HIGH SOLUBILITY OF CELLULOSE EXTRACTED FROM TUNISIAN DATE PALM (*PHOENIX DACTYLIFERA*) IN A NEW IONIC LIQUID

WIEM MARZOUK,[*] RAMZI ZARROUGUI[**] and HATEM MAJDOUB[*]

[*]*Laboratory for Advanced Materials and Interfaces, Faculty of Sciences, University of Monastir, Boulevard of the Environment, 5019 Monastir, Tunisia*
[**]*Laboratory for Methods and Techniques of Analysis, National Institute for Research and Physicochemical Analysis (INRAP), Technology Center, 2020 Sidi Thabet, Tunisia*
✉ *Corresponding author: Hatem Majdoub, hatemmajdoub.fsm@gmail.com*

A quick, straightforward, and environmentally friendly sample preparation method for dissolving cellulose was developed employing an ionic liquid as solvent. In this paper, an attempt to valorize date palm residues was made. The cellulose fibers were extracted from Tunisian date palm petioles. The chemical composition of date palm petioles was determined by assessing holocellulose, α-cellulose, and Klason lignin contents, solvent extractives, as well as ash. The following composition was found: 1.4% of extractives, 27.5% of lignin and 67.7% of hollocellulose. Finally, the solubility of cellulose in the ionic liquid (N-buthyl-N-methylpyrrolidium dibuthylphosphate) as 11% w:w at 80 °C was proven.

Keywords: *Phoenix dactylifera*, cellulose, dissolution, ionic liquid

INTRODUCTION

Limited resources of petroleum and the current fight against global warming have led scientific research in recent years to find new materials with less greenhouse gas emissions. This can be achieved by replacing synthetic polymers with natural ones. In this context, polysaccharides provide a source for biodegradable materials that reduce the recycling problem. Cellulose is a main representative of the polysaccharides family. This is the most common natural biopolymer on earth (more than 50% of the biomass).[1]

Despite its importance, many sources of cellulose, including date palm, are poorly known and unfortunately unexploited. The date palm provides dates with a high fructose rate (30%), presenting a significant feeding source in the desert regions.

In the last few decades, the cellulose derivatives were considerably multiplied. This requires dissolution of the cellulose prior to chemical reactions in a homogeneous medium. It is this aspect that is the motivation of our work.

Dissolving cellulose involves obtaining a good solution where the cellulose chains are not agglomerated. However, such a task remains difficult. The principal hindrance that limits the dissolution is the interaction between the cellulose chains to be broken, as well as the dense network of hydrogen bonds associated with strong hydrophobic interactions.

As well known, the first study on the dissolution of cellulose with an ionic liquid was carried out in 1934.[2] Generally, dissolution occurred in the N-ethylpyridinium chloride in the presence of a nitrogenous base. Unfortunately, this discovery has not been considered as having a lot of importance because of the high melting temperature of the ionic liquid (118 °C). Today, ionic liquids have much lower points of fusion and fall within the definition of green chemistry. In this sense, studies on the dissolution of cellulose in ionic liquids have increased significantly in recent years.[3] Swatloski *et al*. was the first to study the power of dissolution of ionic liquids on cellulose.[4] They studied the dissolution properties of ionic liquids based on imidazolium by varying the nature of the anion and the length of the alkyl chain of the cation. The results show that the solubility decreases as the alkyl chain is

greater than four carbons (butyl). Heinze *et al.*[5,6] showed that the cellulose was dissolved without derivatization in three products. Ionic liquid solubility decreases when the DP of the cellulose increases.

Despite the large number of existing ionic liquids to date, only those with ammonium cations, pyridinium and imidazolium have been reported as capable of dissolving cellulose.[7-9] Asymmetric cations seem to be more effective. It should be noted that the phosphonium and sulfonium cations are not yet described in the literature as solvents for cellulose.

Ionic liquids are not considered solvents for the cellulose derivatization, that is to say, they do not bind covalently with it. This was shown by ^{13}C NMR (spectra of the cellulose in ionic liquids and in DMSO are identical).[10] Nevertheless, the mechanism of solubilization is not known yet. Only BMIMCl has been studied and it was found that the anion Cl$^-$ played a key role in the solubilization of cellulose.[11] The ^{13}C NMR analyzes show that ^{35,37}Cl and the anion is responsible for the breakdown of inter- and intramolecular hydrogen bonds of the cellulose. The mechanism is similar to the dissolution of the cellulose in the LiCl/DMAc. The only difference is the greater involvement of Cl$^-$ due to the greater availability of the ionic liquid.

The maximum solubility of cellulose varies depending on a number of parameters, such as the degree of polymerization (DP), the length of the chains of the cation of the ionic liquid, the nature of the anion *etc*. Thus, in Table 1 we included some ionic liquids reported in the literature and their ability to dissolve cellulose.

EXPERIMENTAL

Date palm petioles

Date palm petioles were collected in March in Monastir (2014). The sample was dried under natural conditions (at 25 °C and 60% relative humidity). Subsequently, the obtained materials were milled and sieved to produce grains between 200 μm and 1 mm. These fibers were cleaned, washed with distilled water and then ground.

Chemical composition of date palm petioles

The chemical composition of the date palm petioles was determined by measuring the contents of holocellulose, α-cellulose, Klason lignin, solvent extractives, as well as ash, using different standard methods. Prior to analysis, the fragments of the studied material were milled and sieved to 40-60 mesh size. There are several standard methods used to determine the chemical composition of the studied lignocellulosic biomass, therefore they are briefly described below:

- Solvent extractives of wood and pulp, Test Method T 204 cm-07: this test determines the amount of solvent-soluble, non-volatile compounds in the raw material. The method consists in an extraction step, which was conducted for 6 hours in a toluene/ethanol mixture (62/38, v/v), using a Soxhlet extractor. This method was found to give the highest amount of extractives, owing to the additional dissolution of low molecular weight carbohydrates and polyphenols.

- Ash in wood and annual plants (Test Method T 211 om-07): the sample was placed in a ceramic crucible and mineralized at 525° ± 25 °C for 4 h. The ash content was calculated by weighing the residue remaining after the mineralization process.

- α-, β- and γ-cellulose in pulp (Test Method T 203 cm-99): α-cellulose is the pulp fraction that was resistant to 17.5 and 9.45% NaOH solutions under the conditions of the test. Beta-cellulose is the soluble fraction that was precipitated on acidification of the solution. Concretely, at 25 °C, the pulp was extracted consecutively with 17.5 and 9.45% sodium hydroxide solutions. The soluble fraction, consisting of beta- and gamma-celluloses, was determined volumetrically by oxidation with potassium dichromate, and alpha-cellulose, as an insoluble fraction, was derived by difference.

- Hollocellulose:[17] date palm petiole fibers were introduced into a flask containing distilled water (200 mL). Subsequently, 1.5 g of sodium chlorite and 0.5 mL of glacial acetic acid were added. The reaction mixture was heated at 80 °C during 1 h. The bleaching process was repeated several times (at least three times) until white fibers were obtained.

- Klason lignin (Test Method T 222 om-06): the lignin content was determined by the Klason method. Dry fiber (1 g) was suspended in a 72% sulfuric acid solution (15 mL) for 2 h at room temperature under stirring. The hydrolysis was continued even after dilution to 3% for 4 h. Subsequently, the precipitate was filtered and thoroughly washed with hot water to remove residual acid moieties. Each experimental test was carried out at least in duplicate and the relative standard deviation (RSD) is 5%.

Extraction and purification of cellulose fibers

The organization of the polysaccharides in the plant cell wall is basically produced by a network of hydrogen bonds between the different polymers. Their separation can be achieved by treatments in order to break the hydrogen bonds. The extraction under alkaline conditions is considered as the best method to remove hemicellulose, break the hydrogen bonds, and the hydrolyzed ester groups.[18] The different stages of extraction and purification processes are sketched in Figure 1. Following the depigmentation process, the extraction was carried out using a hydroxide sodium

solution (2M) at 80 °C during 2 h. The obtained product was subsequently bleached with sodium chlorite in acidic medium.

Synthesis and characterization of Pyr₁₄DBP
Synthesis of Pyr₁₄DBP

One equivalent of 1-methylpyrrolidine and one equivalent of tributhylphosphate were poured into a

flask containing cyclohexane, under argon atmosphere. The flask was brought to 70 °C under stirring in a silicone oil bath for 3 h. The solvent was carefully removed by fractional distillation under reduced pressure and the residue was washed three times with petroleum ether pressure distillation. The ionic liquid was dried under vacuum for 48 h.

Table 1
Examples of ionic liquids and their ability to dissolve cellulose

Ionic liquid	Solubility (w/w %)	Experimental conditions
[Bmim]Cl [12]	10	100 °C, 24 h
[Amim]Cl [13]	5	80 °C, 30 min
[Amim][HCO₂] [14]	10	60 °C
[Emim][(MeO)HPO₂] [15]	10	40 °C, 30 min
[Emim][(MeO)HPO₂] [15]	2-4	Room temperature, 3-5 h
[Bmim][HSCH₂CO₂] [16]	10	70 °C (± 48 h)

Nuclear magnetic resonance spectroscopy (NMR spectroscopy)

NMR spectroscopy was used to characterize the structure of the synthesized ionic liquid. ^{1}H-NMR spectral data were obtained on a Bruker AV 300 spectrometer.

Viscosimetric measurements

A rheometer was used in the study of the ionic liquid viscosimetry (N-buthyl-N-methylpyrrolidium dibuthylphosphate (Pyr₁₄DBP)). The apparatus used was a TA Instruments rheometer (AR 1000) with conical geometry, in the temperature range 25-80 °C.

Conductometric measurements

The conductivity was determined using a Metrohm 712 conductometer, which measures the resistance of a portion of solution comprised between two parallel metal plates. To limit the polarization phenomenon, due to electrolysis of the solution, measurements were performed under alternating current (ac) at low voltage. The ionic conductivity of the ionic liquid was measured in the temperature range varying from 293.15 to 335.15 K.

Turbidimetric measurements

The turbidity of the binary system ionic liquid/cellulose was measured with a Hach Lange turbidimeter, model 2100 P. This device measures the turbidity of the solutions using a white light beam to 860 nm. The measuring tubes have a capacity of about 15 mL. For the study of the maximum solubility of cellulose in an ionic liquid, the following protocol was followed: the measurement of the maximum dissolution of the cellulose was carried out by adding precise amounts of cellulose (10 to 20 mg per addition) in a tube containing the ionic liquid (15 g), equipped with a magnetic stir bar. The turbidity of the sample

was then measured every 15 minutes until a constant value was reached. Then, another addition of cellulose was performed and so on. Between measurements, the tubes were placed in a thermostatic oil bath.

Dissolution and regeneration of cellulose

Prior to use, the extracted cellulose was dried at 50 °C for 2 h. The ionic liquid and cellulose were poured into a flask under nitrogen. Then, once the flask was hermetically closed, the cellulose and the solvent were mixed mechanically at 80 °C for at least 12 hours to make sure that dissolution was complete. Finally, a transparent and viscous cellulose solution was obtained. The solution was then stored at room temperature protected from moisture.

For regeneration of cellulose, deionized water and ethanol were used as an anti-solvent to precipitate the cellulose from Pyr₁₄DBP. An amount of 2 ml of anti-solvent was added to the mixture cellulose/Pyr₁₄DBP. A precipitate formed immediately. The sample was centrifuged briefly and the supernatant was removed. The sample was washed five to six times with additions of ethanol. The resulting cellulose was considered regenerated cellulose. It was characterized by FT-IR.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the original cellulose and of the regenerated cellulose were obtained using a Bio-Rad spectrometer and Omnic software. Scanning was carried out in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}, and 128 scans were averaged for each sample. The disks were prepared from ground samples (2 mg) and KBr (200 mg), using 400 kg/cm² for 5 minutes.

RESULTS AND DISCUSSION
Chemical composition of petiole fibers

The chemical characterization of the obtained particles from petiole fiber was performed and the results were presented in Table 2. The chemical composition of the obtained material was thoroughly compared to that of other parts of date palm, such as leaves[19] and rachis.[20] The results show that relatively high values have been achieved, close to the content normally encountered in the composition of rachis and leaves.

Extraction and purification of cellulose fibers

The organization of the polysaccharides in the plant cell wall is tightly related to a network of hydrogen bonds between different polymers.

Their separation is achieved by treatments to break these bonds.

The extraction under alkaline conditions remains the best method to remove hemicelluloses, break the hydrogen bonds and the hydrolyzed ester groups. This extraction can be performed with a solution of potash or soda in various concentrations. Actually, soda assists hemicellulose potash solubilization. The pulp obtained after extraction is bleached with sodium chlorite in acid medium. The extraction was repeated twice to complete bleaching. The extraction procedure and the bleaching of cellulose are schematically shown in Figure 1.

Table 2
Chemical composition of date palm petiole fibers

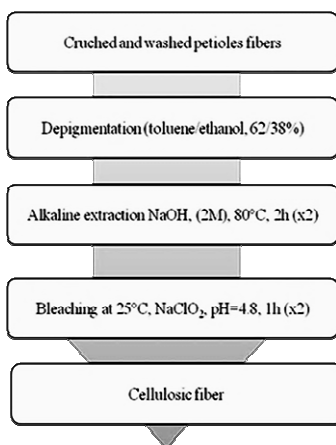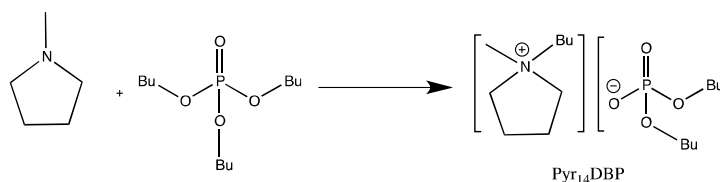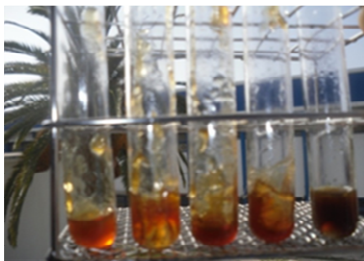| Composition	Our work	Date palm leaves[19]	Date palm rachis[20]
Ash	3.1%	9.6%	2.5%
Lignin (Klason)	27.5%	31.2%	14%
Solvent-soluble extractives	1.4%	11.7%	4%
Holocellulose	67.7%	-	72%
α-cellulose	40.8%	30.3%	44%

Figure 1: Extraction and purification of cellulose from date palm petioles

Scheme 1: Synthesis reaction of Pyr$_{14}$DBP

Figure 2: Solutions of cellulose dissolved in different concentrations of Pyr$_{14}$DBP at 80 °C

Synthesis of ionic liquid Pyr$_{14}$DBP

The synthesis of the ionic liquid involves a reaction of alkylation with 1-methylpurrolidine (Scheme 1). A light brown oily liquid was obtained. As seen in Figure 2, the color of the cellulosic ionic solution was darkening with an increasing amount of dissolved cellulose. We initially thought that this darkening of the color was the result of cellulose degradation in the ionic liquid upon heating. However, the data could not show any degradation products in the regenerated samples.

Characterizations of Pyr14DBP
^{1}H-NMR spectroscopy of Pyr$_{14}$DBP

Structure identification and the purity of the ionic liquid were confirmed by ^{1}H-NMR. Chemical shifts were reported downfield in parts per million (ppm, δ) using tetramethylsilane as internal reference. The data are given as follows:

N-Buthyl-N-methylpyrrolidium dibuthylphosphate ^{1}H-NMR: 3.65 (t, 4H), 3.35 (s, 3H), 3.2 (t, 6H), 1.35 (t, 4H), 1.15 (m, 4H), 1 (m, 2H), 0.9(t, 6H), 0.6 (t, 3H).

Conductometric study of Pyr$_{14}$DBP

The variation of conductivity against temperature is given in Figure 3. Conductivity is generally even more important when the dissociation between the ionic species is high. Thus, ionic liquids that have the lowest inter-ionic interactions will have theoretically high conductivity. However, in this case, the conductivity of Pyr$_{14}$DBP increases with increasing temperature. This can be explained by the strong Colombian attraction between anions and cations of the IL, compared to the energy due to thermal agitation. Generally, the transport of ions is firmly governed by intermolecular conductivity jump, following an Arrhenius

behavior. This means that the logarithmic variation of the conductivity as a function of 1/T is linear.

$$K = A_\kappa \exp \left(-E_{a,\kappa} / RT \right) \tag{1}$$

where A_κ and $E_{a,\kappa}$ denote the frequency factor and the activation energy for conductivity, respectively. In contrast, when the ionic liquid has a glass transition, the conductivity changes with the temperature VTF obeying the model expressed by the equation:

$$K = A_\kappa - (B_{a,\kappa} / R (T-T_0)) \tag{2}$$

where A_κ is a pre-exponential factor (constant), $B_{a,\kappa}$ a pseudo-activation energy, and T_0 represents the glass transition temperature of the ideal ionic liquid (T_0 = 80 °C).

The Arrhenius model was used in the graphs shown in Figure 5, to determine which model fits better to the variations in the conductivity with temperature.

An examination of Figure 4a shows the Arrhenius law is not verified by the Pyr$_{14}$DBP as the natural logarithm of the conductivity. It does not vary linearly with the inverse of the temperature. This behavior is characteristic of ionic liquids for which the Arrhenius activation energy appears as temperature dependent. In contrast, the VTF model is verified by the ionic liquid, as we observe a linear variation of the natural logarithm of the ionic conductivity as a function of $10^3/(T-T_0)$ (Fig. 4b) after adjustment of the value T_0 by linear regression.

Viscosimetric study of Pyr14DPB

In an ionic liquid, each ion is subjected to the action of a very large number of neighboring features so that they vibrate around a mean position. It is recognized that if the temperature rises, it may receive shocks that produce changes in direction and can thus give rise to more or less extensive migration, and hence to an increase in

fluidity of the particle,s which corresponds to a decrease in viscosity. Like all the aprotic ionic liquids, pure $Pyr_{14}DBP$ undergoes a decrease in its

viscosity with increasing temperature (Fig. 5). Unlike conductivity, viscosity values are very sensitive to any variation in temperature.
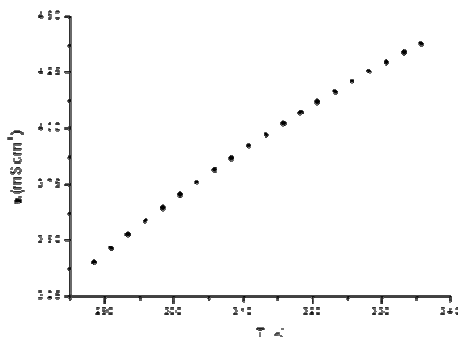
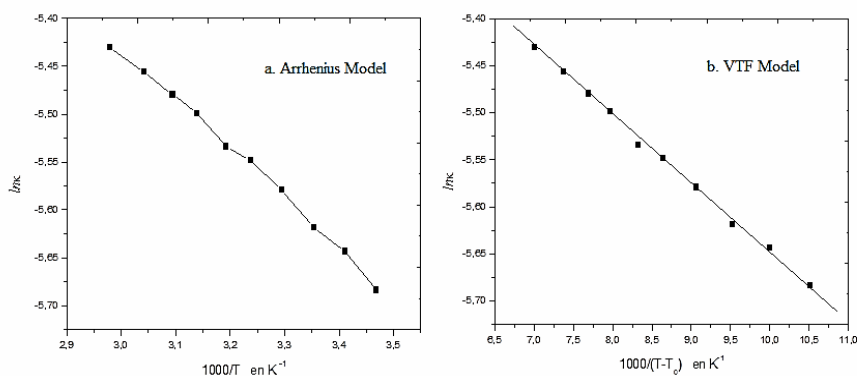Figure 3: Variation of conductivity of $Pyr_{14}DBP$ against temperature (290-335 K)

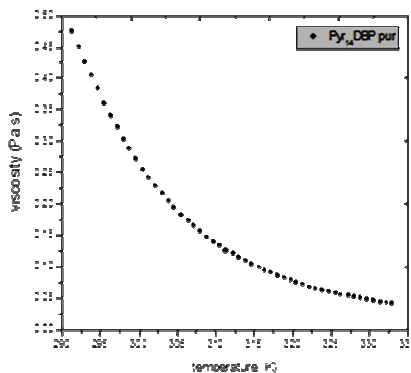Figure 4: Evolution of conductivity of $Pyr_{14}DBP$ against temperature for Arrhenius (a) and VTF (b) models

Figure 5: Evolution of viscosity of $Pyr_{14}DBP$ against temperature (290-335 K)

Dissolution and regeneration of cellulose
Determination of cellulose solubility

The solubility of cellulose in $Pyr_{14}DBP$ was examined using the turbidimetric method. The

results are reported in Figure 6, showing the turbidity against the concentration of cellulose in $Pyr_{14}DBP$. It is important to note that in "Nephelometric Turbidity Units" denoted NTU,

the turbidity detection limit is 1000 NTU). The turbidity of the system cellulose/Pyr$_{14}$DBP increases slightly for low concentrations of cellulose, but remains low. However, the turbidity increases significantly from 11 g of cellulose to 100 g of ionic liquid (Pyr$_{14}$DBP). This change in slope shows the maximum solubility of cellulose in Pyr$_{14}$DBP. Accordingly, the maximum solubility of cellulose in Pyr$_{14}$DBP at 80 °C is 11 g/100 g of ionic liquid. The turbidity of the system should remain low as long as the cellulose is soluble in the ionic liquid. When the maximum solubility is achieved, every cellulose addition should increase the number of undissolved particles in the medium. The turbidity is expected to increase rapidly.

Mechanism of cellulose dissolution in Pyr$_{14}$DBP

The cellulose dissolution mechanism in Pyr$_{14}$DBP is shown in Figure 7. The hydroxyl groups of the cellulose are used as electron pair donor and the hydrogen atoms act as electron acceptors. Similarly, the ionic liquid cations act as electron acceptor centers and anions as electron donor centers. The two centers (donor and acceptor) must be sufficiently close to allow interactions. The oxygen and hydrogen of the hydroxyl groups are separated, which allows the removal of hydrogen bonds between the cellulose chains and, consequently, its solubilization.

Fourier transform infrared spectroscopy (FTIR) of regenerated cellulose

Cellulose regenerated from the prepared sample solutions by the addition of water was washed, dried, and characterized by Fourier transform infrared (FTIR) spectroscopy. Subsequently, the obtained spectrum was compared to that of the original cellulose to elucidate the possible presence of any degradation or reaction of cellulose caused by ionic liquids. The spectra obtained from FTIR are shown in Figure 8.
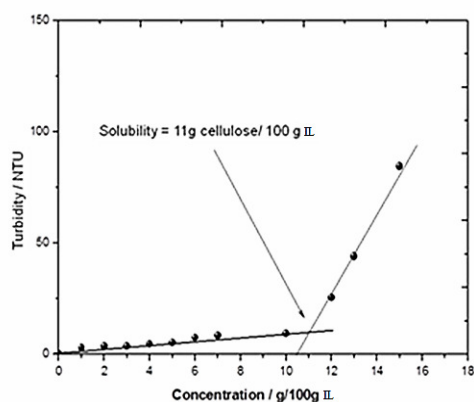

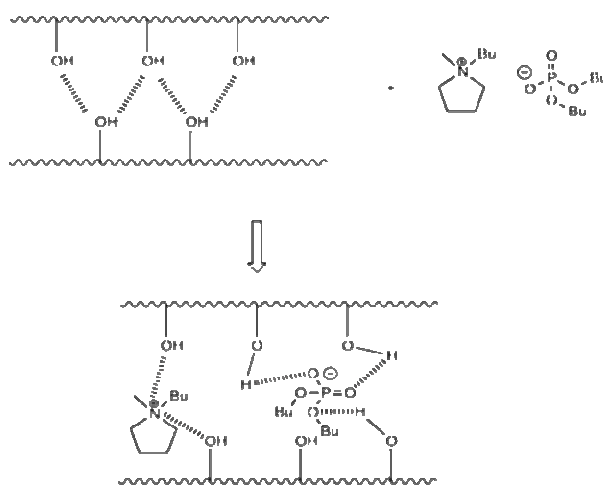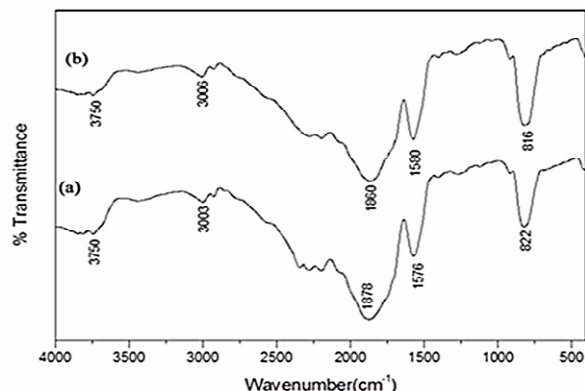Figure 6: Turbidity against concentration of cellulose in Pyr$_{14}$DBP at 80 °C

Figure 7: Mechanism of cellulose dissolution in Pyr$_{14}$DBP

Figure 8: FT-IR spectra of untreated (a) and (b) regenerated cellulose (450-4000 cm^{-1})

FTIR analysis showed that the spectra of the original and regenerated cellulose were similar, indicating the absence of chemical reaction during the dissolution and regeneration steps of the cellulose. This result is similar to previous reports.[21-23] The absorbance observed on the spectrum of the original cellulose at 3750 cm^{-1} was due to the stretching of O-H groups and that at 3003-3006 cm^{-1} was due to C-H stretching, while the peak at 1860-1878 cm^{-1} was due to the bending mode of the absorbed water.[21-22] The peak at 1576-1580 cm^{-1} was due to CH$_2$ scissoring motion.[23] The band at 1407 cm^{-1} referred to C-O stretching, while that at 126-1258 cm^{-1} was due to C-O-C vibration.[22] The peak observed at 816-822 cm^{-1} was due to C-O stretching in the amorphous region.[23] The similarity of the FTIR spectra (except the shift of some of the peaks) of the original and regenerated cellulose shows that there was no effect of the ionic liquid on the cellulose structure. Previously, it was reported that, at relatively low temperatures, Pyr$_{14}$DBP can dissolve biomass with no significant structural chemical changes to its components[24] and that cellulose is the major component of biomass.[25] The observed shift of the O-H stretch, for example, from low frequency in the spectrum of the original cellulose to high frequency in that of the regenerated cellulose is due to the splitting of hydrogen bonding in the cellulose[23] (Fig. 8).

CONCLUSION

The present study not only reveals an environmentally friendly method of dissolving cellulose from date palm petioles under mild conditions, but also provides a new approach for utilizing biomass resources. Through this project, we have managed to develop a derivative of the biomass of the Tunisian flora, which is the date palm. It presents an interesting source of cellulose. We therefore carried out the extraction and purification of cellulose fibers from the date palm petioles with a yield of 42%. Furthermore, we were able to dissolve the cellulose extracted into a new ionic liquid N-N-methylpyrrolidium buthyl- dibuthylphosphate (Pyr$_{14}$DBP), which allowed dissolving 11 g of cellulose per 100 g of this ionic liquid at 80 °C. After dissolution and regeneration in the ionic liquid, the FTIR analysis indicated that there was no effect of the ionic liquid on the cellulose structure.

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