SYNTHESIS AND APPLICATION OF TWO NEW IONIC LIQUIDS IN THE EXTRACTION OF CELLULOSE FROM *BOUGAINVILLEA SPECTABILIS*

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Cellulose is a natural polymer formed by chains of polysaccharide carbohydrates. Traditional processes for extraction of cellulose are expensive and require solvents with high ionic strength and stringent conditions. In this paper, we propose the extraction of cellulose from *Bougainvillea spectabilis* by using a traditional procedure, such as alkaline and acidic hydrolysis extraction, as well as the Vieira extraction method with the aid of two ionic liquids (ILs), with the purpose of using a solvent that allows reducing the harmful impact on the environment and human health. The obtained fibrous materials were analyzed by FTIR spectroscopy and the gravimetric method. According to gravimetric measurements, the results show an efficiency of 99.3% for the proposed extraction method and of 42.97% for acid hydrolysis. These results show that the proposed method allows adequate extraction using ionic solvents.

Keywords: cellulose, Bougainvillea spectabilis, ionic liquids, cellulose extraction method, acid hydrolysis

INTRODUCTION

Natural lignocellulose is the most abundant material on the earth and it is composed of cellulose, hemicellulose and lignin.¹⁻⁴ Cellulose is one of the most abundant biopolymers, it represents the majority of terrestrial biomass and is commonly used as the main constituent in conventional paper.^{5,6} Cellulose is the main component of the cell wall of plants formed by linear molecules with a tendency to form fibers, which provide consistency and stiffness to plants.⁷⁻⁹

Due to its attractive mechanical properties and stability in various solvents, it has generated a growing scientific interest, considering its abundance and low cost as a raw material. However, cellulose technology requires the extraction and processing of this natural polymer from primary sources, using techniques that have changed very little since the beginning of the modern chemical industry, since cellulose and its derivatives can substitute as a source for various chemical compounds.¹⁰⁻¹³

The potential use of cellulose has not been

fully exploited yet, because of the traditional use of petroleum-based polymers, and also because of the limited common solvents in which cellulose is easily soluble.¹⁴ Conventional dissolution processes of cellulose are often difficult or expensive, and require the use of solvents with high ionic strength and in relatively stringent conditions.¹⁵⁻¹⁷ With the increase in industrial pollution and the consequent government regulations, the need to implement "green" processes to avoid contamination with organic solvents, using renewable sources is becoming increasingly notable.

The effectiveness of existing methods for dissolving and extracting cellulose can be significantly improved with the availability of suitable solvents. The use of ionic solvents as a replacement for conventional organic solvents in chemical, biochemical and separation processes has been demonstrated.¹⁸ In addition, a wide and varied range of ionic solvents can be used to provide greater control and flexibility in the processing methodology. Therefore, lignoce-

llulose fractionation and component activation are considered the first challenge towards a competitive bio-economy in terms of materials, chemicals and bioenergy production. This paper proposes the use of two ionic liquids in the extraction of cellulose.

EXPERIMENTAL

Materials

For the extraction of cellulose, fibers of Bougainvillea spectabilis were obtained from waste resulting from the shrub itself, after eliminating traces of bark or remains of other agents. The chemicals: cellulose (powder ≥97%), 1-bromooctane (99%), 1bromodecane (98%). 1-methylimidazole (ReagentPlus®, 99%), sodium hydroxide (ACS reagent, ≥97.0%) 0.1 M, sulfuric acid ACS reagent, 95.0-98.0% 1.2-dichlorobenzene (60% w/w). (ReagentPlus®, 99%), acetonitrile (Anh., 99.8%), nitrogen (99.99% INFRA, purity level 4) and potassium bromide (FT-IR grade, ≥99%) were purchased from Sigma Aldrich, México.

Synthesis of 1-methyl-3-octylimidazole bromide (Br1M3OIm) and 1-methyl-3-decylimidazole bromide (Br1M3DIm)

The ionic liquids, 1-methyl-3-octylimidazole bromide (Br1M3OIm) and 1-methyl-3-decylimidazole bromide (Br1M3DIm) were synthesized under very mild conditions by the Menshutkin reaction.¹⁹⁻²¹ 1-Methylimidazole and 1-alkyl bromide were used as acquired, since the purities of the reagents were greater than 97%, according to Sigma-Aldrich. For the synthesis process, 0.5 mol of 1-methylimidazole and 100 mL of toluene were placed in a balloon flask, equipped with a serpentine and a magnetic stirrer. The reaction was carried out in an inert nitrogen atmosphere and an ice bath. The mixture was stirred for one hour, then an excess of 1-bromooctane (0.55 mol) was slowly added drop by drop using a funnel, keeping the agitation constant and the atmosphere inert. The reaction continued, heating the system up to 75 °C for 24 hours (Fig. 1). To remove the excess 1alkyl bromide, it was washed twice with acetonitrile (100 mL). The remaining acetonitrile was removed by heating under vacuum at 70 °C for 12 hours. The sample was cooled to room temperature and the product obtained was the IL of interest.22-27 Some authors recommend that the reagents be purified to eliminate impurities that appear in ionic liquids with coloration, in addition to protecting the reaction flask from light by covering it with aluminum foil.^{26,27}

1-Methyl-3-octylimidazole bromide (Br1M3OIm)

IR (KBr) v/cm⁻¹ 3436, 3058, 2923, 2854, 1569, 1465, 1378, 1168, 750, 620; ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 7.58 (s, 1H), 7.40 (s, 1H), 4.27 (t, 2H, *J* 7.2 Hz, CH₂), 4.08 (s, 3H, CH₃), 1.86 (m, 2H, CH₂), 1.22 (m, 10H), 0.81 (t, 3H, *J* 5.9 Hz, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 137.31, 123.73, 121.97, 77.48, 77.16, 76.85, 50.15, 36.77, 31.67, 30.34, 29.03, 28.95, 26.25, 22.59, 14.10.

1-Methyl-3-decylimidazole bromide (Br1M3DIm)

IR (KBr) v/cm⁻¹ 3437, 3059, 2925, 2855, 1568, 1460, 1378, 1167, 751, 620; ¹H NMR (400 MHz, CDCl₃) δ 10.31 (s, 1H, CH), 7.55 (s, 1H), 7.38 (s, 1H), 4.29 (t, 2H, *J* 7.2 Hz, CH₂), 4.11 (s, 3H, CH₃), 1.87 (m, 2H, CH₂), 1.26 (m, 14H, CH₂), 0.84 (t, *J* 6.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.46, 123.62, 121.86, 77.45, 77.13, 76.82, 50.19, 36.80, 31.85, 30.36, 29.47, 29.39, 29.26, 29.02, 26.28, 22.68, 14.16.



Figure 1: Synthesis route of 1-methyl-3-alkylimidazole bromide

Preconditioning of Bougainvillea spectabilis fibers

In this work, wood cuttings of *Bougainvillea* spectabilis were used to obtain fibers to extract cellulose. After cutting the branches to sizes of 0.5-0.7 mm, two samples of 100 g each were weighed and crushed to obtain small fibers, which were placed in an oven at 75 °C for 24 hours to remove the moisture contained in the plant.

Depigmentation of preconditioned fibers by alkaline treatment

In this step, 45 g of the dry sample (3 samples of 15 g each) was reacted with 0.1 M NaOH to remove pigmentation (chlorophyll, xanthophylls). The sample

was weighed and added to a 0.1 M NaOH solution, then heated to 45 °C for 3 hours under constant stirring. Followig the treatment with NaOH, the sample was washed with distilled water until the filtrate was clear and the pH was neutral. The washed fibers were dried in an oven at 50 °C for 72 hours. Finally, the obtained samples were weighed and compared with the initial weight.

Acid hydrolysis method

Fibers obtained from the alkaline treatment (3 samples of 3 g each) were weighed and added to 200 mL of 60% H_2SO_4 w/w aqueous solution, at 45 °C for 30 minutes, under constant stirring. Subsequently, the

solution was allowed to cool for 24 hours before filtering and washing. The washes were carried out with distilled water and the obtained samples were left to dry for 24 hours at 75 $^{\circ}$ C.

Extraction method with organic solvent

In this method, 1,2-dichlorobenzene (ODCB) with the boiling point of 180-183 °C was used as organic solvent. ODCB is a liquid that goes from colorless to yellow and with a characteristic odor. It can be absorbed by inhalation, through the skin or ingestion, it is irritating to eyes, skin and respiratory tract. The substance may affect the central nervous system and liver, and its exposure may cause decreased alertness. For this method, 3 samples of 3 g each of alkali treated samples were used. The sample was added to 150 mL of 1,2-dichlorobenzene, then, it was filtered with distilled water until a clear liquid was obtained. The sample was dried for 24 hours at 75 °C.

Cellulose extraction method with ionic liquids

a) 1-Methyl-3-octylimidazole bromide (Br1M3OIm): 3 samples of 3 g each of dried Bougainvillea spectabilis samples treated with 0.1 M NaOH were used. 50 mL of Br1M3OIm was used and heated at 160 °C for 3 hours with constant stirring. Br1M3OIm is a very viscous amber liquid similar to honey. The sample was washed with ethyl alcohol until obtaining a diaphanous filtration. Then, the sample was dried for 24 hours at 75 °C. Water was not used as it can interact with the ionic liquid and it would not be possible to recover it later.

b) 1-Methyl-3-decylimidazole bromide (Br1M3DIm): 3 samples of 3 g each of dried Bougainvillea spectabilis samples treated with 0.1 M NaOH were used. 50 mL of Br1M3DIm was used and heated at 80 °C and 160 °C for 3 hours with constant stirring. At the end of the heating, the sample was filtered and washed with ethyl alcohol. The filtrate was preserved to later recover the ionic liquid and reuse it. The sample was dried for 24 hours at 75 °C.

Characterization by infrared spectroscopy (FTIR)

FITR spectroscopy was used to analyze and compare the fibers obtained by the different methods described above. KBr tablets (potassium bromide) were prepared from each of them, and for comparative purposes, commercial cellulose was used as reference.¹¹ To obtain the FTIR spectra, a Perkin-Elmer spectrophotometer Model Spectrum 100 was used, with 32 scans, in the range of 4000-400 cm⁻¹ at a resolution of 4 cm⁻¹. KBr pellets (5 mg of sample for 100 mg of KBr) were prepared. Three measurements were made for each sample and the average value was considered.

RESULTS AND DISCUSSION

The analyses of the applied methods for the extraction of cellulose fibers from *Bougainvillea spectabilis* are presented below.

Preconditioning analysis of *Bougainvillea* spectabilis fibers

Because the sample was easily burned when dried at 100 °C (a), drying temperature was changed to 75 °C (b), as the drying temperature could affect the obtained sample and the time of cellulose extraction (Fig. 2).²⁸



Figure 2: Dry sample at (a) 100 °C and (b) 75 °C

Analysis of fibers obtained by alkaline treatment

Figure 3 shows the obtained pigment-free fibers after performing the alkaline treatment on preconditioned fibers, and after the filtering and drying process. These fibers were used to obtain cellulose by different methods: acid hydrolysis, the scallop method with 1,2-dichlorobenzene as organic solvent, and the scallop method with ionic solvent. Br1M3OIm and Br1M3DIm were used as ionic liquids in this last method, and the obtained fibers were analyzed by infrared spectroscopy and optical microscopy.²⁹



Figure 3: Washed and dried sample

FT-IR analysis of samples obtained by different chemical methods

The characteristic bands of cellulose were identified in the infrared spectra. The presence of signals between 3500 and 3200 cm⁻¹ is due to the vibration frequency of the -OH group with hydrogen bonds (intramolecular and cm^{-1} intermolecular), band 3000 the at corresponding to the vibration frequency of the -CH group, the band at 1600 cm⁻¹ is attributed to the bending vibration of -OH, the band between 900 and 1300 cm⁻¹ indicates in-plane bending of the -OH group, the band between 1100 and 1200 cm^{-1} corresponds to C–O–C asymmetric

stretching, and the band at 1100 cm^{-1} is due to C–O stretching.^{30,31}

In the spectrum of commercial cellulose (Figs. 4, 5, 6 and 7), the presence of a strong intensity band due to –OH vibration is observed at 3345 cm⁻¹ and the bending of the –OH group at 1638 cm⁻¹. The C-O-C asymmetric stretching is observed at 1163 cm⁻¹ and the C-O vibration band at 1060 cm⁻¹. The small band at 2901 cm⁻¹ is assigned to the stretching vibration of the –CH group. Also, the asymmetric –CH₂ and symmetric –CH₃ vibration stretching is observed at 1431 cm⁻¹ and 1373 cm⁻¹, respectively.



Figure 4: Infrared spectra of commercial cellulose (a) and of cellulose obtained by acid hydrolysis (b)



Figure 5: Infrared spectra of commercial cellulose (a) and of cellulose obtained by the Vieira method with an organic solvent (b)

Analysis of fibers obtained by acid hydrolysis

In the spectrum of cellulose obtained by acid hydrolysis (Fig. 4b), the broad band of strong intensity observed at approximately 3500 cm^{-1} corresponds to the stretching vibration of the -OH group, with the bending of -OH at 1627 cm⁻¹. The asymmetric stretching of C-O-C bonds is notable at 1178 cm⁻¹ and the C-O bond is observed at 1068 cm⁻¹. The stretching vibration of

Analysis of fibers extracted with an organic solvent

Figure 5 (b) shows the spectrum of cellulose extracted by the Vieira method³² with an organic solvent. In this spectrum, we can see the -OH stretching at approximately 3400 cm⁻¹ as a broad band of strong intensity and the bending of -OH is exhibited at 1621 cm⁻¹. The asymmetric C-O-C stretching is localized at 1162 cm⁻¹ and the C-O bond is noted at 1059 cm⁻¹. -CH stretching is shown as a peak of medium intensity at 2922 cm⁻ ¹. The vibration at 1455 cm^{-1} and 1427 cm^{-1} corresponds to asymmetric -CH₃ and -CH₂ bending; while the symmetric bending of -CH₃ is observed at 1372 cm⁻¹ and 1318 cm⁻¹. The bands at 897 cm⁻¹, 731 cm⁻¹ and 616 cm⁻¹ indicate that there is a substituted benzene ring; this can mean that the solvent (1,2-dichlorobenzene) adhered to the fibers, possibly requiring a more thorough washing.

-CH is shown as a weak peak at 2372 cm⁻¹. The vibration at 1463 cm⁻¹ and 1424 cm⁻¹ is assigned to the asymmetric bending of -CH₃. The bands at 885 cm⁻¹ and 850 cm⁻¹ indicate the bending of =CH₂ bonds, and the peak at 576 cm⁻¹ is due to the bending of C=C bonds. This result may indicate that the cellulose was partially removed when the acid medium was used as a solvent.

Analysis of fibers obtained by scallop method with ionic solvent

Figure 6 (b) shows the spectrum of the cellulose obtained by the Vieira method with Br1M3OIm at 160 °C. The -OH stretching is noted approximately between 3400 cm⁻¹ and 3500 cm^{-1} , and the –OH bending at 1630 cm^{-1} . The asymmetric C-O-C stretching is localized at 1165 cm^{-1} , the peaks at 1034 cm^{-1} and 1059 cm^{-1} indicate the C-O vibration. -CH stretching is indicated by two peaks at 2857 cm⁻¹ and 2927 cm^{-1} , respectively. Also, the asymmetric $-CH_3$ bending is observed at 1428 cm⁻¹ and 1463 cm⁻¹, and the symmetric bending of $-CH_3$ at 1373 cm⁻¹. The peak at 621 cm⁻¹ indicates C-Br, which may be due to the solvent used. Some of the bands, such as those corresponding to -OH and -CH, precede the bands from the spectrum of Br1M3OIm. Therefore, the washing of the sample should be improved after extraction.

The FTIR spectra of the cellulose fibers extracted by the Vieira method using Br1M3DIm

at 160 °C and at 80 °C were compared with that of commercial cellulose in Figure 7. –OH stretching can be seen at 3417 cm⁻¹ for the fibers obtained with Br1M3DIm at 80 °C, and at 3350 cm⁻¹ for those achieved at 160 °C. –OH bending is located at 1638 cm⁻¹ for the fibers extracted at 80 °C, and at 1630 cm⁻¹ for those obtained at 160 °C. The asymmetric C-O-C stretching band is observed at 1163.71 cm⁻¹ for the cellulose obtained with Br1M3DIm at 80 °C, and at 1163 cm⁻¹ for that achieved at 160 °C. Meanwhile, the vibration of the C-O bond was localized at approximately 1059 cm⁻¹ for both temperatures.



Figure 6: Infrared spectra of commercial cellulose (a) and of cellulose obtained by the Vieira method with Br1M3OIm (b)



Figure 7: Infrared spectra of commercial cellulose (a) and of cellulose obtained by the Vieira method with Br1M3DIm at 160 $^{\circ}$ C (b) and 75 $^{\circ}$ C (c)



Figure 8: Micrographs of cellulose fibers obtained a) by acid hydrolysis at 75 °C, b) with 1,2-dichlorobenzene, c) with Br1M3OIm at 160 °C, d) with Br1M3DIm at 75 °C, e) with Br1M3DIm at 160 °C, f) white cellulose (commercial)

It is further observed that the –CH stretching is located at 2925 cm⁻¹ and 2925 cm⁻¹, respectively; the asymmetric –CH₃ bending is noted at 1427 cm⁻¹ for the cellulose obtained with Br1M3DIm at 80 °C, and at 1429 cm⁻¹ for that obtained at 160 °C; while the symmetric –CH₃ bending is observed at 1319 cm⁻¹ and 1317 cm⁻¹. The peaks at 620 cm⁻¹ and 619 cm⁻¹ indicate the C-Br bond. Similarly, to the previous spectrum, this may be due to the ionic liquid, considering that bands such as –OH and –CH are placed before the bands of the spectrum of Br1M3DIm.

Optical microscopy analysis of samples obtained by different chemical methods

Figure 8 (a) shows the micrograph of cellulose fibers obtained by acid hydrolysis, revealing dark colored and approximately 6 mm long fibers. The cellulose fibers obtained with the organic solvent ODBC (Fig. 8b) present bright yellow fiber color, without changes in fiber size, compared to alkali treated fibers. The cellulose extracted with Br1M3OIm (Fig. 8c) shows small agglomerated fibers.

As regards the cellulose extracted with Br1M3DIm at 80 °C (Fig. 8d), clear fibers were obtained, of the same size as the sample achieved by the alkaline treatment. Figure 8 (e) shows the cellulose fibers obtained with Br1M3DIm at 160 °C, which are dark colored, but lighter than those obtained with Br1M3OIm at 160 °C. The fibers extracted by Br1M3OIm and Br1M3DIm at 160 °C are the ones that resemble the most closely the

fibers of commercial cellulose, except for the coloration. This is explained by the solvent used and by the fact that no bleaching solution was used. Figure 8 (f) shows the commercial cellulose fibers, which are white.^{17,33}

Evaluation of the effect of the solvent on treated *Bougainvillea spectabilis*

Table 1 shows the mass of Bougainvillea spectabilis (clean and dry) used for each of the systems. In addition, the table lists the average percentages of the fibers obtained in each case (triple experimentation). In the case of the first batch, alkaline treatment was carried out as a for eliminating pretreatment, traces of contaminants, as well as the characteristic pigments of the plant (Figs. 2 and 3). For the treatment in acidic medium, an average percentage of treated mass of 42.5±0.8% was obtained, representing a high mass loss. This is explained by the fact that the acid degrades the samples, which has been also confirmed by the FTIR analysis (Fig. 4b).

For the samples treated by the Vieira method,³² with the use of solvent (1.2-dichlorobenzene), the average mass percentage obtained was in the order of $96.8\pm1.8\%$. This solvent is commonly used in cellulose extraction; however, the cleaning process of the final product is arduous and not always efficient. Despite the high mass percentages obtained, the FTIR study (Fig. 5b) showed traces of the solvent used, which is a contaminant.

Chemical method	Initial mass	Final mass	Average treated mass
	(g)	(g)	obtained (%)
Alkaline treatment	15	12.23	81.5±1.5
Acid hydrolysis (75 °C)	3	1.28	42.5±0.8
Vieira method with organic solvent (75 °C)	3	2.91	96.8±1.8
Vieira method with Br1M3OIm (160 °C)	3	1.39	46.4±0.4
Vieira method with Br1M3Dim (160 °C)	3	1.42	47.2±1.1
Vieira method with Br1M3DIm (75 °C)	3	2.97	98.8±0.5

 Table 1

 Mass percentages of Bougainvillea spectabilis before and after the treatments

The use of ionic liquids is a viable alternative as they are chemically stable when modifying the operating temperature. Table 1 shows the results obtained when using the two ionic liquids studied at 75 °C and 160 °C. When using a temperature of 160 °C, a percentage mass of 46.4±0.4% and 47.2±1.1% was obtained for the fibers extracted with Br1M3Oim and Br1M3Dim, respectively. For the latter, a higher mass percentage was obtained, which can be attributed to the larger ion size of the ionic liquid.^{34,35} The best result was achieved using Br1M3DIm and a temperature of 75 °C, yielding a percentage mass of 98.8±0.5% (even comparing with the extraction with the traditional organic solvent). This demonstrates that ionic liquids yield higher mass percentages of extracted fibers, or in the order of those obtained with conventional organic solvents.36 This supports the major objective of this study of using ion liquids as novel solvents for cellulose extraction, as a way to decrease the temperature of the extraction process and reduce traces of solvent residues.^{37,38}

CONCLUSION

The present study has investigated the possibility of using two ionic liquids in the extraction of cellulose and compared the percentage mass of the fibers obtained with that achieved by other common extraction methods. As a result, it can be concluded that alkaline treatment yielded clean fibers, free of waxes and pigments characteristic of Bougainvillea spectabilis, with a mass percentage of $81.5 \pm 1.5\%$. Depending on the solvent used in cellulose extraction, mass percentages of fibers between 42 and 98% have been obtained, the Vieira method being more efficient than acid hydrolysis (42.5±0.8% for the latter). The application of 1methyl-3-decylimidazole bromide (Br1M3DIm) by the Vieira method improves the extraction of fibers, reaching mass percentages of 98.8±0.5%.

When lowering the extraction temperature to 75 °C, an efficiency of 98.8±0.5% was achieved using Br1M3DIm, this value being similar to that reached with a traditional organic solvent (96.8±1.8%). However, using an ionic liquid allows obtaining cleaner cellulose, without traces of solvents, structurally similar to commercial cellulose. An additional advantage is that ionic liquids are less toxic and can be recovered.

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