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Hotel Maracanã Plaza
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XVII ENCONTRO BRASILEIRO
SOBRE O ENSINO DE
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EXTRACTION AND CHARACTERIZATION OF LIGNIN FROM CASHEW APPLE BAGASSE AIMING FUTURE APPLICATION WITHIN NEW MATERIALS

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ABSTRACT – The lignins resulting of pretreatment from cashew apple bagasse with alkaline hydrogen peroxide and acid/alkali were extracted and characterized. The extracted lignin's showed similar characteristics to those mentioned in the literature, becoming a product of great potential raw for production of different materials. The application of the obtained lignins as material shows a positive impact for the economy.

1. INTRODUCTION

Cashew apple is a pseudofruit from the Northeastern region of Brazil with an outstanding economic role due to the cashew nut exportation. According to the Food and Agriculture Organization of the United Nations the world demand for cashew production grows annually. More than 110 thousand tons of this fruit are exported per year, generating an income of 2 billion dollars (FAO 2006). The industry of juice from cashew apple produce 15% (w/w) of bagasse, representing one of the major waste from the Brazilian agribusiness (Correia *et al.*, 2013; Rocha *et al.*, 2014; Reis *et al.*, 2017). In addition, the composition of cashew apple bagasse (CAB) points the raw material as an alternative and inexpensive lignocellulosic material for the production of ethanol. However, the cashew apple bagasse structure is highly recalcitrant to microbial and enzymatic biotransformation, limiting its use and making its conversion into value-added products not economically feasible. So, the pretreatments are needed to disrupt the recalcitrant structures of the lignocellulosic material to increase the digestibility of the material prior to the conversion into ethanol (Rocha *et al.*, 2011). During the pretreatment of cashew apple bagasse, lignin is discarded and becomes a co-product. Though, it is a potential raw for production of different materials.

Lignin, which consists of 10–35% of the lignocellulosic biomass, is the second most abundant natural polymer and in spite of this fact it is a vastly under-utilized material. It is insoluble in water and stable in nature and acts as the "glue" that binds cellulose and



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hemicellulose. Its structure is three-dimensional and consists of three phenol groups which include: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) (Fengel, 1989). The lignin extracted during pretreatment has been a source of study in several works because it is a fibrous and quite resistant material (Li *et al.*, 2015; Mohan *et al.*, 2015). However, only an insignificant part is used in specialty products, the rest serves as fuel for thermal energy generation. Currently, a wide variety of chemicals can be produced in a sustainable way from the aromatic structures of lignin (Silva *et al.*, 2013). Due to its high molecular weight, lignin can be used to produce carbon fibers, polymer modifiers, adhesives and resins (Frollini and Castellan, 2012). In addition, lignin has antioxidant activity, because of the presence of phenolic groups and benzylic hydrogens.

There are different types of lignin regarding the biomass resource they are obtained, and also depending on the isolation protocol. Then, this research aimed to extract and characterize lignin from cashew apple bagasse, an abundant agro-industrial residue in various countries, in order to use the lignin as new materials.

2. APPROACH

The raw material (cashew apple bagasse, scientific name *Anacardim occidentale* L.) used in this study was kindly donated by the Jandaia Industry of Juice (Ceará, Brazil). The CAB was washed, dried at 60 °C for 24 h and it milled, in order to obtain particles with size between 0.25 and 0.84 mm. The milled CAB was pretreated by alkaline hydrogen peroxide (AHP) and acid/alkali according to the best conditions obtained in the study of Correia *et al.* (2013) and Rocha *et al.* (2009), respectively. A solids concentration of 5% (w/v) CAB, was slurred in hydrogen peroxide H₂O₂ (4.3% v/v) with the H₂O₂ solution adjusted to pH 11.5 using 6 mol.L⁻¹ NaOH. The pretreatment was conducted in an orbital shaker (Tecnal – TE 422, SP, Brazil) at 35 °C for 6 h and 250 rpm. The acid pretreatment was carried out at 121 °C for 15 min using H₂SO₄ 0.6 M and 30% w/v CAB, followed by alkali treatment, water-insoluble solids from the acid pretreatment were impregnated with 4% w/v NaOH at 121 °C for 30 min in autoclave. After pretreatment step, the liquors were separated from the solid fraction by filtration. Then, these liquors were reserved for the precipitation and recovery of lignin. Lignin present in the liquors obtained of the pretreatment was recovered by precipitation with acidification at pH 2 using 50% v/v H₂SO₄. The mass of precipitated lignin was calculated in dry mass basis. The lignin resulting were characterized by the methods of elemental composition analysis, immediate analysis, FTIR and DSC.

3. RESULTS

Of the liquids fractions obtained after pretreatments of cashew apple bagasse, with AHP and acid-alkali, were extracted a mass of lignin of 12.69 g and 16.70 g, respectively, for each 100 g of CAB. Immediate analysis of the extracted lignin with AHP was 5.71% of moisture, 9.67% of fixed carbon, 78.64% of volatiles and 5.96% of ash and for lignin obtained of the acid-alkali pretreatment was 9.43% of moisture, 28.15% of fixed carbon, 57.60% of volatiles and 4.82% of ash.

Contents of carbon, hydrogen and nitrogen in extracted lignin with AHP were 51.5%, 7.34% and 6.66%, respectively, and contents of carbon, hydrogen and nitrogen in the acid-alkali extracted lignin samples was 54.46%, 6.27% and 2.16%, respectively. The values for

elemental analysis found in the literature show variations, possibly caused by the composition of the lignin source material as well as the extraction process. Konduri *et al.* (2015) studied the characterization of hardwood lignin and obtained the following contents: carbon 64.76%, hydrogen 5.78% and nitrogen 0.03%.

The FTIR spectra of the lignins obtained during the pretreatment from CAB using AHP (Figure 1-A) and during the acid/alkali pretreatment (Figure 1-B) showed a successful fractionation, since the bands are well defined in specific wavelengths. The lignins obtained in the present study may be considered free of carbohydrates. According to Lopes *et al.* (2013), since no characteristic bands at 897, 1046 and 1080 cm^{-1} were observed, lignin did not present carbohydrates in its structure. The spectrum obtained exhibited absorption bands typical of lignin and similar to those obtained by LI *et al.* (2015). The aforementioned authors concluded in their spectra that bands with maximum absorbance at 3430 cm^{-1} represent stretching of OH groups, 2962 cm^{-1} stretching CH of methyl or methylene groups, 2854 cm^{-1} CH-vibration of methyl methoxy groups, 1737 cm^{-1} stretch C = O, 1550 cm^{-1} vibration of aromatic rings.

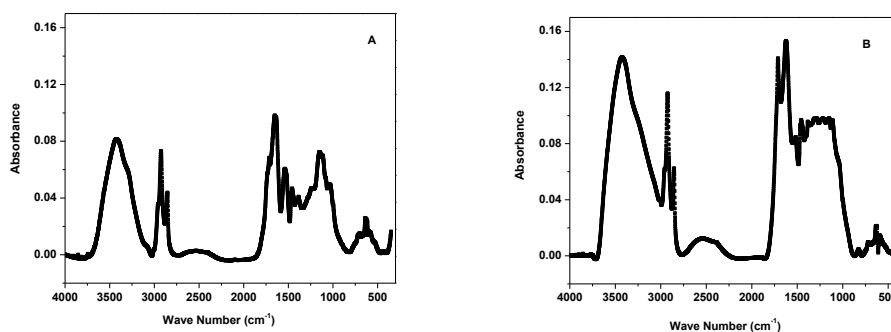


Figure 1: (A) The FTIR spectrum of the lignin obtained during the pretreatment of cashew apple bagasse using alkaline peroxide hydrogen (4.3% v/v, pH 11.5, 5% w/v CAB, 35 °C, 250 rpm for 6 h). (B) The FTIR spectrum of the lignin obtained during the pretreatment of cashew apple bagasse using acid/alkali (pH 13.5).

Thermal stability studies of the lignins extracted from alkaline hydrogen peroxide and acid-alkali pretreatments were carried out through Differential Scanning Calorimetry (DSC). The results of the DSC analysis show the variation of the curve in the degradation process. For two lignins the DSC curves were initiated with endothermic regions due to the heat required for the evaporation of moisture before the heat flow from endothermic to exothermic, being up to 600 °C for lignin from AHP, and up to 450 °C for lignin from acid-alkali pretreatment, that occur a change between 450 °C and 550 °C where shortly after the thermal degradation process restart. The melting enthalpies change the degradation process of the samples too, which matches the values in literature (Mousavioun *et al.*, 2013). Lignin sample takes place the melting change between 600 °C and 700 °C for AHP pretreatment.

4. CONCLUSIONS

Lignins extracted from cashew apple bagasse by pretreatment with alkaline hydrogen peroxide and acid/alkali show characteristics similar to those mentioned in the literature according to the characterization processes. Then, applications are emergent for these lignins



in diverse areas, principally as sustainable alternatives to non-renewable products, such adsorbent, support for enzyme immobilization, and phenolic and epoxy resins.

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