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# Effect of wood sawdust-derived biochar as a substrate component on leachate water quality

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## *ABSTRACT*

This study investigated the effect of biochar addition (14% w/w) on the concentration of nutrient ions present in the leachate from a commercial green roof substrate after contact with rainwater. Biochar sample was produced from wood sawdust at 450 °C via slow pyrolysis. The sawdust biochar was characterized by physico-chemical and hydraluic prosperties and techniques including X-ray fluorescence, Fourier transform infrared spectroscopy, X-ray diffraction, Raman and differential thermal analysis. The physical and chemical properties of green roof substrate were also determined. The biochar effectively reduced the total amount of nitrate, sulfate, and phosphate in the leachates relative to the substrate alone but did not show a significant effect on ammonium leaching. The results indicated that wood sawdust-biochar has appropriate characteristics to be applied as a component of substrates, as it has a porous structure and adsorption capacity, as well as adequate physical-hydric properties. In addition, the management of biochar obtained from agricultural waste can contribute to the achievement of the Sustainable Development Goals when used in sustainable alternatives such as green roofing.

**Contribution/Originality:** This work provides the main physicochemical characteristics of biochar derived from wood sawdust. This study also quantify the effect of wood sawdust-biochar application as a suitable component of green roof substrate to reduce the nutrient leaching.

## 1. INTRODUCTION

In Brazil, according to a trend recorded by the demographic census of the Brazilian Institute of Geography and Statistics, the proportion of persons living in apartments is growing. Changes in municipal legislation and housing financialization process has driven verticalization in large urban centers, such as São Paulo and Porto Alegre. Three Brazilian cities have more than half of their population living in apartments (IBGE, 2002).

Verticalization without planning has caused several significant negative impacts on the environment. The replacement of green areas by buildings and surfaces composed of concrete and asphalt results in an increase in the local temperature, an increase in the flow and volume of rainwater that is runoff superficially and floods. Financial and psychological consequences for the population can also be included (Rashed, 2023; Vujovic, Haddad, Karaky, Sebaibi, & Boutouil, 2021).

Green roof was identified by researchers and public policies as important instrument in the search for sustainability and in the mitigation of negative impacts caused by urbanization on the environment (Mihalakakou et al., 2023; Perivoliotis et al., 2023). It has been adopted for more than thirty years in countries such as Germany, Switzerland, Japan and Canada. There is a proposed law in the Federal Chamber, from 2011, which aims to encourage urban buildings to adopt the green roof on at least 65% of their coverage in Brazil (Dutra & Silva, 2020).

The addition of biochar as a substrate component can enhance green roof performance in several aspects, including the reducing the loss of nutrients in runoff, especially of nitrogen and phosphorus (Beck, Johnson, & Spolek, 2011; Buffam & Boccelli, 2016; CAO, Farrell, Kristiansen, & Rayner, 2014; Piscitelli, Rivier, Mondelli, Miano, & Joner, 2018; Tan & Wang, 2023). Furthermore, biochar production from wastes addresses multiple Sustainable Development Goals challenge, especially contribution to SDG12 (production) (Amalina, Abd Razak, Krishnan, Sulaiman, et al., 2022; Amalina, Abd Razak, Krishnan, Zularisam, & Nasrullah, 2022; Olugbenga, Adeleye, Oladipupo, Adeleye, & John, 2024).

The main uses of biochar in Brazil between 2003 and 2021 is reported by Arias, da Silva, Soares, and Forti (2023). Plant-based materials are the most employed for biochar production in Brazil, mainly of wood origin.

The timber industry is an important source of revenue and employment in Brazil and, especially, for the Amazon region. The timber sector represents the third most economically relevant rural activity for the region, behind only industrial-scale mining and agriculture (Lentini, Sobral, & PLanello, 2019). The municipality of Sinop, located in the northern region of Mato Grosso (Eastern Amazon), is among the five largest in the state and is part of the main timber hub, in which 20% of the state's timber industries are concentrated with 161 establishments related to logging (SFB- IMAZON, 2010; Zaque, Melo, Stangerlin, & Serenine Junior, 2019).

Wood processing industries generate lignocellulosic residues that come from sawn wood and are classified into chips, ribs, shavings, dust and sawdust. It is estimated that at least 35.5 tons of wood waste are generated per year. The amount of waste produced for some species of tropical woods can be higher than 50%, which justifies the use of these residues as feedstocks produce biochar (Fontes, 1994; Garcia, Manfio, Sansígolo, & Magalhães, 2012).

The objective of the current study was a) to characterize the biochar derived from wood residue, b) to characterize substrate produced for planting vegetation on slabs in Brazil, c) to evaluate the reduction in nutrient leaching in the biochar-substrate composite after contact with rainwater.

## 2. MATERIALS AND METHODS

### *2.1. Materials*

All solutions were prepared using ultrapure water and analytical grade reagents unless otherwise stated. Biochar (BC) was produced from sawdust of tropical wood native species, obtained from sawmills located in the city of Sinop, state of Mato Grosso, Brazil. To obtain the BC, sawdust was processed in a slow pyrolysis reactor (vertical furnace), with a 40-minute residence time, at 450°C. Commercial substrate formulated for planting vegetation on slabs was used in the study.

### *2.2. Characterization of Materials*

#### *2.2.1. Biochar Characterization*

Proximate analysis (moisture content, volatile matter, fixed carbon and ash content) was determined according to EBC recommended methods (EBC European Biochar Certificate, 2015).

Dry bulk density, water holding capacity, air-filled porosity and saturated bulk density were determined by methods described in literature (CAO et al., 2014; Duong, Nguyen, Nguyen, & Tan, 2017; EBC European Biochar Certificate, 2015).

Electrical conductivity and pH were measured in a sample/deionized water ratio of 1:10 (w/v) (Singh, Dolk, Shen, & Camps-Arbestain, 2017).

For the cation exchange capacity (CEC), BC was saturated with sodium acetate solution and ammonium acetate solution. $Na^+$ concentration of the resulting solution was determined by Inductively Coupled Plasma Optical Emission Spectroscopy- ICP-OES (Spectrometer – BRAND SPECTRO ARCOS).

For the Point of Zero Charge (PCZ) determination, 0.1 g of BC was mixed with 50.0 mL of 0.1 mol $L^{-1}$ $NaNO_3$ under different conditions of initial pH ($pH_i$), adjusted from 2.0 to 12.0 by the addition of HCl or NaOH solution. The final pH values ($pH_f$) were recorded in the remaining suspensions after 24 h contact time at 120 rpm. The difference between $pH_i$ and $pH_f$ ($\Delta pH$) was plotted against $pH_i$ values and the pH at PZC corresponded to the point of intersection in the resulting curve.

Mineralogical composition was determined by X-ray diffraction analyses (XRD) with an automated Rigaku Miniflex 2 diffractometer with Cu anode using Co Kα radiation at 40 kV and 20 mA over the range (2θ) of 5–80° with a scan time of 0.5 °/min.

Chemical composition was determined by X-ray fluorescence (XRF) spectrometry in Malvern Panalytical, model Zetium.

The Perkin–Elmer Spectrum 400 FT-IR/FT-NIR spectrometer (Perkin–Elmer, Waltham, MA, USA) with the endurance single bounce diamond, attenuated total reflection (ATR) cell was used for spectra registration. The spectra 4000–650 $cm^{-1}$ were recorded. All materials were dried and ground before the measurements.

The mesoporosity of the biochar was determined from the adsorption of molecules from the methylene blue dye solution (Stavropoulos & Zabaniotou, 2005).

The characterization of biochar by Raman spectroscopy was carried out in the Micro Raman equipment WITEC Alpha 300R. This system uses a green $Ar^+$ laser (532 nm), power of 5 mW, objective lens with magnification of 50x and numerical aperture of 0.7 and integration time of 60 s.

Thermal analyses were carried out using a Netzsch Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) 404F3 equipment, utilizing synthetic air and a heating rate of 10 °C/min up to a temperature of 900 °C.

The Boehm's titration method was used for determination of the functional acidic and basic oxygen surface groups (Boehm, 1994; Boehm, 2002).

Some values are expressed as the mean of triplicate and the respective standard deviation.

### *2.2.2. Substrate Characterization*

Methods of the European Standardization Committee (CEN – Comité Européen de Normalisation) were used in the following determinations: electrical conductivity and pH (CEN-DIN EN 13037; CEN-DIN EN 13038); organic matter, ash content, and particle density (CEN-DIN EN 13039); dry density and total porosity (CEN-DIN EN 13041). Moisture was determined according to Normative Instructions No. 17.

CEC was determined by the method described for the BC. To determine the macro (P, K, Ca and Mg) and micronutrients (Zn, Cu, Fe, Mn and B) contents, 100 mL of substrate was mixed 200 mL of deionized water. The suspensions were stirred for 20 min at 120 rpm at room temperature. After this period, the samples were filtered and the filtrate was collected for determination in the ICP-OES (Abreu, Abreu, Sarzi, & Padua Junior, 2007).

#### *2.2.3. Determination of Concentration of Ions in the Leachate of Substrate*

The first sample consisted of simulated acid rain (SAR) prepared by mixing of 2 x $10^{-5}$ mol $L^{-1}$ HCl with $10^{-5}$ mol $L^{-1}$ $H_2SO_4$ at a 1:1 ratio (v/v). A second sample was prepared in the same way with the addition of 0.02 g of each of the following salts: $NH_4Cl$, $Na_2SO_4$, $NaNO_3$ and $Na_6[PO_3]_6$ in the 1 L volumetric flask. The final concentration of each ion was 20 mg $L^{-1}$.

Two types of tests were carried out in batch. In the first, 1 g of substrate was added to 100 mL of SAR, which was considered as a "blank sample" (S). A second sample consisted of substrate with 14% of biochar (% in mass) and was placed in contact with 100 mL of SAR, which was named SB. In the second test, 1 g of substrate (SA) and 1 g of substrate with 14% of biochar (SBA) were placed with 100 mL of SAR containing ions. The samples were stirred for 24 h and after were filtered. The concentrations of $NH_4^+$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$ were determined in the leachate of substrate samples by ionic chromatography (ammonium cation on the DX120 ion chromatograph and anion analysis on the ICS-2100 ion chromatograph). The analyses were performed in triplicate and results are expressed as mean ± standard deviation.

## 3. RESULTS AND DISCUSSION

### *3.1. Characterization of Biochar*

#### *3.1.1. Chemical Composition*

Table 1 presents the major inorganic elements in biochar identified by XRF. It can be observed that the major constituents are $SiO_2$, $Al_2O_3$, and $Fe_2O_3$. The major inorganic elements identified in BC came from the plant biomass that are present naturally (Saleem et al., 2020).

**Table 1.** Chemical composition of the major elements in BC.

| Oxides | Value |
|---|---|
| $SiO_2$ (wt. %) | 5.20 |
| $Al_2O_3$ (wt. %) | 3.05 |
| $Fe_2O_3$ (wt. %) | 1.34 |
| CaO (wt. %) | 0.38 |
| $TiO_2$ (wt. %) | 0.15 |
| $Na_2O$ (wt. %) | 0.08 |
| $K_2O$ (wt. %) | 0.07 |
| MgO (wt. %) | 0.07 |
| $P_2O_5$ (wt. %) | 0.03 |
| $ZrO_2$ (wt. %) | 0.01 |
| Others (wt. %) | $< 0.01$ |
| Loss of ignition (%) | 89.6 |

#### *3.1.2. Proximate and Ultimate Analysis*

Proximate analysis is a measure of total biomass components in terms of moisture content, ash content, volatile solids and fixed carbon of the solid fuel (Qian et al., 2013). The proximate analysis of biochar are shown in Table 2.

A viable adsorbent material as biochar is usually moisture free or contains very little moisture. The lower the moisture the more viable the adsorbents. The observed value is similar to that of biochar produced from pine sawdust (Askeland, Clarke, & Paz-Ferreiro, 2019).

From the results of proximate analysis, the moisture content is within the range for Indian Standard Institution (ISI) standards for adsorbents of 1%–6% (Yahya, Muhammed, Obayomi, Olugbenga, & Abdullahi, 2020).

BC had ash and volatile matter contents relatively low. Ash content is attributable to the different concentrations of ash-forming elements, such as calcium carbonate, potassium silicates, iron and other metals (Lewandowski & Kicherer, 1997).

**Table 2.** Proximate and ultimate analysis of biochar.

| Analysis | Value |
|---|---|
| Proximate analysis | |
| Moisture (%) | 1.003 ± 0.0508 |
| Ash content (%) | 14.0 ± 0.655 |
| Volatile matter (%) | 28.4 ± 1.41 |
| Fixed carbon (%) | 56.5 ± 2.05 |
| Ultimate analysis | |
| C (%) | 66.0 ± 0.078 |
| H (%) | 3.44 ± 0.156 |
| N (%) | 0.855 ± 0.318 |
| O (%) | 29.7 ± 0.085 |
| C/N | 90.0 |
| H/C | 0.625 |
| O/C | 0.336 |

In contrast to ash content, volatile solids retention was primarily affected by the pyrolysis temperature. Biomass typically consists of three components: hemicellulose, cellulose and lignin (Yang et al., 2006). Generally, hemicellulose is the most volatile, cellulose is less volatile, while lignin is the most difficult to volatilize.

Fixed carbon is an important information of biomass quality since it is the most resistant portion that remains in biochar after pyrolysis. It is organized in aromatic chains and is inversely related to volatile materials and ash content (Amonette & Joseph, 2009). The fixed carbon of BC has a high value of 56.5%. The higher the fixed carbon value, the better the quality of the adsorbent becomes. This is because the amount of fixed carbon acts as a main generator of heat combustion.

Elemental analysis and molar ratios based on elemental analysis of biochars are shown in Table 2. The low levels of hydrogen and oxygen in biochar are associated with possible dehydration or dehydrogenation reactions that are responsible for the elimination of hydroxyl groups (OH) and decarboxylation reactions, with the consequent elimination of oxygen.

The proposed biochar certification for European countries and described in the European Biochar Certificate – EBC (EBC European Biochar Certificate, 2015) recommends carbon contents ≥ 50%. The standards proposed by the IBI International Biochar Initiative (2015) classify biochars into classes, with class 2, biochars with carbon contents between ≥ 30% to < 60%, and class 1 with contents ≥ 60%. Following these criteria, the biochar in this study would be considered class 1 by the IBI and would be certified by the EBC.

BC atomic ratios data have been used to estimate the aromaticity and stability (H/C) and polarity (O/C) of biochars. The variation of these ratios are characteristics resulting from the process of removal of polar surface functional groups and formation of aromatic structures with greater or lesser degree of carbonization. A high H/C ratio indicates greater aliphaticity and a lower proportion of aromatic rings. Likewise, a high O/C ratio reflects an increase in the aliphaticity of organic matter (Silva & Mendonça, 2007).

Thermochemically processed materials that have an H/C value greater than 0.7 can be thermochemically "altered" but are not considered thermochemically "converted" (IBI International Biochar Initiative, 2015) preserving part of their original organic residues such as $CH_2$ and fatty acids, lignin (aromatic nucleus) and cellulose (polar fractions) (Chen, Zhou, & Zhu, 2008). As can be seen in Table 2, the BC in the present study presented a H/C value within the required standard (< 0.7).

According to Spokas (2010) biochars with an O/C molar ratio of less than 0.2 are typically the most stable, having an estimated half-life of more than 1000 years; O/C molar ratio of 0.2-0.6 has an intermediate half-life (100-1000 years); and, biochar with an O/C ratio greater than 0.6 has a half-life in the order of 100 years. The BC in the present study is characterized by an intermediate half-life (Table 2).

Pyrolysis of biomass from residues (eg wood or straw), which has large C/N ratios, will result in biochars also with large C/N ratios. Exceptions are biochars produced from food waste and manure that have narrow C/N ratios. Furthermore, N retention during biochar production can also be highly variable, which further contributes to diverse C/N ratios in the resulting biochars (Enders, Hanley, Whitman, Joseph, & Lehmann, 2012). Depending on the raw material and pyrolysis conditions, biochar can have a C/N ratio ranging from 6.5 to 640 (Bonanomi et al., 2017).

Elemental analysis and molar ratios were examined for several samples of biochar originating from wood using different pyrolysis temperatures The analyses confirmed that an increase in pyrolysis temperature causes an increase in the concentration of carbon, whereas there is a reciprocal decrease in the levels of oxygen and hydrogen (Maia, 2011).

### *3.1.3. Physical-Chemical and Hydraulic Properties*

Physical and chemical characteristics and hydraulic property (water holding capacity) of the biochar are shown in Table 3. The dry bulk density of biochars derived from different types of wood processed in different types of traditional ovens ranged from 0.30 kg/L to 0.43 kg/L (Pastor-Villegas, Pastor-Valle, Rodríguez, & García, 2006). The value of the biochar in the present study is close to the minimum value of this range.

The water holding capacity of biochars could improve soil water retention capacity, reduce water leaching, and increase water availability in the root zone of crops. The ability of biochar to retain water is strongly related to the surface area and its porosity, therefore, the smaller the BC particles, the greater the water retention capacity.

Biochars with low ash content, such as those produced using woody feedstocks, generally have lower pH values than biochars with higher ash content (Singh et al., 2017). The biochar sample in the present study has a low ash content and the low pH value indicates that acidic functional groups were not degraded during pyrolysis. Furthermore, cellulose and hemicelluloses decompose around 200–300 ºC, yielding organic acids and phenolic substances that lower the pH of the biochar (Yu, Zhang, Li, & Chen, 2014).

**Table 3.** Physical-chemical and hydraulic properties of biochar.

| Property | Value |
|---|---|
| Dry bulk density (kg/L) | 0.2622 ± 0.0076 |
| Water holding capacity (%) | 317.9 ± 48.54 |
| Air-filled porosity (%) | 10 ± 0.35 |
| Saturated bulk density (%) | 2.84 ± 0.02 |
| pH | 4.6 ± 0.1 |
| Conductivity (µS $cm^{-1}$) | 18.8 ± 0.350 |
| CEC (meq 100 $g^{-1}$) | 3.08 ± 0.050 |
| SSA ($m^2$ $g^{-1}$) | 4.94 ± 0.182 |
| pHpzc | 5.2 ± 0.2 |

The relatively low conductivity value is also related to the low ash content, which probably decreases the dissolution of water-soluble salts. Biochar presented a CEC value close to that of another biochar obtained with pyrolysed sawdust at 350 ºC (Santos, Lustosa Filho, Vergütz, & Melo, 2019). CEC is influenced by the groups carboxylic and phenolic compounds present in the biomass that originated the biochar.

The result obtained for specific surface area (SSA) present a value similar to that of biochar derived from Eucalyptus sawdust dust pyrolysed at 500°C (4.90 $m^2$/g) and close to the value of biochar from wood (SSA of 4.46 $m^2$/g) obtained at 450 ºC with 30 min residence time (Speratti, Johnson, Martins Sousa, Nunes Torres, & Guimarães Couto, 2017; Van Limbergen et al., 2022).

The point of zero charge (pHpzc) determines the value of pH at which the net surface charge on the bicohar is equals to zero. Biochar had a $pH_{pzc}$ value equal to 5.2 (Table 3). The solution pH was lower than the $pH_{pzc}$, indicating that biochar presents a positive surface charge, thereby attracting negatively charged ions.

*3.1.4. Mineralogical Composition*

The X-ray diffractogram of biochar shows a typical band of predominantly amorphous material with a maximum around $2\theta = 20^{o}$ (Figure 1). The occurrence of this band indicates that the cellulose, which is the only crystalline material present in the sawdust was totally destroyed in the pyrolysis process (Chowdhury, Karim, Ashraf, & Khalid, 2016).

Hemicellulose and lignin, which are also part of the composition of sawdust, are both amorphous in nature. The pronounced peak at $2\theta = 26.75^{o}$ is attributed to the presence of $SiO_2$. Silicon is a mineral element that, after being absorbed by plants, polymerizes and accumulates in the cell wall of the epidermis, acting to increase their defenses (Gomes, Moraes, Santos, & Goussain, 2005).

The peak at $\sim 2\theta = 55^{o}$ is attributed to impurities present in the sample or in the pyrolysis process.

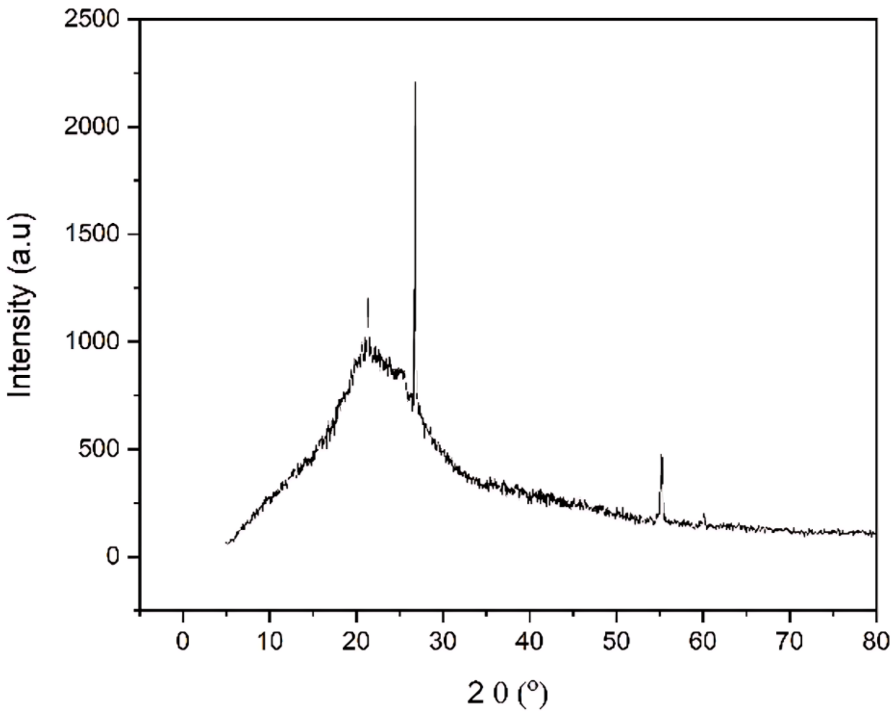


**Figure 1.** X-ray diffractogram of biochar.

*3.1.5. Fourier transform infrared spectroscopy and Raman Spectrum Analysis*

Sawdust is characterized by bands in the Fourier transform infrared spectroscopy (FTIR) spectra of functional groups present in oxygenated hydrocarbons, as it is a material dominated by the carbohydrate structure of cellulose and hemicellulose. The main bands are described in a previous studies (Bajpai, Bajpai, & Rai, 2012; Ghani, 2014). After pyrolysis, the spectra became more simplified which might associate with rupture of various functional groups and progressive carbonization (Shaaban, Se, Mitan, & Dimin, 2013; Wang, Cao, & Wang, 2009).

The only relevant band observed in FTIR spectrum (Figure 2a) of BC is at 1588 $cm^{-1}$ and can be related to functional groups with double bonds with oxygen (C=O), such as carboxylates (carboxylic acids) and carbonyls (conjugated ketones and quinones), normally found in the range of 1600-1750 $cm^{-1}$. This band may also be associated with the presence of sp2 carbon in the C=C bond, linked to the structure of the aromatic ring, referring to the phenolic groups (Zhao et al., 2018).

The Raman spectra of the biochar in the wavelength region of 500–2,000 are exhibited in Figure 2b. The biochar showed two peaks at 1363 and 1588 $cm^{-1}$ referring to the D and G band, respectively. The broad band at

2670 cm⁻¹, whose suggested name is 2D, is attributed to a D-band harmonic, the C−C bond between aromatic rings, or a system with large aromatic rings (Xu et al., 2020).

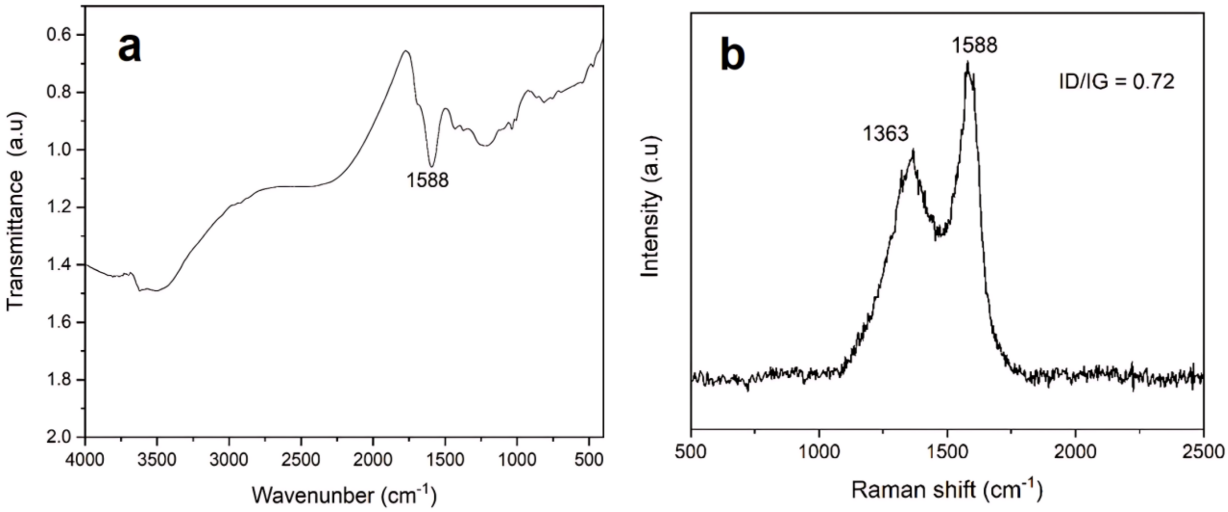


**Figure 2.** FTIR (a) and Raman (b) spectra of biochar.

### *3.1.6. Differential Thermal Analysis*

As seen from Figure 3, the main feature of the differential thermal analysis was a tendency to form a minimum. Minima are consequences of endothermic processes, in which heat is absorbed by the analyte. Endothermic physical processes include melting, vaporization, absorption, desorption, adsorption, and crystallization. Endothermic reactions also include dehydration, reduction in a gaseous atmosphere, and decomposition. The endothermic reaction could be attributable to the decomposition for the biochar of the present study. A similar behavior was observed in biochar produced from Pinus sp. and Eucalyptus sp (Alho, 2012).

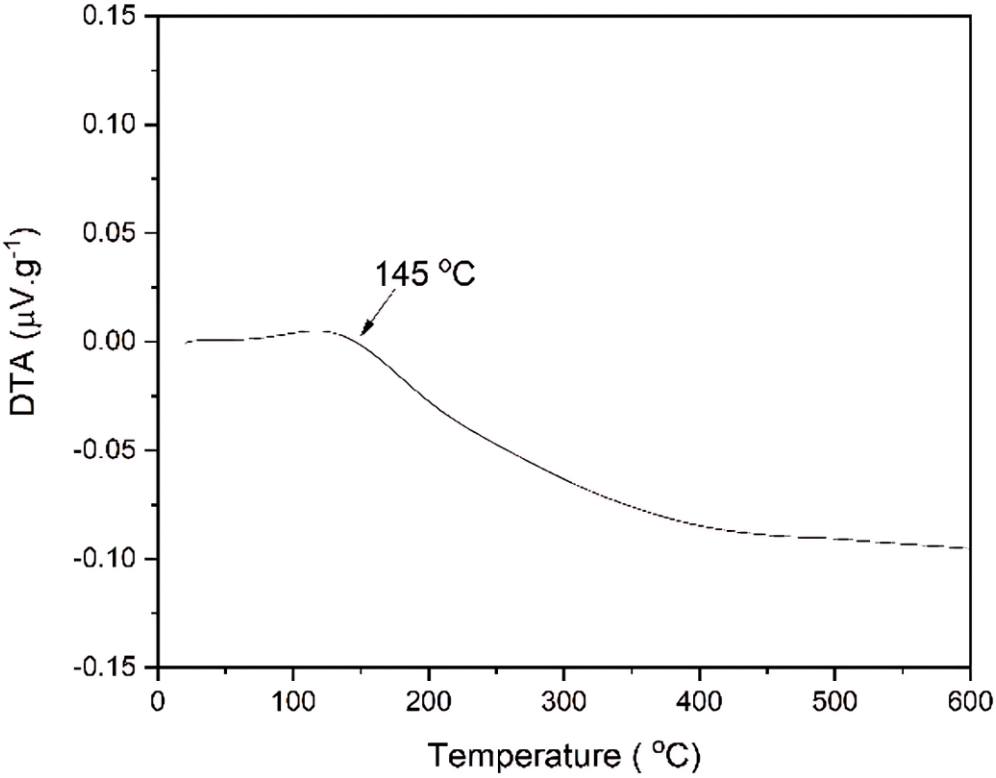


**Figure 3.** Differential thermal analysis curve of biochar.

### *3.1.7. Bohen Titration*

The Boehm's titration method was used to characterize the chemical nature of biochars surface (Boehm, 1994). The content of the functional groups determined on the surface of biochar are presented in Table 4. The obtained results indicate the predominance of basic sites on the surface of the tested biochar. The acidic sites are especially carboxylic type.

**Table 4.** Concentration of acidic and basic active sites on surface of BC obtained by Boehm method.

| Functional surface group | mmol $g^{-1}$ |
|---|---|
| Carboxylic | 6.2 |
| Lactonic | 0.10 |
| Phenolic | 0.90 |
| Surface basicity | 10.3 |

### *3.2. Characterization of Substrate*

Table 5 show the physical and chemical properties of substrate. The moisture content of a substrate affects its density and porosity. It is a very variable value, as a substrate is usually the result of mixing two or more materials and the mixing proportions are as diverse as possible. Among the physical characteristics, it is one of the most important, as there must be enough pore space to allow the diffusion of oxygen and supply of water to the roots (Fermino, 2003; Souza, Lopez, & Fontes, 1995).

Products with moisture contents between 30 and 50% are usually ideal for handling, surface applications, and soil incorporation. The result obtained in this study (Table 5) is within the range of humidity values allowed by Brazilian legislation (Abreu, Dias, Abreu, & Gonzalez, 2012).

**Table 5.** Some physico-chemical analysis of the substrate.

| Parameters | Value |
|---|---|
| Moisture (%) | 44.3 ± 0.250 |
| Organic matter (%) | 38.7 ± 4.11 |
| Ash content (%) | 61.3 ± 4.11 |
| Particle density (g/cm$^3$) | 1.75 ± 0.067 |
| Total porosity (α) | 82.4 ± 3.06 |
| Dry density (g/cm$^3$) | 0.2868 ± 0.00795 |
| pH | 7.17 ± 0.047 |
| Conductivity (dS/cm) | 0.6385 ± 0.0055 |
| Cation exchange capacity (meq/g) | 0.982 ± 0.064 |

Organic matter can greatly improve the chemical and physical properties of the substrate necessary for good plant growth. This is because it provides plant nutrients, improves porosity and water holding capacity. Furthermore, makes the substrate lighter and easier to transport and increases substrate stability.

The ash content is an important parameter indicative of substrate decomposition and mineralization, as it represents the remaining minerals when moisture and organic matter are removed from a sample (Zorzeto, Dechen, Abreu, & Fernandes Junior, 2014). The percentage of ash in the sample can be subtracted from 100 to provide an estimate of percent organic matter. It means that the higher the organic matter concentration, the smaller the amount of ash present and vice versa. The high ash content (~ 61%) indicates high mineral content in the sample.

Particle density ($D_p$) takes into account the mass and volume occupied by the solid particles only. It excludes the volume occupied by air and water. The particle density of substrate derived from minerals containing 70% or more silica and oxygen, is approximately 2.65 g/cm$^3$, the density of quartz. The presence of organic matter reduces the overall particle density value and particle density of organic materials is 1.45 g/cm$^3$ (Boodt & Verdonck, 1972; Martínez, 2002; Rowell, 1994; Zorzeto et al., 2014).

Porosity is another important physical property that affects the aeration, drainage and water holding capacity of a substrate. The total porosity value was 82.4%, demonstrating that the substrate presents a value very close to the optimal point, since an ideal substrate can present porosity above 85% of the volume (Boodt & Verdonck, 1972; Carrijo, Liz, & Makishima, 2002; Verdonck & Gabriels, 1988).

Apparent density or dry of a substrate is defined as the relationship between the mass and volume of the material, including pores and water. Its value is inversely proportional to the porosity, and when the density increases, a restriction to plant root growth may occur. The value considered to be sufficient to support the plants ranges from 0.1-0.8 g/mL (Manuel Abad, Noguera, & Bures, 2001; Singh & Sinju, 1998) defined that the bulk density requirement of an ideal substrate (IS) should be < 0.40 g $cm^3$. Dry density values allowed by Brazilian legislation are found in Abreu et al. (2012). The value observed for the sample in this study is within what is considered ideal to support the plants.

Maintaining the pH within the ideal range is one of the crucial factors in the formulation of substrates. Substrates having pH below 5.0 may cause deficiencies of nutrients and may lead to toxicity due to the increased availability of toxic elements.

On the other hand, high pH may cause deficiencies in phosphorus and micronutrients. For organic substrates, the pH range of 5.5 to 6.5 is considered ideal. The pH of the substrate in the present study is within the range (6.0 to 7.0) that presents an adequate availability of nutrients for mineral substrates (Antunes, Vaz, & Martelleto, 2022; Kämpf, 2000; Schmitz, Souza, & Kämpf, 2002).

Electrical Conductivity (EC) indicates the nutrients or salt levels (salinity) affecting the development and health of crops.

The substrate conductivity ranges suitable for seedlings, bedding plants, and salt-sensitive plants are 0.26 to 0.75 dS $m^{-1}$ by 1:2 dilution method and 1.0 to 2.6 dS $m^{-1}$ by pour thru method.

According to Ansorena (1994) the maximum EC values recommended in commercialized substrates for most plants is 1.8 dS $m^{-1}$. The EC value obtained in this study, 0.64 dS $m^{-1}$ demonstrated that the substrate is within the limits recommended by Brazilian legislation (Abreu et al., 2012).

CEC gives information about the sorption force and buffering ability of a substrate for nutrients. Substrates with high CEC can store more nutrients and plants are fertilized more intensively.

CEC is considered an important substrate characteristic when nutrient solution is not continuously offered and solid fertilizers are used. According to Fontes (1994) the CEC of substrate should vary between 0.06 and 0.15 meq $g^{-1}$, for a wide reserve of nutrients. Handreck and Black (1999) suggested a CEC between 0.05 and 0.10 meq $g^{-1}$. In the present study, the CEC value is related to the ability of the substrate to retain the ammonium ion.

For nutrient content, although there is no current information on adequate ranges in substrates, higher contents are expected to guarantee quality seedlings (Antunes, Vaz, & Martelleto, 2022). Sixteen elements are essential for plant nutrition and they are classified as major and micro nutrients.

The major nutrients are carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulphur (S). The micronutrients (present in much lower concentrations) are iron (Fe), manganese (Mn), copper (Cu), zinc (Zn) boron (B), molybdenum (Mo) and chlorine (Cl).

Table 6 shows the concentrations of macronutrients and micronutrients in substrate. The concentrations follow the orders Mg> K>Ca>P> for macro and Zn> Mn>B> Fe> micronutrients. Others nutrientes were not detected. According to Abad, Martinez, and Martinez (1993) maximum levels of Cu, Zn, Cd, Cr and Pb concentrations in a growth substrate should be less than (in mg/L): 500, 1500, 5, 200 and 1000, respectively. It is evident that heavy metal contents were below these limits.

**Table 6.** Macro e micronutrients content in substrate.

| Macronutrients | Concentration (mg/L) |
|---|---|
| Mg | 78.5 ± 11.7 |
| K | 69.9 ± 11.2 |
| Ca | 38.1 ± 6.22 |
| P | 9.38 ± 2.23 |
| Micronutrients | |
| Zn | 0.861 ± 0.007 |
| Mn | 0.406 ± 0.135 |
| B | 0.102 ± 0.064 |
| Fe | 0.0811 ± 0.0009 |

### *3.3. Biochar Effects on Leachate Quality of Substrate*

The concentration of ammonium, nitrate, phosphate and sulfate ions that leach from the substrate after contact with artificial rainwater was compared with the amount that leaches from the substrate mixed with biochar. In the tests, ion leaching was analyzed after contact with rainwater prepared without the addition of ions (samples S and SB) and with rainwater containing ions (sample SA and SAB). The results obtained are described in Table 7.

Leaching of nutrients can be observed in Figure 4. Nitrate and sulfate were the ions that leached the most after contact of the substrate with rainwater. After adding biochar, the leaching reduction efficiency was as follows:

$PO_4^{3-} > NH_4^{+} > SO_4^{2-} > NO_3^{-}$.

As presented in Table 7, it was also possible to prove that the substrate has little affinity for sulfate and nitrate, as there was a significant increase in their concentrations in the leachate after the addition of rainwater containing 20 mg/L of each ion (Figure 5). On the other hand, the substrate has a great affinity for ammonium and phosphate, as there was no significant increase in the concentration of these ions in the leachate, mainly for ammonium, whose concentration before and after the addition of biochar remained practically the same. The leaching reduction efficiency after adding biochar was as follows: $NO_3^{-} > SO_4^{2-} > PO_4^{3-}$.

**Table 7.** Concentrations of ions in the leachate from substrates samples after contact with rainwater.

| Ion | Concentration (mg/L)* | | | |
|---|---|---|---|---|
| | S | SB | SA | SAB |
| $NO_3^-$ | 18.3 ± 0.885 | 16.5 ± 0.150 | 30.8 ± 0.153 | 26.1 ± 0.110 |
| $PO_4^{3-}$ | 5.72 ± 0.433 | 4.06 ± 0.018 | 16.8 ± 0.505 | 15.4 ± 0.287 |
| $SO_4^{2-}$ | 18.4 ± 0.379 | 15.4 ± 0.087 | 27.4 ± 0.035 | 24.1 ± 0.127 |
| $NH_4^+$ | 1.75 ± 0.032 | 1.42 ± 0.031 | 4.61 ± 0.212 | 4.54 ± 0.019 |

**Note:** (*) S= Substrate and SB=Substrate-biochar with rainwater without the addition of ions; SA= Substrate and SAB=Substrate-biochar with rainwater containing ions.

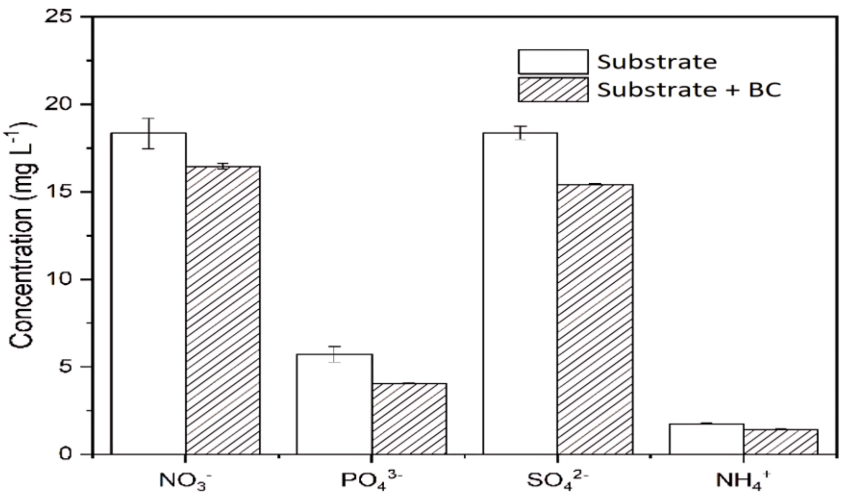


**Figure 4.** Concentration of nutrients in the leachate of substrate samples after contact with rainwater.

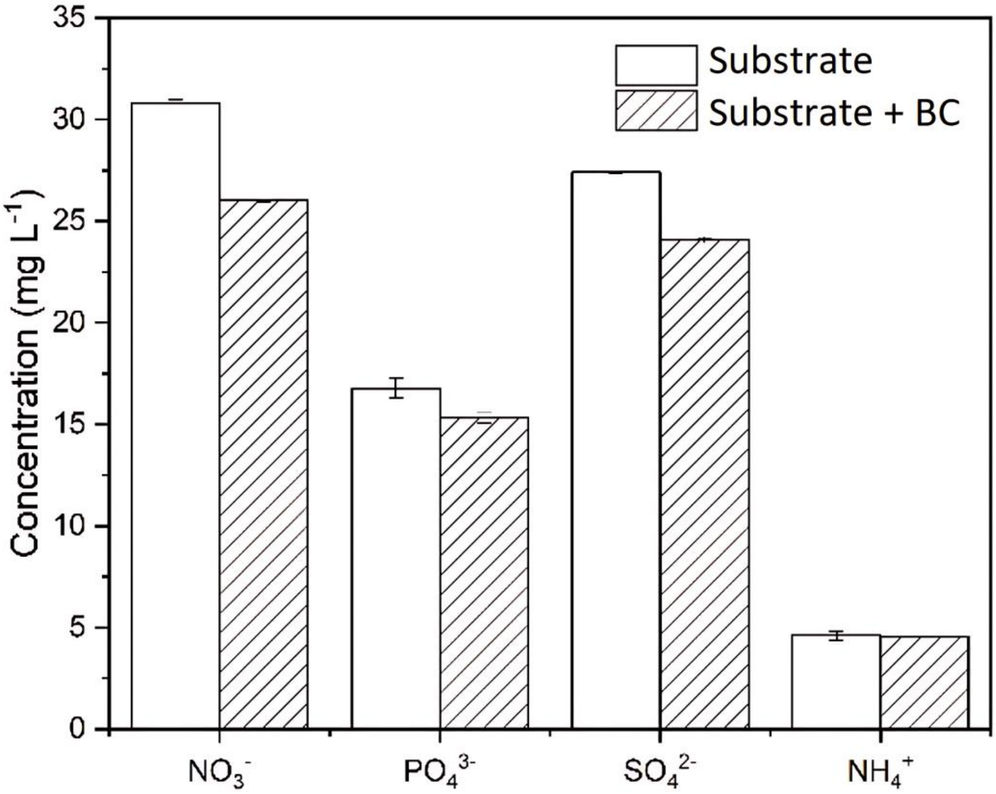


**Figure 5.** Concentration of nutrients in the leachate of substrate samples after contact with rainwater containing ions.

Previous studies have evaluated the ability of wood-based biochar to reduce nutrient leaching from green roof substrate, mainly nitrate and phosphate.

Column studies on biochar-amended vegetated roof substrate was carried out in order to determine the concentrations of ammonium, nitrate and phosphate. Biochar samples used were derived from a wood-based feedstock. The columns were flushed during 24 hours with 1 years' worth of artificial rainwater. The incorporation of biochar substantially reduced and delayed the efflux of $NH_4^+$ and slightly delayed the passage of $NO_3^-$, but had little effect on $PO_4^{3-}$ (Buffam & Boccelli, 2016).

The leachate from a standard peat-based substrate (control) used for producing two ornamental species was compared to peat-based growing media partially replaced by vermicompost and biochar. Biochar was produced by high temperature pyrolysis (600 to 800 °C) of Pinus monticola wood. The amount of nitrate leached from the mixed substrates was reduced compared to the control one in both ornamental species on average 37%. Phosphorous leaching was also decreased 30%, however only for one specie (Alvarez, Pasian, Lal, López, & Fernández, 2019).

A series of column studies were conducted to determine the influence of biochar on nitrate and phosphate retention and leaching in a soilless substrate. A commercial substrate was amended with three different biochar types: gasified rice hull biochar (GRHB), sawdust biochar (SDB), and a bark and wood biochar (BWB). Leachate collection was repeated every day for a total of 12 leaching events. The nutrient leaching curve increases with sampling presenting a maximum concentration peak of leached nutrient. The overall differences in release curve shape suggest that nitrate and phosphate were retained and released more slowly over time in biochar-amended substrates compared with the control substrate. Regarding phosphate, only wood-based biochar materials (SDB and BWB) exhibit this behavior (Altland & Locke, 2013).

In two controlled, replicated experiments, one in the field for 7 months and another in the laboratory for 6 weeks, the amendment of biochar made of birch wood to green roof substrates was studied for its potential to mitigate the leaching of nutrients from green roof Sedum and meadow mats. Nitrogen and phosphorus concentrations were evaluated. In the field experiment, biochar reduced the cumulative leaching of nutrients, even though biochar did not significantly reduce nutrient concentrations. In the laboratory experiment, two different types of commercial biochar were tested; whereas one type of biochar reduced nutrient concentrations and load in runoff, another type had an opposite effect (Kuoppamäki, Hagner, Lehvävirta, & Setälä, 2016).

The biochar created from a blend of mixed hardwoods derived from pyrolysis between 500 and 700 °C was used as a substrate amendment to optimize green roof performance. Each of the levels of biochar (0%, 2.5%, 5%, and 10% w/w) was tested with and without a green roof plant community. Biochar addition in the substrate without plants improved runoff water quality by decreasing phosphorus (about 40% lower). The presence of plants caused a substantial decrease in runoff losses of nitrate (Goldschmidt & Buffam, 2023).

## 4. CONCLUSION

In this study, wood sawdust-derived biochar (BC) produced by slow pyrolysis at 450 °C presented relatively low ash and volatile matter contents. The dry bulk density and CEC values have typical values of wood-derived biochar. Biochar was added to the substrate (14% w/w) that had a high mineral content, with potassium, calcium, and magnesium as the main macronutrients. The addition of biochar reduced the leaching of nitrate, phosphate, and sulfate ions from the substrate after contact with rainwater. The most significant reduction was in nitrate and sulfate, as the substrate has little affinity for these ions. On the contrary, the addition of biochar was not effective in reducing ammonium leaching because the substrate has a high affinity for this ion. The application of biochar derived from wood waste to reduce the leaching of nutrients from green roof substrate follows the principles of the circular economy and sustainable development objectives.

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