SYNTHESIS AND CHARACTERIZATION OF CARBOXYMETHYLCELLULOSE OBTAINED FROM MANGO SEED WASTE

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ABSTRACT

The use of residues rich in lignocellulosic biomass has been of great importance for the development of more sustainable processes in biorefinery. This study evaluated the production of cellulose and carboxymethylcellulose (CMC) from mango seed (MA) waste. The combined acid/peroxide-alkaline (APA) treatment was used to obtain high yields (52%) of good quality cellulose (MACel) and water-soluble carboxymethylcellulose (up to 200% w/w) for commercial application. TG/DTG, XDR and FTIR analyses were performed to prove the efficacy of the synthesis.

Keywords: Biomass. Cellulose. Carboxymethylcellulose.

1 INTRODUCTION

According to the International Energy Agency (IEA), biorefinery is defined as a sustainable processing of biomass into a spectrum of tradable products and energy. Lignocellulosic biomass obtained from refining to produce versatile bio-based materials is of emerging interest and biorefineries can facilitate a sustainable opportunity to build bioeconomy [1][2]. As a result, the scientific community is increasingly interested in reusing industrial waste to create sustainable products with high added value that are more environmentally friendly. As a major agro-industrial producer, Brazil generates a lot of waste, which highlights the potential of biomass from agricultural waste for use in biorefinery systems. Lignocellulosic biomass, composed mainly of lignin, cellulose and hemicellulose, is the most abundant renewable biological material on Earth. Cellulose, which is accessible from a variety of sources, is widely studied and used in the production of various products [3][4]. An important derivative of cellulose is carboxymethyl cellulose (CMC), which has unique physical and chemical properties. Commonly produced as sodium CMC, this biodegradable anionic polyelectrolyte forms water solutions with viscosifying, stabilizing and moisturizing properties. CMC is widely used in adhesives, pharmaceuticals, cosmetics, personal care products, food and fluids for the oil industry [5].The aim of this work is to synthesize cellulose and CMC from mango stone waste (Ma), using green chemistry principles in a sustainable synthesis. Cellulose (Ma) was extracted by acid/alkaline peroxide (APA) treatment and then derivatized into CMC. The carboxymethylation of the cellulose was verified by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG/DTG).

2 MATERIAL & METHODS

The synthesis activities of this work were carried out by the LABTEN-IQ/UFRN team. The characterizations were obtained in partnership with the analytical center of the Institute of Chemistry (FTIR) and by LABPEMOL (DRX, TG/DTG). The reagents used in the syntheses to obtain cellulose and carboxymethylcellulose were sulfuric acid (H2SO4, 95-98%), hydrogen peroxide (H2O2, 30%), sodium hydroxide (NaOH) in microbeads (98%), chloroacetic acid (P. A.), ethyl alcohol (99%), glacial acetic acid (P. A.), sodium chlorite (P. A.) and isopropanol (99.5%). The equipment used was Taylor 752A series sieves, 802D rotary evaporator, 550 water bath heater, TE214S analytical balance, Black+Decker M200-B2 knife mill, QUIMIS ISO 9001 oven, 131B vacuum pump, magnetic stirrer with MA100M36 heating and RW 20 mechanical stirrer.

To obtain the cellulose (MACel) from the biomass of the mango seed, the biomass was initially crushed in a knife mill (Black+Decker M200-B2) and later it was sieved (Tyler mesh sieves), until a particle size of 25 to 50 mesh was obtained, then the biomass was dried at 100º C in an oven (QUIMIS ISO 9001) for 24 hours. The mango biomass was subjected to combined acid/peroxide-alkaline (APA) pre-treatment and bleaching, with the objective of delignification of cellulose. The yields obtained after the treatments were calculated using Equation 1, where m2 is the initial mass of the material to be treated, and m1 is the mass obtained after the treatment.

$$x = \frac{m2}{m1} x\ 100 \quad (1)$$

For the derivatization of MACel in CMC, 1.0 g of bleached cellulose was weighed and transferred to a 125 mL beaker containing 7 mL of 20% NaOH and 40 mL of isopropanol. Then, the suspension was shaken at room temperature for an activation time (RT) of 45 minutes. After TA, 4 g of monochloroacetic acid were added to the reaction medium and the temperature was adjusted to

60º C. The reaction was maintained for a reaction time (RT) of 2 hours, after which time 50 mL of ethanol were added in order to interrupt the reaction, then the pH was adjusted with glacial acetic acid. Finally, the solid obtained was washed with isopropanol and dried in an oven at 50 ºC. The solubility of the CMC was qualitatively tested and the mass yield was calculated according to Equation 2, where mCMC is the mass of the cellulose carboxymethylation product and mCel is the mass of cellulose used in the synthesis.

$$CMC\ (\%) = \frac{mCMC}{mCelulose} x\ 100 \quad (2)$$

3 RESULTS & DISCUSSION

The mango cellulose (MACel) was obtained. Figure 1 presents a comparison between the biomass in natura and its respective cellulose, it is possible to observe the darkened tone in a) still with the presence of lignin, while in b) the bleached appearance confirms the achievement of delignification and the obtaining of holocellulose, which is cellulose with small fractions of hemicellulose. After APA treatment and bleaching, it was possible to obtain a bleached cellulose with a mass yield of 52%.

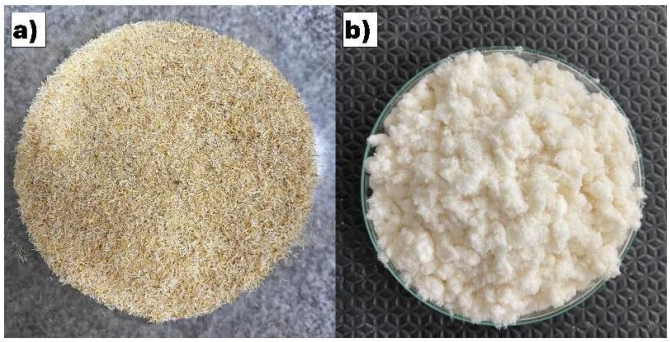

Figure 1. **a)** Biomass in nature from MA, **b)** MACel.

MACel was characterized by TG/DTG and XRD. In the TG/DTG analysis, it was obtained through the change in mass loss as a function of temperature, Figure 2.a), in which it was possible to observe two events, the first at approximately 100 ºC that represents the loss of water present and the second event of mass loss in the range of 300-350 ºC typical of cellulose degradation [6]. It is also possible to observe that no traces of lignin appeared during degradation, proving the efficiency of the treatment in obtaining cellulose [3]. The XRD analysis, Figure 2.b), showed low diffracted intensity at a value of 2θ that represents characteristics of an amorphous cellulose. The peaks at 16.01º and 22.00º are typically characteristic of the structure presented in celluloses, the peaks shown show that the material may be cellulose I and II [7].

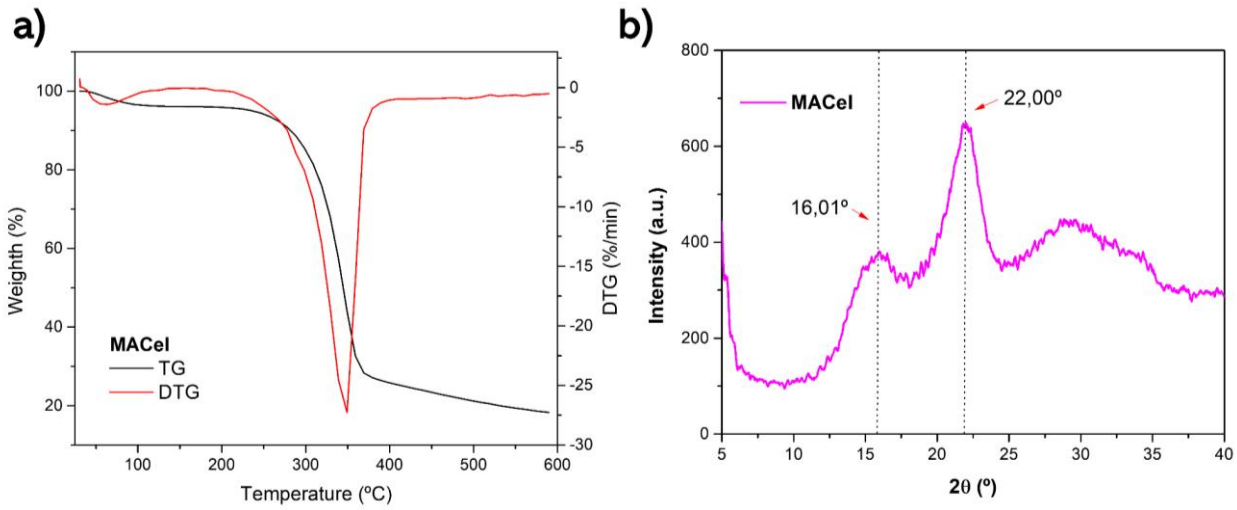

Figure 2. **a)** TG/DTG for MACel **b)** XDR for MACel.

The FTIR spectra were obtained for MA, MACel and MACMC, and are presented in Figure 3, through which it was possible to verify the efficacy of the syntheses. It is possible to observe a change of intensity in the band at 3660 cm^{-1} that belongs to the stretch of the O-H group, for the MACel sample compared to MA, this is associated with the efficiency of the chemical treatment [3]. It is also possible to observe for these samples a reduction in the characteristic bands of lignin and hemicellulose in the regions of 1720 cm^{-1}, At 1635 cm^{-1} and 1240 cm^{-1}, the band at 903 cm^{-1} in MACel refers to the β1,4-glycosidic (C-O-C) bonds between glycan units [8]. For MACMC the FTIR spectrum showed bands at 1590 cm^{-1} corresponding to the stretch vibration of the carboxymethyl compound (COO-), the band at 1410 cm^{-1} corresponding to the vibration of the CMC in the form of salt (-COONa). At 1410 cm^{-1} and 1300 are corresponding to in-plane elongations and symmetrical C-H elongation of the CMC, finally the C-O

elongation of the polysaccharide skeleton can be observed at 1059 cm^{-1} [9][10]. MACMC showed massive yields above 200% (w/w) and proved to be soluble in water.

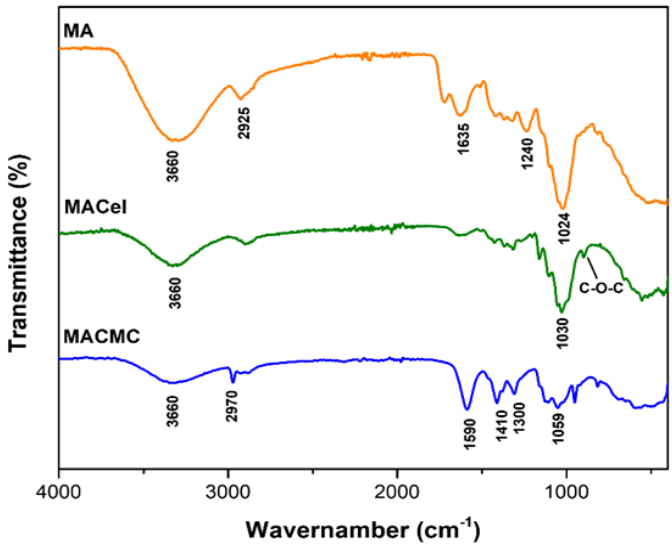

Figure 3. FTIR for MA, MACel, and MACMC samples.

4 CONCLUSION

The treatments used to extract cellulose from the biomass of the mango seed proved to be satisfactory, this fact can be proven by the analysis of TG/DTG, XRD and FTIR. The synthesis of CMC was proven through the presence of characteristic bands of the carboxymethyl group observed in the FTIR spectrum, MACMC showed high mass yields and solubility in water which means that it has great potential to be applied in industrial processes.

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