OPTIMIZATION OF SYNTHESIS FOR CARBOXYMETHYLCELLULOSE (CMC) FROM AGRO-FOOD WASTES BY RESPONSE SURFACE METHODOLOGY (RSM) USING D-OPTIMAL ALGORITHM

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ABSTRACT

This study reports the production of carboxymethylcellulose (CMC) from residual cellulose derived from sugarcane bagasse (SB) and corn cobs (CC). This process was based on various treatments of the biomass in natura, with the aim of extracting high-quality cellulose for CMC synthesis. The combined APA chemical treatment, followed by bleaching, was effective in extracting high purity cellulose. The cellulose obtained was converted to CMC by varying the reaction conditions, determined by a D-Optimal experimental design. Through statistical analysis, it was possible to determine the relevant factors for generating high-quality CMCs.

Keywords: Biomass. Cellulose. Carboxymethylcellulose. Design of Experiments.

1 INTRODUCTION

The world is currently facing a severe environmental crisis resulting in disordered climate change, air and water pollution, and the destruction of the ozone layer [1]. Much of this crisis is attributed to human activities, such as the massive use of fossil fuels and the inadequate management of industrial waste [2]. In response, the scientific community has been looking for sustainable solutions, including the reuse of industrial waste to create high value-added products [3][4]. In Brazil, the agro-industry generates millions of tons of lignocellulosic waste every year from crops such as sugarcane and corn cob, which can be used in biorefineries [5]. Cellulose, the main component of this waste, is a versatile biopolymer that has been widely studied and applied industrially [6][7]. This study focuses on the production of carboxymethyl cellulose (CMC), a cellulose derivative with unique physicochemical properties that make it widely applicable in various commercial products. Produced as a sodium salt, CMC is a biodegradable anionic polyelectrolyte used in adhesives, pharmaceuticals, cosmetics, food and fluids for the oil industry [8]. The sustainable synthesis of CMC was optimized from sugarcane bagasse and corn cobs, using a D-Optimal experimental design to adjust the reaction parameters, such as Activation Time (AT), Reaction Time (RT) and NaOH Concentration. Analysis of variance (ANOVA) and response surface methodology (RSM) allowed us to evaluate the efficiency and solubility of CMC, confirmed by FTIR spectroscopy [8]. This work proves the feasibility of producing high-quality CMC sustainably from agro-industrial waste.

2 MATERIAL & METHODS

The syntheses in this work were developed by the research team at LABTEN-IQ/UFRN. The characterizations were obtained in partnership with the analytical center of the chemistry institute. Reagents and equipment used were sulfuric acid (H_2SO_4), 95-98%, hydrogen peroxide (H_2O_2), 30%, sodium hydroxide (NaOH) in microbeads, 98% and chloroacetic acid, P. A., ethyl alcohol, 99%, glacial acetic acid, P. A., sodium chlorite, P. A. and isopropanol, 99.5%, Taylor 752nd series sieves, 802D rotary evaporator, 550 water bath heater, TE214S analytical balance, Hamilton Beach knife mill, Q-317B252 oven, 131B vacuum pump, MA100M36 heated magnetic stirrer and RW 20 mechanical stirrer. Experiments were carried out with BCA and MI biomass, which was dried, crushed and sieved to obtain fractions between 25 and 50 mesh. The samples underwent acid/peroxide-alkali (APA) pretreatment and bleaching to extract the cellulose fraction. Yields were calculated using Equation 1, where m1 is the initial mass of the material to be treated and m2 is the mass obtained after treatment.

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

Preliminary CMC synthesis tests were carried out with commercial celluloses, BCel and MCel, using a D-Optimal experimental design with 28 experiments in Design-Expert® version 13. Activation Time (AT), Reaction Time (RT), NaOH concentration and cellulose type were evaluated, using ANOVA and RSM for optimization. The FTIR spectra were obtained on the IRAffinity-1

(Shimadzu), the TG and DTG analyses on the SDTQ 600 (TA Instruments), the Raman spectra on the LabRAM HR Evolution (HORIBA), and the XRD patterns on the Bruker D2 Phaser (Madison, EUA).

3 RESULTS & DISCUSSION

The spectra of MCel and BCel (Figure 1) showed similar band profiles to the raw samples (Figure 2), but with variations in intensity. The change in the stretching band of the O-H group (3250-3500 cm^{-1}) indicates an increase in hydrogen bonds due to the chemical treatments, resulting in a larger size of the cellulose crystallites[9]. Spectral analysis revealed a reduction in the hemicellulose (C=O at 1720 cm^{-1}) and lignin (C=C at 1549 cm^{-1} and C=O at 1747 cm^{-1}) bands, suggesting that the BHL treatment with bleaching was effective in removing these fractions and isolating cellulose. The band of β1,4-glycosidic bonds (C-O-C) at 903 cm^{-1} appeared in bleached cellulose, indicating the effective removal of hemicellulose and lignin[10].

With the 28 experiments of the D-Optimal experimental design, it was possible to select specific variables, including minimum, central and maximum levels (-1, 0 and +1). The mass yields were satisfactory in most of the tests, with few results below 100% (m/m). Some experiments exceeded 200% yield, due to the increase in molecular weight due to the chains of the carboxymethyl group (-CH_2-COOH), which has a higher molar mass than the substituted hydrogen atom. Yields below 100% indicate that the conditions did not favor the carboxymethylation of cellulose. In addition, both water solubility and mass yield were impaired with lower NaOH concentrations.

The variance measures the dispersion of the data, where high F values (Fisher's test) and $p < 0.05$ indicate statistical significance. The factors RT, NaOH% and the interaction between AT and RT are statistically significant, influencing CMC yield and carboxymethylation efficiency. The lack of fit of the model was not significant, with a correlation coefficient (R^2) of 0.928 and low standard deviation (7.0x10-⁴), indicating that the model for analyzing the mass yield of CMC is precise and accurate, with 95% confidence.

Based on the results obtained, response surfaces were constructed to show the trends in the variation of the results in relation to changes in the reaction conditions. The surfaces related to the Mass Yield results for SBCel and CCel cellulose are shown in Figure 1. Analysis of these surfaces shows that there are no significant changes between the different cellulose types at RT -1 and +1 times, indicating that the cellulose type factor does not have a statistically significant effect on the CMC yield at a 95% confidence interval. The concentration of NaOH in the reaction medium had a relevant and statistically significant effect ($F=237.06$, $p<0.0001$). This can be explained by the significant increase in CMC yield at NaOH% values between 0 and +1, especially for RT +1. This result highlights the importance of using higher concentrations of NaOH, which acts as an activating agent, increasing the deprotonation of the hydroxyls present in the cellulose monomers and allowing more carboxymethyl radicals to be incorporated into the molecular structure. It was observed that lower AT values result in CMCs with a higher mass yield. This contradicts the majority of literature, which suggests that shorter activation times improve yield by reducing the exposure of cellulose to the NaOH solution and, consequently, the chance of cellulose hydrolysis. The response surfaces related to the Water Solubility result for BCel and MCel cellulose are shown in Figure 2.

As this is a qualitative response, the results are presented in probability form, where insoluble samples are represented by 0 and soluble samples by 1. The results indicate that the NaOH% factor was the most significant, with a wide region of the response surface with NaOH% > 0 comprising soluble samples (red) for BCel, at AT -1 and +1. expressive on the solubility surfaces, thus allowing the synthesis of soluble samples in less time and generating energy and reaction time savings. The cellulose factor was the second most significant factor in the solubility surfaces, with the red region significantly smaller for MCel at both AT times compared to the surface formed by the soluble BCel samples at the same time intervals. The FTIR spectral results for the CMCs obtained from the tests with extremes of NaOH% (10% and 30%) are shown in Figure 2. The presence of carbonyl (C=O) bands at 1650 cm^{-1} and ether C-O-C stretching at 1430 cm^{-1} were observed, indicating the insertion of carboxymethyl groups into the cellulose chains and confirming that the synthesis process was satisfactory. The spectra of the sustainable CMCs obtained are similar to those of commercial samples and others reported in the literature, showing that the polymer was successfully obtained. When comparing the spectra, all the samples with 10% NaOH% show bands at 1650 cm^{-1} and 1430 cm^{-1}, many with high intensity, which corroborates the high efficiency of carboxymethylation with this concentration of NaOH. However, the samples produced with 30% NaOH do not show these bands or show them with little intensity, indicating a lower carboxymethylation efficiency at higher NaOH concentrations. not significantly alter the CMC synthesis process in terms of mass yield, it was relevant for water solubility.

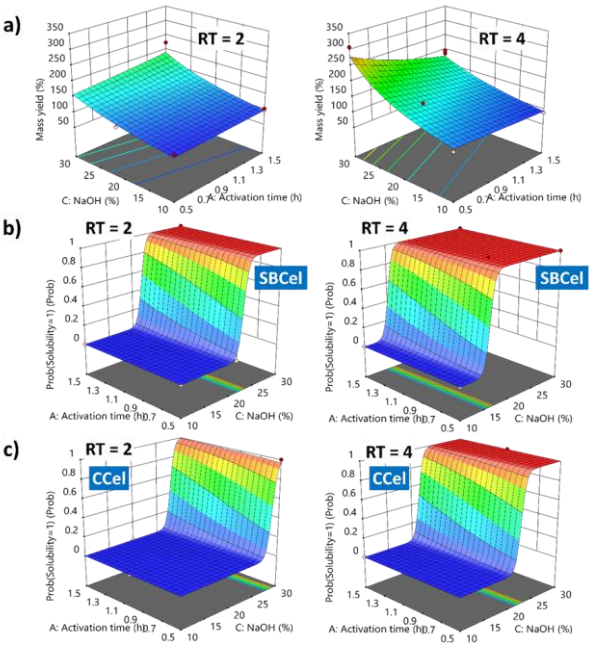

Figure 1. 3-D response surfaces for (a) Mass Yield and Solubility for CMCs produced from (b) SBCel and (c) CCel.

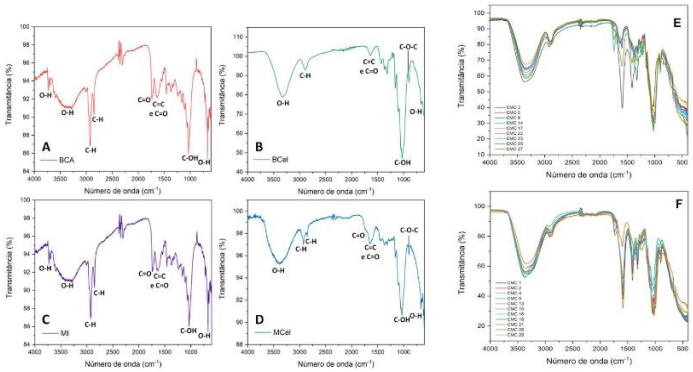

Figure 2. A, B, C, and D. FTIR spectra for the raw biomass (SB and CC) and bleached cellulose (SBCel and CCel), E and F. FTIR spectra for the CMC obtained using the NaOH concentration factors a) 10% and b) 30%.

CONCLUSION

The extraction of cellulose from sugarcane bagasse and corn cobs was successful, removing lignin and hemicellulose, as confirmed by FTIR spectra. The synthesis of carboxymethyl cellulose (CMC) used a D-Optimal experimental design, confirmed by the presence of carboxymethyl bands in the FTIR spectra. Statistical analysis (ANOVA and RSM) showed that NaOH% concentration and Activation Time (AT) were critical factors for CMC yield and solubility, while Reaction Time (RT) had less impact, indicating that high-quality CMCs can be produced with shorter reaction times, saving time and energy.

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