Different Sequential Chemical Treatments Used to Obtain Bleached Cellulose from Orange Bagasse

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ABSTRACT
The development of efficient pretreatments is widely used in biobased products aiming to add value to the residue. In this study, orange bagasse is investigated for cellulose extraction under moderate chemical sequential extraction conditions. Three pretreatments are evaluated: alkaline treatment, organosolv, and residue insoluble alcohol. Then, all pretreated samples are bleached. The results are analyzed by chemical composition, Fourier transformed infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. In general, similar results are observed for all bleaching samples, independently of the pretreatment. A similar cellulose amount is observed among the samples. When compared only to the pretreatments, alkaline shows to be a more effective way of presenting a higher crystallinity index. Hemicellulose and lignin are mostly removed after pretreatment. FTIR and XRD indicated that the pretreatment seems to be more effective in the first step. TG curves presented a more homogeneous pattern due to cellulose removal showing three steps for pretreatment and two steps for bleached samples. The obtained cellulose has numerous potential applications, and a suitable route can be selected according to available reagents.

KEYWORDS
Orange bagasse; chemical treatment; waste bleaching; natural fibers; cellulosic; green solvents

Introduction
Many agroindustrial orange or sweet orange (Citrus sinensis L. Osbeck) is one of the 30 species of Citrus (Roussos 2016), and it is the most common cultivated fruit all over the world. It belongs to the Rutaceae family, being Brazil, the largest orange juice producer (Ashok et al. 2019) in the world. Consequently, the number of underused by-products as peels, seeds, and bagasse (corresponding to around 50% of the total fruit) generated is enormous (López-Linares et al. 2015). These by-products...
can be used for animal feed, but most are disposed of in the environment without any type of treatment, offering a great diversity of low-cost raw materials as the production of bioethanol (a high value-added product). Most plant fibers are formed by a complex structure of crystalline cellulose microfibrils wrapped by an amorphous region consisting basically of lignin, hemicellulose, pectin, extractives, and waxes (Jabbar et al. 2017). Bagasse orange contains peel (60–65%), internal tissues (30–35%), and seeds (0–10%), and it has high levels of soluble sugars, pectin, proteins, hemicellulose, and cellulose (Awan et al. 2013). Thus, to convert these by-products into new value-added ones, different methods are available to separate specific components from the fibers, like cellulose isolation. The treatment methods can be classified as physical, chemical, physicochemical, biological/enzymatic, and combined (Kumari and Singh 2018). Alkaline treatment is a chemical method, and it has high efficiency in removing amorphous/non-cellulosic components like lignin, hemicellulose, extractives, and waxes (Shimizu et al. 2018; Lorenci et al. 2020). Organosolv is a promising approach for pretreatment of biomass since it can solubilize hemicellulose, lignin, and inorganic compounds as silica (SiO$_2$) found in plant cell walls (Ferreira and Taherzadeh 2020). The advantages are as follows: high-quality lignin obtained, value-added in the process, and solvent easily recovered by distillation, which leads to less water pollution. Another example is the alcohol-insoluble residue (AIR), which is dependent on: i) type of starting material and ii) type of analysis to be followed (Waldron and Selvendran 1990). More intracellular/cytoplasmic material is found for coarsely ground or homogenized samples, becoming difficult the removal with subsequent aqueous or solvent extractions. In the bleaching process, some oxidant agents such as hydrogen peroxide (H$_2$O$_2$) are used to cause the oxidation and dissolution of the lignin and hemicellulose remnants (Kabir et al. 2013). After bleaching, the fibers can be treated with a potassium hydroxide solution to remove the residual hemicellulose and produce more pure cellulose fibers (Júnior et al. 2020). Unlike acid or alkaline pretreatment, alkaline peroxide pretreatment can be performed at relatively milder conditions (concentration, temperature) and atmospheric pressure while effectively removing lignin from various agricultural residues.

In the literature, there are several works using vegetal fibers to extract cellulose using different waste and pretreatments like pear, carrot, apple, chokerry, and olive and pineapple crown (Okoro et al. 2021; Pereira et al. 2021). After a mild chemical sequential extraction of lignocellulosic components, solid residues usually contain cellulose, and lignin remnants. Research on the exploitation of orange bagasse residue (OB) has been dedicated to the production animal feed, for H$_2$ and methane production, pectin and limonene, biochar and ethanol production by fermentation (Barbosa et al. 2020) are highlighted. In this context, the extraction of cellulose, hemicellulose, and lignin from the orange bagasse study is very necessary, and only a few studies are found in the literature with an emphasis on this residue. Mariño et al. (2015) reported the extraction of cellulose from orange bagasse, using alkaline and acid treatments, followed by bleaching with sodium chloride. Bicudo and Mustata (Bicu and Mustata 2011) extracted cellulose from orange peel using sequential chemical treatments, including alkaline and sulfite pulping and bleaching steps with hypochlorites and hydrogen peroxide. Cypsyriano, da Silva, and Tasic (2018) reported the use of multistep chemical treatment with sodium hydroxide and sodium chloride to obtain a cellulose-rich material employed for the preparation of nanocellulose.

Based on the literature above, a profound understanding of three different chemical treatments on the orange bagasse regarding chemical composition, chemical structure, crystallinity, and thermal behavior is presented.

**Material and methods**

Orange (*Citrus sinensis* L. Osbeck) used to extract the orange bagasse (OB) were obtained from a popular restaurant at Guaratinguetá city (São Paulo/Brazil) was used as solid waste. OB fibers were previously oven-dried at 60°C for 24 h, cut into a Garthen mill, model GP-1500 AB (1.5 cv), chopped in a knife mill Tecnal model TE-650, and granulometric fractionated until passing by a sieve of 30 mesh (0.595 mm). Reagents employed were: sodium hydroxide (NaOH), acetic acid (C$_2$H$_3$O$_2$),
hydrochloric acid (HCl), ethanol (C₂H₅O), nitric acid (HNO₃), and hydrogen peroxide solution (H₂O₂ 35% v/v), all purchased from Vetec. Untreated orange bagasse fibers were treated following three routes of chemical treatment: (i) alkaline treatment using NaOH, (ii) organosolv with acetic acid, and (iii) AIR using ethanol, which is called the first stage. After this, two stages of bleaching (1B and 2B), following alkaline treatment with KOH solution to remove the residue of hemicellulose first stage all samples were bleached (1B and 2B) and treated with solution KOH.

**Alkaline treatment (AT)**

OB fibers were treated with a 4% (w/v) alkaline solution of sodium hydroxide (NaOH) at a fiber/solution ratio of 1:20 (g/mL) according to (Benar et al. 1999). AT fibers (5 g) were bleaching step was carried out with solution of NaOH 4% (w/v)/ H₂O₂ 30% (v/v) solution at 70°C to (Benar et al. 1999). Finally, after bleaching, fibers were treated with KOH 4% (w/v) solution for 1 h at 80°C, following the pulp: solution ratio of 1:20 g/mL. The solution was vacuum filtered to neutral pH and oven-dried at 60°C for 24 h, which was named 2B/KOH.

**Organosolv Acetic Acid (OAc)**

The acosolv extraction was prepared according to (Pereira et al. 2021). The sequence of bleaching treatments (Bleaching (1B), Bleaching (2B), Bleached (2B/KOH)) was similar to those mentioned above.

**The alcohol-insoluble residue (AIR)**

Orange bagasse fibers were treated using 350 mL of ethanol in one of the balloons coupled to each of the glass tubes, 20 g of milled orange bagasse fiber were added, the balloons were subjected to the heating assembly, while a hose at the top carries cold water causing the vapor to be condensed nature passing through the fiber and removing the soluble residues in ethanol for 24 h. After, the same sequence of bleaching treatments ((1B), (2B), and (2B/KOH)) was followed, as described as mentioned above.

**Characterization of the fibers**

The chemical composition of the OB (in nature), AT, AT_B, AC, AC_B, AIR, and AIR_B was carried out according to (Sluiter, Hames, and Ruiz 2012). Acid-soluble lignin was determined according to (Dence 1992). Monomeric sugars are quantified by high-pressure liquid chromatography (Waters® HPLC) using an HPX-87 H column (Bio-Rad). The temperature of the test was ~45°C, and the samples were eluted with 5 mmol/L sulfuric acid at 0.6 mL/min. To evaluate the functional groups on the surface of the fibers, the ATR (Attenuated Total Reflection) technique was used. The spectra of fibers were determined in a Spectrum GX Perkin Elmer spectrophotometer by taking 8 scans in the range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. X-ray diffraction (XRD) pattern was measured on a Shimadzu diffractometer (XDR-6000 Model), operated at 40 kV and 30 mA with Cu Kα radiation (λ = 0.1542 nm), at angles of incidence of 10–50° (2θ/5 s). The crystallinity index (CI) was determined using the empirical Segal method (Segal et al., 1959), Eq. (1): 

\[ CI = \left[ \frac{I_{200} - I_{am}}{I_{200}} \right] \times 100 \]  

where: \( I_{200} \) is the maximum intensity of the diffraction peak from the (200) plane at 2θ=22°, and \( I_{am} \) is the intensity of the minimum intensity between the major peaks. The values of d-spacing and the crystallite size perpendicular to the plane (L) for different crystalline planes also were calculated. The
d-spacing of each plane was calculated using Bragg’s equation, while the crystallite size was calculated by the Scherrer equation (2) (Ornaghi Jr. et al. 2014) and the crystallite size was calculated using the Scherrer equation

$$L = \frac{(0.94 \times \lambda)}{(H \times \cos \theta)}$$  \hspace{1cm} (2)

where $L$ is the crystallite size perpendicular to the plane, $\lambda$ is the X-ray wavelength (0.1542 nm), $H$ is the full-width at half-maximum in radians, and $\theta$ is the Bragg angle.

Thermogravimetric curves (TG) were analyzed using TGA equipment (TG/DTG SII Nanotechnology Inc., Exstar TG/DTA 6200 model), and were carried out at a flow rate of 60 mL min$^{-1}$, using approximately 10 mg of each sample, at heating rates of 10°C min$^{-1}$ in N$_2$ atmosphere (0.05 L min$^{-1}$), in the temperature range from 25°C to 660°C.

**Results and discussion**

**Chemical composition**

The effect of each chemical treatment step on the chemical composition of orange bagasse is presented in Table 1. The values of the chemical composition differ from other orange bagasse found in the literature (Alvarez et al. 2018; Bhattacharjee and Biswas 2019) due to differences in plant age, variety, geographical region of the plant, among others (Franco et al. 2019). In the first treatment, an increase of cellulose and lignin was observed while the hemicellulose content decreased. The increase of lignin was 13.41% higher after acetosolv treatment due to the lignin solubilization on the fiber surface (Souza et al. 2016). For hemicellulose amount, no significant differences were observed after the first treatment for all samples. With the second step of extraction, the cellulose content increased because of the removal of other components such as lignin, hemicellulose, and amorphous cellulose. The compounds were not entirely extracted after the bleaching treatment. However, relatively higher cellulose (greater than 75%) was obtained regardless of the sequence of chemical treatment content implying the feasibility of cellulose production using orange bagasse as a raw material (Pereira et al. 2021).

**FT-IR spectroscopy**

Figure 1 presents the FTIR spectra for all fibers studied. It is clear differences in absorption by bleached samples, independently of the chemical treatment. Aiming to help the reader visualize the results obtained, FTIR discussion was divided into two main regions (Popescu, Singurel, and Popescu 2009) i) from 4000 cm$^{-1}$ to 2700 cm$^{-1}$ and ii) from 1900 cm$^{-1}$ to 500 cm$^{-1}$. The former includes OH and CH stretching bands at 3400 cm$^{-1}$ and 2900 cm$^{-1}$, respectively. The second is assigned to different stretching vibrations of other groups from cellulose, hemicellulose, and lignin in 1900–800 cm$^{-1}$. Besides, the OH region is particularly useful for elucidating hydrogen patterns while CH stretching

| Fractions (%) | In natura | AIR | AIR_B | AC | AC_B | AT | AT_B |
|---------------|-----------|-----|-------|----|------|----|------|
| Ashes         | 6.2 ± 0.1 | 6.6 ± 0.04 | 3.07 ± 0.04 | 3.06 ± 0.03 | 2.1 ± 0.02 | 6.2 ± 0.02 | 2.92 ± 0.03 |
| Extractives   | 41.6 ± 1.5 | n.a* | n.a* | n.a* | n.a* | n.a* | n.a* |
| Lignin        | 5.1 ± 0.1 | 7.86 ± 0.04 | 2.00 ± 0.15 | 13.41 ± 0.53 | 2.80 ± 1.0 | 6.8 ± 1.0 | 2.60 ± 0.19 |
| Cellulose     | 22.9 ± 0.5 | 31.05 ± 4.1 | 79.34 ± 4.1 | 27.28 ± 3.6 | 78.1 ± 0.7 | 46.2 ± 0.3 | 78.94 ± 1.4 |
| Hemicellulose | 24.1 ± 0.1 | 18.10 ± 3.7 | 16.33 ± 1.9 | 18.31 ± 1.1 | 1.5 ± 0.3 | 4.9 ± 0.1 | 16.49 ± 0.98 |
| Total         | 99.9 ± 2.5 | 63.64 ± 3.8 | 100.7 ± 6.1 | 62.061 ± 1.8 | 79.6 ± 2.1 | 64.1 ± 2.6 | 100.9 ± 2.1 |

*Not analyzed.
mode elucidates carbonyl stretching vibrations of the carboxyl and acetyl groups in hemicelluloses and alkenes stretching of the aromatic ring in lignin (Faix 1991). Hence, both regions were treated separately.

**Hydroxyl stretching absorption**

Each hydroxyl group in fiber gives a single stretching band at a frequency that decreases with increasing hydrogen bonding strength (Popescu et al. 2011). The mixture of inter- and intramolecular hydrogen bonds is responsible for various properties of lignocellulosic materials. Also, it is responsible for the broadening of the OH band in the IR spectra. The chemical treatment can be responsible for changes in peak wavenumber (Wada, Kondo, and Okano 2003).

Regarding the OH stretching region, the broadband from orange bagasse is from variations in the degree of hydrogen bonding between OH groups in the cellulose crystal/aggregated states, hemicellulose, lignin, and water (Cintrón and Hinchliffe 2015). With the removal of hemicellulose and lignin from chemical treatment, the relative increase of absorbance is taken as an indication of more organized cellulose. Consequently, sharper bands with the reduced band are expected due to the vibrations contributing at the same frequency. Thus, a reduction in overall area intensity in the OH region is observed in bleached-treated samples. As a consequence, higher-order suggests higher crystallinity (analyzed in section 3.3). In our study, sharper peaks are observed for bleached samples, but the width seems not to be altered. A shift to a higher wavenumber is observed at the maximum absorbance for hydrogen-bonded in the case of all bleached fibers in the OH stretching region. This could be indicative of a decrease in intramolecular hydrogen bonding. The values obtained for in natura 3298.68 cm\(^{-1}\), AT: 3227.20 cm\(^{-1}\), AT_B:331.41 cm\(^{-1}\), AC: 3327.58 cm\(^{-1}\), AC_B:3332.49 cm\(^{-1}\), AIR: 3307.17 cm\(^{-1}\), and AIR_B:3313.04 cm\(^{-1}\). When compared to in natura fiber, most of the fiber had higher maximum absorbance. Also, all peaks shift for a higher maximum for all bleached fibers. All bleaching processes increased the peak height-more organized structure. Consequently, the crystallinity index tends to increase. Using the values obtained, it is possible to estimate the energy of the hydrogen bonds (\(E_H\)) (Equation 3) and the hydrogen bonding distances (\(R\)) using the Sederholm equation (Equation 4):

\[
E_H = \frac{1}{K} \left[ \frac{v_0 - v}{v_0} \right]
\]

\[
\Delta v (\text{cm}^{-1}) = 4.43 \times 10^3 (2, 84 - R)
\]
where: \(\Delta \nu = \nu_0 - \nu\), \(\nu_0\) is the monomeric OH stretching frequency, is taken to be 3560 cm\(^{-1}\) for the former and 3600 cm\(^{-1}\) for the latter, \(\nu\) is the stretching frequency observed in the IR spectrum, and \(K\) is a constant = 262.5 kJ. Table 2 presents the calculation of FTIR parameters based on the Equations above.

Even with differences in maximum peaks described earlier, the hydrogen bond distance was not significantly altered by treatment. The energy of the overall OH bonds unexpectedly decreases after bleaching. This may be attributed to a loss of overall OH bonds due to hemicellulose and lignin removal and not necessarily to the energy per se.

Since the OH region is composed of two intramolecular, one intermolecular, and one OH stretching (Fan, Dai, and Huang 2012), the results suggest that after treatment, there is a more intense disruption of the hydrogen bonds at the C-3 and C-6 position in the cellulose (Mariño, Rezende, and Tasic 2018). The band referred to the lignin phenolic group (3591/3579 cm\(^{-1}\) = absorbed water weakly bound and intramolecular hydrogen bond) was not observed for all bleached samples. The bands at 3438/3435 cm\(^{-1}\) are assigned to the O-H intermolecular hydrogen bonds involving the C6 position (primary hydroxyl groups). At 3348/3345 cm\(^{-1}\), the frequencies are attributed to the O\(_5\)-H\(_{5\cdots6}\) intramolecular hydrogen bond.

If it is considered cellulose I\(_\beta\) and cellulose I\(_\alpha\) (two crystalline allomorphs): at 3226/3217 cm\(^{-1}\), O\(_6\)-H\(_{6\cdots7}\) intramolecular hydrogen bonds existing only in triclinic I\(_\alpha\) cellulose; while the amount of monoclinic phase I\(_\beta\) is assigned at 3276 cm\(^{-1}\). The results indicate that cellulose I\(_\beta\) is predominant even after chemical treatment.

**CH stretching absorption**

The spectrum is more complex in this region due to different stretching vibrations of the various groups from the main bagasse fiber components. The ranges in the 1800–800 cm\(^{-1}\) are presented in Figure 2. The following groups are attributed to lignin: C = C (1595 cm\(^{-1}\)), C-O stretching (1510 cm\(^{-1}\)), or bending (1270 cm\(^{-1}\)). Other groups as C-H (1460 cm\(^{-1}\)), C-O deformation (1425 cm\(^{-1}\)), C-O bending (1335 cm\(^{-1}\)), or C-O stretching (1220 cm\(^{-1}\) and 1110 cm\(^{-1}\)) are assigned to different groups for lignin and carbohydrates. The bands at 1735, 1375, 1240, 1165, 1060, 1030 cm\(^{-1}\) are assigned to characteristic C = O, C-H, C-O-C, C-O deformation or stretching vibrations of different groups from carbohydrates. Due to the more significant number of cellulose groups presented, the bands assigned to cellulose are higher for pretreatment than their respective bleached samples. The presence of other remaining components is observed in the 1400–1750 cm\(^{-1}\) region. The presence of lignin, hemicelluloses (C = O stretching vibration of carboxyl and acetyl groups in xoglucan), or pectin by the stretching vibration of C-O bond for esters at 1730 cm\(^{-1}\). For NaOH samples, pectin should be discarded due to the acidic pre-treatment (Mariño, Rezende, and Tasic 2018) and chemical composition. Also, the presence of this band is not observed. The bands at 1440–1600 cm\(^{-1}\) are assigned to the stretching vibration of lignin aromatic rings (Mariño,

| Samples | Hydrogen bonding energy (EH) (kJ.mol\(^{-1}\)) \* | Hydrogen bond distance (R) (Å) \* |
|---------|-----------------------------------------------|----------------------------------|
| In natura | 25.26 | 2.77 |
| AT | 30.40 | 2.77 |
| AT_B | 23.99 | 2.77 |
| AC | 23.19 | 2.78 |
| AC_B | 22.83 | 2.78 |
| AIR | 24.65 | 2.77 |
| AIR_B | 24.23 | 2.77 |
Rezende, and Tasic 2018). However, the low intensity of the peaks corroborates the idea of detaching mainly cellulosic products from all samples. All bleached samples showed lower intensity about their pre-treatment.

FTIR spectroscopy can also offer a quantitative lignin determination in fiber. The intensity of the band of aromatic skeletal vibrations around 1510 cm\(^{-1}\) is a measure of the lignin content. Faix (Faix 1988) indicates a non-linear equation which describes well the relation between the lignin content and the height of the 1510 cm\(^{-1}\) band (Equation 5):

\[
\% \text{lignin} = -1.23 + 193.4x - 279.8x^2
\]  

where \(x\) is the band intensity determined by the baseline method.

The lignin content calculated in this study was possible to calculate only for in nature and RIA, and the results found were 31.84% and 9.37%, respectively. The results are in good agreement with the chemical composition (Schwanninger et al. 2004). Faix considers that the calculus is valid only for lignin content from 5% to 30%. But the result obtained for \textit{in natura} showed a good correlation with chemical composition, and it seems to be valid in this case. FTIR calculus so far illustrates that the mean spectra contained specific information that might be useful to distinguish bagasse fiber from most chemical treatments.

**Relative crystallinity based on FTIR analysis**

The total crystalline index (TCI) and the hydrogen bond intensity (HBI) were estimated based on literature (O’connor, Dupré, and Mitcham 1958). TCI is proportional to the crystallinity degree and is calculated by the bands at 1372 cm\(^{-1}\) and 2900 cm\(^{-1}\) bands ratio, and it defines an empirical crystallinity index. HBI is regarded as the degree of intermolecular regularity (crystallinity) and is calculated by the ratio between the absorbance bands at 3400 cm\(^{-1}\) and 1320 cm\(^{-1}\) is used to study the HBI of the OB fibers with different chemical treatments (Oh et al. 2005). Since the structure of the species is the same, a comparable result among other treatments can be done (Carrillo et al. 2018). Table 3 presents TCI and HBI calculated for all samples studied. TCI ratio in bleached samples ranged from 0.25 to 0.44. Regarding HBI, it ranged from 1.51 to 7.94. These values are in agreement with the IR ratios published elsewhere (Carrillo et al. 2018). Since chemical treatment modified chemical composition, it is expected that the band at 897 cm\(^{-1}\) be stronger for cellulose II and amorphous cellulose. Cellulose I change to cellulose II depends on several factors; it can be cited chemical treatment, decrystallization, and changing the crystal polymorph (Mwaikambo and Ansell 2002).
Comparisons are made within each group of samples, given the small variation between the components. IR crystallinity is calculated from two measurements for each sample, and a mean ratio is then calculated. An increase in IR crystallinity with treatment shows that for bleached treatments, there are effective changes in IR spectra. HBI results showed decreased hydrogen bond intensity with bleaching, maybe due to removal of OH intramolecular bonds, hemicellulose, and lignin components.

**X-ray diffraction (XRD)**

X-ray diffraction patterns of the OB fiber with the respective treatments are shown in Figure 3.

Changes in crystal type and chain conformation are feasible and are dependent on solvent, additives, temperature, time, external pressure, among other factors (Mansikkamäki, Lahtinen, and Rissanen 2007). Table 4 shows the apparent lateral crystallites sizes (L) determined by the Scherrer equation and the apparent crystallinity degrees obtained by the Segal method for OB fibers. The result

![Graph](image-url)

**Figure 3.** XRD curve for in nature, AT, AT_B, AC, AC_B, AIR, and AIR_B samples. Dotted line is a guide for the eye representing 200 crystallographic planes.
of OB is in agreement with the literature (Mariño, Rezende, and Tasic 2018) and with values published elsewhere. The lowest crystallinity index was found in natura OB fiber. All treatments promoted an increase in the crystallinity index. All bleached treatments present similar results.

The results obtained from XRD differ from those obtained from FTIR, and no significant correlations could be established between both techniques, except for a general increase in the crystallinity index for bleached samples. But the parameters using FTIR must be used carefully and corroborated with other results. FTIR is sensitive to the polymer chain’s chemical environment and XRD by the crystal lattice structure, so FTIR is an indirect method.

The removal of hemicellulose and lignin increases the regularity of the crystal lattice due to a more organized structure being maintained in the compound, i.e., reduces the amorphous portion of the samples. FTIR calculus uses regions where removing these components is more visible in some specific bands, being less precise concerning XRD results. The removal of less ordered carbohydrates presents a sharper FTIR peak, indicative of a more organized structure, but the values calculated follow a certain trend but are less precise in comparison to XRD results.

According to (Nam et al. 2016), Segal Cr.I. depends on FWHM, crystallite size, and cellulose polymorph, while (Agarwal et al., 2016) (based on Raman spectroscopy) suggested that FWHM from XRD is a measure of the existing disorder in cellulose, which can be considered as the degree of lateral order (DOLO), related with to Cr. I. Changes in FWHM are related to changes in crystal size and may involve changes in DOLO instead of crystallinity, as could be our case if it is assumed that the aggregated state of wood and holocellulose samples are not crystalline.

Regarding the lateral crystallite size (L), a close relationship with the XRD Cr.I. is not observed. The variations of these parameters could be attributed to the removal of lignin, hemicellulose, and less ordered carbohydrates, which could entail the degradation of small crystallites that increase the average lateral crystallite size. Our samples present lower values when compared to the literature.

In this case, the isolation via alkaline extraction mostly removes hemicellulose, low molecular weight, and disordered cellulose chains. Hence, the remaining fraction is mainly constituted of cellulose, and only traces of hemicellulose in the remaining solid are expected, as was confirmed by the reduction of 1740 cm⁻¹ band intensity in FTIR and compositional analysis. As FTIR and XRD indicated, the treatment seems to be more effective in the first step. The alkali solution penetrates the more disordered or amorphous regions, whereby cellulose chains in the amorphous region rearrange into antiparallel cellulose II while the crystalline regions are hardly affected. As the swelling of cellulose continues, the mobility of the cellulose chains is enhanced; hence, the crystalline cellulose gradually diminishes in size.

### Thermogravimetric analysis

The effect of each chemical treatment sequence on the thermal properties of orange bagasse fiber is analyzed based on Figures 4 and 5, and Table 5.

In general, the fibers are composed of hemicellulose, which degrades between 200°C and 350°C or over lower, depending on the experimental conditionals, lignin with an extensive range of degradation temperature (140–800°C) (Galano et al. 2017), the cellulose that presents a high thermal resistance and usually degrades in the range of 300–400°C (Dai et al. 2020) and some impurities such as ash, extractives, waxes,

| Table 4. XRD parameters calculated from diffractograms. |
|----------------------------------|----------------|------------|
| Sample  | L₂₀₀  | FWHM (2₀₀)  | Cr.I.(%) |
| In natura | 5.22  | 1.62  | 15.1 |
| AT      | 3.47  | 2.44  | 42.9 |
| AT_B    | 3.81  | 2.22  | 49.0 |
| AC      | 4.10  | 2.06  | 29.4 |
| AC_B    | 3.47  | 2.44  | 48.3 |
| AIR     | 3.30  | 2.56  | 22.8 |
| AIR_B   | 3.59  | 2.36  | 52.0 |
and inorganic compounds that degrades in the range of 140–800°C (Vassilev et al. 2010). Untreated fibers presented three stages of degradation, while bleached fibers (AT_B, AIR_B, and AC_B) only had two stages, indicating that more homogeneous chemical composition was reached with the chemical treatments applied. Among AT, AC, and AIR fibers, the first presents a more homogeneous degradation with

Table 5. In natura fiber (UT), AT, AT_B, AIR, AIR_B, AC, and AC_B, respectively, and the main mass loss stages.

| Samples  | ΔT (°C) | Tpeak (°C) | Weight loss (%) | Ti (°C) | Residue at 550°C |
|-----------------|---------|------------|-----------------|--------|-----------------|
| In natura       | 30–130  | 57         | 10.22           |        |                 |
|                 | 130–280 | 231        | 29.37           | 124.27 | 29.73           |
|                 | 280–360 | 324        | 18.86           |        |                 |
| AT              | 30–170  | 60         | 10.63           | 133.45 | 20.68           |
|                 | 170–400 | 338        | 61.64           |        |                 |
| AT_B            | 30–140  | 56         | 9.15            | 227.85 | 18.29           |
|                 | 194–404 | 350        | 67.85           |        |                 |
|                 | 30–160  | 62         | 12.39           |        |                 |
| AIR             | 160–279 | 232        | 22.95           | 93.19  | 30.53           |
|                 | 279–360 | 318        | 22.96           |        |                 |
| AIR_B           | 30–130  | 50         | 8.39            | 237.07 | 18.82           |
|                 | 245–390 | 342        | 64.45           |        |                 |
|                 | 30–165  | 62         | 11.75           |        |                 |
| AC              | 165–286 | 250        | 18.37           | 103.52 | 29.40           |
|                 | 286–390 | 340        | 31.34           |        |                 |
| AC_B            | 30–166  | 48         | 8.03            | 243.76 | 21.86           |
|                 | 190–400 | 345        | 63.69           |        |                 |
a shoulder between 150°C and 300°C due to hemicellulose degradation and a narrower peak of cellulose degradation. For AC and AIR samples, the presence of three prominent peaks is an indication that chemical treatments are less efficient in the removal of amorphous components resulting in a material with a more heterogeneous chemical composition. The alkaline treatment causes fiber expansion, increasing the pore size and accessible surface area (Monlau, Kaparaju, and Trably 2015).

On the other hand, during the acetosolv treatment, used to remove mainly lignin, the organic solvents provide the cleavage of the ether bonds of lignin, and also, the oxidation could occur due to the presence of hydrochloric acid as a catalyst reagent (Souza et al. 2016). Finally, AIR treatment is a milder treatment that removes only the alcohol-soluble constituents such as low molecular weight and traces of free galacturonic acid (Oliveira et al. 2016). For all samples, the first stage of degradation is due to the evaporation of adsorbed and absorbed water, as observed in the work of Dai et al. (2020) and Souza et al. (2016). The second one is due to the degradation of hemicellulose (Li et al. 2018), and the third one is due to cellulose degradation (Meng et al. 2019). The main degradation steps are presented in Table 5. The weight loss of each degradation stage can be related to the effect of chemical treatment on removing specific components. The removal of each component gives particular TG curves.

Conclusions

In this study, the importance of utilizing orange bagasse by different chemical pretreatments is demonstrated. A complete chemical structure characterization and discussion are performed, with the advantage of the proper choice of the route, depending on the interest final material. Quantification of the non-cellulosic composites is done after each pretreatment and subsequent bleaching process using FTIR, XRD, chemical composition, and TGA. Higher differences are observed in the crystallinity index and onset degradation curve (shift to higher values), mainly compared to the pretreatment used (alkaline has the best efficiency compared to organosolv and alcohol insoluble residue). All bleaching processes performed after each pretreatment show similar results concerning the techniques analyzed. Moreover, the pretreatment sequence is an essential factor in selecting the adequate chemical method to ensure the most efficient removal of the non-cellulosic materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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