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Carbon Nano Compound from Seeds: Methodology to Obtain a High Added Value Product

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The use of a green chemistry is the philosophy proposed by this work. Development of new energy sources has been developed by many research groups around the world. A high added value product, a carbon adsorbent is the main result of this work. This work was initiated through the drying seeds process. After this stage, oil from the seeds was extracted by hexane by Soxhlet extraction. This process produces two main products. The oil that in general is useful to produce biodiesel and the solid tart. Tart was used to produce charcoal by a low temperature pyrolysis process, at 380°C under nitrogen atmosphere. From this technique were obtained initially four energy sources: Charcoal, gas, pyrolysis oil and water. The charcoal was heated in a muffle furnace at different temperatures range from 500°C to 1,000 °C. This stage was realized in attempt to obtain a most pure charcoal, with higher carbon value. The analysis of Raman spectroscopy and solid NMR show that the best char was obtained at 600°C temperature. By Raman spectroscopy was observed that in higher temperatures were obtained aggregated products and by solid NMR that the products really are good conductors. Charcoal was even characterized by SEM and EDS. After product characterization, was tested the methylene blue adsorption capacity of the obtained material by UV analysis. Results of UV analysis show a great adsorption capacity.

1. Introduction

New technologies have been developed in attempt to solve the many problems caused by high pollution level on Earth atmosphere. Fossil fuel was the main energy source for many years. The high fuel price, the scarcity of its sources and the many pollutants released by the burning of this has directed many research groups to study and develop new energy sources. Alternative renewable energy source has been very useful in attempt to replace the use of fossil fuel due to its regeneration capacity. An example is the use of seeds to obtain energy. Oil seeds have been already used as fuel in the form of biodiesel, replacing fossil fuel, diminishing the release of toxic components in the atmosphere. Crops plantations even help to clean the atmosphere through photosynthesis and even generate jobs, opportunities in rural areas. This social impact is very important, especially at this moment that the planet lives global financial crises. The mix of methyl fatty acid esters, denominated Biodiesel (Prussi et al, 2013), its technology, has reached already a great advance and has been spread used through developed countries such as German, and some others for example and even in the third world, developing countries as Brasil (Figueiredo et al, . The continuous use of seeds in many different processes to produce energy, by biodiesel and even by obtain many products, in general generates a great amount of residue. In attempt to solve, to diminish this problem, first in German and after in Brazil, was developed, studied a methodology of low pyrolysis to obtain alternative energy sources (Romeiro et al, 2012). Low temperature pyrolysis produce main four products: Charcoal, pyrolysis oil, gas and water. All the obtained products are very useful. The oil can be used as fuel, or even to heat systems, as the obtained gas can also be used at heating, the water can be useful to irrigate plantations and the charcoal can also be useful to obtain high added value products, such as catalysts and adsorbent material(Rangabhashiyam et al, 2013)., among others utilities(Deveci et al, 2013). The following figure 1 illustrates this equipment.

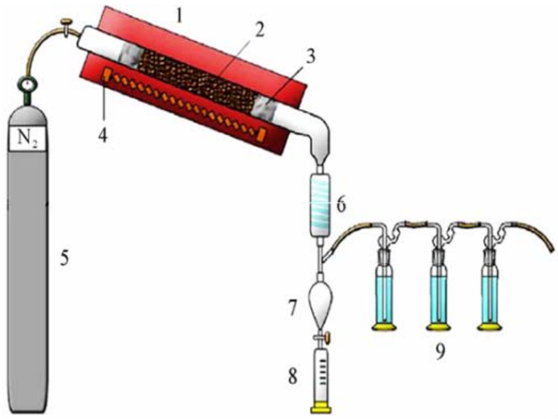

Figure 1. LTC equipment. 1-Oven, 2 – Dried sample, 3 – glass wool, 4 – Electrical resistance, 5 – Inert gas, 6 – Condenser, 7 – separation funnel, 8- liquid receiver and 9- Gas trap

This work focus was the obtaining of an alternative, high added value material from seeds (John et al, 2013). The first step was to characterize and verify how was the behavior of the obtained charcoal by low temperature pyrolysis when submitted to high temperatures under inert atmosphere. Due to the high amount of metals and the structure observed by electronic microscopy (Figure 2) has been tested the adsorption capacity of the obtained material under the form of pyrolysis charcoal and after heating under different temperatures.

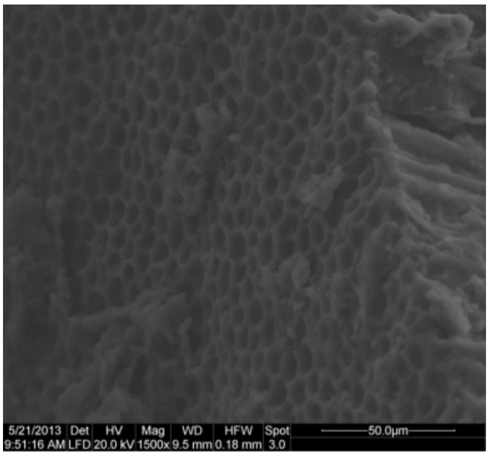

Figure 2. Electronic microscopy (SEM) image of the charcoal obtained from the LTC of Jatropha Curcas seeds that underwent hexane extraction.

2. Materials and methods

2.1 Jatropha Curcas seeds

The seeds were obtained from EMBRAPA – Brazilian Agricultural Research Corporation. The seeds were dried in an oven at 100ºC for 24 h. The dried seeds were crushed in a mini chopper.

2.2 Seeds extraction

The methodology used to extract the oil from the seeds was the Soxhlet extraction procedure. The crushed seeds were packed in the cartridge. The cartridge was placed in the Soxhlet apparatus and the oil was extracted with hexane. After the period of six hours to complete the extraction were obtained two products, the oil and the tart, the solid part inside the cartridge. The tart was dried for two days at ambient temperature to evaporate the hexane residues.

2.3 Low temperature pyrolysis to obtain the charcoal

The dried tart material was packed in the LTC reactor. The process was performed by 2.5 hours, at 380ºC under constant nitrogen atmosphere. After cooling the equipment, the charcoal was removed and stored in a dry recipient.

2.4 High added value charcoal by heating

The charcoal was placed inside a in a stainless steel tube under inert and heated to temperatures ranging from 500°C to 1000°C atmosphere. Each sample was heated for 4 h, so by this methodology were obtained different charcoals, each one at its own heating temperature. To produce all the six samples, from charcoal 500°C to charcoal 1,000 °C this process was repeated by the same manner.

2.5 Physical and chemical characterization of char as adsorptive material

2.5.1 Moisture and ash contents

Moisture and ash contents analyses were done by heating the samples in air to 105 °C for 24 h and 575 °C for 4 h, respectively, and weighting the obtained residue.

2.5.2 pH of biochar in water

The pH of biochar was determined according to Cheng and Lehman. Two grams of biochar were shaken with 40 mL of distilled water for 30 min. The suspension was allowed to stand for 10 min before measuring the pH with a pH electrode 827 pH Lab^{TM}.

2.5.3 Methylene blue adsorption

Solutions with concentrations range from 1 to 20 mg.L^{-1} of methylene blue were prepared and their absorbance measured at 630 nm on a Biochrom System Ultraspec 1,000 UV visible spectrometer. The calibration curve of absorbance against concentration of “MB” was determined and indicated that the Beer Lambert Law is obeyed up to the concentration of 20 mg.L^{-1}. To verify the adsorption of methylene blue on the obtained charcoal from *Jatropha Curcas* seeds, 0.2 g of material was added to 50 mL of 20 mg.L^{-1} methylene blue solution and stirred on a magnetic stirrer of 6 rpm. Aliquots were taken at intervals during 2 minutes until reach 6 minutes time and from 3 to 3 min until reach 15 min. All the aliquots were filtered on filter paper, introduced in disposable cuvettes and the suspensions absorbance were determined.

2.5.4 Raman spectroscopy

Raman scattering measurements were performed at Andor ^{TM} Technologysharmrock sr-303i spectrometer coupled with a charge coupled device detector, in the backscattering configuration using 60x oil immersion and air objective lens.

2.5.5 Scanning electron microscopy

Images were obtained using a Nova nanolab 600 dual platform from FEI, the different charcoal temperature samples were analyzed similarly on the same equipment using 10 Kev accelerating energy and 0.13 nA electron current.

3. Results

3.1 pH of biochar in water

The analysis of the suspensions of biochar in water has demonstrated that the obtained compounds are of basic characteristics. It was observed, that after heating, the biochar, becomes even more basic. The first biochar obtained by pyrolysis has the pH value of 9.78 and all the others derivative of the heating under inert atmosphere process are in the range of 10.58

Table 1: pH of biochar in water analyses results

Biochar (Celsius)	380 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1,000 °C
pH	9.78	10.53	10.57	10.59	10.58	10.56	10.59

3.2 Moisture and ash contents

The obtained result for moisture content in the biochar sample was in the range of 0.22 wt.% and the ash content is in the range of 13 wt.%. The high value, of ash content analyses indicates the presence of minerals in the samples.

3.3 Raman Spectroscopy

The Raman spectra of biochar sample from 500 to 1,000 °C indicates that the charcoal heating does not follow the expect manner to obtain the desired nanomaterial. Verifying the results of crystallite medium size (La) has been observed that is obtained even a different result, the crystallite value diminish when are obtained samples produced with higher heating. The PCA, Principal component analysis of Raman results indicate a certain grouping.

Table 2: Crystallite medium size (La) study of Raman spectra of biochar heating samples from 600 to 1,000 °C

Sample	La	u_La
600 °C	9.06	0.38
800 °C	7.43	0.74
1,000 °C	7.77	0.59

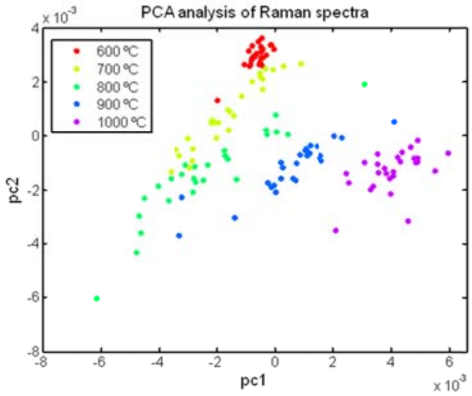

Figure 3. *PCA study of Raman spectra of biochar heating samples from 600 to 1,000 °C*

3.4 Electron Microscopy

The analyses of microscopy images have demonstrated that the material is contaminated with metal, corresponding with the results obtained by ash content and by pH, indicating the presence of alkaline compounds. In the biochars analyses obtained at higher temperature has been observed a higher content of alkali metals, Figure 4 (biochar 500 °C.)Compared to figure 5 (obtained at 1,000 °C) where is observed a high amount of alkaline compounds.

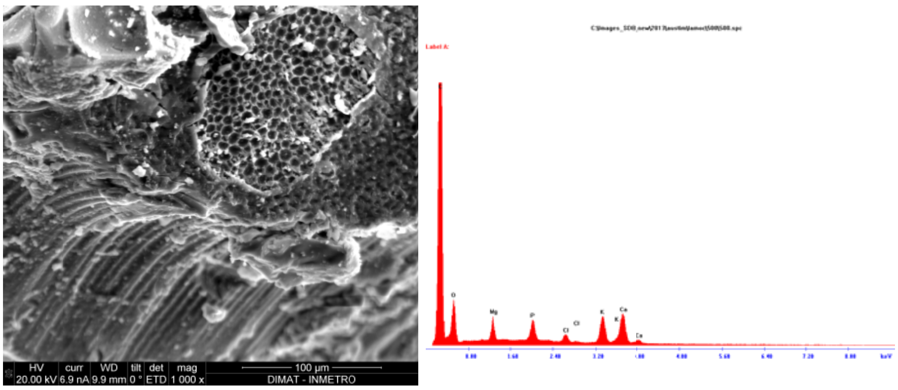

Figure 4. Microscopy image of biochar 500 °C and EDX analyses

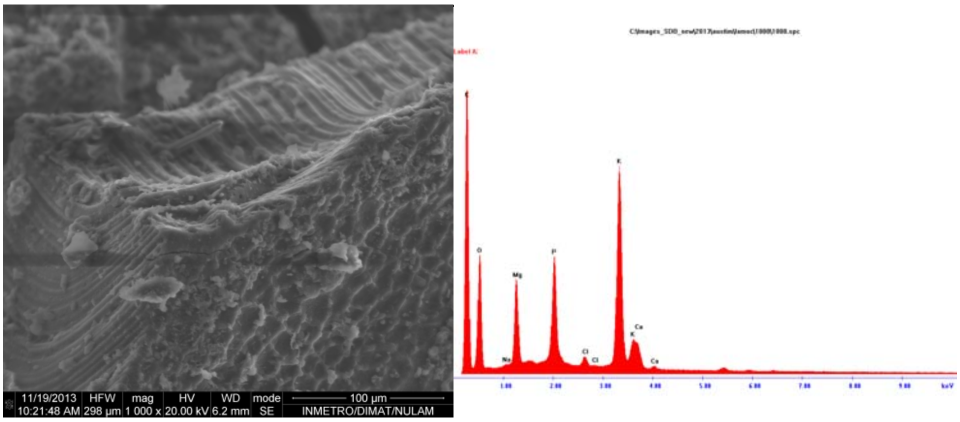

Figure 5. Microscopy image of biochar 1,000 °C and EDX analyses

3.5 Adsorptive biochar capacity

The adsorptive capacity of the obtained biochar was measured through UV using methylene blue. Has been observed that biochar is able to adsorb in little time and the production of biochar in higher temperatures do not affect positively this capacity. Observing the dispersion graphics of Figure 6 it is possible to observe that the material adsorbs the methylene blue in a little time, that after one minute almost all the "MB" is completely adsorb by the obtained biochar. The tentative to produce biochar in higher temperatures do not really produce a better biochar to adsorb the interesting product, methylene blue.

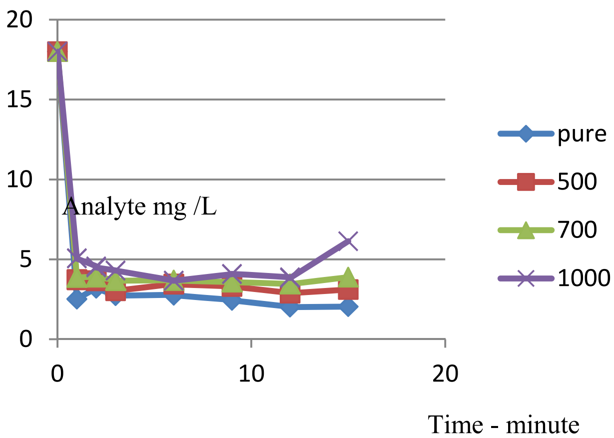

Figure 6. *Obtained graphic (Analyte mgL^{-1} versus time min.) after UV analyses of obtained biochar from various temperatures*

4. Conclusions

This work goal was to obtain a high added value product from seeds. It was observed that from charcoal, a lot of interesting products can be obtained. The focus of this work was to obtain a nano material compound. This was changed due to the high amount of metals obtained by the proposed route. It was proved that the low temperature pyrolysis can produce good chars with adsorptive properties. Charcoal of *Jatropha Curcas* tart, derived of seeds extraction has confirmed its adsorptive property through the initial analyses performed with methylene blue. The increase of temperature indicates that diminishes the porosity property, the microscopy images exhibit it, the micro porous seems to be covered with a thin layer. The increase in temperature also changes the structure compound diminishing it adsorptive capacity. This study indicates, suggests that to produce a nano carbon derived compound from Jatropha seeds by low temperature pyrolysis needs the use of catalysts during the heating to assist the obtaining of the desired product and the use of higher temperatures to diminish the amount of alkali metals. The obtained results show that obtained char from low temperature pyrolysis can be used as high added value product, such as adsorptive and even can be used to produce catalysts, among other products.

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