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CHARACTERISTICS OF WOOD SAWDUST-DERIVED BIOCHAR: POTENTIAL AS ADSORBENT MATERIAL

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ABSTRACT

Biochar is a potential additive for agricultural soil and can be used as an eco-friendly and economical adsorbent material. Biochar properties are affected by several technological parameters, mainly pyrolysis temperature and feedstock, which differentiation can lead to products with a wide range of characteristics. The biochar sample was produced from wood sawdust at 450˚C via slow pyrolysis and was characterized. Parameters characterized to include: physical properties (bulk density, porosity), chemical properties (composition, pH, conductivity, cation exchange capacity), hydraulic property (water holding capacity), proximate analysis, X-ray diffractometry to obtain information on the mineralogical composition, among others. The analysis of biochar properties is important for determining the biochar application.

Keywords: *biochar, characteristics, wood sawdust, slow pyrolysis, physicochemical properties*

1. INTRODUCTION

Biochar is a carbonaceous material generated from biomass pyrolysis under limited oxygen and temperature (<700 ^{o}C). Biomass derived from agroindustrial wastes stands out because it is an inexpensive, abundant, renewable, and biodegradable material. However, it becomes an environmental problem when inadequately disposed (Wang *et al.*, 2020).

Depending on the production conditions and feedstock, biochars' physical and chemical characteristics can vary widely, resulting in biochars with different types and quantities of surface functional groups, surface area, pH, and chemical composition (Tomczyk *et al.*, 2020).

Due to their surface characteristics, including a porous structure, high surface area, and carbonized and non-carbonized domains, biochar can adsorb heavy metals and various organic pollutants in the aqueous phase (Yaashikaa *et al.*, 2020).

This work aims to investigate the properties of wood sawdust-derived biochar to evaluate its suitability as an adsorbent material.

2. MATERIALS AND METHODS

2.1. Biochar production

Biochar (BC) was obtained from native forest species from timber management. To obtain the BC, sawdust was processed in a slow pyrolysis reactor (vertical furnace), with 25 min residence time, at 450°C.

2.2. Biochar characterization

All solutions were prepared using ultrapure water (18.2 MΩ cm resistivity, TOC 10.0 mg L^{-1}) and analytical grade reagents unless otherwise stated. Proximate analysis (moisture content, volatile matter, fixed carbon, and ash content) was determined according to EBC recommended methods (EBC, 2012). Dry bulk density, water holding capacity, air-filled porosity, and saturated bulk density of biochar were determined by methods described in the literature (Duong *et al.*, 2017; CAO *et al.*, 2014; EBC, 2012). Electrical conductivity and pH were measured in a sample/deionized water ratio of 1:10 (w/v) (Singh *et al.*, 2017). BC was saturated with sodium acetate and ammonium acetate solutions for the cation exchange capacity (CEC). Na^+ concentration of the resulting solution was determined by ICP-OES (Spedtroflame — M120). 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 (ΔpH) was plotted against pH_i values. The pH at PZC corresponded to the point of intersection in the resulting curve. The 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.

3. RESULTS AND DISCUSSION:

3.1. Proximate 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 analyses of biochar are shown in Table 1.

Table 1. *Proximate analysis of biochar*

Parameter	Values
moisture (%)	1,003 ± 0,05078
ash content (%)	14,0 ± 0,655
volatile matter (%)	28,4 ± 1,41
fixed carbon (%)	56,5 ± 2,05

It can be seen that the moisture content still presented in the biochar was not zero, even when pyrolyzed at a high temperature.

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 and Kicherer, 1997).

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, and 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 and Joseph, 2009).

3.2. Physical-chemical and hydraulic properties

Physical and chemical characteristics and hydraulic properties (water holding capacity) of the biochar are shown in Table 2.

Table 2. *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	4.10
conductivity (μS cm^{-1})	18.8 ± 0.350
CEC (meq $100g^{-1}$)	3.08 ± 0.0495

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 *et al.*, 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 °C, yielding organic acids and phenolic substances that lower the pH of the biochar (Yu *et al.*, 2014).

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 pyrolyzed sawdust at 350 °C (Santos *et al.*, 2019). CEC is influenced by the groups of carboxylic and phenolic compounds present in the biomass that originated the biochar.

3.2. Chemical composition

Table 3 presents the major inorganic elements in biochar identified by XRF. The major inorganic elements identified in BC came from the plant biomass that are present naturally (Saleem *et al.*, 2020). It can be observed that the major constituents are SiO_2, Al_2O_3, and Fe_2O_3.

Table 3. *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
others (wt. %)	< 0.40
loss of ignition (%)	89.6

3.3. Mineralogical composition

The X-ray diffractogram of biochar shows a typical band of predominantly amorphous material with a maximum of around 2θ = 20° (Figure 1). The occurrence of this band indicates that the cellulose, which is the only crystalline material present in the sawdust, was destroyed in the pyrolysis process (Chowdhury *et al.*, 2016). On the other hand, hemicellulose and lignin, which are also part of the composition of sawdust, are both amorphous in nature.

The pronounced peak at 2θ = 26.75° is attributed to the presence of SiO2. 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 *et al.*, 2005). The peak at ~2θ = 55° is attributed to impurities present in the sample or in the pyrolysis process.

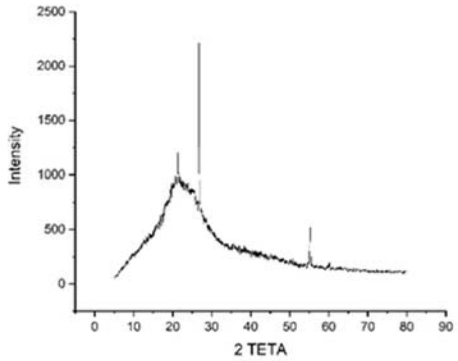

Figure 1. *X-ray diffractogram of biochar*

3.4. Point of zero charge

As seen in Figure 2, biochar had a pHPCZ value equal to 5.2. At a pH lower than this value, the surface charge of biochar will be positive and there will be a preference for adsorbing anions through the electrostatic attraction mechanism. After pHPCZ, the charge will be negative and the attraction of cations to the biosorbent surface will predominate.

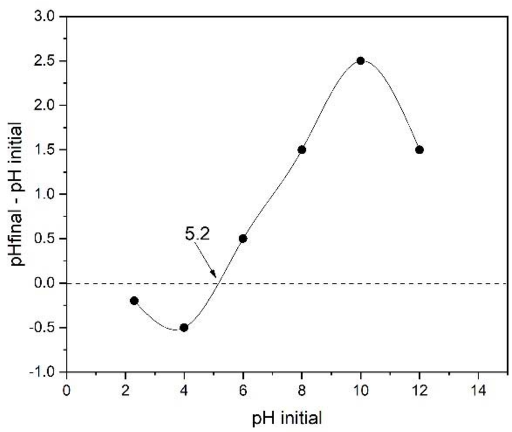

Figure 2. *Point Zero Charge for biochar*

4. CONCLUSIONS:

This study characterized the physical, chemical and hydraulic properties of waste wood-derived biochar (BC) produced by slow pyrolysis. BC presented ash and volatile matter contents relatively low. The pH value in water was low, suggesting that BC may be suitable for improving alkaline soils. The dry bulk density and CEC values are typical of wood-derived biochar. The results of this study may guide the preparation of sawdust biochar and the utilization of this product as adsorbent material.

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6. REFERENCES:

1. Wang, X., Guo, Z., Hu, Z.,Zhang, J. Recent advances in biochar application for water and wastewater treatment: a review, **2020**, PeerJ8:e9164http.
2. Tomczyk, A., Sokołowska, Z., Boguta, P. Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. Rev Environ Sci Biotechnol 19, **2020**, 191–215.
3. Yaashikaa, P.R., Kumar, S. P., Sunita, V., Saravanan, A. A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy, Biotechnology Reports, **2020**, 28:1-15.
4. EBC, **2012**, 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland.
5. Duong, V. K., Nguyen, N., Nguyen, P., Tan, D. X. Impact of biochar on the water holding capacity and moisture of basalt and grey soil. Journal of Science Ho Chi Minh City Open University, **2017**, 7. 36-43.
6. Cao, C. T., Farrell, C., Kristiansen, P. E., Rayner, J. P. Biochar makes green roof soils lighter and improves water supply to plants. Ecol. Eng, **2014**, 71, 368–374.
7. Singh, B., Dolk, M. M., Shen, Q., Camps-Arbestain, M. Biochar pH, electrical conductivity and liming potential. Biochar: A Guide to Analytical Methods, **2017**, 23.
8. Qian, K., Kumar, A., Patil, K., Bellmer, D., Wang, D., Yuan, W., Huhnke, R. L. Effects of biomass feedstocks and gasification conditions on the physiochemical properties of char. Energies, **2013**, 6, 3972–3986.
9. Lewandowski, I., Kicherer, A. Combustion quality of biomass: Practical relevance and experiments to modify the biomass quality of Miscanthus × giganteus. Eur. J. Agron, **1997**, 6, 163–177.
10. Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H., Liang, D. T. In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. Energy Fuels, **2006**, 20, 388–393.
11. Amonette, J. E., Joseph, S. Characteristics of biochar: microchemical properties. In: LEHMANN, J.; JOSEPH, S. (Ed.). Biochar for environmental management science and technology. London: Earthscan, **2009**, p. 34.
12. Pastor-Villegas, J., Pastor-Valle, J. F., Meneses Rodríguez, J. M., García, M. ‘Study of commercial wood charcoals for the preparation of carbon adsorbents’, Journal of Analytical and Applied Pyrolysis, **2006**, vol 76, pp103–108.
13. Yu, H., Zhang, Z., Li, Z., Chen, D. Characteristic of tar formation during cellulose, hemicellulose and lignin gasification. Fuel, **2014**, 118:25–256.
14. Santos, S. R., Filho, J. F. L., Vergütz, L., Melo, L. C. A. Biochar association with phosphate fertilizer and its influence on phosphorus use efficiency by maize. Ciência e Agrotecnologia, **2019**, 43:e025718.
15. Saleem, M.H., Ali, S., Rehman, M., Hasanuzzaman, M., Rizwan, M., Irshad, S., Shafiq, F., Iqbal, M., Alharbi, B.M., Alnusaire, T.S., Qari, S.H. Jute. A Potential Candidate for Phytoremediation of Metals—A Review. Plants, **2020**, 9, 258.
16. Chowdhury, Z. Z., Karim, Md. Z., Ashraf, M. A., Khalid, K. Influence of Carbonization Temperature on Physicochemical Properties of Biochar derived from Slow Pyrolysis of Durian Wood (Durio zibethinus) Sawdust. BioResources, **2016**, 11(2), pp. 3356 - 3372.
17. Gomes, F. B., Moraes, J. C., Santos, C. D., Goussain, M. M. Resistance induction in wheat plants by silicon and aphids. Scientia Agricola, Piracicaba, **2005**, v. 62, n. 6, p. 547-551.