



Coconut fiber biochar alters physical and chemical properties in sandy soils

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ABSTRACT. This work aimed to characterize the biochar produced from residues of coconut fruit and to evaluate how it might beneficially alter the retention capacity of water and nutrients in soils with a sandy texture. The biochar was produced in a retort furnace and later analyzed to determine its chemical and physical characteristics. Experiments to analyze the retention potential of the biochar for water and nutrients were performed in PVC columns filled to a 400 mm depth, with the upper 300 mm receiving treatments that consisted of 0, 1, 2, 3, 4, and 5% (p p⁻¹) biochar mixed with soil. For the nutrient retention experiment, in addition to the biochar concentrations, the treatments received the same NPK fertilization. The experiments were performed in a completely randomized design with four replications. The water retention in the upper 300 mm, as well as the pH, effective cation exchange capacity (ECEC) of the substrate, base saturation, and concentrations of P and K, increased with increasing biochar concentration. Coconut biochar demonstrated potential for increasing water retention and improving nutrient retention in sandy soils.

Keywords: agroindustry residues; nutrient retention; pyrolyzed carbon; sandy soil; soil water retention.

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Introduction

The consumption of coconut water (*Cocos nucifera* L.) and pulp generates a significant amount of residues, represented by the husks. This material is discarded in landfills and dumping grounds, acting, similar to all organic matter, as a potential gas emitter; furthermore, such material contributes to a reduction of the useful life of these deposits, proliferation of the foci of disease-transmitting vectors, foul odors, possible contamination of soil and water bodies, and the inevitable destruction of the urban landscape. From this perspective, several works have aimed to use coconut fruit residues in agriculture as a substrate source for seedling production (Silva Junior, Sousa, Sousa, Lessa, & Silva, 2020; Putrino, Tedesco, Bodini, & Oliveira, 2020) and for the production of biochar (Liu & Balasubramanian, 2014).

Biochar is the solid material obtained from biomass pyrolyzed in an environment with little or no oxygen (Placido, Capareda, & Karthikeyan, 2016); this material is rich in carbon and applied to soil to improve its attributes (Lehmann & Stephen, 2015). In the tropical soils of Brazil, the maintenance and improvement of carbon (C) stocks are challenging since the decomposition of organic C by soil microorganisms is rapid and stimulated by high temperatures and soil moisture (Leite, Iwata, & Araújo, 2014). These characteristics are prevalent in sandy soils, characteristic of the new agricultural frontiers of the country.

Although sandy soils are favorable to mechanization, they also possess a high susceptibility to erosion, low natural fertility, a low surface area of particles, and a low water retention capacity (Uzoma et al., 2011). They also possess high porosity, with the predominance of macropores, which causes water to quickly seep into the soil, with little water retention on the surface in the upper horizons where the crop roots are.

Therefore, the adoption of adequate soil management practices is important to provide regular inputs of organic carbon (C) and to increase carbon stocks. This strategy improves the chemical, physical, and biological properties of soil in the long term (Guimarães et al., 2013). One of the practices used to increase soil organic matter is the use of biochar as a soil conditioner to improve water retention, intensify biological activity, increase carbon sequestration and, consequently, improve soil fertility and crop yield (Głąb, Palmowska,

Zaleski, & Gondek, 2016). However, biochar might present different properties depending on the source from which it was produced. Therefore, this work aimed to characterize the biochar produced from coconut fruit residues and to evaluate the benefits of its application in sandy soils in terms of the retention capacity for water and nutrients.

Material and methods

Soil Collection and Biochar Production

The sandy-textured soil (75.6% sand, 5.6% silt, and 18.8% clay), classified as a Quartzarenic Neosol (Santos et al., 2018), was collected in an area with native vegetation in the Chapada dos Guimarães plateau, Mato Grosso state, Brazil (15°25.707' S 55°46.746' W). The soil was dried and sieved (2 mm mesh size), and the chemical characterization was performed according to the method by (Teixeira, Donagemma, Fontana, & Teixeira, 2017) (Table 1).

Table 1. Chemical characterization of the soil.

pH Water	pH CaCl ₂	P mg dm ⁻³	K mg dm ⁻³	Ca mg dm ⁻³	Mg cmol _c dm ⁻³	Al cmol _c dm ⁻³	H g dm ⁻³	OM g dm ⁻³	SB cmol _c dm ⁻³	CEC cmol _c dm ⁻³	BS %
5.6	4.8	11	26	2	0.6	0	3.3	20.6	2.15	5.4	39.8

O.M. – Organic matter, SB – Sum of bases, CEC – Cation exchange capacity, BS – Base saturation.

The green coconut fruits were collected, crushed, and dried naturally. The coconut biochar was produced in slow pyrolysis in a handcrafted retort furnace, and the internal temperature was monitored with a type K thermocouple, reaching a maximum of 661.9°C. The biochar was crushed, ground and sieved through sieves with 2 and 0.2 mm mesh sizes, and the fraction used in the experiment was that retained between both sieves.

Biochar characterization

Coconut biochar was characterized in terms of its gravimetric yield, bulk density (Teixeira et al., 2017), pH, electrical conductivity, and effective cation exchange capacity (ECEC) (Ministério da Agricultura, Pecuária e Abastecimento [MAPA], 2014). The contents of carbon (C), hydrogen (H), and nitrogen (N) were determined in a CHN analyzer (Series 680, LECO Corporation World Headquarters, St. Joseph, MI, USA). The contents of macro- (P, K, Ca, Mg, and S) and micronutrients (Zn, Cu, Fe, Mn, and B) were determined according to the methodology described in the Manual of Chemical Analyses of Plants (Silva, 2009). Raman scattering measurements were performed using a spectrometer (Horiba, INC. model HR-800) coupled to a microscope (50X objective lens), through which a laser beam produced by a HeNe excitation source was fired and collected with a wavelength of 633 nm. The spectra obtained were analyzed to obtain the intensity, line width at half height, and wavenumber (or Raman shift). The thermal stability of the *in natura* coconut fruit and its biochar was determined by using a thermal analyzer (DTG-60H Shimadzu Corporation, Japan) in a compressed air atmosphere with a flow of 100 mL min⁻¹ and heating rate of 10°C min⁻¹ from ambient temperature to 700°C. Images were obtained using a scanning electron microscope (SEM), model SSX-550 (Shimadzu Corporation, Japan). Based on images, the diameter of pores was measured using Measure software (C Thing Software). The specific surface area of biochar was determined by the principle of adsorption of polar liquid (Brunauer, Emmett, & Teller, 1938).

Water Retention in Soil Columns

The evaluation of biochar water retention capacity was performed by using PVC cylinders (100 mm diameter and 500 mm length) (Eykelbosh, Johnson, & Couto, 2015). To avoid soil loss, a 0.25 mm mesh and a thin layer of fiberglass were placed at the bottom of the tubes.

The first 100 mm of each tube was filled with soil, after which the tubes were filled with soil containing biochar until reaching 400 mm. The treatments consisted of 0, 1, 2, 3, 4, and 5% biochar per weight of air-dried soil. For each treatment, four replications were performed. Samples from each treatment were collected to determine the initial soil moisture. The drainage hole in each PVC tube was sealed, and distilled water was added until reaching a water depth of 20 mm under the soil. After 48 hours of saturation, drainage of the gravitational water was performed with the aid of a vacuum pump (-30.0 kPa) coupled to the drainage hole of each column. After drainage, samples from the 0-100, 100-200, 200-300, and 300-400 mm layers were

removed for moisture content determination. The retained moisture was determined from the difference between the final saturated mass and initial mass and the dry mass.

Nutrient Retention in Soil Columns

Nutrient retention experiment followed the same procedure as that used for moisture retention evaluation. The experiment was performed in a completely randomized design, with four replications and six treatments: 0, 1, 2, 3, 4, and 5% biochar per weight of air-dried fine earth and fertilizer (2.198 g of P_2O_5 and 0.5495 g of KCl). The tubes were filled in such a manner that the first 100 mm from the bottom contained only fertilized soil. From this point to 300 mm above, the columns were filled with mixtures of soil and biochar specific to each treatment and supplemented with fertilizer. To each tube, 750 mL of distilled water was added to reach the field capacity of the soil. Daily, for eight days, 250 mL of distilled water was added (31.8303 mm irrigation depth) via dripping in the center of each column. After this period, soil in the upper 300 mm from each column was removed and homogenized, and a sample was removed for chemical analysis according to the methodology of Teixeira et al. (2017).

Statistical analysis

Effects of coconut biochar application on water and nutrient retention in the soil was analyzed through regression analysis. For the data that did not present a normal distribution, Monte Carlo analysis was performed. Statistical analyses were performed using the statistical software R commander (R Core Team, 2019).

Results and discussion

Biochar characteristics

The pyrolysis of coconut fruits resulted in a gravimetric yield of approximately 1/3 of the raw material weight ($36.28 \pm 1.33\%$) and a low bulk density ($220.00 \pm 0.01 \text{ kg m}^{-3}$). The electrical conductivity of biochar ($125.8 \pm 0.01 \mu\text{S m}^{-1}$) was high in relation to that of the *in natura* coconut fruit ($35.2 \pm 0.005 \mu\text{S m}^{-1}$) due to increase in the concentration of soluble salts during the pyrolysis process (Limwikran, Kheoruenromne, Suddhiprakarn, Prakongkep, & Gilkes, 2018). The biochar possessed an alkaline pH (9.03 ± 0.05), in contrast to acid pH of the *in natura* coconut (4.50 ± 0.01). The alkalinity of biochar is influenced by presence of organic functional groups (COOH and OH), carbonates (CaCO_3 and MgCO_3), and alkaline salts (Prakongkep, Gilkes, & Wiriyakitnateekul, 2015). The influence of organic functional groups on pH decreases with increases in pyrolysis temperature due to thermal decomposition, whereas the formation of carbonates and alkaline metals is favored by temperatures above 500°C (Yuan, Xu, & Zhang, 2011).

The ECEC was $9.53 \pm 0.57 \text{ cmol kg}^{-1}$, so this biochar had low negative charges, with an ECEC value similar to those of 1:1 phyllosilicates such as kaolinite. ECEC varies as a function of pyrolysis temperature (Jegajeevagan et al., 2016); high pyrolysis temperatures can volatilize or decompose acid functional groups (Song & Guo, 2012), resulting in fewer cation exchange sites.

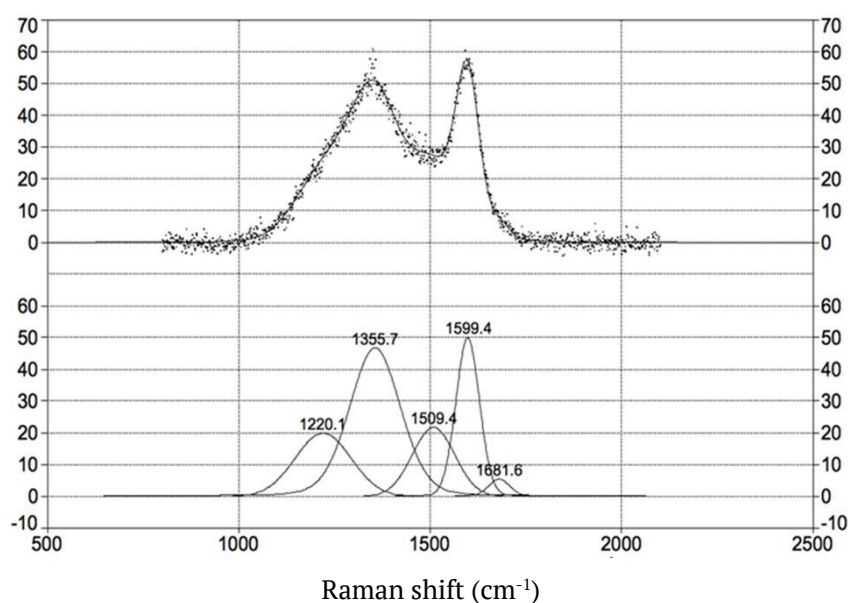
The C contents in coconut fruit and its biochar were 45.31 and 71.68% on a dry matter basis, respectively (Table 2); this increase in carbon content occurred due to the loss by volatilization of main biomass constituents (hydrogen, oxygen, and carbon) during pyrolysis (Lehmann & Joseph, 2009). The concentration of N for coconut fruits was 0.5%, and for biochar, it was 0.99% on a dry matter basis (Table 2). High N concentration occurred due to low pyrolysis temperature, given that an increase in temperature reduces the concentration of N in biochar (Zheng, Wang, Deng, Herbert, & Xing, 2013a).

The concentration of H in the biochar was lower than concentration in the *in natura* coconut fruit (Table 2). A reduction in H content after pyrolysis was also reported by (Liu, Quek, Kent Hoekman, & Balasubramanian, 2013), and this loss of H in the pyrolysis process occurs due to a reduction in hydroxyl functional groups (OH) and due to dehydration process (Zielińska, Oleszczuk, Charnas, Skubiszewska-Zięba, & Pasiieczna-Patkowska, 2015). Low H:C elemental ratio (Table 2) indicates development of aromatic structures in the biochar, given that lower the H:C ratio is, greater the development of aromatic structures in the biochar (López, Marco, Caballero, Laresgoiti, & Adrados, 2011; Wu et al., 2012), and greater its recalcitrance (Zheng et al., 2013b).

Table 2. Chemical characteristics of the *in natura* Coconut Fruit and Coconut Biochar.

	Units	<i>In natura</i> Coconut Fruit	Coconut Biochar
C	%	45.31 ± 0.04	71.68 ± 0.21
H	%	6.15 ± 0.02	2.87 ± 0.01
N	%	0.5 ± 0.02	0.99 ± 0.008
C:N	-	90.62 ± 4.09	72.40 ± 0.36
H:C	-	0.14 ± 0.00	0.04 ± 0.00
P	g kg ⁻¹	1.2 ± 0.00	3.33 ± 0.05
K	g kg ⁻¹	15.03 ± 0.05	8.46 ± 0.05
Ca	g kg ⁻¹	2.03 ± 0.11	6.16 ± 0.15
Mg	g kg ⁻¹	1.36 ± 0.05	3.30 ± 0.20
S	g kg ⁻¹	0.70 ± 0.00	1.76 ± 0.05
Zn	g kg ⁻¹	0.012 ± 0.36	0.068 ± 0.58
Cu	g kg ⁻¹	0.004 ± 0.32	0.012 ± 0.25
Fe	g kg ⁻¹	0.252 ± 1.73	1.102 ± 9.00
Mn	g kg ⁻¹	0.012 ± 1.00	0.04 ± 1.00
B	g kg ⁻¹	0.028 ± 0.78	0.049 ± 3.55

Figure 1 shows the behavior of the D-band (1,355.7 cm⁻¹) and G-band (1,599.4 cm⁻¹) positions for the coconut biochar sample. According to the degradation model (Ferrari & Robertson, 2000), the amorphization route results in a ratio between the integrated areas of the D and G bands ($I_D I_G^{-1}$) of 0.9360 and a growing G band shift with the transformation process of crystalline graphite into nanocrystalline graphite.

**Figure 1.** Raman spectrum of the coconut biochar with D (1,355.7 cm⁻¹) and G (1,599.4 cm⁻¹) bands.

The presence of D band is a signature of degree of amorphization, since this band is not related to the selection rules of the detectable vibrational modes through Raman scattering, according to structure of the graphite crystalline lattice (Tuinstra & Koenig, 1970). Formation of amorphous structures probably occurs due to decomposition of amorphous organic structures during the pyrolysis process (Mendonça, Cunha, Soares, Tristão, & Lago, 2017).

The thermogravimetric analysis indicated a higher thermal stability of biochar than coconut fruits since thermal decomposition of biochar began at higher temperatures. The first mass loss occurred at approximately 100°C due to water loss of the materials; however, for the biochar, this water loss was subtle (Figure 2). The greater thermal stability of biochar is demonstrated by temperatures at beginning of the second mass loss, 204 and 326°C for coconut fruits and biochar, respectively. At end of thermogravimetric analysis, the residual mass percentage was 8.76% higher for the biochar (12.43%) than coconut fruits (3.76%). This lower mass loss for biochar occurred due to its greater thermal stability. The thermogravimetric analysis, Raman spectroscopy, and H:C ratio studies evidenced the recalcitrance of coconut fruit biochar, a factor that confers to the biochar greater resistance to decomposition and a longer residence time in soil.

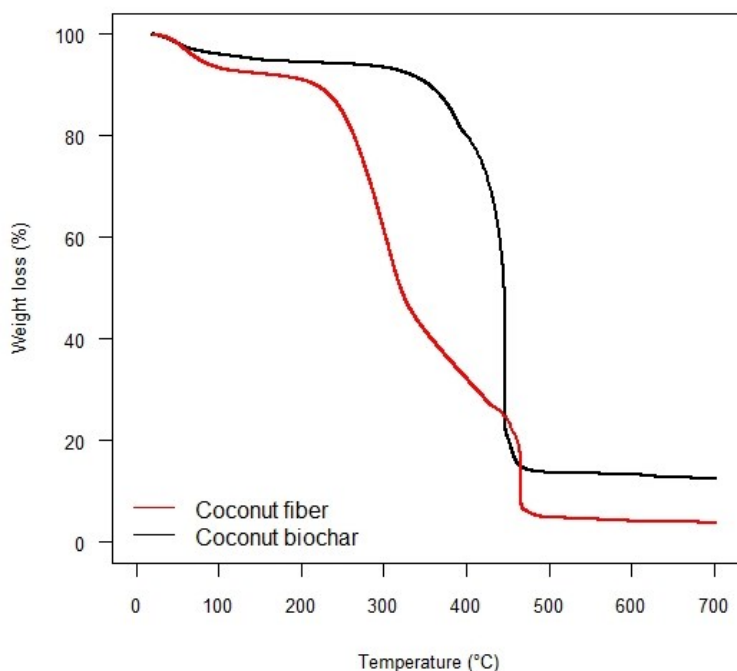


Figure 2. Thermogravimetric Analysis Curves of in natura coconut fruits and their biochar.

SEM analysis allowed visualization of the remaining porous structures in the biochar (Figure 3). Coconut biochar presented a pore diameter of $9.51 \pm 3.44 \mu\text{m}$ due to the resistance of cell structures, such as cell walls. This value is similar to that reported by Batista et al. (2018), in which the value is approximately $10 \mu\text{m}$. The thermal decomposition of cellulose and hemicellulose revealed the cell wall structure, which is mostly composed of lignin (Lee et al., 2013). The large specific surface area of biochar ($208.53 \pm 2.43 \text{ m}^2 \text{ g}^{-1}$), evidenced the biochar potential for nutrients and water retention. The porous structure and specific surface area reinforce the potential of biochar for retention of nutrients, solutes, organic compounds, and gases (Lima et al., 2018).

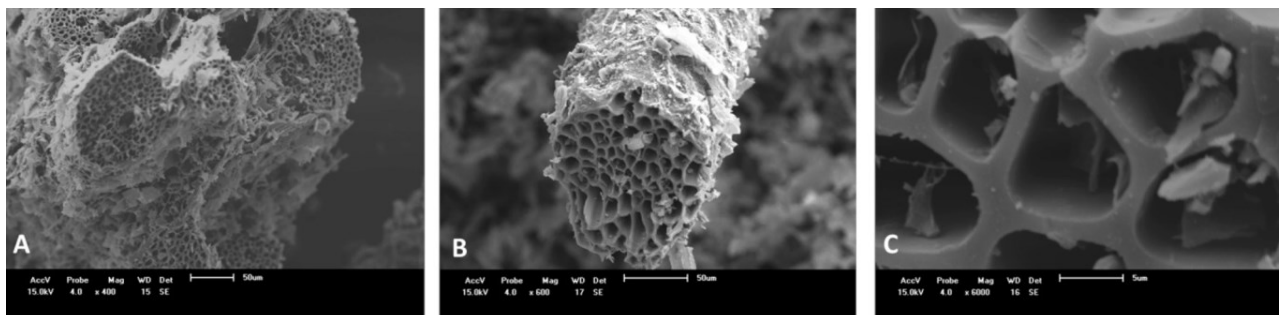


Figure 3. Scanning Electron Microscopy Images of coconut biochar. (A, B, and C) Coconut biochar at magnitudes of 400X, 600X, and 6,000X, respectively.

Water Retention Capacity of Soil with Biochar

In all treatments, soil moisture increased with depth. The moisture was reduced, however, in treatments with biochar at a depth of 300–400 mm, a strip in which there was no biochar incorporation (Figure 4). Water retention was also higher with higher biochar contents at all depths of samples in which the material was incorporated. This result means that the efficiency of water retention is dependent on incorporation of biochar into the soil.

The ability of biochar to retain water is strongly related to a large surface area and porosity of the biochar (Suliman et al., 2017), characteristics that are corroborated by analyses of the specific surface area and diameter of pores in coconut biochar. These characteristics reveal the utilization potential of coconut biochar to increase water retention in soil, especially in soils that possess low water retention capacity, such as in the case of Quartzarenic Neosol, which possesses a predominance of macropores and mesopores ($>50 \mu\text{m}$ and $30\text{--}50 \mu\text{m}$, respectively) and low amounts of organic matter and clay.

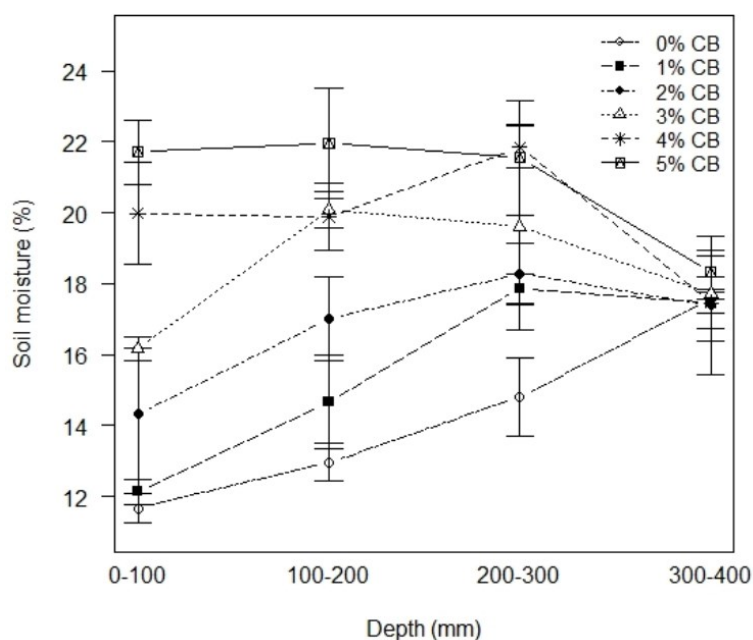


Figure 4. Soil moisture in the different treatments with coconut biochar (CB) versus soil depth.

The application of biochar, in addition to increasing organic matter, favors moisture conservation and can be a useful tool in the management of sandy soils. The maintenance of soil moisture is fundamental for the establishment of crops and ensures that plants suffer less stress in critical periods of hydric deficit (Cha et al., 2016). The application of biochar in sandy soils reduces hydric stress and increases the photosynthetic activity of plants (Tan et al., 2017). Furthermore, the effects of biochar on soil water retention are similar to those provided by humus (Bruun, Petersen, Hansen, Holm, & Hauggaard-Nielsen, 2014).

Changes in the Chemical Properties of the Soil and Nutrient Retention

The addition of coconut biochar to the sandy soil promoted alterations in chemical characteristics that are essential to improve soil fertility. Characteristics such as soil pH, ECEC, and base saturation increased (Monte Carlo, $p = 0.001$, randomizations: 1000) (Figure 5). The rise in soil pH is associated with the presence of hydroxyls (OH^-) and bicarbonate (HCO_3^-) (Norström, Bylund, Vestin, & Lundström, 2012). The increases in ECEC and base saturation occur mainly due to biochar being a porous material and consequently possessing a large surface area that can be oxidized and increase ECEC (Tan et al., 2017) and due to the presence of negative charges in the carboxylic groups of the biochar (Chintala, Subramanian, Fortuna, & Schumacher, 2016).

Treatments with addition of biochar presented greater retention of phosphorus and potassium (Figure 5), also suggesting that any biochar concentration is better than the control for this type of soil (Monte Carlo, P and K, $p = 0.001$, randomizations: 1000). Increases in the concentrations of phosphorus and potassium in the soil with the addition of biochar occurred due to pH increase (5.07 for the control and 6.05 for the treatment with 5% biochar) and ECEC increase through the increase in C content. Management systems and land use approaches that favor the preservation of soil organic matter (MOS) contribute to a higher availability of P in the soil, mainly related to the increase in P_o (organic phosphorus), reducing the effects of the inorganic adsorption of phosphorus in the mineral phase of the soil (Cunha, Gama-Rodrigues, Costa, & Velloso, 2007).

The availability of Ca and Mg did not change with the addition of biochar (Monte Carlo, Ca – P = 0.004, and Mg – P = 0.001, randomizations: 1000) (Figure 5). Although the concentrations of Ca and Mg increased with the pyrolysis process (Table 2), these changes were not enough to increase their concentrations in the soil. The chemical improvements observed are important for the management of sandy soils since they reduce the precipitation of phosphorus with Al and Fe and decrease the losses of Ca, Mg, and K through lixiviation, decreasing the risks for agriculture in such areas.

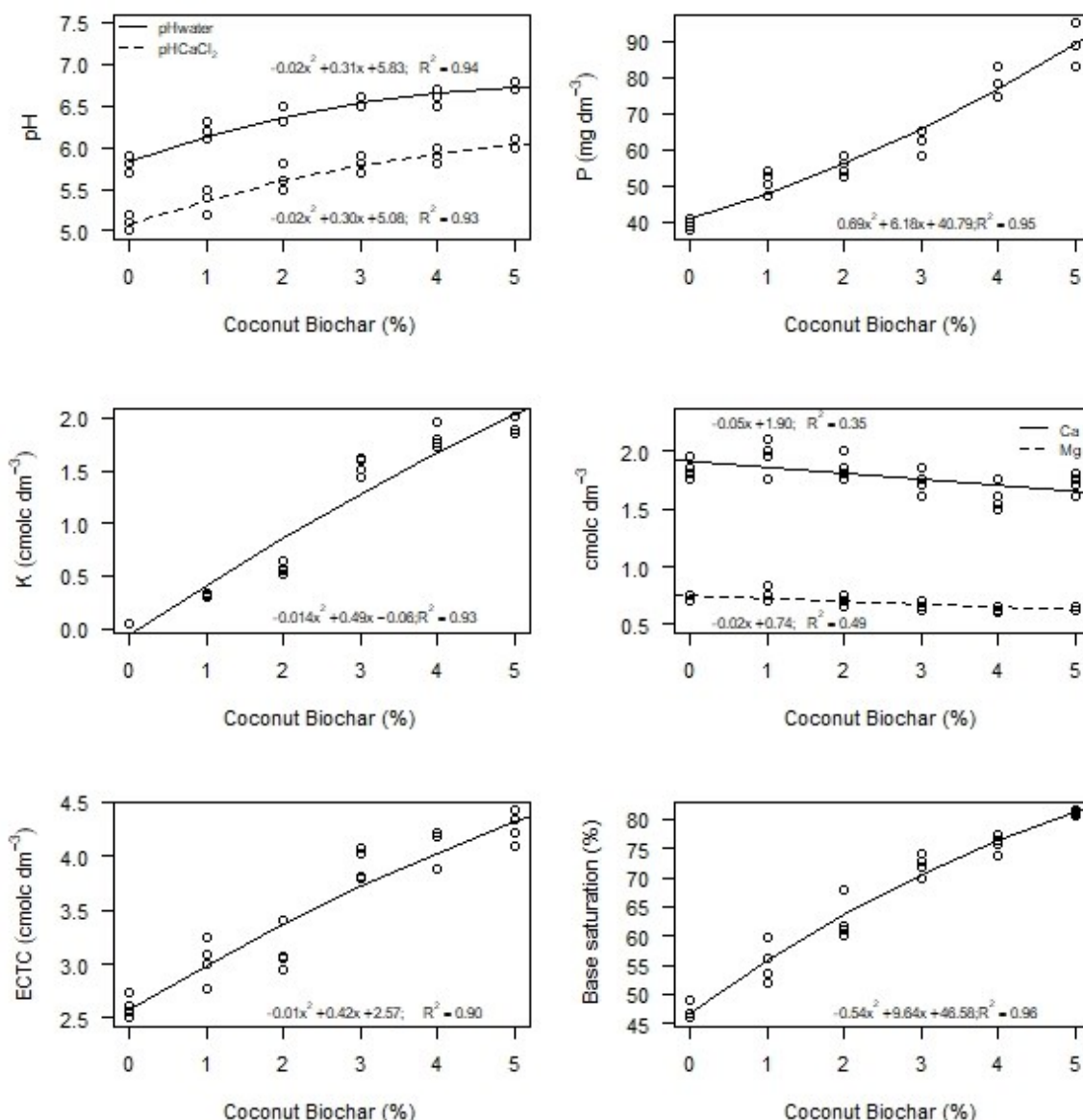


Figure 5. Chemical attributes of the sandy soil with coconut biochar and fertilization after 8 days of incubation and drainage. Effective cation exchange capacity (ECEC) = K + Ca + Mg + Al.

Conclusion

The addition of coconut biochar to the sandy soil increased the water retention capacity at all sampled depths. Therefore, the application of biochar might be a useful tool in the management of sandy soils to reduce stress of plants in critical periods of water restriction.

The application of coconut biochar raised the pH, ECEC, and BS, as well as the retention of phosphorus and potassium in sandy soil, thus promoting improvements in fertility and cropping possibility in areas with similar soil characteristics.

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