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Characterization, water retention and availability of different types of biochar from animal and plant origin

Caracterização, retenção e disponibilidade de água de diferentes tipos de biocarvão de origem animal e vegetal

Caracterización, retención y disponibilidad de agua de diferentes tipos de biocarbón animal y vegetal

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Abstract
The increase in food production to meet global demand has generated a large volume of organic waste. When reinserted into the production chain, this waste can provide various environmental services, mainly not referring to the quality and quantity of two water resources. The biocarvão presents great potential as a solo corrector, source of nutrients, and conditioner, increasing water retention. This study produced and characterized biochars from six types of biomass (sugar cane bagasse-SBB, dry coconut husks-DCB, green coconut husks-GCB, sludge sludge-SSB, corn cobs-CCB, and orange bagasse- OBB). The main objective was to assess the water retention of biochar. The biochar was produced through slow pyrolysis at a temperature of 550ºC, ground and penetrated to determine porosity, specific surface area, electrical conductivity, pH, cation exchange capacity, morphology structural, immediate and elemental analysis, particle size distribution, water retention capacity (WRC), retention curve and available water (AW). All biochars presented great variability in their characteristics. A WRC varied from 88% to 628 % as follows: SSB < OBB < GCB < CCB = DCB < SBB A AW varied from 10% to 140% where SBB > DCB > CCB = GCB > OBB > SSB. Hence, SBB showed higher water retention, and SSB was the least efficient.
Keywords: Water resources; Organic waste; Pyrolysis; Carbon; Climate change.

Resumo
O aumento da produção de alimentos para atender a demanda global tem gerado um grande volume de resíduos orgânicos. Quando reinseridos na cadeia produtiva, esses resíduos podem prestar diversos serviços ambientais, principalmente no que se refere à qualidade e quantidade dos recursos hídricos. O biocarvão apresenta grande potencial como corretivo do solo, fonte de nutrientes e condicionador, aumentando a retenção de água. Este estudo produziu e caracterizou biocarvões a partir de seis tipos de biomassa (bagaço de cana-SBB, casca de coco seca-DCB, casca de coco verde-GCB, lodo de esgoto-SSB, sabugo de milho-CCB e bagaço de laranja-OBB. O objetivo principal foi avaliar a retenção de água do biocarvão. O biocarvão foi produzido através de pirólise lenta a uma temperatura de

550ºC, moído e peneirado para determinar porosidade, área superficial específica, condutividade elétrica, pH, capacidade de troca catiônica, morfologia estrutural, análise imediata e elementar, distribuição de tamanho de partícula, capacidade de retenção de água (WRC), curva de retenção e água disponível (AW). Todos os biocarvões apresentaram grande variabilidade em suas características. A WRC variou de 88% a 628% da seguinte forma: SSB < OBB < GCB < CCB = DCB < SBB. A AW variou de 10% a 140% onde SBB > DCB > CCB = GCB > OBB > SSB. Assim, o SBB apresentou a maior retenção de água, sendo o SSB o menos eficiente.
Palavras-chave: Recursos hídricos; Resíduo orgânico; Pirólise; Carbono; Mudanças climáticas.

Resumen

El aumento de la producción de alimentos para satisfacer la demanda mundial ha generado un gran volumen de residuos orgánicos. Cuando se reinsertan en la cadena productiva, estos residuos pueden brindar varios servicios ambientales, especialmente en lo que se refiere a la calidad y cantidad de los recursos hídricos. El biocarbón tiene un gran potencial como enmienda del suelo, fuente de nutrientes y acondicionador, lo que aumenta la retención de agua. Este estudio produjo y caracterizó biocarbón a partir de seis tipos de biomasa (bagazo de caña de azúcar-SBB, cascarilla de coco seca-DCB, cascarilla de coco verde-GCB, lodo de depuradora-SSB, mazorca de maíz-CCB y bagazo de naranja-OBB. El objetivo principal fue evaluar la retención de agua del biocarbón El biocarbón se produjo mediante pirólisis lenta a una temperatura de 550ºC, molido y tamizado para determinar porosidad, área superficial específica, conductividad eléctrica, pH, capacidad de intercambio catiónico, morfología, análisis estructural, inmediato y elemental, distribución del tamaño de partículas, capacidad de retención de agua (WRC), curva de retención y agua disponible (AW). Todos los biochars mostraron una gran variabilidad en sus características. WRC varió de 88% a 628% de la siguiente manera: SSB < OBB < GCB < CCB = DCB < SBB. AW osciló entre 10 % y 140 % donde SBB > DCB > CCB = GCB > OBB > SSB. Por lo tanto, SBB tuvo la mayor retención de agua, siendo SSB el menos eficiente.
Palabras clave: Recursos hídricos; Residuo orgánico; Pirólisis; Carbón; Cambios climáticos.

1. Introduction

The recycling of organic waste in Brazil and the world has become a necessity for the better use of natural resources in the face of increasing demand for food. The use of these residues in agriculture, for instance, improves soil quality, increases crop productivity, contributes to food security, reduces mineral fertilizer applications, and contributes to soil carbon sequestration (Lal, et al., 2015; Lal, 2018). From the standpoint of agricultural management in hydrographic basins, in areas under high production pressure, organic waste as soil amendment and conditioner reduces soil erosion and contributes significantly to the conservation of water resources. There are a variety of organic residues from animal and plant origin found everywhere, mostly facing disposal and environmental problems.

Sewage sludge, a semi-solid residue from wastewater treatment, has excellent potential as a soil amendment. It is estimated that sewage sludge production in Brazil is between 150 and 220 thousand tons of dry matter per year. In Sergipe alone, the sludge production is around 9 tons day-1. However, despite the large-scale production, the final destination is complex, and its inadequate disposal can result in hazardous effects on water quality. However, in the form of biochar, sewage sludge presents a lower pathogen load and reduced environmental risk for land use (Singh, et al., 2020).

Another essential source of organic residues with agricultural potential is agroindustries. They are present in large numbers in Brazil and produce large amounts of hard-to-dispose wastes. Furthermore, agroindustries have residues with high lignocellulosic compounds content (hemicellulose, cellulose, and lignin around 20-40%, 40-60%, and 10-25%, respectively) (Ferreira, 2014). In the state of Sergipe, these companies generate sugarcane bagasse, green coconut husk, and dry coconut, corn cobs, passion fruit husks, orange bagasse, among others.

The production of residues derived from green coconut is increasing in the northeast region, including the state of Sergipe, the second-largest producer in the northeast. In rural areas, green coconut shells are deposited near cultivated areas, while in urban areas, they form large piles until they are collected and transported to a controlled landfill. This practice generates environmental damage, including soil and river pollution, groundwater contamination, emission of polluting volatile gases, and the proliferation of disease-transmitting insects.

Sugarcane residues are also produced in large quantities and result mainly from the sugar and alcohol industries. In addition to industrial production, sugarcane bagasse is also generated in the urban area, at open markets. Orange residues come from industrial extraction of fruit juice and use in cafeterias and restaurants, resulting in significant residues (peel, bagasse, and seeds). All these residues can be used to produce biochar for agricultural use (Gonzaga, et al., 2021).

Biochar is the product obtained from biomass heated in a closed environment, with little or no oxygen and a temperature ranging from 350 to 700ºC (Nair, et al., 2020), to be used as a soil conditioner (Guo, et al., 2020). In addition, Biochars produced from different types of biomass, lignocellulosic or not, have other characteristics regarding fixed carbon content, volatile matter, ash, nutrients, porosity, specific surface area, morphology, cation, and anion exchange capacity and retention of water (Liu, et al., 2016, Feitosa, et al., 2017, Batista, et al., 2018; Wijitkosum & Jiwnok, 2019, Tomczyk, et al., 2020; Huang, et al., 2021). Furthermore, all biochars present high recalcitrance and aromaticity, regardless of the feedstock, contributing to their long permanence time in the soil (Nair, et al., 2020).

One of the most critical biochar properties is the high water retention capacity (Gondim, et al., 2018; Batista, et al., 2018); Razzaghi, et al., 2020; Ndede, et al., 2022). Gondim, et al. (2018) reported the high water holding capacity of wood-based biochars and attributed the results to the high microporosity. Ndede, et al. (2022) observed high water retention capacity in biochar from woodchip, poultry litter, and bagasse. However, there is significant variability between the different biochar types. Therefore, a detailed characterization of each biochar from different feedstocks is crucial to define specific uses, either as a conditioner or input in the soil or as a filter to treat water and effluents. Thus, the present study aimed to produce biochars from sewage sludge, green and dry coconut shells, orange bagasse, corn cob, and sugarcane bagasse and characterize them, aiming at properties that contribute to water retention.

2. Methodology

2.1 Biochar preparation

The organic residues used in the study for the production of biochar were sewage sludge (SSB), green coconut husk (GCB), dry coconut husk (DCB), orange bagasse (OBB), sugarcane bagasse (SBB), and corncob (CCB).

The sewage sludge was collected at the Municipal Effluent Treatment Station (ETE) in Aracaju-SE. The material was removed from drying beds and spread to dry before pyrolysis. The green coconut husks were collected in open markets in Aracaju, crushed in a mill explicitly designed to mill green coconut. Sugarcane bagasse was collected at sugarcane juice outlets in São Cristóvão. After drying, the feedstock was pyrolyzed. Dry coconut residues were obtained from a rural property. There was no need for further drying as the residues were already collected in a dry state. The orange bagasse was procured in a cafeteria located on the University main Campus, in São Cristóvão-SE, and air-dried before biochar production.

The residues were pyrolyzed in a TLUD (top-lit updraft) reactor that initially works by burning waste as fuel; however, from a certain point onwards, the process starts to be fed back with the gases released from the waste destined for biochar. In this way, the vapors and non-condensable gases produced and released during the thermal conversion of waste are burned to provide energy and continue the pyrolysis process. The oven temperature reaches, on average, 550ºC.

The production time varied between the types of residues, and for lignocellulosic residues (those of vegetable origin), pyrolysis occurred after 1 hour, and for sewage sludge, the process lasted 3 hours. After the pyrolysis process, the biochars were spread on benches in an agricultural oven for drying, ground, passed through sieves with a 2 mm mesh opening, and packed in plastic bags.

2.2 Biochar characterization

a) Total porosity, specific surface area, and morphology

The surface structures of biochar were determined by previously gasifying the samples at a temperature of 150°C, for two hours. Then, the 77 K nitrogen adsorption technique was used to determine the specific surface area, the pore volume, and the average pore size, using the NOVA 1200 equipment (Quantachrome, USA), using the BET method (Brunauer-Emmett-Teller). The method is based on the adsorption and desorption of gas volumes at different pressures.

The morphology of the biochars was obtained by scanning electron microscopy (SEM), using an Express electron microscope, model Aspex, operated under high vacuum, with an electron beam acceleration of 15 kV. The samples were previously fixed on double-sided carbon tapes and metalized with gold to visualize the structure.

b) Moisture, volatile matter, ash content, and fixed carbon

The moisture content was determined by weighing approximately 1g of biochar and transferring it to a porcelain crucible and taken to an oven previously heated to 105 ± 5ºC for 24 hours. The residual material was taken to a muffle oven previously heated to 950 ± 10ºC for 6 minutes and weighed to calculate the volatile matter. The residual material was returned to the muffle furnace at a temperature of 750ºC for 6 hours to determine the ash content (ASTM D1762). The equation 1 determined the fixed carbon content:

Fixed carbon = 100 – (moisture + volatile matter + ash content) Eq. 1

c) pH and electrical conductivity

Biochar pH and electrical conductivity (EC) were determined in a 1:5 (m/v) ratio of biochar and distilled water. Exactly 5 g of biochar were weighed in a 125ml Erlenmeyer flask and, after adding 25ml of distilled water, the samples were shaken on a reciprocating shaking for 1h30min, at 250 rpm. After 1 hour of rest, the pH was determined in a benchtop potentiometer, and the EC was determined in a benchtop conductivimeter (Gaskin, et al., 2008; Rajkovich, et al., 2011).

d) Particle size distribution

The particle size analysis of biochar was performed based on the ASTM D5158-98 methodology. Approximately 20-25 g of air-dried biochar was transferred to a set of mesh sieves: 2mm, 1mm, 0.5mm, 0.25mm, and 0.10mm. A lid was placed on the first sieve and shaken for 20 minutes in an orbital shaker, rotating at 4-4.5 rpm. The biochar retained in each sieve was collected in aluminum cans and weighed.

e) Water retention capacity (WRC)

Samples of biochars were oven-dried at 105ºC to determine the hygroscopic moisture. The water retention capacity (WRC) was determined according to Bhadha, et al. (2017). Briefly, 5 g of biochar were transferred to a funnel lined with a paper filter and attached to a hose with a closure device at the lower end. Next, 50ml of distilled water was added slowly and uniformly for complete contact and saturation of the biochar. After resting for 30 minutes, the end of the hose was opened, allowing water to drain for 30 minutes. The drained water was collected in a beaker for later measurement of the volume in a graduated cylinder.

The water retention capacity (WRC) was calculated as follows:

WRC (%) = [(50ml – DW – FW+ HW) / 5g] X 100. Eq. 2

Where:

DW= Drained water (mL);

FW= water retained in the filter paper (mL);

HW= Hygroscopic water.

f) Water retention curves and plant available water.

The biochar´s water retention curve was determined in the Richards pressure chamber. The samples were placed in polyvinyl chloride (PVC) rings, measuring 5 cm in diameter and 2 cm in height, saturated in trays for 24 hours, weighed, and transferred to the pressure chamber at water potentials of - 6, -33, -100, -500, and -1500 kPa. After reaching the equilibrium state, the samples were removed from the chamber, weighed (m1), taken to an oven at 105oC, and weighed (m2).

The water content (WC) was calculated as shown in Equation 3:

$$WC(\%, w/w) = \{(m1 - m2)/m2\} x\ 100 \qquad \text{Eq. 3}$$

g) Ultimate analysis and CEC

The total carbon (C), hydrogen (H), and nitrogen (N) contents of the biochars were determined using the CHN Elemental Analyzer model 1420 (Perkin-Elmer) equipment. The percentage contents of C, N, and H, obtained from the analysis, were divided by the respective atomic mass of that element to calculate the atomic ratios. The oxygen content was calculated as 100 – (C + H + N). Finally, the H/C, O/C, and N/C ratios were calculated.

The CEC was calculated by summing the results for Ca, Mg, K, Na, and Al.

2.3 Statistical analysis

The completely randomized design model was used in this experiment, with six types of biochar feedstocks and four replications, totaling 24 experimental units. Some results are presented as means of four replicates, with standard deviation. Differences between means were compared by Tukey test at 5% significance.

3. Results and Discussion

3.1 pH, electrical conductivity (EC), CEC, specific surface area, porosity, and density

Biochars´ pH, electrical conductivity (EC), cation exchange capacity (CEC), specific surface area, and porosity are shown in Table 1.

Table 1 – pH, electrical conductivity (EC), CEC, specific surface area, porosity, and density of the biochars from sugarcane bagasse (SBB), corncobs (CB), sewage sludge (SSB), orange bagasse (OBB), dry coconut husks (DCB), and green coconut husks (GCB).

Biochar	pH	EC (dS m^{-1})	CEC (cmolc kg^{-1})	Specific surface (m^2 g^{-1})	Porosity (cm^3 g^{-1})	Density (g cm^{-3})
CCB	10.2	1.90	30.2	193	0.017	0.11
DCB	10.5	4.20	69.7	122	0.064	0.10
SSB	7.50	7.30	22.2	98.8	0.082	0.56
OBB	9.60	4.20	63.5	99.2	0.022	0.25
SBB	9.90	1.00	10.7	112	0.012	0.10
GCB	8.30	0.67	27.0	147	0.077	0.20

Source: Authors.

The pH values varied from 7.5 to 10.5, confirming the alkaline nature of the biochars. Typically, this variation in pH values is likely due to the production process, temperature, and type of biomass. In the present study, all biochars were produced using the same method and temperature; therefore, differences in pH are associated with the kind of biomass used. For example, the SSB presented the lowest pH value (7.50), whereas CCB and DCB had the highest values (10.2 and 10.5, respectively). The alkaline nature of biochars is of great interest for agriculture since very acidic soils (pH <5.0) need correction to allow adequate growth and development of crops, which have better performance in soil pH between 5.5 and 6.5.

The different biochars also showed significant variation concerning EC values, between 0.67 - 7.30 dS m^{-1}, with 50% between 4.2 and 7.3 dS m^{-1} and 50% between 0 .67 to 1.90 dS m^{-1}. Interestingly, the BLE, with the lowest pH value, presented the highest EC (7.3 dS m^{-1}), which configures a high salinity value. Green coconut biochar (GCB) had the lowest EC value, which may be related to the biomass washing process after milling. One of the main limiting factors for using green coconut residues to compost and biochar production is the high salinity level; Therefore, we ground and washed the feedstock before pyrolysis, which promoted the leaching of soluble salts and enabled the use of green coconut residue.

One of the main characteristics of biochar for agricultural use, especially in tropical soils, is CEC. The evaluated biochars presented significant variation in CEC between 10.7 and 69.7 cmolc kg^{-1}; There was also variation between the different types of biomass. The DCB and OBB showed the highest CEC values, whereas the lowest CEC was observed in SBB. Thus, the DCB presented CEC 6.5 times greater than the SBB. Tomczky, et al. (2020) found CEC results below 5cmolc kg^{-1} in two sugarcane bagasse biochars, confirming the influence of biomass on characteristics such as the CEC of the biochar. Applying biochar with high CEC can increase the soil CEC and, consequently, improve the nutrient and water retention capacity, reducing the ion leaching process and increasing soil fertility and nutrient utilization by plants.

The specific surface area and porosity of biochar are two physical characteristics related to the ability of biochar to interact with soil components, that is, with mineral and organic particles, ions, water, and microorganisms. These properties of biochar arise with the increase in temperature during the pyrolysis process (Rafiq, et al., 2016; Tomczky, et al., 2020). In the present study, SBB, DCB, GCB, and CCB biochars had a specific surface of 112 to 197 m^2 g^{-1}, and the OBB and SSB biochars presented specific surface area < 100 m^2 g^{-1}. The CCB contributed a specific surface 200% larger than the SSB, which showed the lowest value, 98.8 m^2 g^{-1}. However, observing the results presented in Table 1, there does not seem to be a correlation between specific surface and porosity of the biochars, which is easily noticed when comparing SSB with OBB, two biochars with similar surface area, but with different porosity. Such results confirm the importance of the type of biomass in obtaining the biochars. In addition, there may be different types of pore size and shape, which influences the surface area.

The porosity of the biochars ranged from 0.012 – 0.082 cm^3 g^{-1} (Table 1), showing significant differences depending on the raw material, where SBB had the lowest porosity, followed by CCB and OBB, respectively. The other DCB, GCB, and SSB were 6, 7, and 8x, respectively, higher than the SBB. Some production factors such as raw material, pyrolysis temperature, and carbonization residence time can be helpful to produce biochar with variable porosity (Liu, et al., 2017). For example, Huang, et al. (2017) produced biochar from sewage sludge at a temperature of 500oC. They obtained porosity of 0.061 cm^3 g^{-1}, a value much higher than that found in this work, which shows the influence of temperature on the final product characteristics.

Biochar´s density ranged from 0.10 to 0.56 g cm^{-3}, with SSB > OBB > GCB > CCB = SBB = DCB (Table 1). Brewer, et al. (2014) evaluated different types of biochar and found density values ranging from 0.25 to 0.60 g cm-3. Although the methodology used by the authors was different from that applied in the present study, their results are very similar and confirm the great variability between biochars of different biomasses. Density and porosity are important physical properties of biochar related to material movement in soil and other environmental compartments. In addition, materials with a density lower than water (1 g cm^{-3}) tend to float, facilitating transport, especially by erosion (Rumpel, et al., 2009). These properties influence hydrological processes, water retention, and its availability to plants. The low density of biochar also makes its application in

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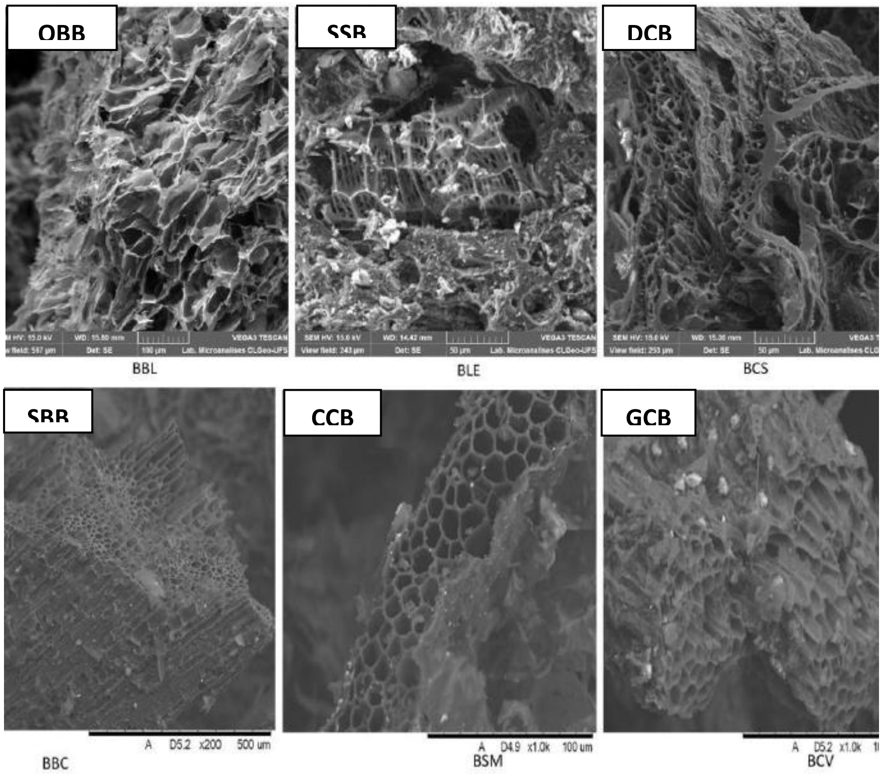
the field difficult, requiring care and strategies to avoid impacts on both farmers and the environment.

3.2 Morphological characterization

Figure 1 shows scanned micrograph images of the different biochars used in the present study OBB (a), SSB (b), DCB (c), SBB (d), CCB (e), and GCB (f). The images revealed defined porosity in the biochars (GCB, CCB, SBB, and DCB), with a predominance of cylindrical holes interconnected by large tubes, forming channels. In the DCB, the images also revealed the presence of heterogeneous pores with irregular shapes. The SBB and CCB stood out to the others; there was a predominance of pores with diameters between (20 - 50 µm) and (50 - 100 µm) respectively, indicating high inner porosity. In general, pore sizes were between 20 to 500 µm (Figure 1). The OBB and SSB biochars did not show well-defined morphology.

These morphological differences observed between the different types of biochar used in the present study define two groups according to the composition of the feedstocks. Thus, in DCB, CCB, SBB, and GCB biochars, the porous structure seems to be related to the lignocellulosic characteristics predominant in the dry coconut husk, corn cob, sugarcane bagasse, and green coconut, respectively. On the other hand, as sewage sludge does not have a significant lignocellulosic composition, it has less than 4% lignin, but rather a mixture of several organic and inorganic compounds without a defined form, its biochar reflected this trend. The morphology of OBB is related to the composition of orange pomace, which has a significant amount of soluble carbohydrates and only 3% or less of lignin.

Figure 1 – Scanned micrograph images (SEM) of different biochars (OBB: Orange bagasse; SSB: sewage sludge; DCB: dry coconut husks; SBB: sugarcane bagasse; CCB: corn cobs; GCB: green coconut husks).



Source: Authors.

Biochars with well-defined and elongated pores such as DCB, CCB, SBB, and GCB can probably indicate a high water retention capacity as they form storage channels (intrapore). According to Liu, et al. (2017), biochars with high intraporosity and irregular shapes can efficiently increase water storage. This characteristic is often related to the large specific surface area and adsorption capacity for water and nutrients. Some references compare biochar with a sponge, visibly observed in SEM images. Devens, et al. (2018) characterized the orange peel and green coconut biochars, produced at a temperature of 350°C, through SEM images. They observed a complex network of heterogeneous pores in the orange biochar and cylindrical cracks interconnected by large tubes in the coconut biochar.

3.3 Particle size distribution

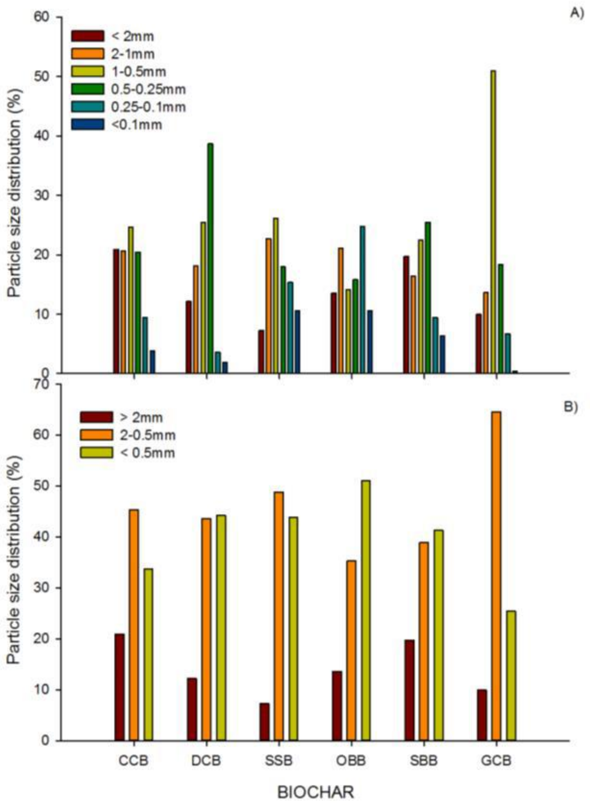
The particle size distribution was obtained by sieving the biochar in 6 particle size classes, varying between (> 2 mm and < 1 mm), as shown in Figure 2(A and B). All biochar types presented a very different particle size distribution , confirming the information found in the literature, that all biochar is different from one another, which reinforces the need to evaluate different materials. The highest proportion of particles > 2mm was observed in the CCB and SBB, reaching approximately 21%. The presence of a large amount of particles with a larger diameter offers advantages for the application of biochar to the soil under field conditions, as it reduces drift and pore clogging, and increases the longevity or permanence of the biochar in the soil, which is beneficial for carbon sequestration (Brewer, et al., 2014).

However, all biochars presented a percentage equal to or below 21% in the range > 2mm. DCB and GCB showed the smallest proportions of particles < 1mm, which reduces drift during the application; however, they have large proportions of intermediate particles (0.50-0.25mm: DCB and 0.50- 1mm: GCB). It is interesting to observe that the two biochars with the lowest lignin composition (SSB and OBB) had the highest proportions of small particles (< 0.25 mm), which may imply more significant drift during application and greater leaching of these particles in the soil profile. This result is related to the higher density values found in these two biochars (Table 1). A higher proportion of smaller particles favors a more compact packing and arrangement, increasing density.

The CCB, SSB, and OBB presented above 20% of particles in the range of (1 – 2mm) and other values between 13 and 18% of the sample. However, in the range (0.5 – 1.0mm), GCB had the highest granulometric fraction (51%). In the range of (0.25 – 0.5mm), the DCB obtained 39%, followed by the SBB, OBB, GCB, respectively. The CCB and SSB showed less than 20% of particles in this class. In the range of 0.10 to 0.25mm, the OBB obtained 25% of the sample fraction, followed by the GCB and SSB. The SBB and CCB presented close to 9%, and the DCB, below 5%. Particles < 1mm were present in (SSB and OBB), (SBB and GCB), (CCB and DCB) with percentages of approximately 10%, 7%, 4%, respectively.

The particle size distribution in the different biochars influences the pore space distribution, the specific surface area, and water retention (Liu, et al., 2017). In addition, the varied granulometry of biochar can affect the soil pore size distribution, either reducing or increasing it, depending on the soil and biochar particle size. Tiny biochar particles can reduce soil macroporosity in coarse texture soils; Conversely, large biochar particles can increase macroporosity in fine texture soils.

Figure 2 – Particle size distribution of biochar (CCB: corn cobs; DCB: dry coconut husks; SSB: sewage sludge; OBB: Orange bagasse; SBB: sugarcane bagasse; GCB: green coconut husks).



Source: Authors.

3.4 Proximate analysis

The immediate analysis separates biomass components (fixed carbon, ash content, and volatile material) to assess the variation in their proportions in the different materials formed by the thermal transformation process (Mitchell, et al., 2013). Figure 3 shows the relative percentage of fixed carbon, ash content, and volatile material in each pyrolyzed biochar. The results will be presented here in partial form since it was impossible to analyze all biochars in triplicate. In general, the proportions of the elements that make up the immediate analysis, unlike most of the characteristics of biochars, showed slight variation between the treatments CCB, DCB, SBB, and GCB, with ash values between 7-8%, volatile matter between 11-13% (except GCB: 19%), and fixed carbon between 70-80%. All these biochars have more remarkable similarities regarding biomass with high lignin content. On the other hand, the SSB and OBB treatments have more distinct compositions. OBB maintained a higher proportion of fixed carbon but had a higher ash and volatile matter content concerning other biochars of plant origin.

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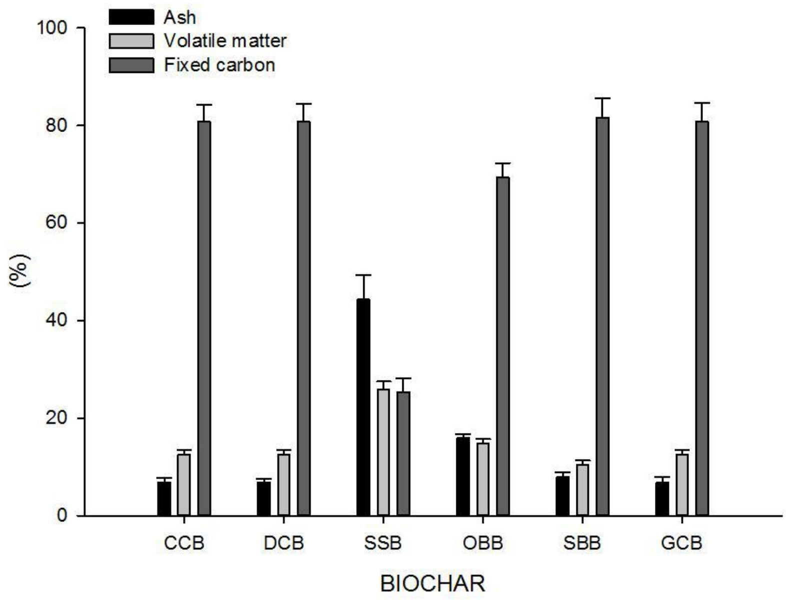
Figure 3 - Percentage of ash, volatile matter, and fixed carbon of biochar (CCB: corn cobs; DCB: dry coconut husks; SSB: sewage sludge; OBB: Orange bagasse; SBB: sugarcane bagasse; GCB: green coconut husks).



Source: Authors.

The influence of the composition of the original material was quite evident in the SSB, which presented more than 40% ash and around 25% volatile matter, characteristics that are not very desirable in this biochar. In addition, its low proportion of fixed carbon is a disadvantage, as it does not significantly contribute to soil carbon sequestration. However, the high ash content can increase its potential as an immediate supplier of nutrients to plants. The ash content tends to increase as it depends on the amount of mineral matter present in the biomass, which does not volatilize at normal carbonization temperatures, remaining entirely in the ash of the biochar. In this way, SSB stood out from the others. Chen, et al. (2011) suggest that biochar derived from smaller feedstock particles generally has a higher ash content, which may increase the effects of liming. The largest share of volatile material in the SSB confirms that part of the toxic materials present in the sludge is volatilized in the pyrolysis, producing more significant amounts of volatile matter and smaller amounts of fixed carbon, with ash persisting (Tan, et al., 2014). Generally, the values of volatile material in the biochar are related to the pyrolysis temperature, which was not the objective of this study.

Among the components of the proximate analysis, the proportion of fixed carbon is the most important element because it is the most resistant material, the one that remains after the release of moisture, volatile material, and ash. Fixed C is related to longevity and recalcitrant carbon input.

Many works have been published on the characteristics and composition of different biochars (Jindo, et al., 2014; Sun, et al., 2016). For example, in Jindo, et al. (2014), percentages of volatile matter below 10% were observed in rice husk and rice straw biochars. In work by Sun, et al. (2016), the authors found proportions of ash, volatile matter, and fixed carbon similar to those found in the study for biochars of plant origin.

3.5 Ultimate analysis

The elemental analysis of biochars is of fundamental importance for the characterization and evaluation of the degree of degradation of the biomass after the pyrolysis process. Table 2 displays the results of C, H, N, O, H/C, O/C, and N/C of the biochars in this study. An increase in carbon content is expected after the thermal process, as other compounds and elements

(N, H, and O) are released, with a consequent concentration of C at the end of the process (Jindo, et al., 2014). The higher the concentration of C, the greater the longevity and potential of biochar for sequestering C in the soil (Wijitkosum & Jiwnok, 2019). C concentrations ranged from 43.8 to 85.6% among biochars in the present study, with higher values observed in plant-based biochars (SBB, DCB, CCB, and OBB).

Table 2 – Ultimate analysis of biochar (CCB: corn cobs; DCB: dry coconut husks; SSB: sewage sludge; OBB: Orange bagasse; SBB: sugarcane bagasse).

Biochar	C	H	N	O	H/C	O/C	N/C
	---------------------- %	---------------------					
CCB	81.8	2.43	4.54	11.2	0.03	0.14	0.06
DCB	83.5	2.12	3.49	10.9	0.02	0.13	0.04
SSB	43.8	3.66	3.95	48.5	0.08	1.11	0.09
OBB	75.4	2.39	2.72	19.5	0.03	0.26	0.04
SBB	85.6	1.74	3.91	8.72	0.02	0.10	0.05

Source: Authors.

On the other hand, SSB obtained a result of 50% less concerning the largest, the SBB. The concentration of H varied from 1.74 to 3.66%, with the highest value for the SSB and the lowest for the SBB. The concentration of N shows similar values among the studied biochars, ranging from 2.72% to 4.54%. The highest concentration of N (4.54%) was observed in the CCB, probably due to the lower loss of N by volatilization during the pyrolysis process (Feitosa, et al., 2020).

According to Francioso, et al. (2011), who used Pinus pinea charcoal produced at low temperature, the carbon contents in the samples are influenced by the granulometry of the carbonaceous material, where smaller granulometry is related to the lower C content. The particle size distribution of SSB and SBB were exceptionally assorted. However, the predominant range was 1.0 to 0.5mm in the studied biochars, except for OBB, which shows that this characteristic alone may not determine the results. The C content of biochars is more related to the source material and the pyrolysis temperature. Among the biochars studied, SSB had the highest percentage of H and O, and SBB had the lowest rate. The N concentration of biochars is not of significant interest in agriculture since this element is not available. However, the relationships between the concentrations of different factors (H/C, O/C, and N/C) provide essential information about the recalcitrance and longevity of biochars (Nguyen & Lehmann, 2009).

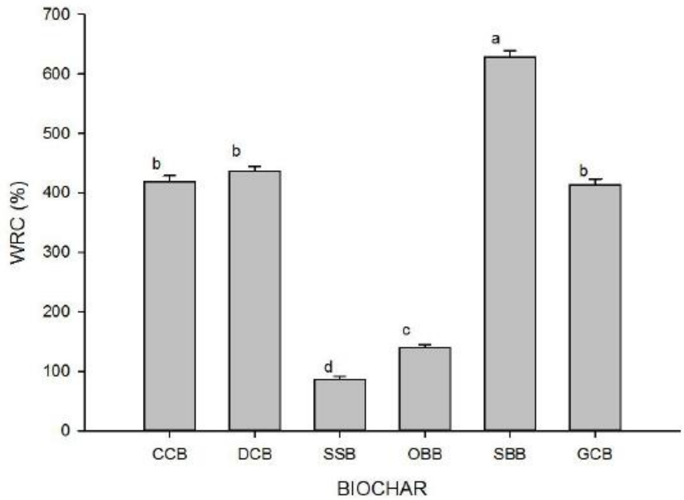
The lower the H/C, O/C, and N/C ratios, the greater the recalcitrance of biochar (Spokas, 2010). Therefore, the results indicate that our biochars have high stability by forming condensed aromatic structures (Wang, et al., 2013). However, there were differences between biochars. For instance, the H/C (0.08), O/C (1.11), and N/C (0.09) ratios of the SSB indicate lower stability and recalcitrance compared to the others. In addition, the O/C and N/C ratios can infer biochar reactivity related to functional groups of oxygen and nitrogen. According to Spokas (2010), the high temperatures reached during the pyrolysis process promote significant losses of O and H, causing changes in the structural arrangement and increasing the formation of aromatic rings and graphite-like crystal structures.

The same type of biomass may result in biochar with different elemental concentrations. For instance, Wijitkosum & Jiwnok (2019) found concentrations of C (41.6%), H (6.84%), N (0 .74%), and O (50.7%) in corn cobs biochar produced through slow pyrolysis. However, their results differ from ours (81.8% C), likely due to production, carbonization time, and feedstock maturity. In addition, the use of green corn cobs may result in a lower proportion of C than dry corn cobs since there is a higher lignin content in the latter. Wijitkosum and Jiwnok (2019) found high H/C (1.97) and O/C (0.91) values, which may indicate an incomplete pyrolysis process.

3.6 Water retention capacity (WRC)

The water retention capacity (WRC) based on the weight of the different biochars varied from 86.7 to 628% and is shown in Figure 4. The WRC was SSB < OBB < GCB < CCB = DCB < SBB. Therefore, SSB is the least efficient at retaining water, and SBB is the most efficient. The structural pores created during the biomass thermal decomposition and the increase in functional groups (mainly carboxylic and hydroxyl) are responsible for the absorption and adsorption of water in biochars. Although SSB presented a slightly larger pore volume than the other biochars, its smaller CEC and surface area probably (Table 1) contributed to the low WRC. In the present study, we did not evaluate the functional groups, making it difficult to address their contribution to the WRC further.

Figure 4 - Water retention capacity (WRC, %) of biochar (CCB: corn cobs; DCB: dry coconut husks; SSB: sewage sludge; OBB: Orange bagasse; SBB: sugarcane bagasse; GCB: green coconut husks).



Source: Authors.

In addition, biochars have different degrees of hydrophobicity (Hallin, et al., 2015; Liu, et al., 2016; Mao, et al., 2019), a characteristic that can reduce the water retention capacity even in highly porous biochars. The hydrophobicity of biochars is closely related to certain surface functional groups, such as alkyls (Mao, et al., 2019), aliphatic chain groups formed in more significant quantities when biochar is produced at lower temperatures. According to Hallin, et al. (2015), the feedstock functional groups remain in the biochar prepared at temperatures lower than 500ºC, developing hydrophobicity; however, these functional groups are volatilized at higher temperatures resulting in biochar with hydrophilic groups, which attract water molecules.

Even though CCB and DCB were produced from different feedstocks, they show similar WRC (425%). On the other hand, DCB presented higher WRC than the GCB despite the same feedstock. In this case, the higher CEC (Table 1) and percentage of particles with a diameter between 0.5-0.25 mm granted better results to DCB (Figure 3). However, the highest WRC was observed in the SBB (628%), which increases its potential as a soil conditioner, mainly for tropical soils with low water storage capacity. Furthermore, laboratory observations showed a slow saturation rate and ease of compaction of the SCB, which likely influenced the water sorption pattern. On the other hand, the OBB showed a smaller WRC (140%) than the other plant-based biochars. Hence, the similarities observed in the particle size distribution of SSB and OBB may have contributed to their lower WRC results; however, the granulometry of these two biochars may improve aeration and drainage in fine-textured soils.

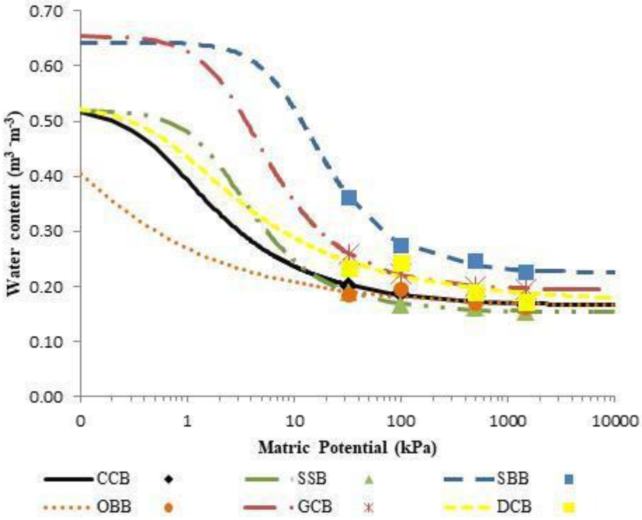
According to Liu, et al. (2016), biochar surfaces can present different levels of hydrophobicity and hydrophilicity, which mainly depends on the pyrolysis temperature (Mao, et al., 2019) and the type of biomass. The hydrophobicity and pore connectivity in biochar can interfere with water's effective absorption and storage (Gondim, et al., 2018). In the absence of hydrophobicity, water penetrates the pores and, if there is connectivity, there will be a faster flow in larger-diameter pores than in smaller pores. On the other hand, if there is hydrophobicity, there will be no effective water penetration, especially in the smaller pores of the biochar. Generally, hydrophobicity tends to be higher in biochars produced at low temperatures. Therefore, characteristics such as hydrophobicity and pore connectivity, which were not evaluated in the present study, may have influenced the water retention capacity of the biochars and made it difficult to correlate with more apparent characteristics such as porosity and specific surface area.

3.7 Water retention curves and available water (AW) of biochar

Figure 5 illustrates the water retention curves of biochars. Although mainly applied to soils, the estimation of the water retention curve for the different biochars showed a similar pattern as seen for soils. The biochar water curves coherently estimated the capacity of the pyrolyzed material to store water in its structure when subjected to different matric potentials. Observing the maximum retention capacity ($\psi m = 0$), there was a separation of the biochars into groups that show some similarity in relation to this characteristic, that is, SBB = GCB (65%) > SSB = DCB = CCB (52%) > OBB (40%). The SBB and GCB biochars offered greater resistance to water release as the tension increased until the potential of - 1 kPa. From that point, these two biochars showed differences in the retention pattern, and the SCB presented higher moisture content than the GCB. For example, in $\psi m = - 10$ kPa, the SBB presented a moisture content of approximately 50%, while in the GCB, this value was around 35%. At $\psi m = -33$ kPa, the differences between the two biochars decreased, with 36% for SBB and 26% for GCB.

Similarities in the retention pattern of the SSB, DCB, and CCB group decreased along the curve. Compared to CCB and DCB, SSB retained more water at $\psi m < -10$ kPa and less water at $\psi m > -10$ kPa. DCB offered greater resistance to water loss at $\psi m > -10$ kPa. However, at $\psi m = - 33$ kPa, these three biochars had similar moisture contents (19-23%). To determine the equilibrium moisture points in the soil, it was proposed the value of -33 kPa for field capacity (FC) and -1500 kPa for the permanent wilting point (PWP); however, to assess water retention in biochar, there is still no standard methodology. The OBB retention curve showed rapid release of water with the increase in the matric potential until approximately -10 kPa. From that point on, the OBB behaved like the others.

Figure 5 - Water retention curves of biochar (CCB: corn cobs; DCB: dry coconut husks; SSB: sewage sludge; OBB: Orange bagasse;; SBB: sugarcane bagasse;; GCB: green coconut husks).



Source: Authors.

In the highest matric potential (ψm = - 1500 kPa), the SSB presented the lowest moisture content (15%) and the SBB, the highest (22%). Although moisture contents retained at high potentials (ψm = -1500 kPa) are not readily available for most plants, the presence of biochar in the soil must favor the maintenance of more significant volumes of water.

Basso, et al. (2013) observed an increase in biochar water retention between 0 and -10 kPa, attributed to capillary effect and pore distribution, corroborating our results. According to Feitosa, et al. (2017), high water retention in biochar is probably related to the high specific surface area, which increases the amount of water adsorbed on the surface and micropores.

The available water (AW) in the biochars was calculated by subtracting the moisture content at – 33 kPa from that obtained at – 1500 kPa (Figure 17). There was a great variation between biochar, which followed the trend SBB > DCB > CCB = GCB > OBB > SSB. SBB presented a high percentage of AW (136%), which is seventeen times higher than the SSB (8%). Therefore, it is imperative to characterize the materials to elucidate their potential for application in agriculture.

The AW variation among biochars may also be related to the biochar´s particle size distribution (Figure 13). According to Abel et al. (2013), the granulometry of biochar varies from a few millimeters to nanometers. The assortment of particles provides large (interpores) and small (intrapores)spaces in the biochar structure, which results in different retention energy intensities. For instance, SBB retains a lot of water at -10 kPa and – 33 kPa but not so much at -1500 kPa, which may indicate that the assortment of particles favors the existence of a more significant amount of interpores. Similar to what happens in soils, smaller pores in biochar can attract and retain water by capillarity longer than larger pores.

4. Conclusion

Considering that biochar was produced through the same pyrolysis process and at the same temperature, the vast variation observed in our study is attributed to the different feedstocks. However, the differences in the particle size distribution, porosity, and specific surface did not fully explain the variation in the water retention capacity of biochar, suggesting the need for further evaluation of functional groups and hydrophobicity. These characteristics can change patterns of water absorption and storage. All biochars showed great potential for water retention; however, the most efficient was sugarcane bagasse biochar, and the least efficient sewage sludge. Given the variation observed in the different biochars, future research to evaluate the effect of particle size distribution and hydrophobic groups on water retention should shed light on the adequate pretreatment and application of biochar.

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