

SEPARATION AND CHARACTERIZATION OF NEW CELLULOSIC FIBRES FROM THE *JUNCUS ACUTUS* L PLANT

Amel El Ghali,^{a,*} Imed Ben Marzoug,^b Mohamed Hassen V. Baouab,^c and Mohamed Sadok Roudesli^a

Cellulose fibres from the *Juncus acutus* L plant were isolated and characterized. The isolation of the fibres was performed by sequential NaOH treatment and H₂O₂ bleaching under different extraction conditions. The chemical and surface morphological structures of the *Juncus acutus* L fibres were characterized with FTIR, SEM, AFM, DSC, surface energy, diameter, density, and lignin content determination. Changes in structure and properties of the obtained fibres were observed by varying the concentration and the treatment time of the applied process. Results revealed that the optimum conditions to remove most of non-cellulosic materials from the *Juncus acutus* L plant were 7M NaOH, 3h and 100°C for alkaline procedure, and 10 mL.L⁻¹ H₂O₂, 45 minutes and 95°C for bleaching treatment.

Keywords: Cellulose; *Juncus acutus* L; Isolation; Characterization

Contact information: a: Laboratoire des Polymères-Biopolymères, Matériaux Organiques (LPBMO), Faculté des Sciences de Monastir, Bd. de l'environnement, 5019, Université de Monastir, Tunisia ; b : Laboratoire de Génie Textile, 5017, Université de Monastir, Tunisia ; c : Institut Préparatoire aux Etudes d'Ingénieurs de Monastir, 5019, Université de Monastir, Tunisia ; * Corresponding author : amelelghali@yahoo.fr

INTRODUCTION

In recent years, there has been a growing interest in more efficient use of plant fibres, also known as lignocellulosic fibres, as raw materials for a variety of applications such as composite preparation (Habibi et al. 2008; De Rosa et al. 2010) and paper production (Ates et al. 2008), depending on their composition and physical properties. Cellulose, the most common organic substance in nature, is the main structural component that contributes strength and stability to the plant cell walls. It is found in the cell walls as a network of microfibrils embedded in a soft hemicelluloses and lignin matrix. Considerable research has been focused on the isolation of lignocellulosic fibres from many plants like esparto grass (Ben Marzoug et al. 2010), wheat straw and soy hulls (Alemdar and Sain 2008), soybean straw (Reddy and Yang 2009), and sugarcane bagasse (Sun et al. 2004).

The fibres studied in this work were extracted from Samaar morr (*Juncus acutus* L) commonly known as sharp rush or spiny rush, which is an erect plant that forms a perennial tussock up to 2 meters high. It belongs to the Juncaceae family and grows in western and southern Europe, Africa, and North and South America. Traditionally, this biomass has been employed by artisans and, as far as we know, there is only one publication that has reported the use of this plant as a raw material for papermaking (El Sayed 2004). Therefore, the exploitation of the *Juncus acutus* L plant in this unique application should create a great deal of research interest.

In the present study, the isolation of cellulose fibres was achieved by the use of alkaline solution followed by bleaching treatment. The lignin amount, the density, and the diameter of these fibres were measured. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and surface energy were also evaluated. The effect of treatment conditions such as time, NaOH, and H₂O₂ concentrations on the above properties of isolated fibers were examined in this paper.

EXPERIMENTAL

Materials

The *Juncus acutus* L plants used in this study were collected at Monastir in the east of Tunisia during the period of March-April. Sodium hydroxide pellet for scouring, hydrogen peroxide (H₂O₂) [30% (W/W)] for bleaching, sodium silicate a stabilizer for H₂O₂, and carbon tetrachloride (CCl₄), an immersion medium for evaluation of apparent density of the fibre, were used as received without further purification.

Procedure for the Extraction of Cellulose Fibres from Samaar morr Plant

The isolation of cellulose fibres required the removal of other components such as lignin, hemicellulose, and pectin from the Samaar morr plant. This was accomplished in alkaline medium using NaOH solution at different concentrations and treatment times, followed by bleaching procedure at various H₂O₂ concentrations and at pH 11. The fibres were extracted using a liquid to plant ratio of 10:1. At each step of the different treatments, the insoluble residue was extensively washed with distilled water until reaching neutral pH. The treatments and codifications of the samples are summarized in Fig. 1.

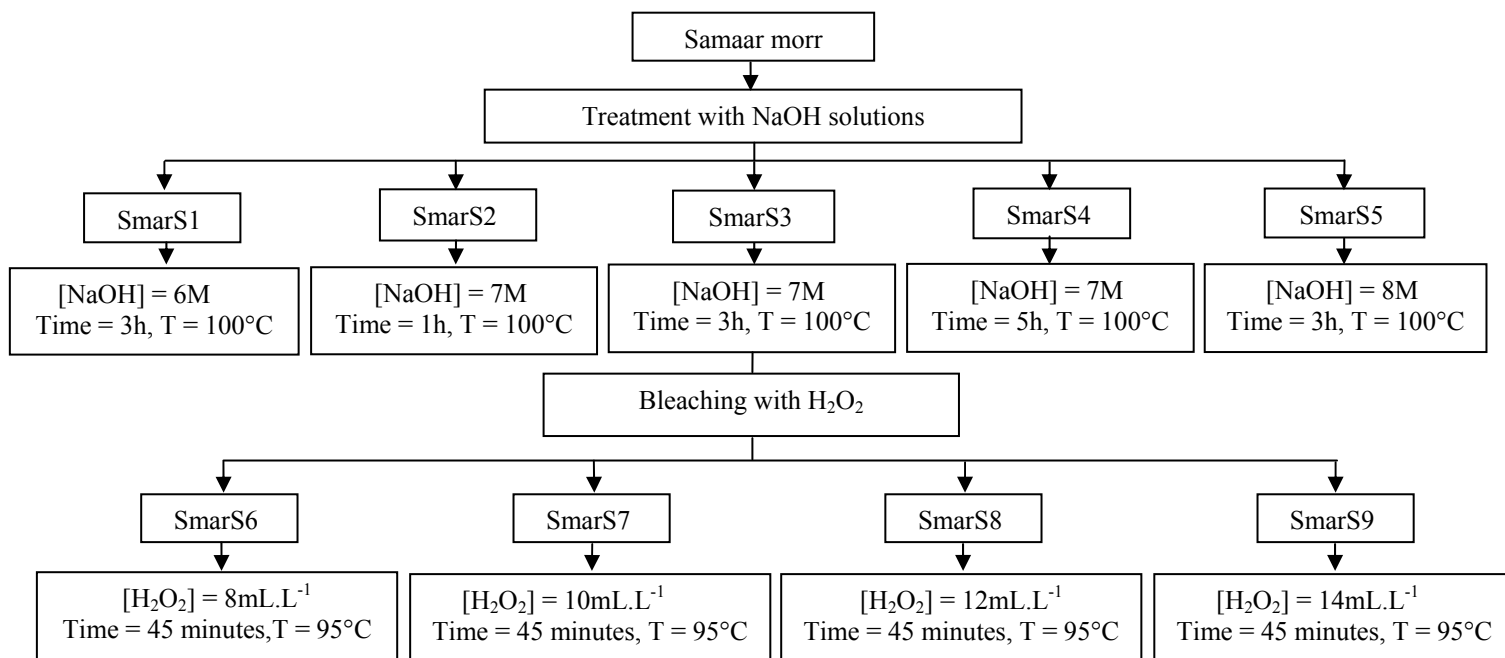


Fig. 1. Isolation scheme of cellulose fibers from Smaar morr plant by different chemical treatments

Characterization of Extracted Fibres

Fibre diameter

The diameters of the fibres were measured using a projection microscope with a magnification of 200. Twenty chosen readings samples were taken from each extraction procedure. The diameter was measured at 10 points, and the average value was then calculated.

Fibre density

The apparent fibre density was determined with a picnometer using carbon tetrachloride as the immersion liquid according to NFT 20-035 standard method at 25°C. This parameter was calculated using the following equation,

$$\rho_{fibre} = \rho_{CCl_4} \times \frac{m_{fibre}}{(m_l - m_t + m_{fibre})} \quad (1)$$

where ρ_{CCl_4} is the density of carbon tetrachloride (1.595 g.cm⁻³), m_{fibre} is the mass of dried sample (g), m_l is the mass of the picnometer containing carbon tetrachloride (g), and m_t is the mass of the picnometer containing both carbon tetrachloride and the mass of dried sample (g).

Lignin content

Lignin content in the extracted fibres was estimated by determining the dry mass remained after treating with 72% sulphuric acid according to the Klason's method (Le Digabel and Avérous 2006). About 3 g of the sample was placed in a 100 mL flask, with 3 mL of 72% (w/w) H₂SO₄. The mixture was steeped for 2h at 20°C with frequent mechanical stirring. Afterwards, it was diluted with 40 mL of distilled water and heated under reflux for 3 h. It was then filtered, and the insoluble lignin was washed thoroughly with water to free it from traces of acid, dried at 105°C, and weighed.

Scanning electron microscopy (SEM)

The morphology of the various extracted fibres samples was investigated by using scanning electron microscopy (XL30 ESEM).

FT-IR spectral analysis

Fourier transform infrared (FTIR) spectroscopy was carried out to qualitatively identify the constituents of the various extracted fibres. The dried samples were ground into fine particles and mixed with KBr. They were then compressed into pellets and analyzed with Nicolet® 510M spectrophotometer operating in a transmission mode in the range of 500-4000 cm⁻¹.

Differential scanning calorimetry (DSC)

Thermal analysis was performed using a Setaram differential scanning calorimeter. Each fibres sample was heated from room temperature to 500°C at a rate of 10°Cmin⁻¹, under dynamic flow of air.

Surface energy

The contact angles (θ) were measured using three different liquids: ultrapure water, diodomethane (Aldrich, 99%), and formamid (Aldrich, 99%). The measurements were performed at room temperature (20°C). The surface energy was calculated according to the Owens-Wendt method, based on the Young-Dupre and Fowkes equations (Bessadok et al. 2007).

AFM analysis

The surface topography of extracted fibres was studied with a Nanoscope III atomic force microscope (Digital Instruments, Santa Barbara, USA). AFM images were recorded in the tapping mode, which consists in sweeping the surface of the sample using a tip oscillating at a frequency close to that of the cantilever resonance.

The contact with the surface was done when the tip reached the maximum amplitude of oscillation. Contrary to the contact mode, the siliceous tip, which intermittently contacts the surface, did not modify the state of this surface (El Ghali et al. 2011).

RESULTS AND DISCUSSION

Fibre Diameter

The results of diameter determination for extracted fibres from the Samaar morr plant are shown in Table 1. As can be seen, there were significant differences between the various studied samples assessed by the obtained coefficients of variation (CV %). The obtained results concerning the alkaline procedure exhibited a decrease in diameter value with the increment of NaOH concentration or the exposure time.

The SmarS3 sample showed the lowest coefficient of variation (CV = 6.74%). This revealed that the other extracted fibres probably presented surface irregularities caused either by the partial removal of the cementing materials around the fibre-bundles or the degradation of the isolated fibres.

The treatment of SmarS3 alkaline treated fibres with H₂O₂ promoted a decrease in the diameter values that did not present great differences between each other. This could be attributed to the removal of surface impurities (lignin) during the hydrogen peroxide bleaching. The fibres treated with H₂O₂ presented an average diameter of 11.33 µm. This revealed that the applied treatment has removed the non-cellulosic substances without significantly altering the extracted fibres. The best coefficient of variation was obtained for the fibres bleached with 10 mL.L⁻¹ of H₂O₂ (SmarS7), having an average diameter value of 11.75 µm.

The diameter of SmarS7 fibers was considered small compared to that of other natural ones like coir (Saw et al. 2011), coconut (Brígida et al. 2010), okra (De Rosa et al. 2010), etc., and comparable to glass (Sezer and Aran 2001) and carbon (Yao et al. 2003) fibers. This result appears promising in terms of possible use of these extracted fibers for the obtainment of a sounder interface.

Table 1. Diameter and Density Values of the Different Extracted Fibers

Sample	SmarS1	SmarS2	SmarS3	SmarS4	SmarS5	SmarS6	SmarS7	SmarS8	SmarS9
Diameter (μm)	19.765	18.380	12.030	7.317	9.870	11.875	11.750	11.517	10.215
Coefficient of variation (%)	13.022	11.910	6.740	33.250	19.250	6.450	5.360	7.240	15.550
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.719	2.670	1.584	0.508	0.660	1.442	1.369	1.313	1.046

Fibre Density

The influence of chemical treatments on the fibre densities is illustrated in Table 1. As can be seen, this parameter was highly affected by the extraction conditions. The decrease in density values of extracted fibres suggested the reduction of hemicelluloses, lignin, and pectin amounts after the alkaline procedure. However, the low-density values obtained in the case of SmarS4 and SmarS5 samples showed the degradation of these fibres. This can be explained by the fact that the chemical attack was probably stronger, inducing structural changes of the extracted fibres. The obtained results could also be attributed to the entrapped air on and among the fibrils due to poor wetting of the fibre by carbon tetrachloride. Thus, the applied treatment conditions caused a mass loss and considerably reduced the fibre volume, indicating that these materials have a more porous structure. The density of SmarS3 sample value was found to be equal to $1.584 \text{ g}\cdot\text{cm}^{-3}$, which is comparable to that of cotton fibres (Spinacé et al. 2009).

The bleaching of SmarS3 fibres caused a reduction of the density values (Table 1) confirming that the amount of lignin detached from the extracted fibres was improved by the hydrogen peroxide treatment. This could produce void spaces between the fibrils, causing a decrease of this parameter values. The low variability of the measured densities for SmarS7 and SmaS8 samples suggested that these fibres possibly exhibited homogeneous surfaces and contained low quantities of non-cellulosic materials.

The increase of H_2O_2 concentration in the case of SmarS9 sample corresponded to a decrease in the density value, suggesting probably that fibrillation took place. In this case, the air volume became more important which caused a reduction in the density value, as can be seen in Table 1.

The measured density of SmarS7 fibers is comparable to those of other cellulosic materials such as banana (Deepa et al. 2011), date palm rachis (Khiari et al. 2011), and sisal (Satyanarayana et al. 2007), and higher than those of curaua (Satyanarayana et al. 2007), *Stipa tenacissima* L (Bessadok et al. 2007), and luffa (Satyanarayana et al. 2007) fibers.

Lignin Content

Chemical pulping processes are designed to remove the majority of lignin in order to release the fibres. The efficiency of the treatment methods was evaluated through the determination of lignin content. Table 2 reveals that the rise of NaOH concentration or treatment alkaline time was accompanied by a reduction in insoluble lignin content. Results also showed that the amount of lignin contained in SmarS3, SmarS4, and SmarS5 were relatively stable. This indicated that strong conditions did not significantly affect the lignin amount, but it could lead to the degradation of the extracted fibres. The hydrogen peroxide bleaching resulted in a considerable decrease in the lignin content particularly when the concentration of H_2O_2 was increased.

Table 2. Lignin Content and Energy Surface Values of the Different Extracted Fibers

Sample	SmarS1	SmarS2	SmarS3	SmarS4	SmarS5	SmarS6	SmarS7	SmarS8	SmarS9
Lignin content (%)	10.370	9.950	9.150	8.950	9.050	7.400	6.200	6.010	5.980
Surface energy (mJ.m ⁻²)	57.300	52.800	46.800	41.300	45.200	46.300	45.400	45.100	46.800

Scanning Electron Microscopy (SEM) Analysis

The changes in cellulose structure induced by the different chemical treatments were also corroborated by other physicochemical tests such as SEM examinations (Figs. 2 and 3). Figures 2(a) and 2(b) showed the overlapping of non-cellulosic substances along the length of the fibres that are bonded firmly together by the cemented materials that give strength to the bundle as a whole. This could be attributed to a low treatment duration or NaOH concentration.

These two parameters were insufficient to remove a great percentage of these substances. However, in some cases, where the chemical attack was probably stronger, the fibres appeared to be deformed with an opened structure, indicating the damage on its surface caused by the increase in the treatment time, as can be seen in Fig. 2 (d).

Figure 2 (c) indicates that the SmarS3 sample consisted basically of elementary cellulose fibres still incorporating lignin compounds, as demonstrated by the presence of some deposits on the surface of the extracted fibres. This can be explained by the fact that during alkaline treatments, constituents like pectin and hemicelluloses are usually hydrolyzed by the action of NaOH solutions, whereas lignin can be removed during an additional bleaching step using hydrogen peroxide.

The SEM micrograph of SmarS5 (Fig. 2(e)) sample did not show a clear separation of extracted fibres in spite of the increase in NaOH concentration (8 M). This image cannot give, in this case, considerable information about the morphological surface of the obtained fibres.

Owing to the fact that some of lignin content was still not completely removed from the SmarS3 sample, bleaching treatment was carried out in this study. SEM examinations of the longitudinal surface of bleached smaar fibres are depicted in Fig. 3. Figure 3 (a) shows the presence of some impurities on the surface of SmarS6 fibres (treatment with 8 mL.L⁻¹ H₂O₂), indicating the partial removal of lignin that interconnect the cellulose fibres.

SEM picture of SmarS7 sample (Fig. 3(b)) visually suggested the removal of non-cellulosic materials after H₂O₂ treatment using a concentration of 10 mL.L⁻¹ resulting in smooth, compact, and clean fibre surfaces that are well defined and separated. The obtained fibres are reasonably uniform in cylindrical shape. When the concentration of H₂O₂ exceeds 10 mL.L⁻¹ (Figs. 3(c) and 3(d)), we observed irregularities in the diameter of the extracted fibres revealing that the applied treatment conditions have affected their final size.

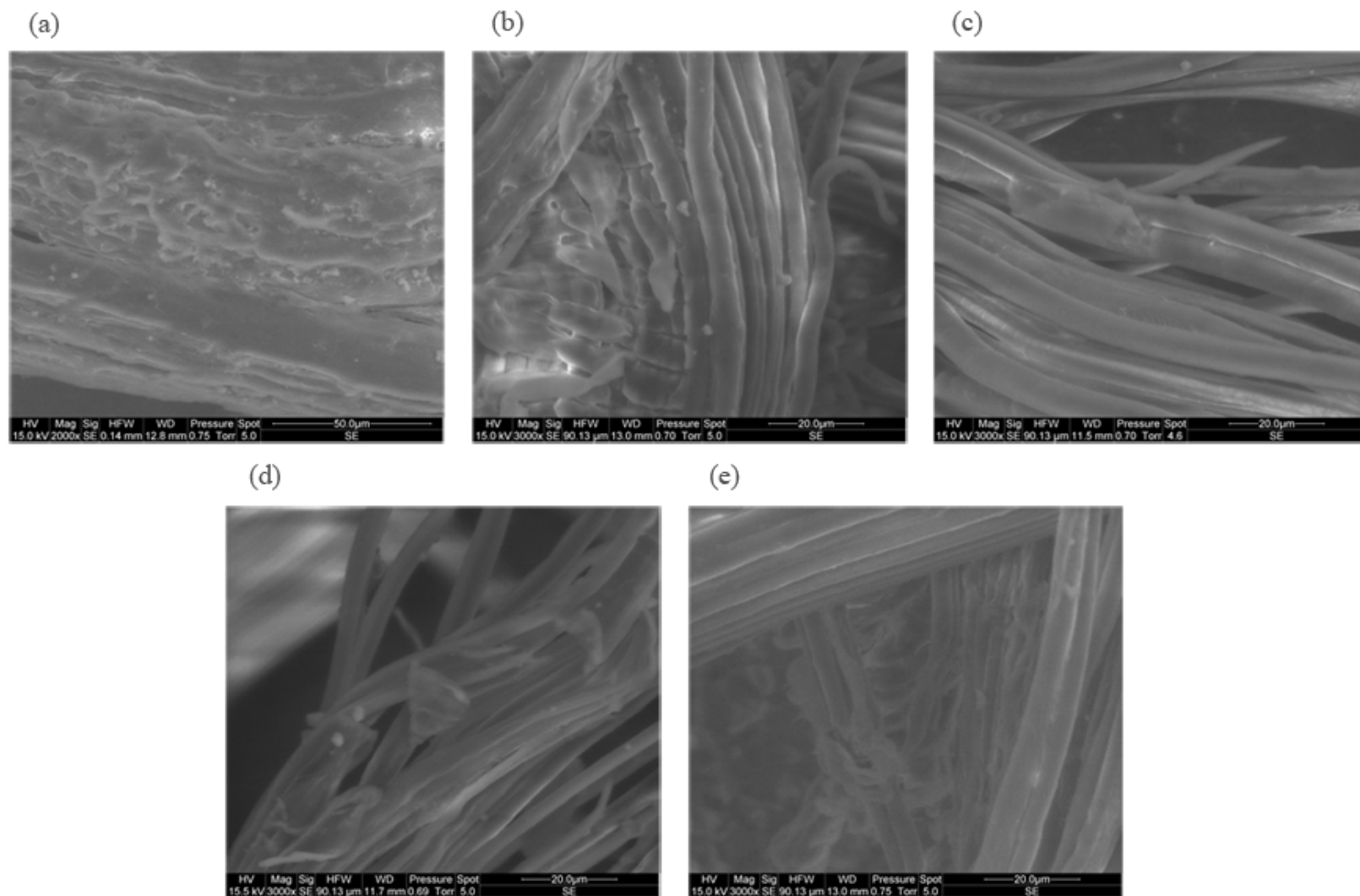


Fig. 2. SEM micrographs of extracted fibers by NaOH treatment: (a) SmarS1, (b) SmarS2, (c) SmarS3, (d) SmarS4, and (e) SmarS5

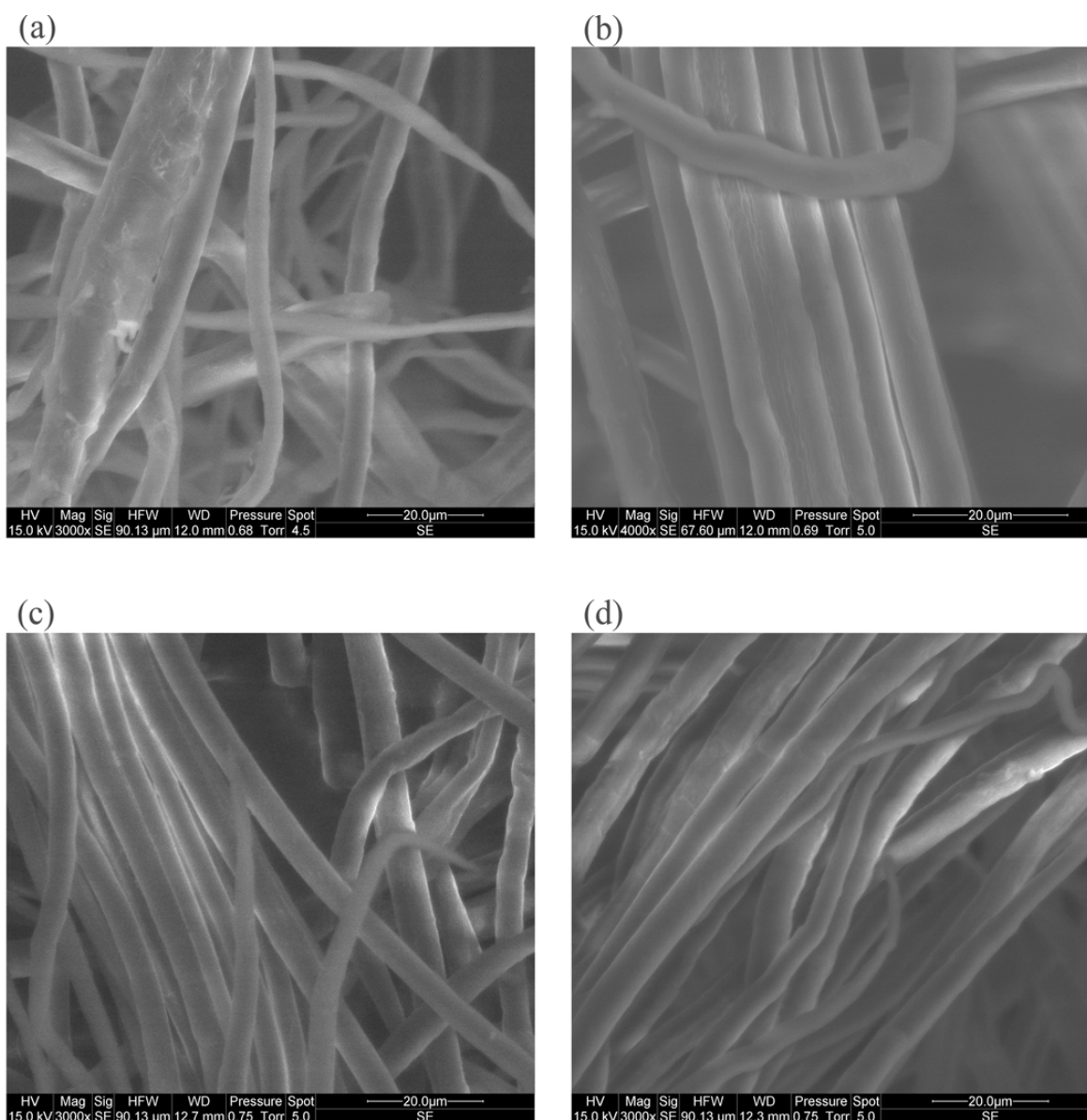


Fig. 3. SEM micrographs of bleached fibers by H_2O_2 : (a) SmarS6, (b) SmarS7, (c) SmarS8, and (d) SmarS9

Spectroscopic Analysis

FTIR spectroscopy is an appropriate technique by which to establish the variations introduced by different treatments on the chemical structure of the isolated fibres. Figures 4 and 5 showed the FTIR spectra of the different isolated fibres from the Smaar moor plant. All these spectra revealed a broad peak at 3424 cm^{-1} , suggesting hydrogen bonded $\nu(\text{O-H})$ stretching vibration of α -cellulose. The bands at 2921 cm^{-1} and 2851 cm^{-1} are characteristics of the C-H stretching vibration from CH and CH_2 in cellulose component (Jayaramudu et al. 2010; Marais et al. 2008). The 1424 cm^{-1} band could be attributed to the CH_2 symmetric bending present in cellulose (Bessadok et al. 2008; De Rosa et al. 2011). Furthermore, the

absorbance at 670 cm^{-1} corresponds to the C-OH bending deformation (Sgriccia et al. 2008). The band at 1376 cm^{-1} represents symmetric C-H bending from the methoxyl group (Adel et al. 2010). The band around 1059 cm^{-1} is probably due to the C-OH stretching vibration of the cellulose backbone (ν C-O secondary alcohol) (Bessadok et al. 2008). In addition, the band at 1161 cm^{-1} corresponds to C-O-C stretching at the $\beta(1,4)$ - glycosidic linkage (Zhou et al. 2009). The peak, observed at 895 cm^{-1} , is attributed to the β -glycosidic linkages (De Rosa et al. 2010).

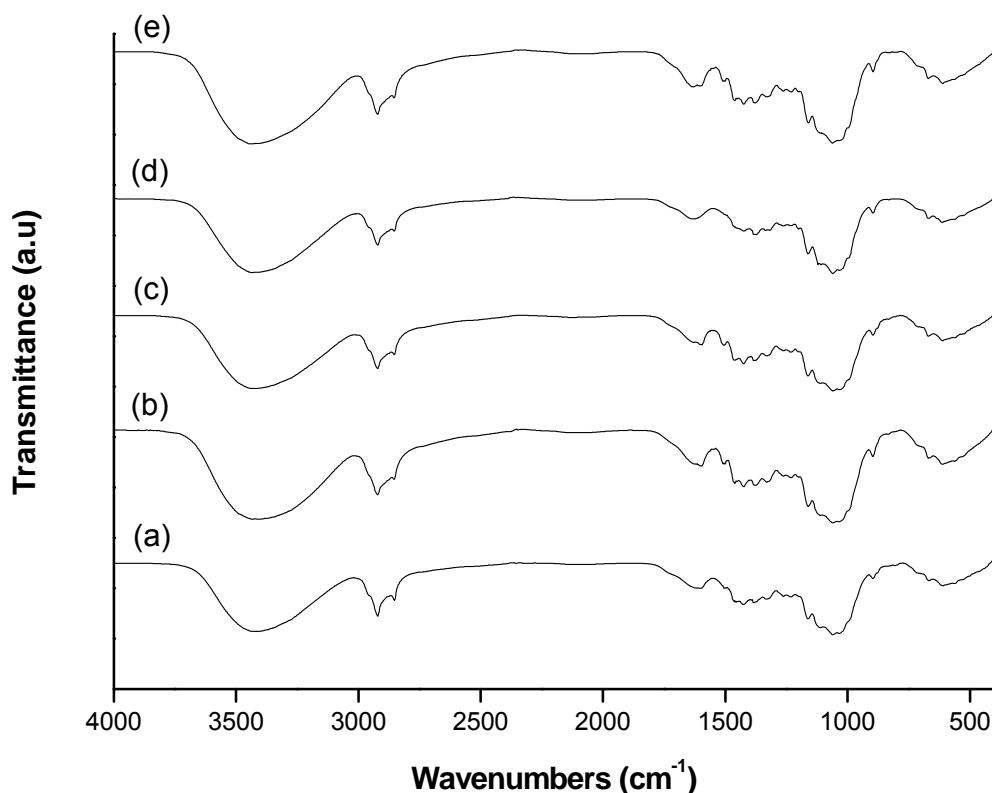


Fig. 4. FT-IR spectra of extracted fibers by NaOH treatment: (a) SmarS1, (b) SmarS2, (c) SmarS3, (d) SmarS4, and (e) SmarS5

All IR spectra showed the lack of a band at 1731 cm^{-1} that would be characteristic of the C=O stretching of the acetyl groups of hemicelluloses (Abrahama et al. 2011). This means that hemicelluloses had been effectively dissolved and removed by the alkaline treatment.

The presence of lignin component was also assessed by the IR spectroscopy analysis. In all cases, the band observed at around 1615 cm^{-1} is attributed to the C-O stretching of lignin (Jayaramudu et al. 2010). The IR spectra illustrated in Fig. 4 shows the presence of a peak around 1505 cm^{-1} , which could be assigned to the aromatic C=C stretch of aromatic rings of lignin (Alemdar and Sain 2008). The intensity of this band decreased in

the IR spectra of bleached fibres (Fig. 5), confirming the efficiency of the hydrogen peroxide treatment.

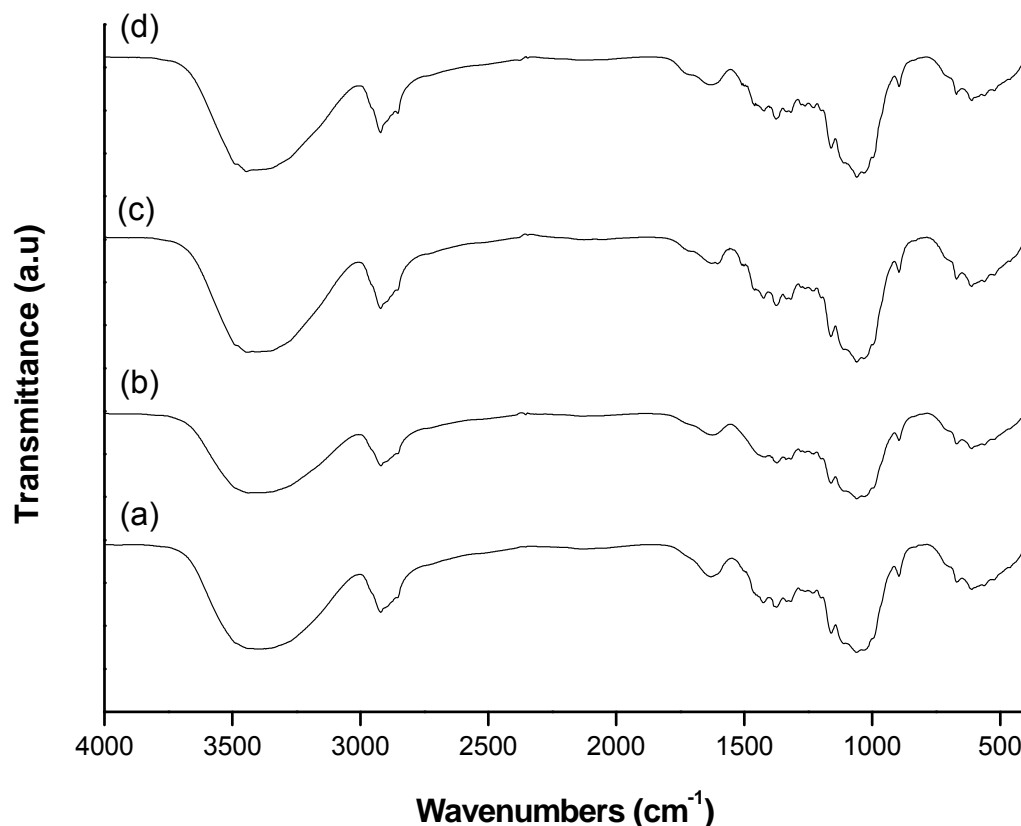


Fig. 5. FTIR spectra of bleached fibers by H_2O_2 : (a) SmarS6, (b) SmarS7, (c) SmarS8, and (d) SmarS9

The various IR spectra showed also the absence of some bands that characterize the lignin component. These bands are identified in Table 3.

Table 3. Assignment of Some Lignin absent FT-IR Peaks and their Relative Intensities

Band position (cm^{-1})	Band assignments	Reference
1740	Carbonyl C=O stretching vibration	Subramanian et al. 2005
830	C-H out-of-plane vibration	Oujai and Shanks 2005
1036	Symmetric stretching of C=O groups	Jayaramudu et al. 2010
1308	Asymmetric stretching of C–O–C	Jayaramudu et al. 2010

The results in Fig. 5 showed that: (1) the amount of cellulose was high, as confirmed by the presence of many bands characterizing these materials, (2) hemicelluloses were completely removed from the different extracted fibres, and (3) the absence of the majority of characteristic lignin peaks in the spectra of alkaline treated fibers as well as for the bleached ones, which was believed to be due to the removal of lignin after the chemical treatments.

Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry (DSC) is one of the most widely used techniques to monitor the structural dependence on the thermal degradation of natural lignocellulosic fibres. DSC analysis of Samaar-extracted fibres using alkaline treatment followed by bleaching are shown in Figs. 6 and 7, respectively. It can be noted that the endothermic peak of all the studied samples, at approximately 104°C, can be related to the water loss associated with moisture present in the extracted fibres.

During the thermal characterization of lignocellulosic fibers, the decomposition of lignin compound takes place within the temperature range of 250 to 500°C (Shen et al. 2009) and could also be occurring from a temperature of 340°C (Yang et al. 2004). It is well known that the processes used in the removal of lignin from plants are conducted under conditions where lignin is progressively broken down to lower molecular weight fragments, resulting in change of physico-chemical properties, including thermal characteristics (Mousavioun and Doherty 2010). As can be seen from Fig. 6 and 7, the thermal behavior of lignin component varied from one sample to another, depending on the applied extraction process. The curves in Fig. 6, relative to SmarS1, SmarS2, and SmarS3 samples, showed similar thermal behavior. Indeed, only one endothermic transition was observed around 374, 378, and 380°C, respectively. However, SmarS4 and SmarS5 samples presented two transitions, indicating that the decomposition of lignin component in this range of temperature occurs in two steps: the first is situated at 342°C and the second at 374°C. This means that the lignin contained in the first three samples (SmarS1, SmarS2, and SmarS3) had undergone only one transformation, whereas the two other samples (SmarS4 and SmarS5) had undertaken two state transformations that could be attributed either to a higher NaOH concentration or higher treatment alkaline time. The obtained results also exhibited that SmarS4 and SmarS5 samples contained two types of lignin: the first is amorphous, which could be related to the thermal decomposition of the aliphatic moiety (Saw et al. 2011), whereas the second is compact and more crystalline, which is probably related to the decomposition of aromatic rings of this molecule (Saw et al. 2011). This confirmed the heterogeneity of these extracted fibres.

The DSC thermograms of SmarS2 and SmarS3 samples, treated with 7M NaOH concentrations, are almost confused. However, and although that SmarS1 sample showed similar thermal behavior, it needs a greater flow heat for lignin decomposition than the other two samples (SmarS2 and SmarS3). This revealed that the SmarS1 material contained a greater amount of lignin than the other ones, which could be attributed to lower NaOH concentration, confirming the results previously indicated in this paper. It can be also noted that between 250 and 320°C, representing the decomposition zone of cellulose fragment (Xiao et al. 2001), the SmarS3 sample needed greater heating flow compared to that of SmarS2 sample. This revealed that the thermal stability of SmarS3 is slightly higher than that of SmarS2, indicating that the latter contained a lower amount of cellulose (Kim et al.

2004). This signifies that its cellulose amount was greater than that of SmarS2 sample. The obtained results justify the choice of SmarS3 sample for the bleaching treatment.

The DSC thermograms of the bleached SmarS3 sample at various H_2O_2 concentrations are illustrated in Fig. 7. The thermal behavior of the SmarS6 sample revealed that the bleaching treatment induced the division of lignin into two parts; the first one was amorphous and the second was more crystalline. These two types of lignin required more heating flow to be decomposed as compared to the other bleached samples. This revealed that the SmarS6 sample contained higher amount of lignin than the other ones.

The curves shown in Fig. 7 also exhibited that the decomposition of the amorphous part of lignin contained in the SmarS7 sample took place at around 339°C . However, in the case of SmarS8 and SmarS9, this temperature increased towards 346 and 343°C , respectively. The obtained result revealed an increasingly important fragmentation of lignin, which decreased the molecular cohesion of this compound that exists in these two samples (SmarS8 and SmarS9). This could be attributed to the fact that the amorphous zone of lignin decreased with the increment of H_2O_2 concentration. In this case, SmarS8 and SmarS7 samples present an increase in the crystalline zone of lignin, which requires higher temperature to be decomposed.

The DSC thermal analysis of SmarS7, SmarS8, and SmarS9 samples showed a weak transition at about 377°C . This suggested that the lignin included in these samples has undergone an intensive fragmentation (lignin in its crystalline form) by comparison to that of SmarS6 sample.

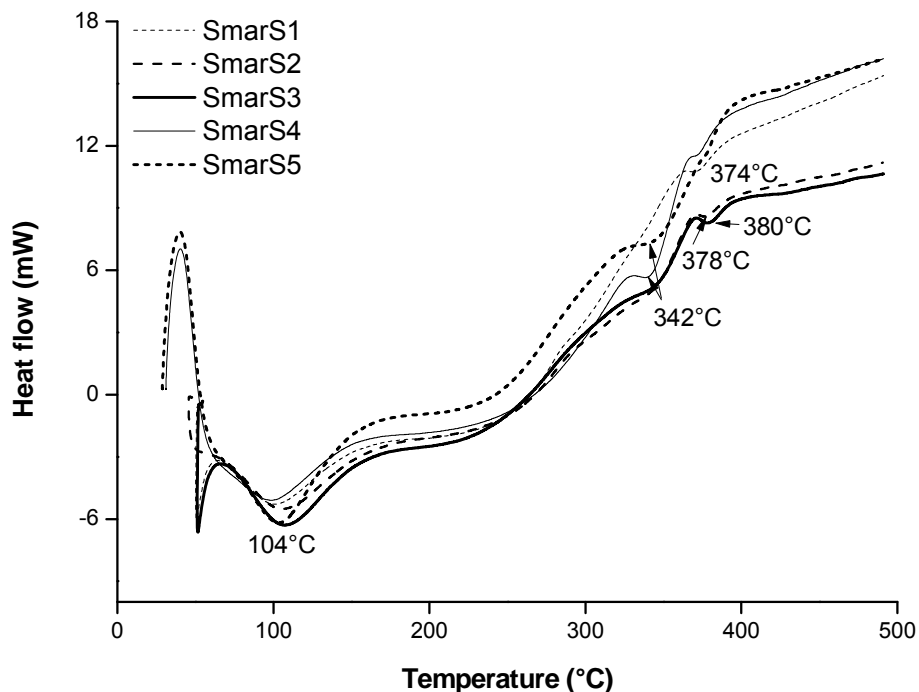


Fig. 6. DSC analysis of extracted fibers by NaOH treatment

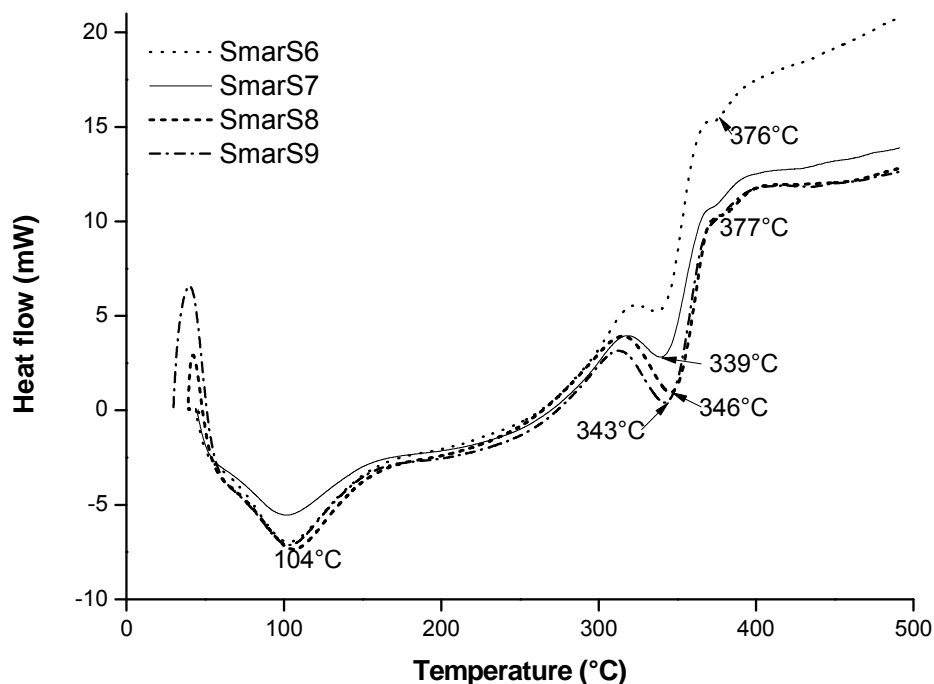


Fig. 7. DSC analysis of bleached fibers by H₂O₂

Surface Energy

The surface energy of alkaline treated fibres calculated from contact angles are given in Table 2. The analysis of data showed that the increment, in NaOH concentration or in treatment time, was accompanied by a decrease in the total surface energy. This reduction is mainly due to the decrease of lignin amount. Indeed, SmarS1 and SmarS2 samples showed the highest surface energy with values near to that of lignin (Lucia 2009). This revealed that these samples still contained other substances than cellulose, and that such substances induced a decrease of their absorptivity involving higher surface energies. However, the SmarS3, SmarS4, and SmarS5 presented lower values of surface energy and consequently lower amounts of lignin. It can also be noted that SmarS4 and SmarS5 displayed surface energy values less important than those of the SmarS3 one. Since the characterizations previously carried out in this paper showed that these two samples are more heterogeneous than the SmarS3 material, the later will be bleached by different H₂O₂ concentrations.

After the bleaching treatment, the value of surface energy became stable towards a value of 45 mJ.m⁻². The obtained value is close to the surface energy of *Stipa tenacissima* L fibres that were extracted with a minimum of degradation (Ben Marzoug. 2009).

AFM Analysis

The wettability tests have shown variability in the energy surface values for the alkaline treated fibres. For this, we chose to evaluate the surface ultrastructures of SmarS2,

SmarS3, and SmarS4 samples using AFM analysis in order to assess the effect of NaOH treatment time on the surface morphology of the extracted fibres. The AFM characterization of SmarS7 bleached sample was also investigated. The surface morphology of the isolated fibres is observed to undergo significant change, as can be seen in Fig. 8.

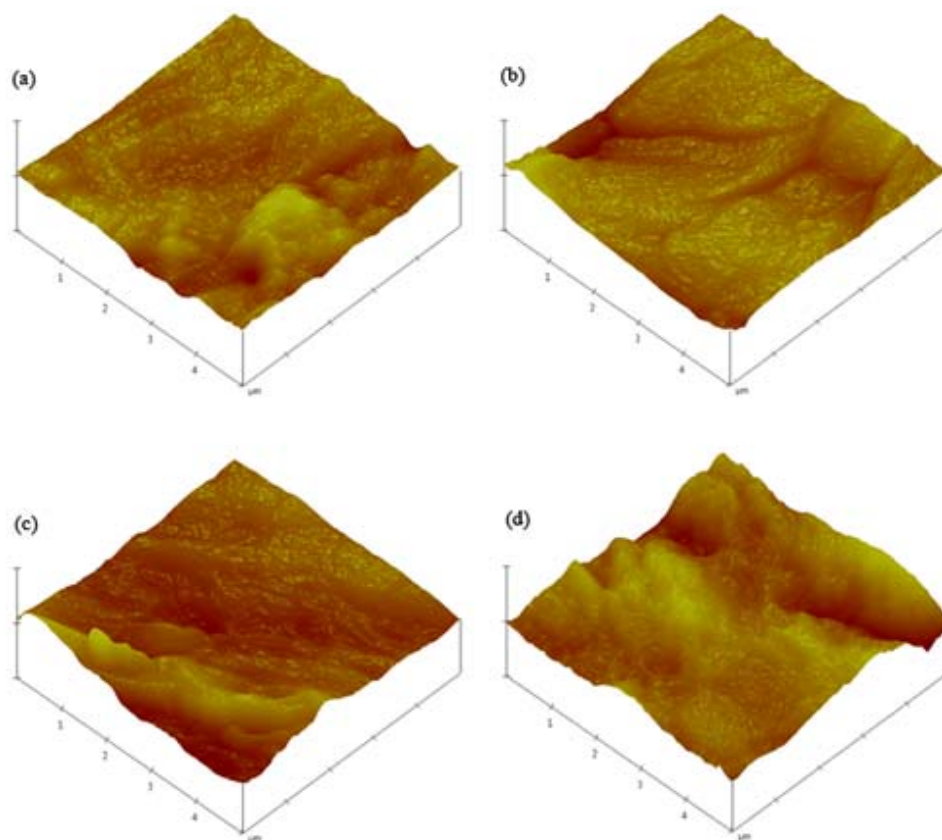


Fig. 8. AFM images of: (a) SmarS2, (b) SmarS3, (c) SmarS4, and (d) SmarS7

This change was confirmed by the determination of the roughness values (Table 4). Indeed, the SmarS2 sample exhibited a roughness value of 89.143 nm. This roughness decreased for SmarS3 sample, which has undergone a treatment alkaline time of 3 h and then increased again for the SmarS4 sample. These nanometric variations are not in accordance with the results found in the energy surface values, which decreased by increasing the duration of the alkaline treatment.

The decrease of roughness by the increase of alkaline treatment time from 1h to 3h, could be attributed to the removal of non cellulosic materials such as hemicelluloses and lignin (Deepa et al. 2011). However the increase of roughness when the treatment time was fixed at 5h may be attributed, in this case, to the degradation of the extracted SmarS4 sample.

The obtained result proved the choice of the SmarS3 sample to be bleached by H₂O₂ treatment. Table 4 shows that the roughness increased after the bleaching treatment,

inducing a complete change in the surface of extracted fibres. This could be probably explained by the fact that the OH groups of cellulose increased after the H₂O₂ exposure inducing a polarity difference.

Table 4. Roughness Values of Smars2, Smars3, Smars4 and Smars7 Samples

Sample	SmarS2	SmarS3	SmarS4	SmarS7
Roughness (nm)	89.143	57.039	59.084	65.530

CONCLUSIONS

We have reported in this work the extraction of new cellulosic fibres from the *Juncus acutus* L plant by sequential alkaline treatment and hydrogen peroxide bleaching. The properties of the extracted fibres showed a dependence on the conditions used in the hydrolysis process. By means of SEM, AFM, FTIR, DSC, surface energy, diameter, density, and lignin content analysis, it was possible to study the effect of the extraction treatments on the morphology and structure of the resulting products. Hydrolysis of the cemented materials with 7M NaOH for 3h at 100°C followed by 10mL.L⁻¹ of H₂O₂ concentration for 45 minutes at 95°C was found to be the optimum extraction condition. Indeed, the purified cellulose obtained was found to be relatively free of bound hemicelluloses and lignin, revealing the success of the applied chemical treatment.

REFERENCES CITED

- Abraham, E., Deepa, B., Pothan, L. A., Jacob, M., Thomas, S., Cvelbar, U., and Anandjiwal, R. (2011). "Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach," *Carbohydr Polym.* 86, 1468-1475.
- Adel, A. M., Abd El-Wahab, Z. H., Ibrahim, A. A., and Al-Shemy, M. T. (2010). "Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis," *Bioresource Technol.* 101, 4446-4455.
- Alemdar, A., and Sain, M. (2008). "Isolation and characterization of nanofibres from agricultural residues -Wheat straw and soy hulls," *Bioresource Technol.* 99, 664-1671.
- Ates, S., Ni, Y., Akgul, M., and Tozluoglu, A. (2008). "Characterization and evaluation of *Paulownia elongota* as a raw material for paper production," *Afr. J. Biotechnol.* 7(22), 4153-4158.
- Ben Marzoug, I. (2009). "Caractérisation et modification des fibres d'alfa en vue de leur utilisation en application textile, thesis," page 89, University of Monastir.
- Ben Marzoug, I., Sakli, F., and Roudesli, S. (2010). "Separation of Ultimate and Technical Fiber of Esparto Grass: Comparison between extractions methods," *J. Tex. Inst.* 101 (12), 1050-1056.
- Bessadok, A., Marais, S., Gouanve, F., Colasse, L., Roudesli, S., Zimmerlin, I., and Metayer, M. (2007). "Effect of chemical treatments of Alfa (*Stipa tenacissima*) fibres on water-sorption properties," *Compo. Sci. Technol.* 67, 685-697.

- Bessadok, A., Marais, S., Roudesli, S., Lixon, C., and Métayer, M. (2008). "Influence of chemical modifications on water-sorption and mechanical properties of Agave fibres," *Composites: Part A*. 39, 29-45.
- Brígida, A. I. S., Calado, V. M. A., Gonçalves, L. R. B., and Coelho, M. A. Z. (2010). "Effect of chemical treatments on properties of green coconut fiber," *Carbohyd Polym*. 79(4), 832-838.
- Deepa, B., Abraham, E., Cherian, B. M., Bismarck, A., Blaker, J. J., Pothan, L. A., Leao, A. L., de Souza, S. F., and Kottaisamy, M. (2011). "Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion," *Bioresource Technol*. 102, 1988-1997.
- De Rosa, I. M., Kenny, J. M., Maniruzzaman, M., Moniruzzaman, Md., M. Monti, Puglia, D., Santulli, C., and Sarasini, F. (2011). "Effect of chemical treatments on the mechanical and thermal behavior of okra (*Abelmoschus esculentus*) fibres," *Compo Sci Technol*. 71 (2), 246-254.
- De Rosa, I. M., Kenny, J. M., Puglia, D., Santulli, C., and Sarasini, F. (2010). "Morphological, thermal and mechanical characterization of okra (*Abelmoschus esculentus*) fibres as potential reinforcement in polymer composites," *Composites Science and Technology*. 70, 116-122.
- El Ghali, A., Baouab, M. H. V., and Roudesli, M. S. (2011). "Preparation, characterization and application of a [copper(II)/ethylenediamine–cotton] complex for the removal of AB25 from aqueous solution in a laboratory scale column," *Chem. Eng. J*. 174, 18-26.
- El Sayed, E. (2004). "Evaluation of Samaar morr (*Juncus acutus*) plant as raw material for paper making," *J. Sci. Ind. Res*. 63 (2), 163-171.
- Habibi, Y., El-Zawawy, W. K., Ibrahim, M. M., and Dufresne, A. (2008). "Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues," *Compos. Sci. Technol*. 68, 1877-1885.
- Le Digabel, F., and Avérous, L. (2006). "Effects of lignin content on the properties of lignocellulose-based biocomposites," *Carbohyd Polymer* 66, 537-545.
- Lucia, L. A., and Rojas, O. J. (2009). *The Nanoscience and Technology of Renewable Biomaterials*, 1st Edition, Blackwell Publishing Ltd, see page 191.
- Jayaramudu, J., Guduri, B. R., and Varada Rajulu, A. (2010). "Characterization of new natural cellulosic fabric *Grewia tilifolia*," *Carbohyd Polym*. 79(4), 847-851.
- Khiari, R., Mhenni, M. F., Belgacem, M. N., and Mauret, E. (2011). "Valorisation of vegetal wastes as a source of cellulose and cellulose derivatives," *J. Polym. Environ*. 19, 80-89.
- Kim, H. S., Yang, H. S., Kim, H. J. and Park, H. J. (2004). "Thermogravimetric analysis of rice husk flour filled thermoplastic polymer composites," *J. Therm. Anal. Calorim*. 76, 395-404.
- Ouajai, S., and Shanks, R. A. (2005). "Composition, structure and thermal degradation of hemp cellulose after chemical treatments," *Polym Degrad Stabil*. 89, 327-335.
- Mousavioun, P., and Doherty, W.O.S. (2010). "Chemical and thermal properties of bagasse soda lignin," *Ind. Crops Prod*. 31(1), 52-58.
- Reddy, N., and Yang, Y. (2009). "Natural cellulose fibres from soybean straw," *Bioresource Technol*. 100, 3593-3598.

- Satyanarayana, K. G., Guimarães, J. L., and Wypych, F. (2007). "Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications," *Compos Part A*. 38, 1694-1709.
- Saw, S. K., Sarkhel, G., and Choudhury, A. (2011). "Surface modification of coir fibre involving oxidation of lignins followed by reaction with furfuryl alcohol: Characterization and stability," *Appl. Surf. Sci.* 257, 3763-3769.
- Sezer, M., and Aran, A. (2001). "Fatigue behavior of discontinuous glass fiber reinforced polypropylene," in: *Plastic Failure, Analysis and Prevention*, Plastic Design Library, New York, 18.
- Shen, D. K., Gu, S., Luo, K. H., Bridgwater, A. V., and Fang, M. X. (2009). "Kinetic study on thermal decomposition of woods in oxidative environment," *Fuel*. 88, 1024-1030.
- Sgriccia, N., Hawley, M.C., and Misra, M. (2008). "Characterization of natural fibre surfaces and natural fibre composites," *Composites: Part A* 39, 1632-1637.
- Spinacé, M. A. S., Lambert, C. S., Feroselli, K. K. G., and De Paoli, M. A. (2009). "Characterization of lignocellulosic curaua fibres," *Carbohyd Polym.* 77, 47-53.
- Subramanian, K., Kumar, P. S., Jeyapal, P., and Venkatesh, N. (2005). "Characterization of ligno-cellulosic seed fibre from *Wrightia tinctoria* plant for textile applications – An exploratory investigation," *Eur. Polym. J.* 41, 853-861.
- Sun, J. X., Sun, X. F., Zhao, H., and Sun R. C. (2004). "Isolation and characterization of cellulose from sugarcane bagasse," *Polym Degrad Stabil.* 84(2), 331-339.
- Zhou, W., Zhu, D., Langdon, A., Li, L., Liao, S., and Tan, L. (2009). "The structure characterization of cellulose xanthogenate derived from the straw of *Eichhornia crassipes*," *Bioresource Technol.* 100, 5366-5369.
- Yang, H., Yan, R., Chin, T., Liang, D. T., Chen, H., and Zheng, C. (2004). "Thermogravimetric analysis-Fourier transform infrared analysis of palm oil waste pyrolysis," *Energ. Fuel*. 18, 1814-1821.
- Yao, W., Chen, B., and Wu, K. (2003). "Smart behavior of carbon fiber reinforced cement-based composite," *J. Mater. Sci. Technol.* 19(3), 239-242.
- Xiao, B., Sun, X. F., and Sun, R. C. (2001). "Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw," *Polym Degrad and Stabil.* 74, 307-319.

Article submitted: January 17, 2012; Peer review completed: February 19, 2012; Revised version received and accepted: March 12, 2012; Published: March 15, 2012.