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Thermal and Chemical Characterization of Bleached Cellulose From Horse Grass (Andropogon Tectorum)

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Research Article

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Abstract

Horse grass fibers were pretreated with 10% (w/v) sulfuric acid solution to eliminate hemicelluloses and obtained cellulose fibers. Cellulose fibers obtained were then de-lignified with 25% methanol, 60 min cooking time at 121^0C, and later subjected to hydrogen peroxide–acetic acid (HPAC) bleaching process. Fourier transform infrared (FT-IR) spectrometry, Thermogravimetry analysis (TGA), and X-ray diffraction (XRD), analysis was applied to analyze treated cellulose fibers obtained from horse grass. The chemical analysis showed cellulose yields of 48.10%, 82.74%, and, 92.59% for raw horse grass fibers, methanol-treated fibers, and hydrogen peroxide acetic acid treated fibers respectively. The FT-IR spectral characterization has established the elimination of hemicelluloses and lignin. TGA analysis results showed that treated fibers have high thermal stability. XRD results show diffraction peaks that are comparable to cellulose pulp. It was, therefore, concluded that horse grass fibers can serve as alternative raw materials for cellulose production.

Introduction

In the study of wood chemistry and especially in its application to the pulp and paper industry, cellulose, hemicelluloses, and lignin are the major natural polymer components. The usage of wood as the major source of raw materials for pulp and paper production has led to deforestation and inorganic chemicals for pulping causing environmental pollution has necessitated the search for alternatives (Jun *et al.* 2016). The longer year of maturity of wood justifies the use of non-wood raw materials derived from biomass such as annual plants and agricultural waste for paper pulp manufacturing (Susi et al., 2015; Ruiz et al., 2011). The annual plants and other non-wood biomass have short life cycles and low lignin contents, which make it easy to pulp with less energy and fewer chemicals (Afifah et al., 2016). The basic knowledge is that lignin acts as cement that ties together the holocellulose parts of lignocellulosic biomass (Ashogbon, 2017). Cellulose is a linear, renewable, and biodegradable natural polymer material (Jun *et al.* 2016; Habibi et al. 2010). Due to its abundant renewable polymers, the use of cellulose is becoming increasingly important. Many annual plants and agricultural plants, such as bagasse, and wiry love grass have been used for the production of cellulose, with applications as composites, nanocrystalline cellulose, pulp, and paper (Susi et al. 2015Brinchi et al. 2013). Therefore, cellulose can be obtained by different methods such as mineral acids hydrolysis, and enzymatic hydrolysis, during the period of hydrolysis the lignin will break down into soluble substance in the liquor (Praveen et al., 2019; Suryadi et al., 2017; Arshadi et al., 2016). Since removing the lignin requires the usage of chemicals, in this regard, environmentally friendly chemicals such as organolsov pulping have to be considered, because it eliminates sulfur emission and is biodegradable (Khristova, 2006). With the arrangement of the lignin sugar complex, pulping may not be sufficient enough to remove all the lignin and hemicellulose residue from the materials, therefore extra procedures like bleaching processes have to be engaged (Wi et al. 2015). With our extensive research, no comprehensive facts regarding the properties of cellulose isolated from horse grass are presented in the scientific literature to the best of our knowledge. Therefore, considering waste to wealth, due to the availability of annual plants, especially horse grass, it

is necessary to convert its usage for cellulose production. This paper aims to generate cellulose from horse grass, by organosolv treatment using methanol as a solvent

Materials and method

Materials

The 2g of air-dried samples of horse grass grounded in a hammer mill, with a fraction of particle size 0.5-1mm was selected as raw material in this study.

Chemical analysis

The chemical characterization was performed using standard methods: Ash content, cellulose, hemicelluloses and lignin by TAPPI T 211om-93, TAPPI T 203 om-99 and TAPPI T 222om-99, alcohol-benzene extractable, water, and an alkali (1%NaOH) were determined by TAPPIT 204 om-97, TAPPI T 207 om-93, TAPPI T 212 om-98, respectively (Anonymous, 1992–1993).

Preparation of unbleached and bleached cellulose:

50g of air-dried samples of horse grass was pretreated with 10% (w/v) sulfuric acid solution inside a 1L reactor at 120^0C for 10 min, followed by centrifugation to isolate the rich pentosans. Cellulose fibers obtained were then de-lignified with 25% methanol, 60 min cooking time at 121^0C. 20g of unbleached cellulose was taken and bleached with hydrogen peroxide and acetic acid HPAC (1:1) v/v at 80^0C for 2h. The bleached cellulose fibers were later dried in an oven at 50^0C for 12h using (Wi et al. 2015).

Fourier Transform Infrared (FTIR) spectroscopy

FT-IR was used to determine the chemical structure of obtained cellulose fibers. The measurement of the resulting cellulose fibers was taken using Shimadzu FTIR 8400s equipped with MIRacleTM ATR. Each scan recorded 21 scans in the range from 4000 − 500 cm-1 with a resolution of 4 cm-1.

Thermogravimetric analysis (TGA)

TGA curves of cellulose fibers were obtained by the use of a thermogravimetric instrument. Thermal behavior of the preparations was obtained by recording the TGA curves in the range 25 to 7000C under conditions of nitrogen atmosphere using weighed samples in the range 10 to 15mg, at 200C min-1.

X-Ray Diffraction Analysis (XRD)

The XRD analysis instrument used was SHIMADZU XRD-6000 operating at 40kV/30mA with a Cu-Kα radiation (λ = 0.154nm). The cellulose fibers data were collected at ranges 50 to 800 on the 2θ.

Results and Discussion

The chemical properties of horse grass

The chemical analysis results presented in Table 1 show that Horse grass has cellulose, hemicelluloses, and lignin contents of 48.10%, 26.10%, and 18.50%, respectively, ash content of 2.58%, 1% Alkalinity of 30.80%, Alcohol-cyclohexane extractible 2.7%, cold water, and hot water extractible of 2.35%, and 4.25%. The study showed that most of the results such as cellulose, hemicelluloses, lignin, 1% alkali, and alcohol extract are comparable to grasses and non-wood fibers as reported by (, Gülsoy and Şimşir; 2018; Moradbak et al., 2016; Susi et al., 2015). From Table 1, the chemical analysis results of unbleached horse grass cellulose fibers were 82.74%, 12.81%, and 3.12%, and the results of hydrogen peroxide acetic acid (HPAC) bleached horse grass cellulose fibers were 92.59%, 5.32%, and 0.15% for cellulose, hemicelluloses, and lignin respectively. The results showed that cellulose in the treated fibers was higher than in raw horse grass fibers. The above results are comparable to alkali-treated agave fibers, but higher than the Fruit and Vegetable Pomaces (Monika et al., 2017; Rosli *et al.*, 2013). After the methanol-water pulping process, it was observed that hemicelluloses declined in high percentage, this can be attributed to their amorphous nature which made them more easily degraded by sulfuric acid. The crystalline and stable nature of cellulose makes it very hard to be broken by a mineral acid with low concentrations (Praveen et al., 2019). It also shows that hydrogen peroxide–acetic acid (HPAC), was very effective in bleaching horse grass fibers because the extracted cellulose had a lignin content of 0.15. The low lignin content of the Horse grass is an advantage in the pulping process.

Table 1
Chemical composition of raw, Methanol, and HPAC-treated fibers

Parameters	Raw horse grass	Methanol treated cellulose	HPAC treated cellulose
Ash (%)	2.58	1.32	1.81
Cellulose (%)	48.10	82.74	92.59
Hemicellulose (%)	20.10	12.81	5.23
Lignin (%)	18.50	3.12	0.15
Cold water (%)	2.35	-	-
Hot water (%)	4.25	-	-
1% alkalinity (%)	8.42	-	-
Alcohol- cyclohexane extractible (1:2v/v) (%)	2.70	-	-

Fourier Transform Infrared (FTIR) spectroscopy

The primary variations concerning the functional group inside the horse grass fibers and in the cellulose that was obtained can be seen on the infrared spectra peaks as exhibited in Fig. 1. The peak at 3420cm^{-1} relates to the hydroxyls of cellulose, hemicelluloses, lignin, and water molecules. (Zhang et al., 2018). The differences among the spectra of raw, unbleached, and bleached cellulose of horse grass fibers have been observed within the vicinity from 3500 to 700cm^{-1}. The absorption bands at 1732 cm^{-1}, 1606 $cm^{-1,}$ and 831 cm^{-1} were no longer discovered inside the spectrum of the cellulose that was extracted from horse grass (Fig. 1). The absorptions are credited to the functional groups present inside the lignin which can be associated with cellulose and hemicelluloses before the delignification and bleaching of horse grass. (Ayu *et al.*, 2019; Obi et al., 2014).

Figure 1, shows some absorptions that should be emphasized, the bands at 1514 cm^{-1}; 831 cm^{-1}; 1058 cm^{-1}; 1035 $cm^{-1,}$ and 1031 cm^{-1}. The band at 831 cm-1 is not present in both unbleached cellulose and bleached cellulose and the band 1514 cm-1 decreased in unbleached cellulose fiber but completely disappeared in the spectrum of bleached cellulose fibers. These absorption bands 1514 cm^{-1} and 831 cm^{-1} are essential because their absence in the bleached cellulose fibers spectra shows that the lignin has been removed. After the removal of lignin, the crude cellulose and bleached cellulose display a brand-new sharp band at round 1058 $cm^{-1, which}$ seems like a doublet with 1035cm^{-1} for unbleached cellulose and 1031 cm^{-1} for bleached cellulose, and this can be discovered after the elimination of lignin and other extractives (Pandey,1999). After pulping and bleaching the absorbance 1433, 1319, 1035, and 896 cm^{-1}, which are typical cellulose was found in the hydrogen peroxide-acetic acid (HPAC) bleached cellulose peaks (Do et al., 2016, Lamamin et al., 2015).

Thermogravimetric Analysis (TGA)

TGA curves as shown in Fig. 2, the TGA curves occur in two stages; the first stage of weight loss occurs at around 30-100^{0}C (both fibers), which corresponds to water vaporization heat in the sample (Yang et al., 2007; Poletto et al., 2012).

The main degradation of three main components; cellulose, hemicelluloses, and lignin happened in the second stage of decomposition. The degradation of cellulose and hemicelluloses takes place at 200^{0}C-500^{0}C; while the degradation of lignin takes place at the third stage 250^{0}C-500^{0}C. Since hemicelluloses happen to be the most reactive components their degradation will come first, at somewhere around 200 and 350^{0}C as reported by (Caroline et al., 2011). Followed by cellulose, and lignin comes last, which breaks down between 250-500^{0}C (Araceli et al., 2010), at this point, the decomposition of larger parts of hemicelluloses, some part of cellulose, and lignin happen in thermal reactions. It was observed that the TGA curves of horse grass fibers follow the trend of typical biomass pyrolysis as reported by (Nkateko et al., 2017). From the insert, the residue from degradation temperature can be seen, at 14.7, 13.8, and 2.8 wt%. for raw, unbleached, and bleached horse grass fibers. The small amount of residue in bleached fibers of horse grass may be the result of lignin removal during acid hydrolysis (Shah et al., 2017, Ruzene et al., 2009). The thermal properties of the fibers results showed that raw horse grass fiber had the

lowest thermal stability at a lower temperature of approximately 345.4^{0}C while the Methanol-treated fibers and Hydrogen peroxide acetic acid-treated fibers started to degrade at 430.1^{0}C and 436.5^{0}C respectively. The thermal results of bleached horse grass fibers clearly show that hydrogen peroxide acetic acid (HPAC) treatment enhances its thermal stability, this can be noticed from degradation temperature, which can be attributed to the removal of hemicellulose and lignin.

X-ray Diffraction analysis (XRD)

Figure 3 shows the effect of treatment on horse grass fiber using a high-resolution X-ray diffractometer. The crystallinity of horse grass fiber was calculated from an X-ray diffractogram using crystallinity index (CI) calculation based on $CI\,(\%) = I\,(002) - I\,(Am)\,/I\,(002)\,x100$ (Rosli *et al.*, 2013) Where I (002) is the peak height at 22.4 (2θ) and I(Am)is the peak height of amorphous cellulose to 16.5 (2θ). The pattern of raw horse grass fibers, methanol treated fibers, and hydrogen peroxide acetic acid treated fibers can be seen from Fig. 4, X-ray diffractogram, and the peaks around 2θ = 16^0, 22^0, 35^0, signified cellulose structure. The peaks at 160 and 220 show evidence of treatment on the fibers. These peaks indicate that methanol and hydrogen peroxide acetic acid (HPAC) treatment, was able to dissolve the lignin and hemicelluloses to give pure crystalline materials from horse grass, this is in agreement with (Fatah et al., 2014). From Fig. 3, diffractogram, hydrogen peroxide acetic acid treated fibers give the highest crystallinity index peak at 2θ of 35^0. The crystallinity index of raw horse grass fiber, methanol-treated fiber and hydrogen peroxide acetic acid-treated fiber are 51.6%; 59.3%, and 61.9% respectively, which are comparable to the results reported (Afifah et al., 2016).

Both untreated and treated fibers showed similar patterns, but raw horse grass fibers have less crystalline than methanol and hydrogen peroxide acetic acid treated fiber. The hydrogen peroxides acetic acid treated fiber exhibited the highest crystallinity which showed that it is more efficient in removing the amorphous parts and has higher orderliness of crystalline structure, this is in agreement with (Fatah et al., 2014).

Conclusion

The experimental results showed that horse grass is another new good source of cellulose production. A low concentration of Methanol used on horse grass fibers, degraded substantial amounts of hemicelluloses, while HPAC treatment removed all the residual lignin. The bleached horse grass fibers showed the highest thermal stability and the highest percentage of crystallinity.

The research concluded, that using 25% methanol, with 60min cooking time at 121^{0}C was excellently good for the treatment of horse grass fibers. It is therefore recommended that horse grass fibers can serve as alternative sources for cellulose production.

Declarations

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Authors contributions

Conception and design: OO and AOA,

Formal analysis and investigation: OO and AOA, Data collection and analysis: OO,

Writing-first draft preparation: OO, Writing—review and editing: OO and AOA, Supervision: AOA.

Conflict of interest

We jointly declare that there is no conflict of interest of any sort.

Ethical approval and funding

“Not applicable”

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Figures

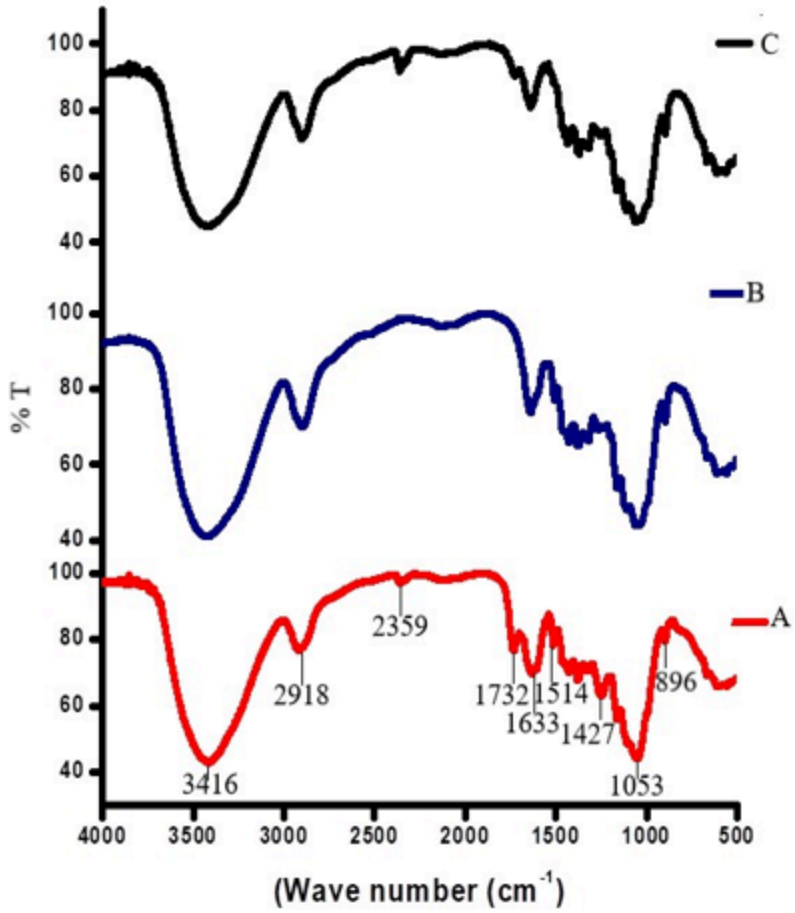


Figure 1

FTIR spectra of horse grass (wavelength 4000 to 500 cm^{-1}). (a) Raw horse grass fibers (b) Methanol-treated fibers and (c) HPAC-treated fibers of horse grass

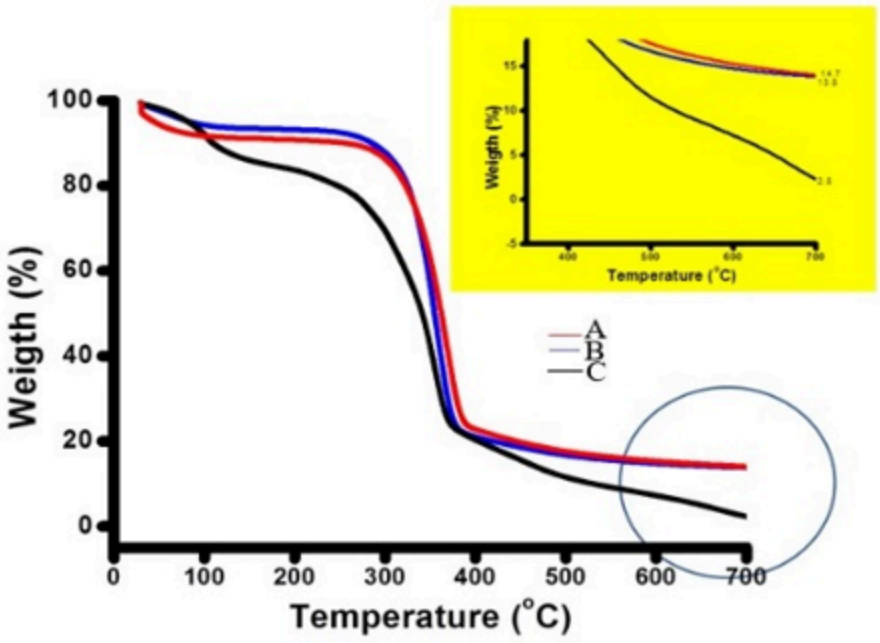


Figure 2

TGA curves (a) Raw horse grass fibers (b) Methanol-treated fibers and (c) HPAC-treated fibers of horse grass

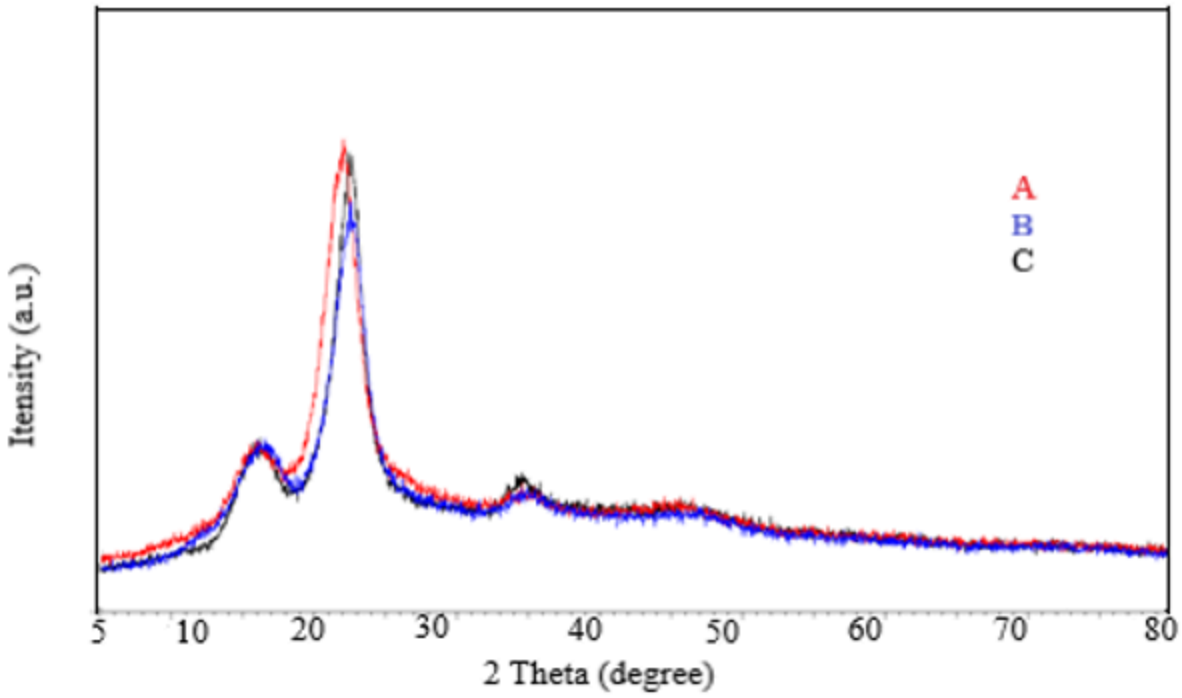


Figure 3

X-ray diffraction patterns for (a) Raw horse grass fibers (b) Methanol-treated fibers and (c) HPAC-treated fibers of horse grass