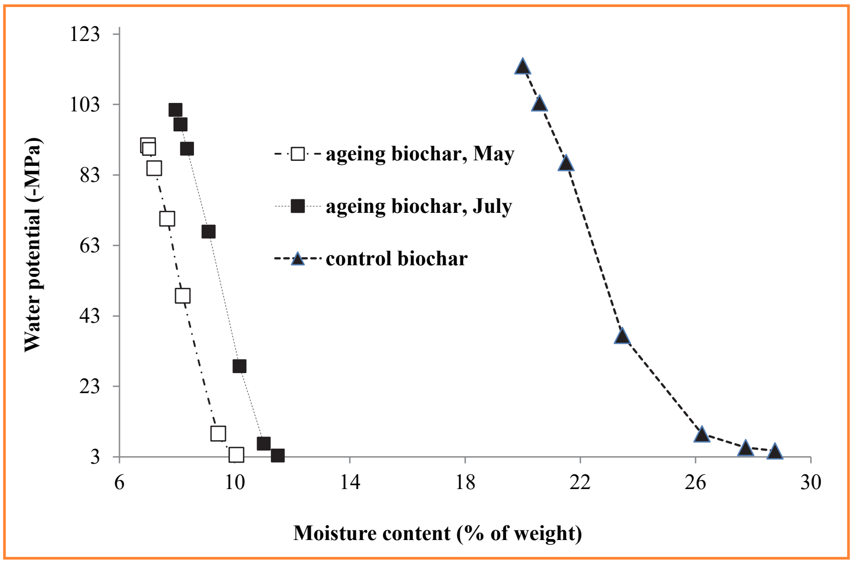

Figure 2 Water retention curves of control biochar and ageing biochar in May and July

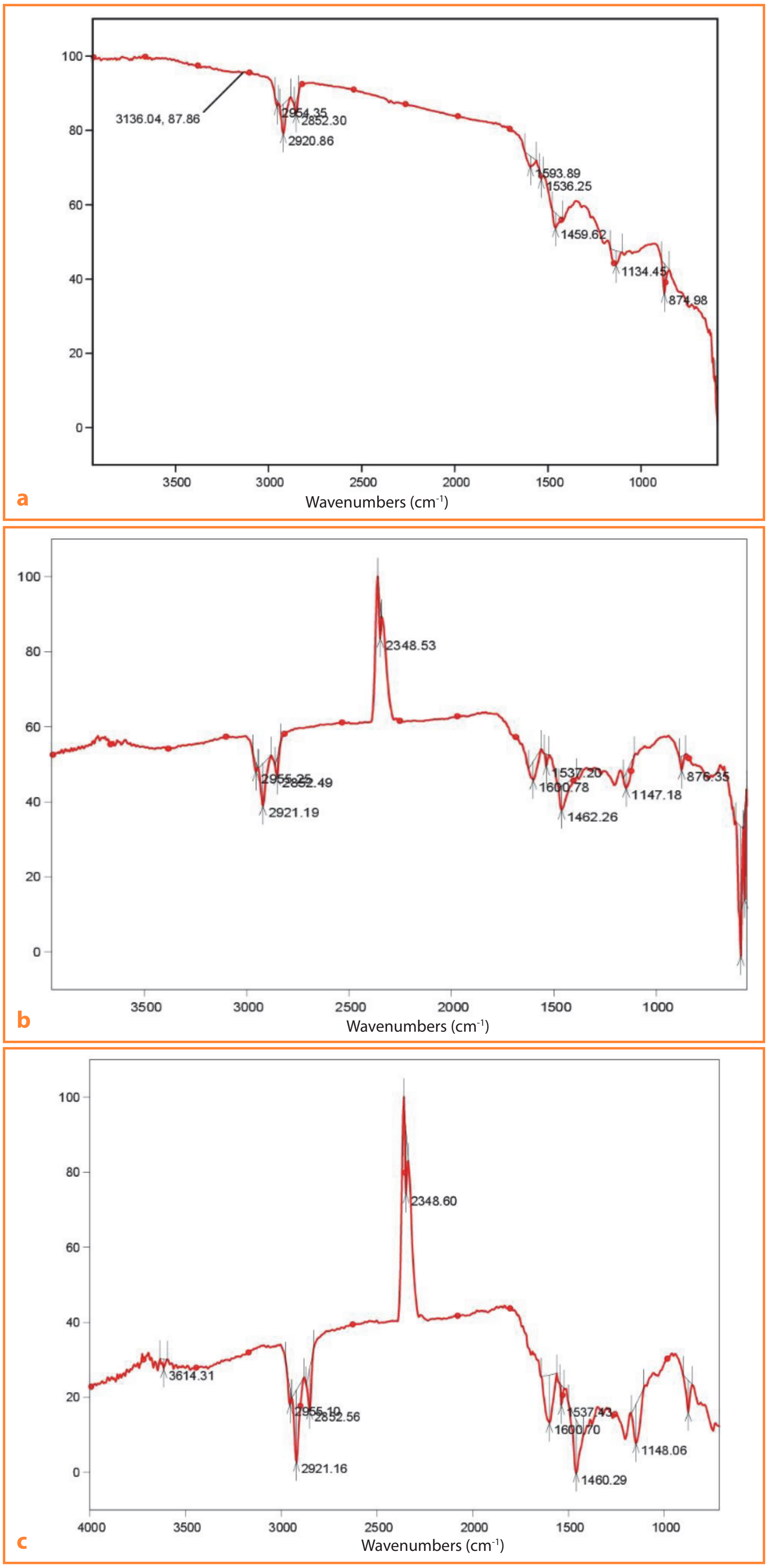

Figure 3 Distribution of areas of adsorption bands of the control biochar (3a), aging biochar in May (3b) and July (3c)

to stronger chemical interactions with soil minerals with subsequent physical occlusion in organo-mineral fractions (Lehmann et al., 2011).

The changes in retention capacity of adsorbed film water by the soil could contribute to a temporal increase in that by aging biochars. First of all, the results of our studies of adsorption – desorption of water vapors on the surfaces of biochars showed that the control biochar had demonstrated a higher retention capacity of adsorbed film water than aging biochar in May and July (Fig. 2).

The surface of the control biochar could be affected by a higher air oxidation and by a subsequent greater hydrophilization than aging biochar in soil with a low aeration. Besides, clay particles could clog meso- and macropores of aging biochar and decrease its retention capacity of adsorbed film water (Ren et al., 2016). The retention capacity of adsorbed film water by control biochar was significantly (p <0.001) higher than that by aging biochar in May and July. The results also showed that the retention capacity of adsorbed film water by aging biochar was only insignificantly (p = 0.08) higher in July than in May (Fig. 2). Thus, aging of biochar in the soil was accompanied by increasing hydrophilization of its surface. These changes in hydrophysical properties of aging biochar could reflect an increase in density of OFGs which participated in the adsorption – desorption of water vapors. Molecules of water are stronger (by two orders) associated with carboxylic functional groups than with other OFGs (Brennan et al., 2001, Liu et al., 2017).

The results of FTIR studies of all the biochars are presented in Figures 3a, b. c. The highest areas of adsorption bands of structural fragments of organic substances with OFGs on surfaces of studied biochars were recorded in spectra of wavenumbers of 1,400–1,100 cm^{-1} and 1,600–1,400 cm^{-1}.

The areas of adsorption bands are considered to reflect densities of OFGs. At the spectra of wavenumbers of 1,400–1,100 cm^{-1} the areas of adsorption bands were equal to 1.44% (control biochar), 0.88% (aging biochar, May) and 2.66% (aging biochar, July). The distribution of areas of adsorption bands (or densities of oxygen-containing functional groups) at the spectra of wavenumbers of 1,600–1,400 cm^{-1} showed a following order: 2.46% (control biochar), 2.83% (aging biochar, May), 7.86% (aging biochar, July).

All the biochars demonstrated a temporal increase in the densities of OFGs on their surfaces. The highest increase in the density of OFGs on the surface of aging biochar in July was probably induced by the highest increase in the content of hydrophilic organic substances: lipide fractions (fatty acids) and carbohydrates of plant origin. Our results showed that the temporal increase in the density of OFGs on the surfaces of aging biochar could contribute to increase in a degree of hydrophilicity of surface of aging biochar and its activity in physicochemical interactions with organo-mineral soil phase.

4 Conclusions

The results of studies showed that the increase in retention capacity of adsorbed film water by soil from May to July was probably induced by a temporal increase in contents of hydrophilic organic compounds (fatty acids and carbohydrates) of plant origin. The temporal increase in retention capacity of adsorbed film water by aging biochars was caused by increasing density of oxygen-containing functional groups (carboxylic, hydroxylic, phenolic) associated with structural fragments of different organic compounds on their surfaces.

Acknowledgements

This study was supported by the Russian Foundation for Basic Research (grant No. 19-016-00038-A).

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