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Caracterização de Biocarvões Provenientes de Resíduos de Cascas de Coco Verde e de Laranja

Resumo: Resíduos orgânicos do processamento do coco verde e da laranja são amplamente gerados no Brasil. Esses resíduos agroindustriais possuem potencial de aproveitamento, mas geralmente são destinados a aterros sanitários. Neste estudo, biocarvões provenientes de cascas de coco verde (CSB) e de cascas de laranja (OPB) foram produzidos pela pirólise da biomassa na temperatura de 350ºC por uma hora. Os biocarvões foram caracterizados por pH, condutividade elétrica, densidade aparente, distribuição do tamanho de partículas, análise imediata e microscopia eletrônica de varredura (MEV) para identificação do tamanho de poros. CSB e OPB apresentaram altos valores de carbono fixo (59% para OPB e 34% para CSB), material volátil (30% para OPB e 29% para CSB) e pH (8,78 para OPB e 8,41 para CSB). As imagens de MEV mostraram uma rede complexa de poros heterogêneos para OPB, e fendas cilíndricas interconectadas por grandes tubos para CSB. Os resultados indicam que OPB e CSB podem ser usados como condicionadores de solo e como adsorventes de baixo custo em processos de adsorção.

Palavras-chave: Resíduos agroindustriais; biomassa; pirólise; aproveitamento.

Abstract

Organic wastes from the processing of green coconut and orange are widely generated in Brazil. These agroindustrial residues have the potential of reuse, but mostly they are destinated for landfills. In this study, biochar from green coconut shell (CSB) and orange peel (OPB) were produced by pyrolysis of the biomass at the temperature of 350ºC for one hour. Biochar is characterized for pH, electrical conductivity, bulk density, particle size distribution, proximate analysis and scanning electron microscopy (SEM) analysis for identification of pore size. The CSB and OPB presented high values of fixed carbon (59% for OPB and 34% for CSB), volatile matter (30% for OPB and 29% for CSB) and pH (8.78 for OPB and 8.41 for CSB). The SEM images showed complex network of heterogeneous pores for OPB, and cylindrical crevices interconnected by some large tubes for CSB. The results indicate that OPB and CSB can be used as a soil amendment and as low-cost adsorbents in adsorption process.

Keywords: agroindustrial waste; biomass; pyrolysis; reuse.

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Characterization of Biochar from Green Coconut Shell and Orange Peel Wastes

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1. Introduction

The productive chain of green coconut (*Cocos nucifera* L.) begins in the agricultural production, passing through the processing for extraction of the pulp or processing of the coconut water that goes to the consumer´s market. In Brazil, the consumption of the fruit´s water *in natura* stands out. However, about 80 to 85% of the gross weight of the green coconut is considered waste, generally destinated to landfill, and with estimated average time for complete decomposition of eight years.[1] About 70% of the organic waste generated on brazilian beaches is composed of green coconut, which is not reutilized.

The high moisture (about 85%) and the characteristics of the fiber of the immature coconut reduce its reuse in relation to the shell of mature coconut. The green coconut shell fibers are mainly composed of lignins of the mesocarp, and are characterized by their hardness when compared to other natural fibers.[2] They can be used on the production of clothing, mattresses, brushes, ropes, cork, among others. The endocarp is used in the production of activated carbon.[3]

Another productive chain that stands out in Brazil is orange (*Citrus sinensis* (l.) osbeck), being the most cultivated species of citrus. The country owns more than half of the world's production of orange juice, exporting approximately 98% of the production.[4]

The industrialization of orange juice generates as waste: the seeds, the peel and the bagasse, that in general are disposed to landfill. This material is equivalent to 50% of the weight of the fruit and has a moisture of approximately 82%.[5] Among the reuse possibilities of the orange peels are: obtaining organic fertilizers, essential oils and enzymes.[6,7]

An alternative way to reuse the residues of green coconut shell and orange peel may be the production of biochar. The biochar is a carbon rich product obtained when a biomass or organic material undergoes thermal decomposition under limited supply of oxygen. It has been used for different purposes such as soil conditioner with increasing crop yield,[8] reducer of fertilizer costs and also reducer of environmental impacts on soil and water,[9] mitigating climate change through carbon sequestration and reducing greenhouse gases,[10] recovery of contaminated areas,[11] water and wastewater treatment[12] and composting.[13]

Biochar has a relative structure on carbon matrix with high degree of porosity, extensive surface area,[14] presence of alkaline cations, functional groups,[15] and heterogeneous composition with different content of moisture, volatile matter, ash and fixed carbon, according feedstock biomass.

The purpose of this study is the production of biochar from green coconut shell and orange peel and its characterization for pH, electrical conductivity, bulk density, particle size distribution, proximate analysis and scanning electron microscopy (SEM).

2. Material and Methods

The wastes of orange peel and green coconut used for this study were collected in local commerce on the city of Campo Mourão (Brazil). Biochar production by pyrolysis was carried separately in pyrolytic reactor using a muffle oven, in laboratory, at the temperature of 350 ºC for one hour. After pyrolysis, the biochar was milled in knives mill and sifted at sift of 10 mesh size (nominal sieve opening = 2.00 mm), without any type of biochar cleaning before milling.

The pH and electrical conductivity were measured (in duplicate) in a aqueous extract 1:20 (w:v), after agitation for 1.5 hours for pH determination, and after 12 hours of repose for electrical conductivity.[16]

The proximate analysis (moisture content, volatile matter and ash) were obtained according to the gravimetric method of the American Society for Testing and Materials - ASTM D1762-84,[17] and the fixed carbon was calculated according with ASTM D3172-13,[18] in duplicate.

The indication by analysis of bulk density was conducted using adapted ASTM D2854,[19] where the samples, in duplicate, were inserted in graduated beaker with 500 mL capacity until the volume of 200 mL. The mass of volume of 200 mL measured was determined in analytical balance.

In the particle size distribution analysis, the same samples used in determination of apparent density were placed in the sieves column in the mechanical agitator. The sieves used were of 4, 8 and 40 mesh size.

Surface morphology of biochar was studied by scanning electron microscopy (SEM). SEM images were obtained using a resolution of 15 nm and a magnification x600, x800 and x1500 K.

3. Results and Discussion

Results of the biochar characterization are showed in Table 1. The pH of both biochar was alkaline, with high value for OPB. The alkaline cations of the feedstock are largely retained in the biochar, where it concentrates due to the gradual loss of C, H and O during pyrolysis.[20] The increase in temperature, although caused loss of oxygen, also resulted in the formation of some oxygen groups of the cellulose thermal processing and may be associated with increasing pH.[21-22]

Table 1. Physical and chemical properties of the produced biochar

Parameter	Biochar	
	OPB	CSB
pH	8.78 ± 0.13	8.41 ± 0.25
Electrical conductivity (µS cm^{-1})	1420.00 ± 0.02	2880.00 ± 0.09
Moisture content (%)	1.48 ± 0.00	2.5 ± 0.03
Volatile matter (%)	30.00 ± 2.26	29.53 ± 8.77
Ash (%)	9.26 ± 0.7	33.56 ± 0.41
Fixed carbon (%)	59.26 ± 2.98	34.41 ± 8.39
Bulk density (g cm^{-3})	0.41 ± 0.06	0.27 ± 0.03
Particle size distribution (%)		
> 4.76 mm	0.29	0.30
4.76 – 2.38 mm	0.36	0.075
2.38 – 0.42 mm	55.95	57.41
< 0.42 mm	43.38	42.21

OPB: orange peel biochar; CSB: green coconut shell biochar

Variations of the biochar electrical conductivity (EC) occurs according to the feedstock nutrient content. The CSB showed higher EC than OPB (Table 1), possibly due to higher concentrations of Na and K commonly found in coconut shell[23]. Biochar bulk density varied slightly with feedstock, the OPB was denser than CSB, probably due to the fixed carbon content.

The proximate analysis separates components as moisture, volatile matter, ash and fixed carbon, to evaluate the change in its proportions on the biochar formed by the thermal treatment. The volatile matter is considered a portion of the mass of the original material that is lost during pyrolysis, composed by labile materials. Volatile matter values for OPB and CSB were approximately equal.

Ash content is related to the minerals present in the material, which varies in function of the composition of the feedstock. The ash content quantified, varied mostly of biochar, being that CSB (33.56%) was higher than that OPB (9.26%), presumably due to passive accumulation of mineral elements during decomposition of organic C, O and H,[24] which is also evidenced by the higher electrical conductivity.

The volatile compounds and the carbon content are influenced by the pyrolysis method. The slow pyrolysis provides a lower concentration of volatiles and higher fixed carbon concentration, when compared to fast pyrolysis.[25] Therefore, occurs the increase of the carbon concentration by dehydration, decarboxylation and condensation reactions, effect more evident on higher pyrolysis final temperature.[26]

Fixed carbon is a measure of the material portion that does not constitute volatile material, moisture or ash. Therefore, is the element in its form most resistant that remains in the biochar after the pyrolysis. The fixed carbon was high in OPB (59.26%) followed by CSB (34.41%).

Biochar properties such as volatile matter and fixed carbon level have different effects on soil fertility. The volatile matter may have an immediate enhancement effect on the soil organic carbon, where biochar is applied in the dirt. On the other hand, fixed carbon is chemically and biologically recalcitrant, and its degradation can persist over hundreds to thousands years.[27,28]

Particle size distributions of biochar (OPB and CSB) showed that they do not have much resistance to breakage, since the highest rates were found in the smaller mesh of the sieves (2.38 – 0.42 mm and <0.42 mm).

Scanning electron microscopy (SEM) was used to evaluate the physical surface morphology of the biochar (Fig. 1).

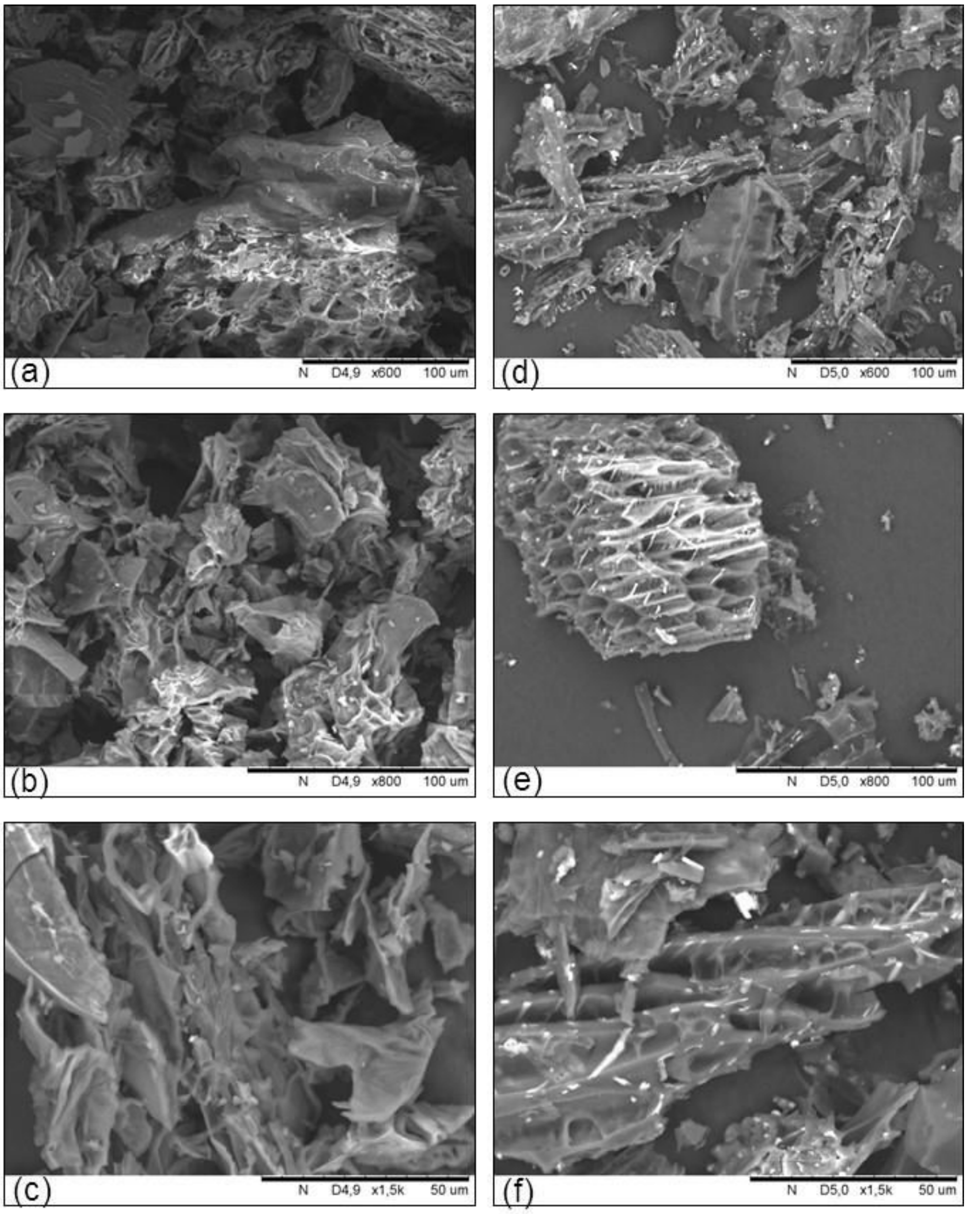

Figure 1. Scanning electron microscopy (SEM) micrographs of biochar. OPB: **(a)** x600; **(b)** x800 and **(c)** x1500. CSB: **(d)** x600; **(e)** x800 and **(f)** x1500

The porous structure of the biochar shows different shapes and scales of micro-pores, mesopores, and macropores. The OPB and CSB exhibit plan and dense surfaces with complex network of heterogeneous pores (Figure 1a), also with cylindrical crevices interconnected by some large tubes, seeming honeycomb-like (Figure 1e). The porosity of biochar is mainly attributed to the intrinsic physical structure of the precursor biomass, and may be influenced by the sample pyrolysis temperature.

Based on the SEM results, the biochar OPB and CSB can be utilized as some low-cost adsorbents in adsorption processes for water and wastewater treatment, because of vascular bundles structure and formation of internal pore structures, which play an important role in the adsorption of various contaminants.[12,14,29-31]

4. Conclusion

Through pyrolysis process was possible the conversion of the green coconut shell and orange peel wastes in biochar. The CSB and OPB had high values of fixed carbon, volatile matter and pH, indicates that they can be used as a soil amendment, increasing soil carbon, reducing the emission of greenhouse gases and maintaining positive agronomic effects over longer periods of time. Moreover, the porous structure of the biochar shows the possibility of its use as low-cost adsorbents in adsorption processes.

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