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Effects of Chemical Treatment on Structural Properties of *Jatropha curcas* Seedcake

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Abstract: Biodiesel is a biofuel obtained through a transesterification reaction using vegetable oils and animal fats. After oil extraction, the seedcake is a by-product, which can be used as a biofertilizer. This work evaluated the modifications in chemical structures that occurred in Jatropha cake after its submission to different treatments with distilled water and vapor of 10% v/v aqueous solution of acetic acid. Seedcakes were characterized by chemical analysis of acidity, water solubility, conductivity and infrared spectroscopy. The following values were observed in untreated cake (% w/w): moisture 6.1 ± 0.2, ash 5.2 ± 0.3, crude protein 26.5 ± 0.9, potassium 1.7 ± 0.1, crude fiber 34.9 ± 5.8, phosphorous 4.7 ± 0.4 and crude fat 13.8 ± 0.5. Ash, crude fiber and phosphorous content had no significant modifications, whereas crude protein decreased after acid treatment. Moisture and potassium content decreased after both water and acetic acid solution treatments. The acidity of the soluble fraction presented values around 5.8. Conductivities ($\mu S \cdot cm^{-1}$) of the soluble fraction for cakes *in natura*, treated with water and treated with acetic acid were, respectively, 430.8 ± 13.6, 362.9 ± 8.1 and 599.3 ± 26.8 and solubilities (g 100 g^{-1} H_2O) were 0.309 ± 0.008, 0.241 ± 0.008 and 0.373 ± 0.012, respectively. These results showed that structures like hemicellulose and lignin were probably modified through acid hydrolysis, producing ionic groups and leading to higher conductivity and solubility. Similar infrared spectra were obtained for three cake samples. In general, Jatropha cake underwent slight modification concerning composition after acetic acid treatment.

Key words: Jatropha seedcake, chemical treatment, structural properties, fertilizer.

1. Introduction

The shortage of fossil fuel and increasing demand for energy has increased the need to obtain other sources of energy. Biodiesel has received attention for many years as a replacement for petroleum diesel due to advantages such as renewable raw material, biodegradable, non-toxic and not producing sulfur and aromatics [1]. Biodiesel is produced through a transesterification reaction using vegetable oils and animal fats as raw material, an alcohol such as methanol and a catalyst.

Jatropha curcas L. is a plant from which the oil is used as raw material for biodiesel production [1]. The plant is a small tree or large shrub and belongs to the Euphorbiaceae family. It is well adapted to a wide range of environmental and soil conditions allowing its cultivation in different regions. The seeds should be harvested at maturity, which occurs 90 days after flowering [2].

Mechanical expellers or chemical processes can be used to extract the oil from the seeds [3]. After oil extraction, the waste obtained results in an important by-product with suitable physicochemical properties for many applications. This residue has nutrients with good quality for use as organic fertilizer [4, 5], as it is rich in nitrogen, phosphorus and potassium, with levels higher than usual organic fertilizers. Press cake has high calorific values and can be used as combustible fuel after pressing it into cake-briquettes, obtaining higher energy content per kg [3]. In addition, biogas can be produced through anaerobic fermentation of press cake [6]. Jatropha cake presents natural fibers such as cellulose, hemicellulose and lignin, which can

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be used as biocomposite reinforcement in order to improve mechanical properties of polymeric matrices [7].

Jatropha cake has toxic constituents, which make its use as human or animal food inappropriate. Phorbol esters, a group of diterpenes [8], are the main toxic compounds detected in the cake besides trypsin inhibitor, lectin, saponins and phytate [9]. Detoxified cake is obtained through chemical treatment with organic solvents that remove phorbol esters [10]. Other toxic constituents can be removed using heat treatment. Moreover, in Mexico, a non-toxic species of Jatropha plant that produces seeds without toxic compounds was identified; consequently, this seedcake may be appropriate for nutritional applications [11].

Among the applications of Jatropha cake, its use as a fertilizer has attracted many researchers studying plant growth with this cake. KUMAR [12] investigated the effects of different amounts of Jatropha and mustard cakes on the growth and essential oil yield of the *Mentha piperita* L. plant. The best growth responses concerning the addition of Jatropha cake were when plants were treated with up to 50% concentration, and maximum oil contents were, respectively, 0.51 and 0.46% for treatments with Jatropha and mustard cakes in the same growth conditions. In tomato crop, Jatropha cake revealed the potential to be used as an organic fertilizer [13]. The *Lycopercicum esculatum* plant was cultivated using different concentrations of cake and ages of plant life-cycle. Morphological parameters (plant height, number of leaves, flowers per plant, number of fruit and yield) and nutritional parameters of the fruit (total soluble solids, vitamin C, protein, reducing sugars, lycopene and pectin) were measured. The results demonstrated that 2 and 3% (w/w) of Jatropha cake in the soil increased the plant yield for 60 days of the plant life cycle. At 2%, the yield was the highest, and the nutrient level was not affected, whereas at 3%, both yield and nutrient levels were significantly high.

Investigating procedures for using residues, in this case, Jatropha cake from biodiesel production contributes to environmental and biomass technology. In this sense, the aim of this work was to submit the Jatropha cake to chemical treatment with vapor of aqueous acid solution in order to obtain modifications in structural properties, which likely increase the residue's potential as an organic fertilizer.

2. Material and Methods

2.1 Sample Preparation and Collection

Jatropha seeds were acquired from Biojan NNE Minas Agroindústria LTDA, located in the north region of Minas Gerais State, Brazil. The seedcake was obtained through hot extraction, triturated in a knife mill and stored in dark packaging.

Two treatments were carried out using vapor of distilled water and vapor of 10% v/v aqueous solution of acetic acid. Samples were submitted to these treatments for 3 h. After treatment, seedcakes were placed in an oven at 80 °C for 2 h and triturated using a pestle and mortar.

2.2 Seedcake Characterization

Chemical analysis was performed to evaluate crude fiber, crude protein, potassium and phosphorous contents. Crude fiber was obtained through the gravimetric method after acid and alkaline digestion of defatted samples and the micro Kjeldhal method was used to determine crude protein [14]. Flame photometry and spectrophotometry were used to determine potassium and phosphorous contents, respectively [15].

Water solubility as well as acidity and conductivity in the soluble fraction of the seedcake was also evaluated. For measurements, 1.0 g of seedcake and 50 mL of water (submitted to reverse osmosis) were mixed, left under agitation for 1 h at room temperature and filtrated. The liquid part was used to perform acidity and conductivity analyses, while the solid part was used to obtain solubility through mass difference.

FT-IR spectra were recorded on Perkin-Elmer 240c equipment in the 4,000–400 cm^{-1} wave number range using KBr pellets.

All analyses cited previously were performed in triplicate in the samples submitted to treatments and in the *in natura* sample.

2.3 Data Analysis

The mathematical assumptions for the Analysis of Variance were previously measured. Comparison of mean values was performed through One-way ANOVA and the Tukey test was used to identify the treatments which presented significant differences to 5% level of significance.

3. Results and Discussion

Chemical analysis is shown in Table 1. Concerning the *in natura* seedcake, some values are in accordance with the literature (% w/w): moisture 5.55 ± 0.20 [16], ash 4.50 ± 0.14 [16] and 3.4–5.0 [9], crude protein 24.60 ± 1.40 [16] and 19.0–30.0 [9], potassium 1.2–1.68 [5]. On the other hand, crude fiber and phosphorous presented discrepant values of 10.12 ± 0.52% w/w [16] and 1.4–2.09% w/w [5], respectively. Crude fat values depend on the extraction oil method and indicate residual oil in the seedcake.

Ash, crude fiber and phosphorous content had no significant modifications, whereas crude protein decreased after acid treatment. Possibly, hydrolysis of the proteic structure in the Jatropha cake contributed to leaching this nutrient. A similar effect occurred with moisture and potassium content after both water and acetic acid solution treatments. In general, Jatropha cake underwent a slight modification concerning composition after acetic acid treatment.

The acidity of the soluble fraction of the cake presented a value of approximately 5.8 (Table 2), which is an interesting result since it demonstrates that no acid waste remained in the seedcake. The solubility value decreased for water treatment. This result showed that hemicellulose and lignin were likely removed or partially removed after the use of vapor [17]. Smaller amounts of these structures contributed to the lower hydrophilic character of seedcake and it is according to lower solubility and moisture for water treatment. Otherwise, a higher solubility for acetic acid treatment was observed. Besides removing hemicellulose and lignin, there is the possibility of producing ionic groups and smaller structures [18] and leading to higher conductivity and water solubility. In the case of the water treatment, non-ionic structures can be formed, thus decreasing the conductivity.

Fig. 1 presents the results of the absorption spectra in the infrared region. Similar infrared spectra were obtained for three cake samples, demonstrating that functional groups were maintained after the treatments.

Broad absorption bands around 3,307 (a), narrow medium peaks around 2,924 (b) and weak peaks around 2,854 (c) cm^{-1} can be assigned, respectively, to free and intermolecularly bonded hydroxyl groups, the stretching vibration of the C-H group [19] and the

Table 1 Chemical analysis of Jatropha cakes.

Measurements	*In natura*	Treatments	
		Water	Acetic acid
Moisture*	6.1 ± 0.2ab	2.5 ± 1.2a	3.6 ± 0.4b
Ash*	5.2 ± 0.3	4.1 ± 1.4	4.8 ± 0.2
Crude fat*	13.8 ± 0.5	14.4 ± 0.3	13.8 ± 0.4
Crude fiber*	34.9 ± 5.8	34.4 ± 0.3	33.8 ± 1.6
Crude protein*	26.5 ± 0.9a	26.2 ± 0.7	24.5 ± 0.4a
Potassium**	17.4 ± 0.1ab	16.1 ± 0.2a	16.0 ± 0.4b
Phosphorous**	4.7 ± 0.4	4.9 ± 0.1	4.7 ± 0.0

*% w/w, ** g kg^{-1}. Samples followed by the same letter in line differ statistically by Tukey test ($\alpha = 0.05$).

Table 2 Physico-chemical properties of Jatropha cakes measured in soluble part.

Properties	*In natura*	Treatments	
		Water	Acetic acid
Solubility (g 100 g^{-1} H_2O)	0.309 ± 0.008ac	0.241 ± 0.008ab	0.373 ± 0.012bc
Acidity (pH)	5.88 ± 0.31	5.81 ± 0.20	5.78 ± 0.27
Conductivity (μS cm^{-1})	430.8 ± 13.6ac	362.9 ± 8.1ab	599.3 ± 26.8bc

Samples followed by the same letter in line differ statistically by Tukey test (α = 0.05).

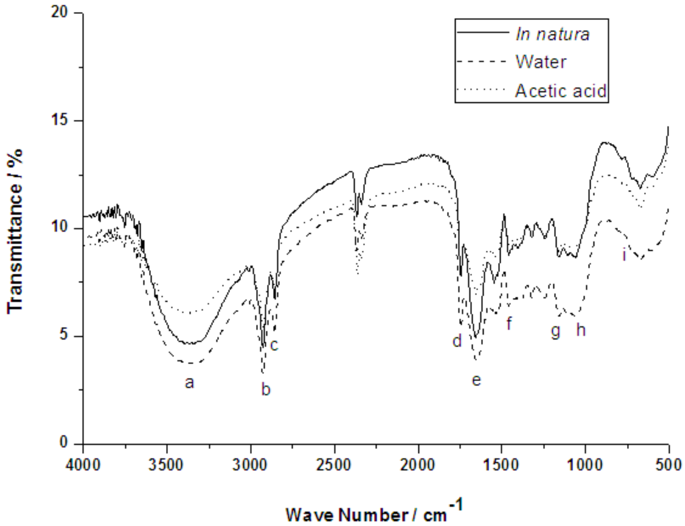

Fig. 1 Infrared spectra of Jatropha cakes submitted to different treatments.

stretching vibration of the CH_2 of alkyl group [20]. The presence of a carbonyl group is confirmed by the peak at 1,743 cm^{-1} (d). Strong medium peaks around 1,651 cm^{-1} (e) are related to the stretching vibration of C=C of conjugated diene and triene groups. Weak peaks at 1,462 cm^{-1} (f) can be attributed to deformation of CH_3 of an alkyl group, while peaks at 1,161 cm^{-1} (g) and 1,056 cm^{-1} (h) can be attributed to the stretching vibration of an O-C-C of ester group. In addition, absorption bands at 2,854, 1,743, 1,651, 1,161 and 1,056 cm^{-1} can indicate the presence of phorbol esters [20] in seedcake.

Spectra infrared analysis demonstrated that the main constituents of seedcake did not undergo considerable modifications in their structures. Vegetable materials are complex systems that need harsher treatments to modify their structures. Nevertheless, other analyses performed to characterize the seedcake revealed slight modifications, such as increasing solubility and conductivity. An important result was obtained concerning the chemical composition analysis, which is that the seedcake maintained its composition in general. Thus, there was no significant loss of nutrients after treatments. These properties strongly suggest that the procedure allowed Jatropha cake for fertilizer to be mineralized more easily. Conditions such as the type of acid, concentration and time can be varied in order to obtain significant modifications in the Jatropha seedcake.

3. Conclusion

The parameters chemical composition, acidity, solubility and ionic conductivity used in this work to investigate the effects on Jatropha seedcake after its chemical treatment with vapor of distilled water and vapor of 10% v/v solution aqueous of acetic acid revealed slight modifications in the structure of seedcake constituents.

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