VALORIZATION OF OAT HULLS: ECO-FRIENDLY EXTRACTION OF CELLULOSE AND HYDROGEL PRODUCTION FOR AGRICULTURAL APPLICATIONS

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ABSTRACT

Brazil's agro-industry generates a lot of oat hulls, a by-product of oat milling, with production reaching 1.1 million tons in 2023. Due to its high cellulose content, oat hulls are a promising source for cellulose extraction. Traditional extraction involves aggressive treatments with chlorinated products over long periods. This study aimed to extract cellulose from oat hulls using an environmentally friendly one-step process with 16% w/v H_2O_2 and 5% w/v NaOH. The process resulted in over 62% cellulose content extraction. FTIR analysis confirmed the removal of most lignin and hemicellulose. This eco-friendly method successfully isolated cellulose with minimal lignin and hemicellulose residues at a rapid extraction time (1 hour).

Keywords: Recovery of residues. Oat hulls. Agroindustrial residues. Bioeconomy

1 INTRODUCTION

The valorization of agro-industrial residues into high value-added products is one of the main objectives within the context of the circular economy, aimed at maximizing the use of lignocellulosic biomass to reduce the generation of residues in agriculture and other industries. Global production of lignocellulosic biomass in 2022 reached approximately 220 billion tons in terms of dry mass.[1] The final disposal of this residue generally involves burning in open spaces, generating a large amount of pollution that affects human health and the environment.[2]

Brazil's agro-industry produces substantial residues, such as oat hulls, a by-product of oat milling, with 1.1 million tons produced in 2023.[3] Oat hulls are rich in cellulose, a widely used natural polymer in food, paper, textiles, and pharmaceuticals due to its mechanical properties, biocompatibility, non-toxicity, and low water solubility.[4]

Typically, cellulose is extracted from cotton and wood using harsh treatments that generate toxic effluents.[5] A greener alternative uses synergistic treatments like alkaline peroxide, composed of NaOH and hydrogen peroxide, which has a low environmental impact as it decomposes into water and oxygen.[6] This study uses eco-friendly one-step processes to extract cellulose from oat hulls.

2 MATERIAL & METHODS

EXTRACTING CELLULOSE FROM OAT HULLS

The extraction was performed according to the methodology described by Gabriel, [7] with modifications made. For 20 g of CA, an alkaline peroxide solution composed of 16% w/v H_2O_2 (110 mL of H_2O_2 + 90 mL of H_2O) and 5% w/v NaOH (10 g of NaOH + 200 mL of H_2O) was used for a total of 400 mL. First, the oat hulls were mixed with the NaOH solution, and then the H_2O_2 solution was slowly added to the system. The process took place under constant stirring at 60 ºC for 1 hour. After the treatment, the cellulose fibers were filtered and neutralized with 2 L of a solution composed of water and 0.5 M HCL. The retained material was placed on a Petri dish and subjected to drying in an oven for 2 days at 30°C, then ground and stored for subsequent analyses

DETERMINATION OF LIGNOCELLULOSIC CONTENT

The determination of cellulose and hemicellulose contents was performed according to the methodology described by Van Soest.[8] For this, 0.5 g of dried sample was placed in 125 mL Erlenmeyer flasks with an acid detergent solution for ADF (acid detergent fiber) and a neutral detergent solution for NDF (neutral detergent fiber) in a water bath at 97°C for 1 hour. Subsequently, the solutions were vacuum-filtered and washed with 800 mL of water and 40 mL of acetone at the end. Finally, they were oven-dried and weighed. The lignin content was determined following the standard method of the Technical Association of the Pulp and Paper Industry (TAPPI) T222 om-88.[9] For this analysis, 1 g of dried sample was treated with 72% sulfuric acid at 60°C for 7 minutes with vigorous stirring. The solutions were autoclaved at 121°C for 30 minutes, then vacuum filtered, washed, dried, and weighed.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR analyses were performed with a Prestige spectrometer. The FTIR spectra of CA, CN, and hydrogels were recorded in the 4500 to 400 cm−1 spectral range. The CA and CN samples were analyzed dry without additional treatment.

X-RAY DIFFRACTION (XRD)

To evaluate the crystallinity of CA and CN, a PANalytical X'PERT PRO MDP diffractometer was used, with copper Kα radiation (λ = 1.5418 Å) and operating conditions of 40 kV and 30 mA. The relative crystallinity index (CI) was calculated according to the previously established method,[10] with the following equation:

$$Ic(\%) = \left(1 - \frac{I_{am}}{I_{200}}\right) x\ 100\ \%$$

Where I_{200} is the intensity of the crystalline peak (2θ ~ 22.8°), and I_{am} is the intensity of the amorphous phase (2θ ~ 18.6°).

STATISTICAL ANALYSIS

Statistical analysis was performed using R. Student's t-test was used for all results. The significance level was set at 5%.

3 RESULTS & DISCUSSION

DETERMINATION OF LIGNOCELLULOSIC CONTENT

Table 1 shows that after treatment with alkaline peroxide, the cellulose content increased from 16.45% to 62.42%, with a significant decrease in hemicellulose and lignin content, respectively. The process yield was 37.6 g of bleached material/100 g of oat hulls.

Table 1. Cellulose, hemicellulose, and lignin content in CA and CN.

Samples	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Yield (%)
Oat hulls (CA)	16,45 ± 1,03[a]	36,69 ± 0, 71[a]	31,96 ± 0,67[a]	37.60 g bleached material/100 g oat hulls.
Bleached material (CN)	62,42 ± 1,20[b]	7,68 ± 0,72[b]	17,33 ± 1,00[b]	

(a-b) Superscript lowercase letters in each column indicate significant differences between the means of the treatments (p ≤ 0.05).

In a previous study, cellulose was extracted from sugar palm, yielding 82.88%-86.99% cellulose, 5.34%-2.90% lignin, and 11.60%-9.95% hemicellulose using alkaline peroxide. These results showed lower lignin and higher cellulose percentages than in this study, with hemicellulose at a lower rate (7.68%).[11] Another study on oat hulls reported higher cellulose (94.2%) and lower lignin and hemicellulose (1.0%-1.4%).[12] Variations are due to raw material type, extraction conditions, climate, location, or crop age. Warm environments can alter hemicellulose and lignin composition, while cellulose remains unaffected by climate.[13]

In this study, a one-step alkaline peroxide pretreatment was applied, resulting in over 62% cellulose content. However, considering factors such as temperature, agitation, different extraction times, and concentrations, a more comprehensive evaluation is suggested, as these aspects were not initially considered.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In Figure 1, for CA and CN, peaks around 3441 cm^{-1} and 1636 cm^{-1} are evident, representing the stretching vibrations of the -OH and C-H functional groups of cellulose. Additionally, the peak around 2900 cm^{-1} corresponds to C-H stretching. The peak at 1250 cm^{-1} in CA corresponds to C-O stretching of the aryl group of lignin; the absence of this peak in the CN spectrum indicates that, after bleaching with alkaline peroxide, most of the lignin and hemicellulose were removed. Similarly, the peaks at 1054 cm^{-1} and 896 cm^{-1} in CN are related to C-O stretching and C-H bending vibrations of cellulose. The results obtained are consistent with those of other authors.[14,15]

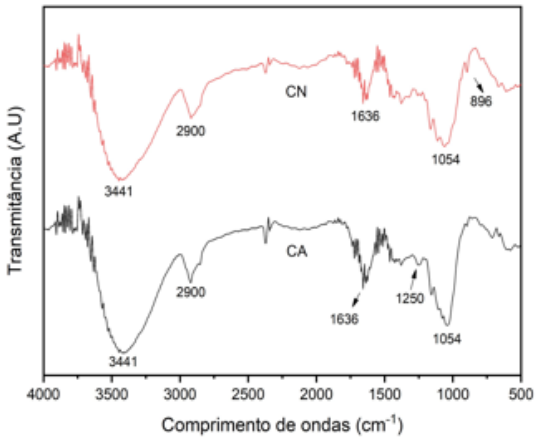

Figure 1. FTIR of oat hulls and extracted cellulose

X-RAY DIFFRACTION (XRD)

In figure 2, a peak at 2θ=22° was observed in both CA and CN, with CN showing a more pronounced peak due to removing lignin and hemicellulose. Additionally, it was noted that the cellulose present corresponds to type I, as evidenced by the absence of a doublet in the intensity of the prominent peak (2θ=22°). These results corroborate previous studies, which reported that cellulose was responsible for the crystalline fraction due to the hydrogen bonds formed between the cellulose molecules, resulting in a monoclinic crystalline network.[16] Peaks at 2θ=34° were also observed for both CA and CN and at 2θ=16° for CN, which are also characteristic of type I cellulose.

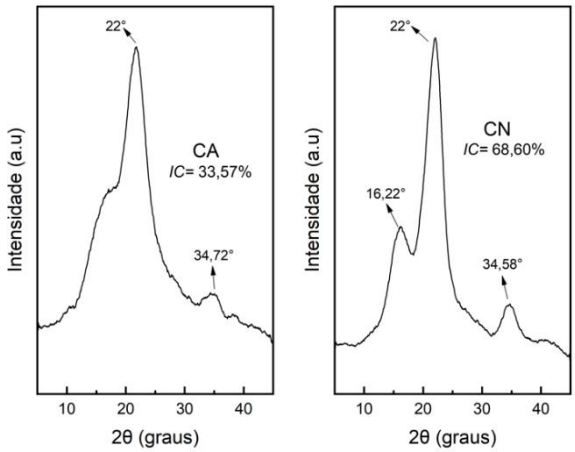

Figure 2. X-ray diffraction patterns and crystallinity index of oat hulls (CA) and extracted cellulose (CN)

The CI of oat hulls was 33.57%, increasing to 68.60% for the extracted cellulose after bleaching. This rise in crystallinity is due to the partial removal of lignin and hemicellulose by alkaline peroxide treatment. The crystallinity of lignocellulosic materials is attributed to cellulose's crystalline structure.[12] These results align with other studies using hydrogen peroxide for extraction.[17,15]

4 CONCLUSION

Using a one-hour eco-friendly hydrogen peroxide treatment, cellulose was successfully isolated from oat hulls (> 62% extracted content) with minimal lignin and hemicellulose residues. Future studies should consider factors like temperature, agitation, extraction times, and concentrations to assess their impact on cellulose content. Additionally, cellulose, hemicellulose, and lignin contents were measured before and after extraction, with FTIR and XRD spectra confirming the characteristic peaks of cellulose.

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