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ORIGINAL RESEARCH

Synthesis of carboxymethylcellulose from corn straw waste: comparison between pre-treatments with sodium hydroxide and low-cost ionic liquid

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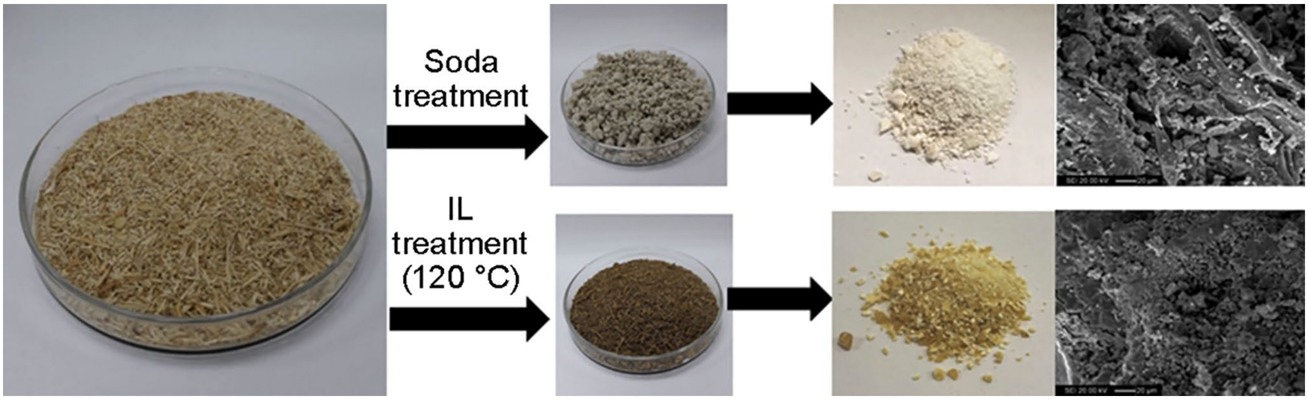
Abstract

In this work, the possibility of using corn straw to obtain carboxymethylcellulose (CMC) was verified. However, to obtain CMC from lignocellulosic residues, it is necessary to carry out initial treatments to reduce the levels of lignin and hemicellulose. In this context, studies have been conducted to enable the use of an ionic liquid (IL). The *n*-butylammonium acetate was used to treat the straw instead of the pulping stage for the subsequent attainment of CMC. For comparison, we determined the composition of the resulting material after the stages of NaOH pulping (NaP) or treatment with the IL (at 80 °C—ILP80 and 120 °C—ILP120) and bleaching, to analyze the purity of the cellulose obtained. It was also possible to verify that the treatment at 120 °C was more effective to remove inorganic materials and lignin, leading to cellulose with $91.45 \pm 0.11\%$ purity when compared with its treatment at 80 °C. CMC was successfully synthesized and presented similar morphologies accordingly. Consequently, the attainment of CMC was confirmed by analyzing the data obtained via FTIR, NMR, and XRD techniques, as well as the analyses of degree of substitution. It was also possible to recover the ionic liquid at a purity of 95.93%.

Graphical abstract



Keywords Lignocellulosic material · Waste · Corn straw · Ionic liquid treatment · Carboxymethylcellulose

Introduction

Currently, the search for new production methods that are less harmful to the environment and can efficiently replace stages of conventional industrial processes has become

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essential. As a result, there has been an increase in studies that aim to use products from renewable sources as raw material or even the use of different types of waste, such as lignocellulosic materials, which are generally not reused in the best way and cause great environmental impacts when misused [1]. Considering global warming and climate change [2], there is no room for this kind of environmental issues.

Wastes can be all materials discarded during or after a production process, as well as being derived from organic matter from plant sources. However, lignocellulosic waste can be considered a renewable source. As examples of lignocellulosic residues, it is possible to mention sugarcane bagasse, corn or cob straw, bamboo, coconut fiber, sawdust, grass, board, among many other materials [1, 3].

This type of waste is characterized by having components such as lignin (16–45%), cellulose (13–50%), and hemicellulose (0.20–40%) in its structure. Lignin is a hydrophobic phenylpropanoid natural macromolecule that has a highly branched three-dimensional structure consisting of an irregular arrangement of several units of phenylpropanoids which, in turn, contain hydroxyl and methoxy groups as substitutes for the phenyl group. Cellulose is a natural linear polymer consisting of units of the β-*D*-glucose monosaccharide joined through β-1,4 glycoside bonds, with water molecule elimination. Hemicellulose is considered as a heterogeneous polysaccharide due to the presence of a mixture of different sugar units. The main ones are: β-*D*-xylose, β-*D*-mannose, β-*D*-glucose, α-*L*-arabiose, α-*D*-galactose, β-*D*-glucuronic acid, β-*D*-galactouronic acid, and α-*D*-4–0-methylglucouronic acid in several proportions in their composition [1, 4, 5].

Lignocellulosic materials also have other constituents present in lesser quantities, such as inorganic compounds, proteins, and pectin substances. The percentage of each of these compounds in the waste defines in which types of processes they can be used, and may be cited in the production of bioethanol, composites, and cellulosic derivatives such as carboxymethylcellulose and cellulose acetate, among others [1, 6].

Of these, carboxymethylcellulose [β-D-glucose and β-D-glucopyranosyl-2-O-(carboxymethyl)-sodium salt] [7], one of the most common cellulose-derived biopolymers [8], is an anionic long-chain and linear polysaccharide that has different degrees of substitution and different industrial applications, e.g., in food, pharmaceutical, detergent, cosmetic, paint, and textile industries. These properties make it possible to use it as a thickening agent, viscosity modifier, emulsifier, fluid stabilizer, ironing agent, and adhesive agent [9–11].

Regarding residues, corn straw is considered an agricultural residue that is commonly incinerated or used in rural properties, being little used to generate income, except as handicrafts. This residue is used in the production of cigarettes, packaging, and handicrafts; however, because it is a lignocellulosic material, an economic interest arose in using it as a raw material for obtaining cellulose and its derivatives such as cellulose acetate and carboxymethylcellulose, a component widely used in several industrial sectors [12–14].

However, to obtain derivatives such as carboxymethylcellulose from lignocelluloses, it is necessary to carry out a series of chemical processes that can promote the disruption of the hemicellulose–lignin–cellulose association present in the biomass structure. For this purpose, pre-treatment techniques such as pulping, bleaching stage, and etherification stage of pre-purified cellulose are necessary, which, on an industrial scale, use a significant volume of solvents, mainly organic, which generate problems related to process safety and environmental impact when discarded [15–17].

In general, the possible pre-treatment methods fall into four different categories: physical (grinding, microwave, and extrusion), chemical (acid, alkaline, and ionic liquid), physico-chemical (steam explosion, hydrothermal treatment, and wet oxidation), and biological [18, 19]. The choice of the best process to be used depends on the degree of separation desired and purpose of the material [20]. Of these, the alkaline method is one of the main processes, while soda and Kraft or sulfate process are the most popular methods used industrially. Lignin is degraded by the medium, while polysaccharides remained unaffected, giving rise to an insoluble residue, which is the cellulosic pulp [21]. However, in these processes, a lot of waste is generated.

Therefore, in an attempt to minimize these problems, some studies have been developed in search of greener processes such as those using ionic liquids (ILs), which showed a variety of applications with possibility of recovery, giving a possible alternative for the pre-treatment of lignocellulosic residues [18, 22].

Ionic liquids are compounds that have melting points below 100 °C, high viscosity, low conductivity, low vapor pressure even at high temperatures, are non-corrosive, have high thermal and chemical stability, and are easy to recover. They are formed by several cations and anions, which open the possibility of making numerous combinations that allow changes in their characteristics [23, 24].

Due to these properties, ionic liquids have been increasingly explored as solvents and/or reagents in several applications as a result of their sustainable character, as well as their adjustable physical, chemical, and biological properties. They have been used in compounds that have low solubility in organic solvents, such as cellulose, as well as in several other processes [25–27].

Among the possible applications, we highlighted their use in extraction and separation processes, catalysis, biocatalysis, organic and pharmaceutical synthesis, nanomaterial synthesis, among others. As an example, it is possible to mention their use in the treatment of lignocellulosic materials in replacement of the pulping processes due to the ease of recovery of cellulose and the possibility of their recycling, thus being able to be reused and reduce costs [26–28].

The excellent results that have been obtained in these types of treatments are also noteworthy, since an electron donor–acceptor complex is formed during their use and the intra- and inter-molecular hydrogen cellulose bonds are broken [25, 26]. This causes a modification in its crystallinity, increasing cellulose surface accessibility or reducing the particle's size. Therefore, treatments with ILs can provide the removal of lignin and hemicellulose, which can be reused in other processes or favor the breaking of hydrogen bonds. This favors the increase in the availability of hydroxyls to carry out substitution reactions, as in the case of CMC production [29–31].

Therefore, in this study, the synthesis of CMC was carried out from an agro-industrial waste—corn straw—and the *n*-butylammonium acetate IL was used as an alternative technique in the pre-treatment to replace pulping, aiming at a more sustainable production. In this context, this work showed the obtainment of a widely used product with a high-added value, CMC, from a lignocellulosic material, corn straw, considered an agricultural residue that is commonly underused, which reduced the accumulation of agro-industrial residues. The use of a low-cost ionic liquid and its possibility of recovery should also be noted, which will result in the reduction of industrial waste in the process.

Experimental

Materials

Analytical grade reagents were used to prepare all solutions. Ionic liquid and CMC were acquired from Sigma-Aldrich (USA) or Dinâmica Reagentes (Brazil). Ethanol (92.80%) was purchased from Tuppi (Brazil). Corn straw was supplied by CEAGESP (Brazil). Microcrystalline cellulose was acquired from SYNTH (Brazil).

Obtaining and characterizing the *n*-butylammonium acetate

The ionic liquid *n*-butylammonium acetate was obtained through the reaction between an acid and a base. For this, the acetic acid was added dropwise in a 1:1 stoichiometric ratio into *n*-butylamine. This system was kept under mechanical stirring (Fisaton, Brazil) at 300 rpm and the temperature was controlled between 15 °C and 40 °C. After the addition of the acid, the solution was kept under stirring for another 2 h, and then, it was stored in an amber flask.

The ionic liquid was characterized via nuclear magnetic resonance (NMR) on a Bruker Avance III 600 HD (Germany) NMR spectrometer, using deuterated chloroform as solvent. Finally, the hydrogen and carbon spectra were obtained.

n-butylammonium acetate: H^1 NMR (600 MHz, $CDCl_3$): δ 1.9 (s, 3H), 2.80 (t, 2H), 1.60 (q, 2H), 1.37 (s, 2H), 0.92 (t, 3H), 7.10 (s, 3H).

C^{13} NMR (150 MHz, $CDCl_3$): δ 179.05, 30.43, 39.38, 24.60; 19,94; 13.72.

Corn straw treatment

The corn straw was separated from the rest of the components and then subjected to an oven drying process at 80 °C. After drying, the corn straw went through a grinding process, using a Willye knife mill (Tecnal, Brazil), subsequent washing to remove soluble components, and drying again in an oven at 80 °C until constant weight. After this stage, it was submitted to the treatment process with the soda solution or ionic liquid.

Soda and ionic liquid pre-treatments

The soda pre-treatment process used a 5 L batch reactor from Metalquim (Brazil) in which 300.00 g of crushed, washed, and dried raw straw and 3.00 L of a 9.00 wt% sodium hydroxide solution was added. The system was maintained under agitation of 120 rpm, pressure of 2.50 atm, and temperature of 137 °C for 6 h. After this period, the product was washed with running water to eliminate residues from the process and dried in an oven at 80 °C [32].

During the ionic liquid pre-treatment, 50.00 g of crude crushed straw were added to 300.00 mL of the ionic liquid *n*-butylammonium acetate and 150.00 mL of tetrahydrofuran (used to decrease the viscosity of the solution). Subsequently, the system was placed in a silicone oil bath at 120 °C or 80 °C, under mechanical stirring at 300 rpm under reflux, for 25 h. After this period, the product was washed with running water and subsequently dried in an oven at 80 °C [24, 30].

After the pre-treatments, the bleaching step was performed. For this, 100.00 mL of hydrogen peroxide solution (4.20%, pH 12) were used for each 5.00 g of corn straw pulped or treated with the ionic liquid. This mixture was kept in a thermostatic water bath at 40 °C, under mechanical stirring at 200 rpm under reflux, for 6 h. After being removed from the bath, the product was washed with running water, filtered, and then dried in an oven at 80 °C [30].

All materials were characterized by determination of holocellulose, cellulose, hemicellulose, lignin using TAPPI methods, humidity (using an infrared moisture analyzer

IV2000-GEHAKA, Brazil), and ash [33, 34]. Analyses were also performed via FTIR, XRD, and SEM.

The infrared spectroscopy analysis was performed using a Thermo Scientific Nicolet 6700 (USA) FTIR spectrophotometer. The attenuated total reflectance spectra (ATR-FTIR) were collected in the range of 4,000–500 cm^{-1} with a resolution of 4 cm^{-1} and 128 scans per sample. The results were analyzed basically to determine small changes in the intensity of the absorption bands.

An X-ray diffraction (XRD) analysis was performed on a Shimadzu XRD-7000, (Japan) X-ray diffractometer. The operating voltage and current were maintained at 40 kV and 35 mA, respectively, and the angular range was 3–135°. The diffraction spectra were collected using the θ–2θ method. The samples were scanned in the 2θ range 5–40° in steps of 0.015°. The radiation (Cu KαX-ray source) wavelength was 1.5406 Å.

SEM micrographs of materials were obtained on a high-resolution JSM 7500F (JEOL) microscope (Japan), equipped with an energy-dispersive spectroscopy (EDS) detector using an accelerating voltage of 2 kV and a magnification of 500 times. The samples were submitted to carbon deposition.

Ionic liquid recovery

The advantage of using ionic liquid in the process of treating lignocellulosic materials is that it can be recovered after its use. In this way, the mixture obtained after the pre-treatment process of corn straw with the ionic liquid was vacuum distillation, first removing the THF and then the recovered ionic liquid. After this stage, the IL was submitted to analysis via NMR to confirm if it suffered from any degradation, as well as checking its degree of purity.

Synthesis of carboxymethylcellulose

Carboxymethylcellulose was synthesized from corn straw treated with soda or ionic liquid. For this, 15 g of the treated corn straw (soda or ionic liquid) were mixed with 400.00 mL of isopropanol and 40.00 mL of distilled water, separately. The system was subjected to agitation in a water bath at room temperature for 30 min. After completing this step, 100.00 mL of the soda solution (40.00 wt%) were added dropwise for 30 min. After the addition of this solution, the system was kept under stirring for 1 h. Then, a solution consisting of 40.00 g of monochloroacetic acid and 50.00 mL of isopropanol was added dropwise for 15 min. Afterward, the bath temperature was changed to 55 °C and the system was kept under agitation for another 4 h [11, 24]. After the reaction, the pH of the solution obtained was measured and neutralized with glacial acetic acid until it reached a value of 7. The system was filtered, and the retained product was washed with 80% ethanol and then washed three times with absolute ethanol. The CMC was dried at 60 °C in an oven.

The synthesized carboxymethylcellulose was characterized by FTIR, XRD, and SEM techniques, and used the ASTM D1439-61T method to determine the degree of substitution.

Results and discussion

Corn straw treatment

During the carboxymethylcellulose attainment from corn straw, chemical treatments were initially carried out to break down lignin–hemicellulose–cellulose interactions. For this, two different chemical treatments were carried out to verify the efficiency of the treatment with ionic liquids. The first is based on the soda pulping process (NaP), while the second uses the *n*-butylammonium acetate ionic liquid at two different temperatures (80 °C-ILP80 or 120 °C-ILP120).

After the pre-treatment process (soda or ionic liquid treatment), all materials were subjected to the peroxide bleaching process and characterized via determination of holocellulose, cellulose, hemicellulose, lignin, humidity, and ash contents (Table 1), as well as by use of FTIR, XRD, and SEM techniques.

By analyzing the results, it was possible to see that the pulping process with soda provided a reduction in the lignin content of 79.76% in relation to raw corn straw, while the treatment with ionic liquid at 120 °C reduced the lignin content by only 22.68%. Despite having a much lower delignification compared to the first process, the result was as expected, since this type of treatment does not aim at removing the lignin but increasing cellulose surface accessibility due to the breakage of hydrogen bonds which leaves hydroxyls free for the next step of the CMC production.

Regarding the treatment process with the IL at 80 °C, there were no changes in the total lignin content, which can be explained by the possible preservation of the phenylpropanoid structure of lignin. When analyzing the levels obtained during the bleaching processes, it is observed that, for the pulped and bleached sample, there was a reduction of 61.38% in relation to the straw that was only pulped. For the straw treated with the IL at 120 °C and bleached, there was a reduction of 4.33% in relation to the fiber only treated at this temperature. When treated with the ionic liquid at 80 °C, a reduction of 16.68% was observed in relation to the raw straw only.

Through the analysis of the results, a higher holocellulose content was found in the pulped and bleached samples, which was 97.02 ± 0.10%. Since the holocellulose content of a sample corresponds to the percentage of cellulose and hemicellulose present in it, the results obtained

Table 1 Corn straw composition before and after each treatment

Content	Crude corn straw (%)	NaP (%)[a]	ILP80 (%)[b]	ILP120 (%)[c]
Holocellulose	80.76 ± 0.39	96.40 ± 0.39	83.74 ± 0.03	82.93 ± 0.49
Cellulose	35.66 ± 1.18	88.96 ± 0.39	41.66 ± 0.35	41.73 ± 0.67
Hemicellulose	45.10 ± 1.57	7.45 ± 0.00	42.08 ± 0.32	41.20 ± 0.18
Lignin	14.93 ± 0.28	3.04 ± 0.16	15.73 ± 0.02	11.89 ± 0.09
Humidity	4.00	4.70	6.60	6.80
Ash	1.13 ± 0.03	0.80 ± 0.01	0.73 ± 0.01	0.68 ± 0.01
Materials after the bleaching process				
Holocellulose	–	97.02 ± 0.10	90.00 ± 0.07	85.33 ± 0.59
Cellulose	–	91.45 ± 0.11	42.84 ± 0.07	43.38 ± 1.03
Hemicellulose	–	5.57 ± 0.01	47.16 ± 0.14	41.95 ± 1.62
Lignin	–	1.12 ± 0.09	13.36 ± 0.21	11.00 ± 0.05
Humidity	–	3.50	8.60	3.60
Ash	–	0.58 ± 0.02	0.75 ± 0.01	0.81 ± 0.02

[a] Soda pulping process (NaP), [b] treatment with *n*-butylammonium acetate ionic liquid at 80 °C (ILP80), [c] treatment with *n*-butylammonium acetate ionic liquid at 120 °C (ILP120)

corroborate the results referring to the analysis of the lignin content, since the higher the value of holocellulose obtained, the greater the removal of lignin and, thus, the greater the purity of the cellulose obtained.

Analyzing the results of the cellulose content, it was possible to observe that the sample that presented the highest content of this component was the corn straw that passed through the pulping and bleaching processes, with a value of 91.45 ± 0.11%. The sample that underwent treatment with the ionic liquid at 120 °C and bleaching showed final a cellulose content of 41.82 ± 1.03%, with an increase of 22.17% in relation to the raw corn straw. Regarding the holocellulose content, it was observed that pulping was more efficient in removing the hemicellulose from the raw straw than the treatment with the IL at 120 °C, with a reduction of 82.69% for the first process and 10.76% for the second one.

Through analyses via FTIR spectroscopy, it was possible to identify the main connections attributed to the main functional groups present in each sample before and after each treatment (Fig. 1). By analyzing the spectra of the samples obtained through the soda treatment (spectra 3 and 4 in Fig. 1a), it is possible to see that both [NaP (spectrum 3 in Fig. 1a) and pulped and bleached corn straw–NaP-B (spectrum 4 in Fig. 1a)] are closer to the spectrum of pure cellulose (spectrum 1 in Fig. 1a) than raw straw (spectrum 2 in Fig. 1a). This indicates that, after the proposed treatments, there was a reduction in the level of undesirable components such as lignin and hemicellulose, thus leaving a significant amount of cellulose behind. There was also an increase in the characteristic band of the O–H bond at 3,670 cm^{-1}, indicating an increase in the number of free hydroxyls, which was expected, since most of the lignin was removed.

Figure 1b shows the spectra 1–4 that are for pure cellulose, raw corn straw, ILP80 (corn straw treated with IL at 80 °C), and ILP80-B (corn straw treated with IL at 80 °C and bleached), respectively. In this case, the processed samples had a composition similar to raw straw, with spectra almost coincident, indicating the small removal of unwanted components such as lignin and hemicellulose; however, there is an increase in the OH-bond band, indicating a rise in the free hydroxyls. Figure 1c shows the spectra 1–4 that are for pure cellulose, raw corn straw, ILP120 (corn straw treated with IL at 120 °C), and ILP120-B (corn straw treated with IL at 120 °C and bleached), respectively. In this case, the processed samples continued with a composition similar to the raw straw, as shown in Fig. 1b, indicating a not so efficient reduction of the unwanted components mentioned above and, still, there was a small increase in the band of the O–H bond. However, at this temperature, it can be noted that there was an approximation with the spectrum of pure cellulose, which indicates a greater delignification of the straw, compared to the treatment at 80 °C.

Through the SEM analysis (Fig. 2), it was possible to perform the morphological characterization of the material before and after each treatment. Therefore, Fig. 2a shows the micrograph of the crude corn straw. Through the micrographs obtained, it was possible to observe a rigid and compact structure that presented certain elevations in relation to the plane, which probably represented the cellulose–hemicellulose–lignin groups of which the raw corn straws were composed. The cellulose fibrils are surrounded, structured, and interconnected by several lignin molecules and, therefore, it was not possible to identify them separately, as in the corn straw treated micrographs (Fig. 2b-d). In the micrograph of Fig. 2b, it is possible to clearly see the separation

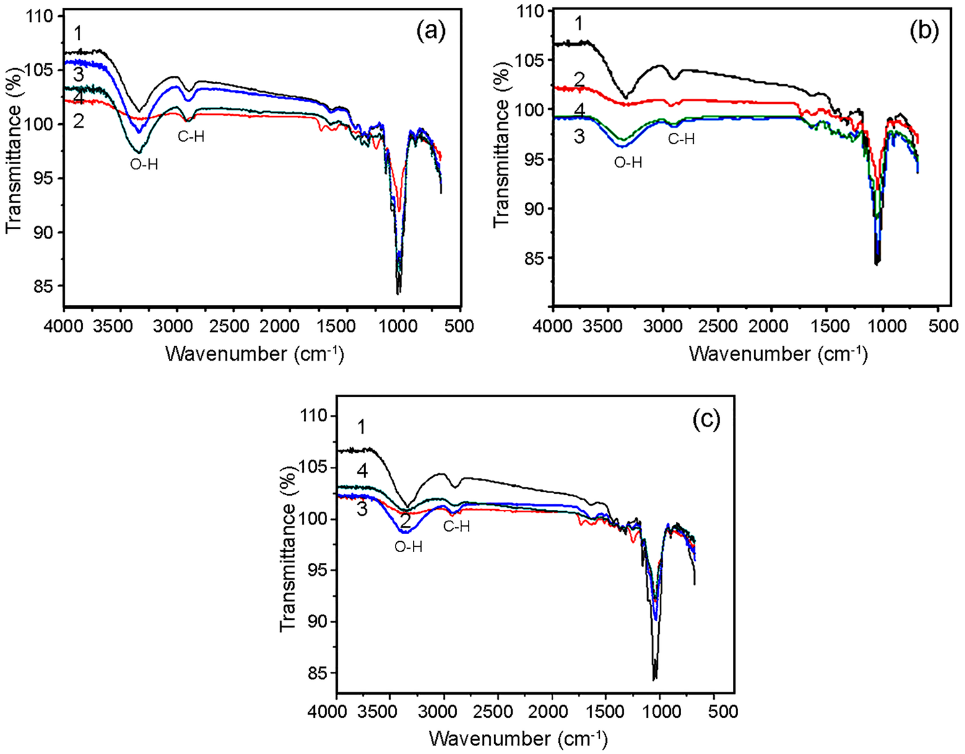

Fig. 1 FTIR spectra of: **a** NaP, **b** ILP80, and **c** ILP120 samples. (**1**) Cellulose, (**2**) corn straw, (**3**) corn straw IL treated (NaP; ILP80; or ILP120), (**4**) corn straw IL treated and bleached (NaP-B; ILP80-B; or ILP120-B)

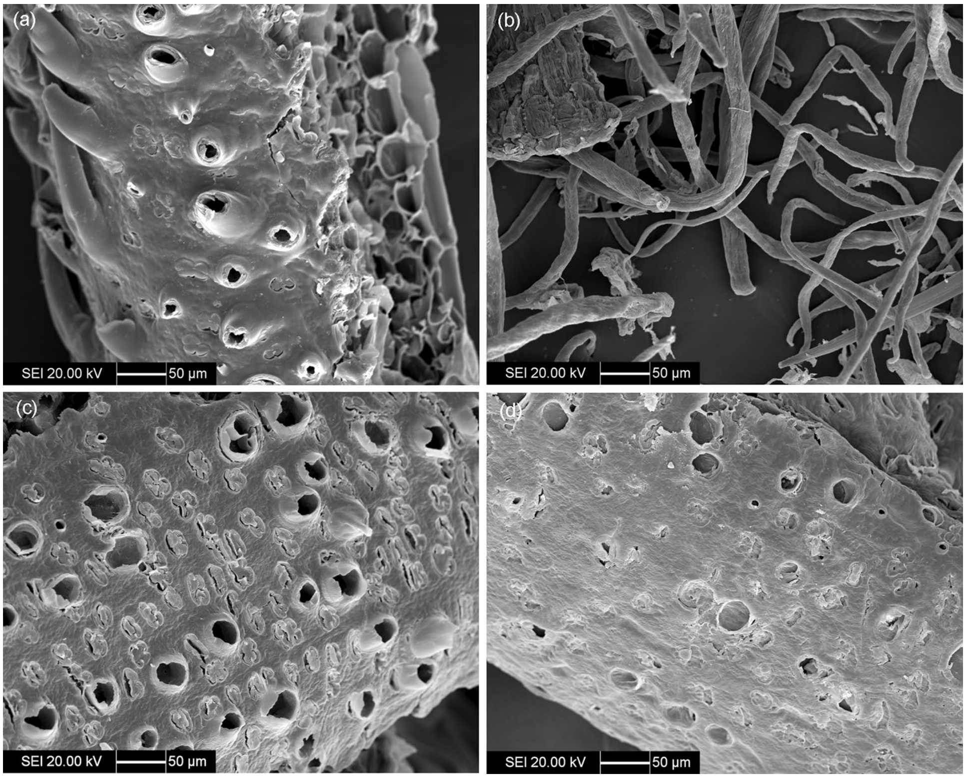

Fig. 2 SEM micrographs with 250 × magnification for: **a** raw corn straw, **b** NaP-B, **c** ILP80-B, and **d** ILP120-B

of the cellulose fibrils and the removal of the lignin wrap presented in the raw corn straw, which was already expected according to the analyses of the lignin content.

Through the micrographs represented in Fig. 2(c and d), it is possible to observe that the treatment with the *n*-butylammonium acetate ionic liquid was not able to promote

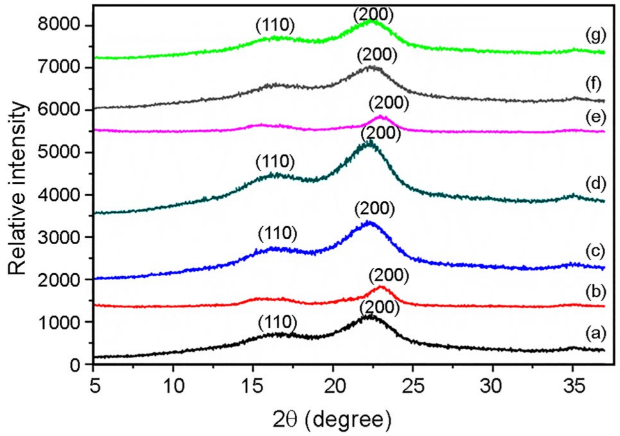

Fig. 3 XRD patterns of the samples after chemical treatments: **a** corn straw; **b** NaP; **c** ILP80; **d** ILP120; **e** NaP-B; **f** ILP80-B; and **g** ILP120-B

Table 2 Crystallinity index of the samples before and after chemical treatments

Sample code	CI (%)
Raw corn straw	56.04
NaP	65.08
NaP-B	66.37
ILP120	56.15
ILP120-B	56.99
ILP80	56.08
ILP120-B	56.01

Table 3 Degree of substitution (DS) of CMC samples

Sample code	DS
CMC standard	0.67
CMC-NaP-B	0.90
CMC-ILP120-B	0.73
CMC-ILP80-B	0.72

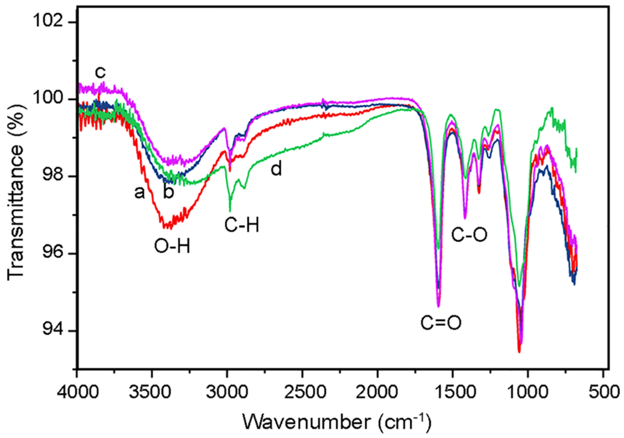

Fig. 4 FTIR spectra of the synthesized CMCs: **a** CMC-NaP-B; **b** CMC-ILP80-B; **c** CMC-ILP120-B, and **d** CMC standard

delignification of the material; however, the treatment with ILs promotes the rupture of hydrogen bonds, favoring the subsequent production of the lignocellulosic derivative, i.e. CMC [30, 31].

Corroborating the results, through the XRD analysis (Fig. 3), the presence of peaks in the regions close to 16° and 22°, corresponding to the crystallographic planes (110) and (200), is characteristic of the cellulose type I [35].

By determining the crystallinity index of the samples (Table 2), it can be noted that the initial pulping treatment resulted in an increase in the crystallinity index, since this procedure guaranteed the breakdown of the lignin–cellulose–hemicellulose structure and increased the amount of hydrogen bonds and organization of the chains. However, after the bleaching procedure, this index remained practically constant, since there were no significant changes in the crystallinity of the material.

It should be noted that the small change in the crystallinity index may be the result of the interaction between cellulose chains that were not modified. However, it should be taken into account that the use of ionic liquids in pretreatments can lead to the retention of the cellulose structure and this fact favors the subsequent etherification stage, since the presence of ionic liquids increased the dissolution in the first stage of the CMC production process (solubilization in a basic medium). This justifies the results observed during the enhanced synthesis and efficiency in the production process of the desired derivative [31].

Carboxymethylcellulose attainment

After the characterization of corn straw before and after each treatment, the carboxymethylcellulose (CMC) was obtained from NaP-B, ILP80-B, and ILP120-B. The obtained materials (CMC-NaP-B; CMC-ILP80-B, and CMC-ILP120-B) were characterized by FTIR, SEM, and NMR techniques, and by determining the degree of substitution and percentage of CMC to evaluate the effectiveness of the treatment with the synthesized ionic liquid in the subsequent attainment of CMC.

When analyzing the data obtained regarding the degree of substitution, it is possible to see that the values obtained for the samples treated with IL were similar to the values obtained for the standard CMC (Table 3). The analysis of FTIR data (Fig. 4) showed that CMCs synthesized from celluloses obtained by the three methods studied were very similar to the standard CMC, which indicated that even starting from materials with different compositions, they reach the same desired end product.

It can also be observed that the carboxymethylcellulose obtained from the ionic liquid treatment route presented spectra closer to the characteristic spectrum of the product sold, both at 80 °C and 120 °C (CMC-ILP80-B and CMC-ILP120-B). When comparing the spectrum of the CMC standard with that obtained for CMC-NaP-B, the characteristic bands of the O–H bond were verified, in the region of 3670 cm^{-1}, which indicated the amount of similar free hydroxyl groups.

It is also possible to see an increase in the bands in the regions of 1600 and 1400 cm^{-1}, respectively, as well as an increase in the number of C = O bonds of carboxylic/carbonyl groups, and a band in the region of 1220 cm^{-1} which corresponded to an increase in the number of carboxylic acid groups in CO bonds. In addition, the displacement of the band from 3400 to 3600 cm^{-1} demonstrated that O–H groups were no longer linked by intra- and inter-molecular bonds, confirming that a portion of them had been replaced by carboxymethyl groups.

SEM micrographs of carboxymethylcellulose samples synthesized from corn straw (Fig. 5) showed several structural changes in the samples that have gone through the carboxymethylation process. Analyzing the micrograph of the carboxymethylcellulose synthesized from the pulped and bleached straw samples (Fig. 5a), it is possible to verify the presence of some intact cellulose fibrils with the structures corresponding to the CMC groups distributed throughout its surface. This characteristic can also be observed in the carboxymethylcellulose samples obtained from corn straw treated with ionic liquid under both conditions, i.e. 80 °C and 120 °C (Fig. 5b and c).

The analysis via X-ray diffraction (Fig. 6) shows a widening of the peak in the region of 21°, when compared to that obtained for samples of the lignocellulosic material after the treatments proposed for cellulose isolation. This change was related to the decrease in the degree of crystallinity, which may indicate the introduction of groups in the structure, causing changes in the ordered arrangement of cellulose

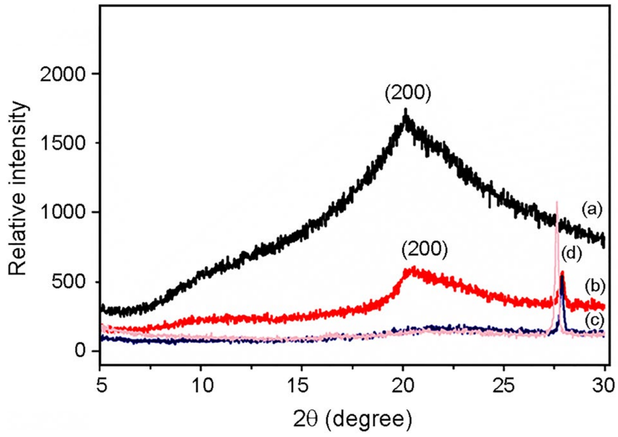

Fig. 6 XRD patterns of CMC samples: **a** CMC standard, **b** CMC-NaP-B, **c** CMC-ILP80-B, and **d** CMC-ILP120-B

Fig. 5 SEM micrographs with 500 × magnification: **a** CMC-NaP-B, **b** CMC-ILP80-B, and **c** CMC-ILP120-B samples

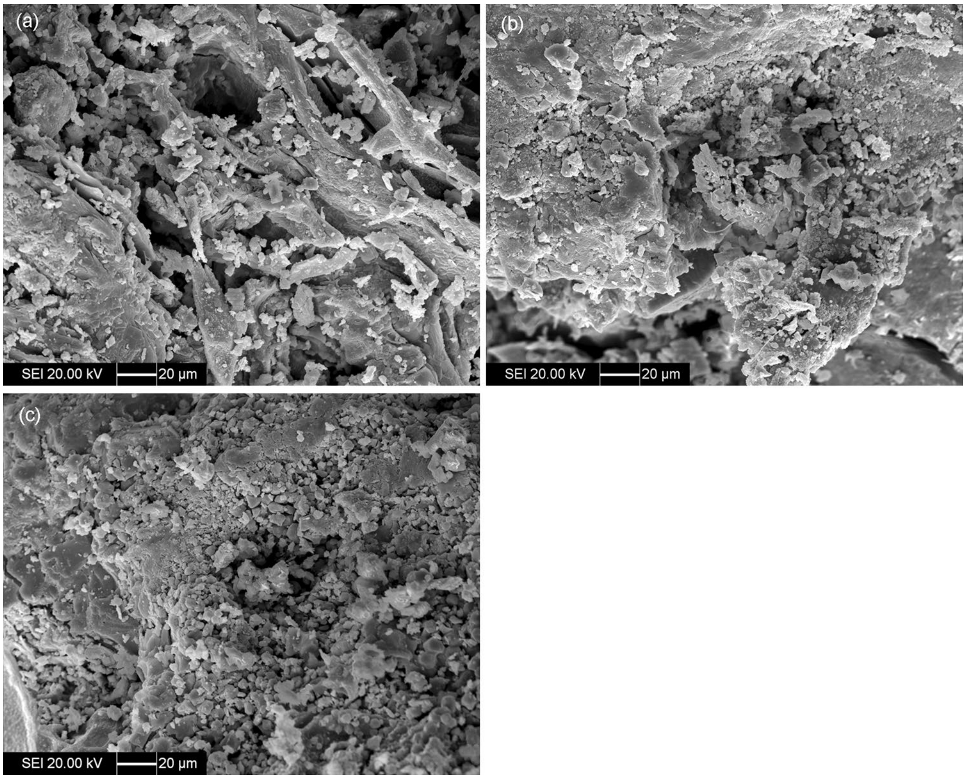

Table 4 Crystallinity index (CI) for CMCs obtained

Sample code	CI (%)
CMC standard	57.44
CMC-NaP-B	37.53
CMC-ILP80-B	38.25
CMC-ILP120-B	36.07

chains. These data can be confirmed by the values obtained from the crystallinity index presented in Table 4.

The crystallinity index was modified according to the degree of substitution of the cellulose (number of carboxymethyl groups introduced). Since the CMC standard used has a degree of substitution of 0.67 and the CMC samples obtained higher values, changes in the arrangement of the cellulose chains were verified due to the interactions between the chains mainly via hydrogen bonds.

Ionic liquid recovery

The *n*-butylammonium acetate ionic liquid was recovered by vacuum distillation after its use in the treatment of corn straw. After this stage, it was characterized via NMR and, by analyzing the H^1 NMR spectra; it was possible to verify the efficiency of the technique in the purification of the ionic liquid and thus the possibility of its reuse. The calculation of IL purity after recovery was determined via H^1 NMR and it was possible to see that the ionic liquid showed a purity of 95.93%.

n-butylammonium acetate: H^1 NMR (600 MHz, CDCl$_3$): δ 1.9 (s, 3H), 2.80 (t, 2H), 1.60 (q, 2H), 1.37 (s, 2H), 0.92 (t, 3H), 7.10 (s, 3H). C^{13} NMR (150 MHz, CDCl$_3$): δ 179.05, 30.43, 39.38, 24.60; 19,94; 13.72.

n-butylammonium acetate recovered: H^1 NMR (600 MHz, CDCl$_3$): δ 1.95 (s, 3H), 2.83 (t, 2H), 1.61 (q, 2H), 1.38 (s, 2H), 0.93 (t, 3H), 7.75 (s, 3H). C^{13} NMR (150 MHz, CDCl$_3$): δ 178.15, 30.09, 39.33, 23.48; 19,94; 13.70.

Conclusion

After the synthesis, characterization, and application of the *n*-butylammonium acetate ionic liquid in the treatment of corn straw aiming at the production of CMC, it was possible to verify the efficiency in the production of the ionic liquid that was obtained with a purity of 99.40%, as well as the possibility of recovery after its use in the treatment, obtaining a purity of 95.93%. Analyzing the celluloses obtained after each treatment, it can be seen that the IL treatment was not able to promote the total separation of the cellulose fibrils within the matrix. However, the IL used was able to promote the rupture of the cellulose–hemicellulose–lignin complex, which favored the production of CMC. The use of other low-cost ionic liquids should be evaluated to consider the characteristics of the pre-treated materials in future studies to optimize the production of the cellulose-derived biopolymers. Additionally, it was not enough to remove the lignin wrap, as it also occurred in the pulping process. The CMCs obtained from the straws that underwent treatment with the IL showed a lower degree of substitution when compared with the CMC obtained from the pulped straw. All values were within the expected range and the CMC obtained from the treatment with the IL showed values similar to those of the standard CMC, which showed efficiency of the process used.

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