

ALFA FIBER: ALKALINE EXTRACTION TOGETHER WITH STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION

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Received February 8, 2018

Cellulosic fibers were extracted from Alfa stems (*Stipa tenacissima* L.) using alkaline methods only and without any fiber pretreatment in order to reduce the environmental impact and the extraction costs. A simple post-treatment that consisted of subsequent manual fiber disintegration was studied. The extraction quality was improved according to a two-step investigation. Firstly, the processing temperature, duration and the sodium hydroxide (NaOH) concentration, together with the usefulness of the post-treatment, were studied based on visual examinations. Then, a second set of NaOH concentrations was selected and their effect on the non-cellulosic components removal and on the crystallinity degree of the native crystalline cellulose I was studied. Fibers were characterized by means of Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD), High Performance Anion Exchange Chromatography equipped with Pulse Amperometric Detection (HPAEC-PAD), together with optical microscopy and Scanning Electron Microscopy (SEM). It was shown that the best pulp was obtained by treating the stems in a NaOH solution with a concentration of 3.25 M at 100 °C during 2.5 hours, together with applying the post-treatment. The resulting pulp consisted mainly of single fibers with a smaller amount of bundles and nano-fibrillated cellulose (NFC). Besides, the crystallinity of cellulose I was of 88% and the fibers had an average diameter and length of 10.19 μm and 1082 μm, respectively. Furthermore, the XRD study showed that treating the fibers with NaOH concentrations beyond 3.25 M resulted in a significant drop in the cellulose I crystallinity.

Keywords: Alfa fibers, *Stipa tenacissima*, Esparto grass, alkaline extraction, single fibers

INTRODUCTION

In the last few decades, the use of natural cellulosic fibers has been deeply investigated in the academic field due to their low density, biodegradability and mechanical properties.^{1,2} Cellulosic fibers are used in different fields, such as the textile industry, paper making and packaging.³ Cellulose can be found in different crystalline forms and its native form is called cellulose I.⁴ Cellulose is the main component of fibers, providing mechanical strength and stiffness, and it coexists with other non-cellulosic components, such as hemicellulose, lignin and pectin.⁵ The extraction of fibers from grass means the removal of the middle lamella, which is a mixture of non-cellulosic components binding fibers.¹ This fiber disintegration increases hence

the surface to volume ratio⁶ of fibers, resulting in a better mechanical loading transfer from the matrix to the fibers in the applications of natural fiber composites.^{7,8} Different extraction methods can be mentioned, namely mechanical crushing,⁹ chemical treatments using alkaline solutions,¹⁰ steam explosion,¹¹ retting in salt water or dew retting,¹² together with enzymatic extraction.¹³ Several post-extraction treatments have been reported in the literature, as having contributed significantly to further fiber disintegration and hence to a further increase in the surface to volume ratio, for instance, bleaching with sodium hypochlorite (NaClO₂), TEMPO oxidation or homogenization in water suspension at high pressure.^{14,15} However, these post-treatments

require the use of different additional chemicals and a high amount of energy, making them expensive and not environmentally friendly.

Alfa grass grows in semi-arid regions in Libya, Tunisia, Algeria, Morocco and Spain. In Tunisia, the surface that is covered by Alfa grass measures approximately 600,000 ha.⁵ Currently, the annual production of Alfa grass in Tunisia is of about 40,000 tons and is exclusively harvested by the National Company of Cellulose and Alfa Paper to produce pulp and high quality paper.¹⁶ Alfa fibers have been studied in several works^{2,10,17} to enhance the mechanical behavior of natural fiber composites. For instance, Espinach *et al.*¹⁰ found that blending a starch based polymer with 35% wt:wt of Alfa fibers that were treated in a 5% wt:wt sodium hydroxide (NaOH) solution resulted in an increase in the modulus of rigidity from 2.5 to 7.2 GPa. In all the previously cited works, Alfa stems were first treated mechanically by combing or crushing before the alkaline treatments in order to improve the impregnation of chemicals inside the fibers. However, to our knowledge, no treatments leading to purely or mainly single Alfa fibers have been reported in the literature yet. The purpose of this work was to obtain a pulp made mainly from single Alfa fibers using alkaline extraction methods without any mechanical pretreatment. Different extraction parameters were investigated and a post-treatment that consisted of manual disintegration of the extracted fibers was studied. The extracted fibers were analyzed visually and by means of Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD), High Performance Anion Exchange Chromatography equipped with Pulse Amperometric Detection (HPAEC-PAD), optical microscopy together with Scanning Electron Microscopy (SEM).

EXPERIMENTAL

Materials

Alfa stems were harvested from the region of Kasserine in Tunisia. The stems have a cylindrical shape with one tip that is thick and rigid and the other – thin and soft. Subsequently, they have been stored in plastic bags at room temperature and away from light. A representative image of the stems is shown in Figure 1. Sodium hydroxide (NaOH) (purity $\geq 98\%$) was supplied Honeywell International Inc.

Alkaline extraction

Extraction without post-treatment

Alfa stems were treated according to the parameters that are listed in Table 1. The choice of these

parameters was based on methods described in the literature. For example, Arrakhiz *et al.*⁹ treated Alfa fibers in a 1.6 M NaOH solution for 48 hours at room temperature, while Espinach *et al.*¹⁸ used a 1.25 M NaOH solution for 2.5-4 hours at 98 ± 1 °C. Treatments at 60 and 100 °C were not studied for the durations of 24 and 48 hours for the following reasons: (1) they were difficult to control because of water evaporation, and (2) because of the higher consumption of energy, and thus it was assumed that the process will not be industrially viable (for instance, the well-known Kraft process used to extract fibers from wood, which is performed at 150-170 °C, lasts roughly 1-2 hours). The fiber/solution ratio was of 1 g/20 ml and corresponded to the minimum volume that fully covered the raw stems. Subsequently, Alfa fibers were rinsed with tap water to remove the excess NaOH solution until a neutral pH was reached and then dried at 105 °C for 1 hour.

Extraction with post-treatment

In order to further disintegrate the fibers, a simple post-treatment that is presented in Figure 2 was applied, where the stems were washed subsequent to the alkaline extraction and then further disintegrated manually for roughly 5 minutes using a system made from a pestle and a mortar.

According to this post-treatment method, a second set of treatments that was called “set A” was performed, as listed in Table 2, where the treatment parameters were selected according to the treatment that previously corresponded to the highest level of fiber disintegration based on visual examinations and the treatment duration was further investigated. Afterward, the treatment time that corresponded to the highest level of fiber extraction based on visual examination was fixed and the NaOH concentration was further studied, as listed in Table 2, and this set of treatments was called “set B”. The fibers were subsequently washed with tap water until a neutral pH was reached, then filtered using a Buchner funnel and dried at 105 °C for 1 hour.

Characterization

Fourier Transform Infrared spectroscopy (FTIR)

The effect of NaOH concentrations, which are listed in Table 3, on the removal of non-cellulosic components was investigated using a Perkin-Elmer Model 2000 Fourier Transform Infrared (FTIR) spectrometer. Spectra were studied within the range between 400 and 4000 cm^{-1} , where the resolution was equal to 4 cm^{-1} . Samples were prepared according to the standard potassium bromide (KBr) pellet method, where small particles were mixed with the KBr and pressed into discs.¹⁹ A method that was described by Yuen *et al.*²⁰ was applied in order to compare the different treatments, which involved comparisons based on the ratio of the studied band intensity of that particular group in the sample divided by the intensity

of an arbitrarily chosen reference band.²¹ In this study, the reference band was centred at 1400 cm^{-1} , which is linked to the O-H bending of acid.

X-ray Diffraction (XRD)

The Segal method²² was applied to determine the crystallinity of cellulose I for the different treatments listed in Table 3. An X'PERT Pro PANAnalytical X-ray diffractometer, with a CuK α radiation ($\lambda = 1.54\text{ \AA}$), was used and analyses were conducted within a 2θ

range between 5 and 80° with a step of 0.02° during 5 minutes. The $\theta/2\theta$ scanning method was applied and the crystallinity (χ) was calculated according to Equation 1:

$$\chi = (I_{002} - I_a) / I_{002} \quad (1)$$

where I_{002} is the intensity of the crystalline phase at $2\theta = 22.8^\circ$ matching planes (002), and I_a is the minimum intensity between the (002) and (110) peaks corresponding to $2\theta = 18^\circ$.

Table 1
Alkaline extraction parameters – without post-treatment

Temperature ($^\circ\text{C}$)	NaOH concentration (M)	Time (hours)
Room temperature	0.25	3; 6; 24; 48
	1	
	1.75	
	2.5	
	3.25	
60	0.25	3; 6
	1	
	1.75	
	2.5	
	3.25	
100	0.25	3; 6
	1	
	1.75	
	2.5	
	3.25	

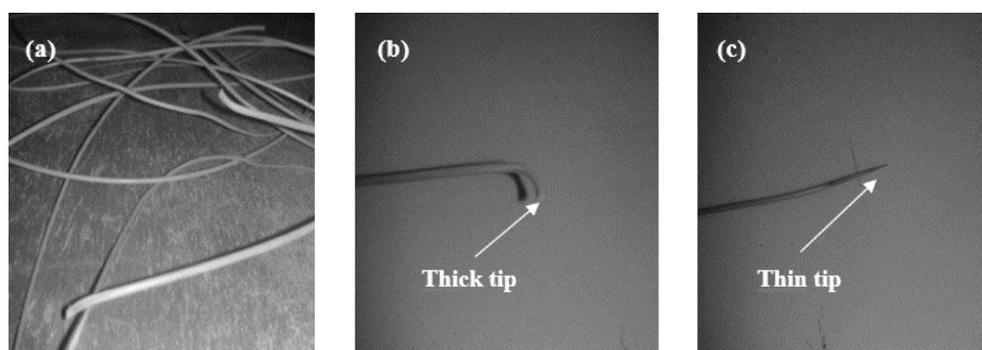


Figure 1: Alfa raw stems: (a) holistic view; (b) thick tip; (c) thin tip

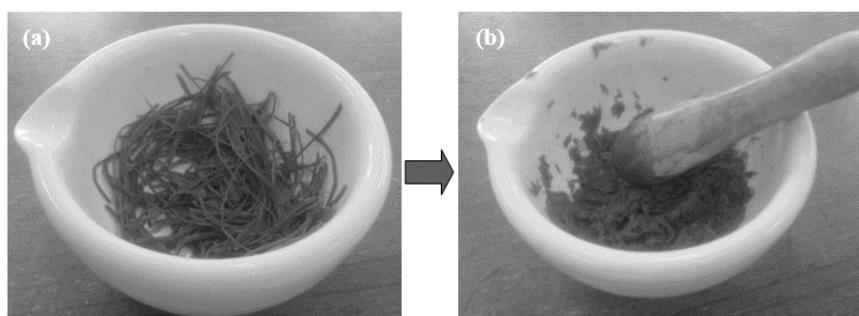


Figure 2: Treated fibers: (a) after alkaline extraction; (b) after manual fiber disintegration

Table 2
Alkaline extraction parameters with post-treatment for fixed NaOH concentration (set A) and for fixed treatment duration (set B)

	Temperature (°C)	NaOH concentration (M)	Time (hours)
Set A	100	3.25	1; 1.5; 2; 2.5; 3; 3.5
Set B	100	1.75; 2.5; 3.25; 5.5; 7	2.5

Table 3
Effect of NaOH concentrations on cellulose I crystallinity of alkaline extracted fibers at 100 °C during 2.5 hours with post-treatment

NaOH concentration (M)	1.75	2.5	3.25	5.5	7
Crystallinity (%)	90	90	88	77	73

Chemical composition

The chemical compositions of raw stems and fibers that corresponded to the best extraction method were investigated according to the National Renewable Energy Laboratory of the United States standard²³ NREL/TP-510-42618. Fibers were first subjected to mild milling, using a Wiley mill model N°2, and subsequently treated with 72% wt:wt sulfuric acid to hydrolyze cellulose, hemicellulose and acid soluble lignin (ASL). The monosaccharides coming from cellulose and hemicellulose were analyzed using a Dionex ICS-3000 High Performance Anion Exchange Chromatography equipped with Pulse Amperometric Detection (HPAEC-PAD). The monosaccharides percentage was converted into carbohydrates percentages, using correction factors based on data on birch fibers.²⁴ ASL was analyzed by a Shimadzu UV-2550 spectrophotometer within a wavelength range between 200 nm and 300 nm. The ASL calculations were based on values for bagasse fibers, where the absorption intensity was recorded at 240 nm and the absorption coefficient was 25 L (g cm). The acid insoluble lignin (Klason lignin) was first filtered using crucibles (porosity 3) and subsequently dried overnight at 105 °C to remove moisture and then weighed. Then, the total lignin content was calculated by summing contents from acid soluble and acid insoluble lignin. The mineral content was determined using ISO 1762 (2001) standard,²⁵ where the organic materials were burned at 525 °C for 5 hours and subsequently the residue was weighed.

Optical microscopy

Different images corresponding to fibers that were treated according to the best extraction method were collected using a LEICA DM 1000 LED optical microscope with light reflection mode. Afterward, the recorded images were analyzed by a software called "ImageJ" in order to measure the dimensions of the

fibers. 250 measurements for each of the fiber diameters and lengths were performed.¹²

Scanning Electron Microscopy (SEM)

Fibers that were treated according to the best extraction method were first distributed over a carbon tape and then a thin platinum layer was sputtered on top of them, using a Leica EM ACE600 device, to ensure conductivity. A Zeiss Sigma VP SEM was used to study fiber morphology.

RESULTS AND DISCUSSION

Fiber extraction

Extraction without post-treatment

During the alkaline treatments, non-cellulosic components, such as pectin, lignin and hemicellulose, which are naturally rich in hydroxyl (OH) groups, react with the sodium hydroxide and are broken down to shorter molecules. The following chemical formula is widely accepted in the literature to describe the alkaline hydrolysis of natural fiber components:



Then, the hydrolyzed parts react with water molecules and are removed from the fiber.

The color of the NaOH solutions turned to dark green after a few minutes of processing and corresponded to the beginning of the removal of non-cellulosic components. The experiments that were conducted at room temperature and at 60 °C did not yield any fiber separation and the resulting fibers looked the same. This was probably caused by the slow kinetics of NaOH reactions with fiber components at relatively low temperatures. A representative sample from these treated fibers is shown in Figure 3a. As a result of the alkaline treatments, the stems softened because such

treatments lead to changes in the orientation of cellulosic chains and act as a plasticizer.⁸ Fibers

started to disintegrate in treatments using NaOH 2.5 M at 100 °C.

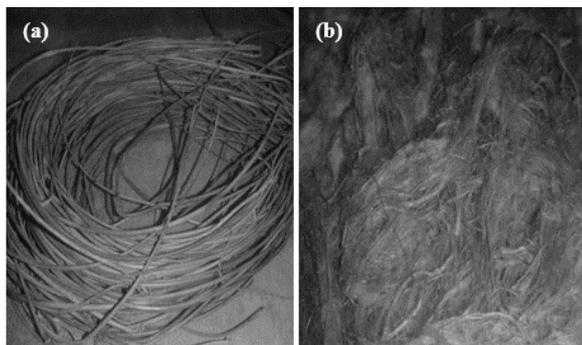


Figure 3: Fibers treated with NaOH 3.25 M during 3 hours: (a) at room temperature; (b) at 100 °C

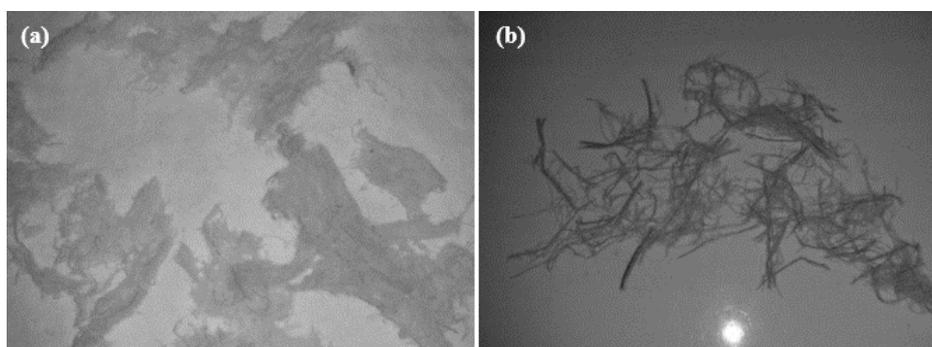


Figure 4: Fibers treated with NaOH 3.25 M at 100 °C during: (a) 2.5-3.5 hours, and (b) 1-2 hours

However, the amount of thick fiber bundles and undissolved stems was significantly high. When the stems were treated in a solution of NaOH 3.25 M at 100 °C during 3 and 6 hours, they totally disintegrated into thin bundles with lower amounts of single fibers. A representative sample from these fibers is shown in Figure 3b. Therefore, the increase in the processing temperature and NaOH concentration improved the quality of fiber extraction. These results are in agreement with those reported by Borchani *et al.*,⁶ who studied the extraction of Alfa fibers and found that the increase in NaOH concentration reduced the fiber dimensions as a consequence of the higher removal of non-cellulosic components. Ayala-Soto *et al.*²⁶ studied the extraction of corn fiber arabino-xylans (a complex made of pectin and hemicellulose) and found that the increase in the NaOH concentration and the treatment temperature resulted in a higher amount of extractives. The fibers that were treated during 3 and 6 hours looked the same, so the best treatment parameters were then as follows: NaOH 3.25 M, 100 °C and 3 hours, and this treatment will be named “treatment A”. However, the aim of this

study was to get a pulp composed mainly from single fibers. Therefore, further improvements needed to be conducted.

Extraction with post-treatment

First, the post-treatment that was described in Figure 2 was applied subsequent to the treatment A. As a result, the obtained pulp consisted mainly of single fibers, as shown in Figure 4a. Hence, manual disintegration had significantly improved the quality of the extraction. The reason behind this is the additional removal of non-cellulosic components that leached away from the fibers after washing with water. In fact, these parts that remained trapped inside the middle lamella subsequent to the alkaline extraction were then removed by the action of mechanical shear forces that resulted from the manual disintegration.

Furthermore and again based on treatment A, a second set of treatments was investigated, as listed in Table 2 – Set A, where the processing duration was further studied. It was found that the pulps subjected to treatment durations of 1 to 2 hours looked the same and yielded thin fiber bundles (Fig. 4b). However, when the duration of

the treatments was between 2.5 and 3.5 hours, the quality of the extraction significantly improved and the pulps looked the same (Fig. 4a). This is consistent with the findings of Yilmaz,²⁷ who studied the effect of corn husk alkaline extraction and concluded that the increase in treatment duration resulted in a lower residual fraction due to the removal of non-cellulosic material. Similar results were also found by Ayala-Soto *et al.*²⁶

Then, it was concluded that the duration of 2.5 hours was the optimum and that the treatment duration played a significant role in the extraction of Alfa fiber.

Effect of NaOH concentration (with post-treatment)

The effect of the NaOH concentration was studied for treatments listed in Table 2 – Set B, with subsequent post-treatment.

Effect of NaOH concentration on the removal of non-cellulosic materials

Different concentrations, between 1.75 and 7 M, were studied in order to determine which treatment is the most efficient with regard to the removal of pectin and lignin (Fig. 5). The graph related to the raw fibers exhibits a band centered at 1730 cm⁻¹, which corresponds to the stretching vibration of C=O groups of pectin.^{2,17} However, the band that was initially present disappeared for the fibers subjected to the different studied treatments, indicating the removal of pectin. This was expected since pectin is the principal component of the cementing middle lamella, which binds fibers for grass.¹ The band centered at 1652 cm⁻¹, which is attributed to the carboxylic

acid COOH originating from the aromatic group of lignin,²⁸ had the lowest intensity ratios when the NaOH concentrations were between 1.75 and 3.25 M, while at higher concentrations this band intensity ratio increased. In addition, the band centered at 1452 cm⁻¹, which is attributed to the C-H deformation of lignin²⁹ had the lowest intensity ratio for the fibers that were treated with NaOH 3.25 M. Hence, NaOH 3.25 M was the concentration that contributed the most to the removal of lignin.

Since lignin is also a part of the cementing materials that bind the fibers, it can be then concluded that NaOH 3.25 M is the best concentration that contributes to the removal of the middle lamella and therefore to the fiber extraction.

Effect of NaOH concentration on the cellulose I crystallinity

The increase in crystallinity can result in higher yield stress and modulus of rigidity for polymers³⁰ and hence highly crystalline fibers should result in better mechanical behavior if one considers that the fibers will be used to make natural fiber composites. Table 3 presents the cellulose I crystallinity as a function of NaOH concentration.

The fibers that were treated with concentrations between NaOH 1.75 and 3.25 M exhibited high and constant cellulose I crystallinity. These results are in agreement with the findings of Borchani *et al.*,⁶ who treated Alfa fibers in NaOH with concentrations of 1 (~0.25 M) and 5% (~1.3 M).

Table 4
AF extraction parameters

NaOH concentration (M)	Temperature (°C)	Time (hours)	Fiber to solution ratio (g:ml)	Post-treatment
3.25	100	2.5	1:20	X

They concluded that the cellulose I crystallinity did not depend on the studied NaOH concentrations. However, higher concentrations resulted in a significant drop in crystallinity. Similar results were reported by Choi *et al.*,³¹ where the increase in NaOH concentration from 8 (~2 M) to 18% (~5 M) was found to lead to a decrease in the crystallinity of the alkaline extracted wood fibers. The reason behind this change in the crystallinity should be the formation

of new amorphous regions as a result of the reactions of hydroxyl groups (OH) with NaOH.⁸ Figure 6 shows a representative example of the studied XRD patterns and corresponds to fibers that were treated with NaOH 3.25 M. Four peaks that are linked to the crystalline cellulose I appear, corresponding to the planes (110), (110), (200) and (004).⁴

Conclusion about the best treatment

Taking into account the previous findings regarding the effect of NaOH concentration on the removal of non-cellulosic materials and on the cellulose I crystallinity, the treatment that resulted

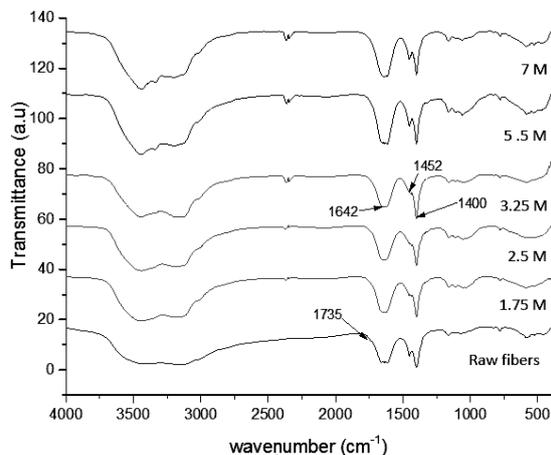


Figure 5: Effect of NaOH concentration on chemical modification of alkaline extracted fibers at 100 °C during 2.5 hours, with subsequent post-treatment

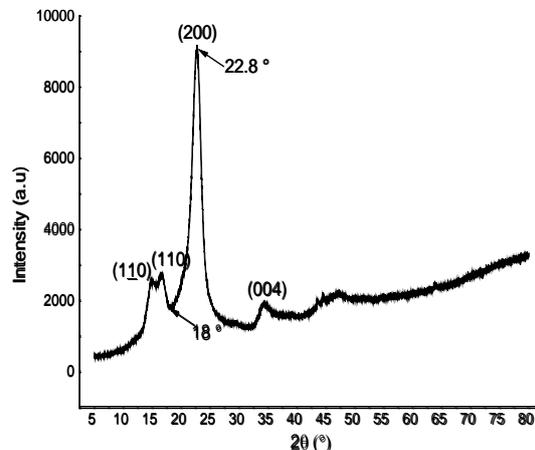


Figure 6: XRD pattern of fibers treated with NaOH 3.25 M

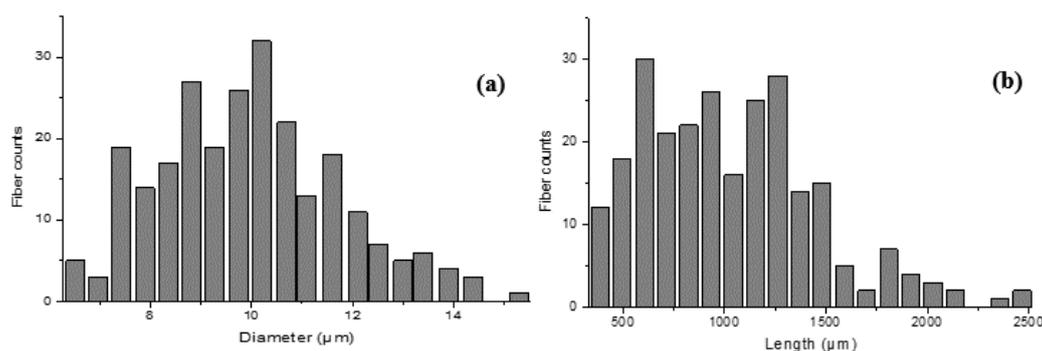


Figure 7: Histograms of (a) fiber diameters, and (b) fiber lengths

Table 5
Chemical composition of the AFs

Fibers	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Minerals (%)
Raw stems	44.2	23.0	25.4	2.4
AFs	77.8	5.3	6.7	1.5

Table 6
Dimensional characteristics of Alfa treated fibers

Study	Mean diameter (μm)	Mean length (μm)	Aspect ratio
Borchani <i>et al.</i> ⁶	26	540	21
Zrida <i>et al.</i> ¹²	185.2	1000-2000	5-10
This study	10.19	1082	106

Characterization of AFs

Chemical composition

Table 5 shows the chemical composition of the raw stems and the extracted AFs. The cellulose

in the best pulp was defined as described in Table 4. Alfa fibers that were treated accordingly were named “AFs” and were previously presented in Figure 4b.

percentage increased by 76% and conversely hemicellulose, lignin and minerals were significantly reduced by 77, 74 and 38%, respectively. Similar results were found in a study

by Hanana *et al.*,¹³ where the alkaline extracted Alfa fibers had 75% higher cellulose content than the raw stems.

These results are in agreement with the previous findings about the efficiency of the

applied NaOH treatments on the removal of the non-cellulosic materials, which induces fiber disintegration.

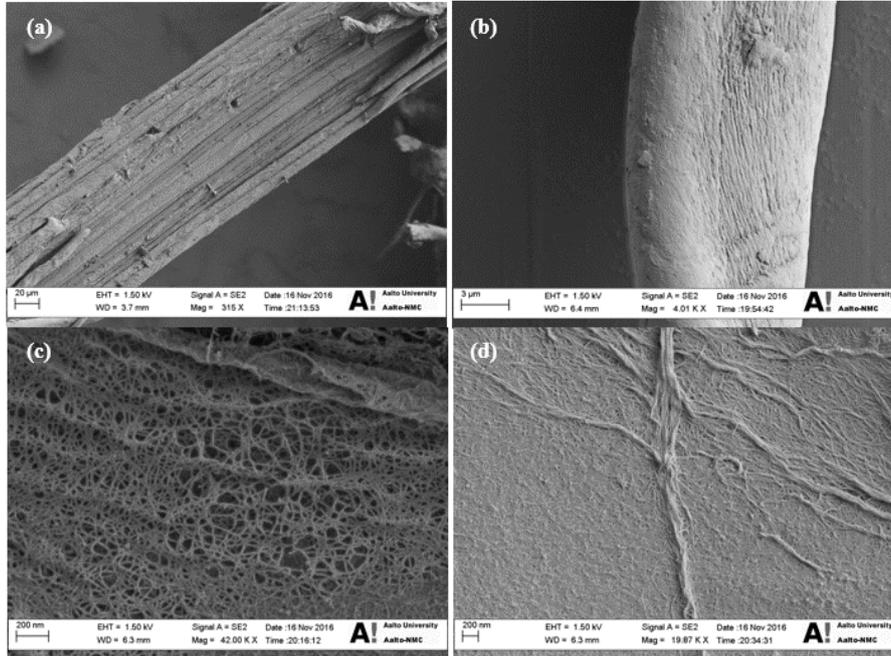


Figure 8: SEM images of: (a) fiber bundle; (b) single fiber; (c, d) Nano-fibrillated cellulose (NFC)

AFs morphology

Figure 7 presents the histograms of AF diameters and lengths. AF diameters were between 6.5 and 15.3 μm , while the lengths were between 387 and 2466 μm . This important reduction of fiber dimensions after the alkaline treatment, followed by manual disintegration, was due to the breakdown of fiber bundles as a result of the removal of the non-cellulosic materials that bind Alfa fibers.¹ The aspect ratio, which is defined as the ratio between fiber length and diameter, affects the final mechanical properties of natural fiber composites, where high aspect ratio is needed in order to guarantee the efficiency of the fibrous reinforcement.^{6,7,18} The average diameters and lengths, together with the calculated aspect ratios, are listed in Table 6, where a comparison between the results from this study and data from the literature is presented. The AFs that were obtained in this study had the lowest average diameter and the highest aspect ratio due to the applied manual disintegration. Then, this post-treatment should be considered, if larger scale production of Alfa fiber composites is planned.

Figure 8 shows SEM micrographs of the AFs. The morphological study showed that AFs are composed mainly of single fibers (Fig. 8b), along with smaller amounts of fiber bundles (Fig. 8a) and nano-fibrillated cellulose (Figs. 8c and 8d). The surface of single fibers was clean and the presence of cellulose nano-fibrils confirmed the efficiency of the applied alkaline treatment that was followed by manual disintegration with regard to the removal of non-cellulosic components. In fact, cellulose is present inside natural fibers in the form of nano-fibrils, which are embedded into cementing hemicellulose, lignin and pectin.^{14,32} As a reminder, the treatment applied to the raw fibers has been done in order to obtain single fibers. However, nano-fibrillated cellulose (NFC), which is known to require complex treatments in processing, using high energy consumption,¹⁴ was also obtained – this type of cellulose was present all over the surface of the carbon tape.

Moreover, the removal of these cementing materials led to a rougher fiber surface due to the stripping of the cellulosic fibrils (Fig. 8b) and should result in better mechanical interlocking

with polymeric matrices³³ and then in better mechanical properties.

CONCLUSION

Fibers were successfully extracted from Alfa grass, using an alkaline method that was followed by manual disintegration. The combined treatment induced a significant reduction in the non-cellulosic components, namely hemicellulose, lignin, pectin and minerals. The stems that were treated accordingly yielded mainly single fibers with lower amounts of bundles and nano-cellulose due to the manual disintegration. These fibers also had a relatively high aspect ratio and rough surface, which makes them good candidates for developing natural fiber composites on a larger scale and with improved mechanical properties. The experimental study also showed that a temperature of 100 °C is required in order to achieve fiber separation and that the treatment duration and NaOH concentration dictate the quality of the resulting fibers. Besides, it was shown that the cellulose I crystallinity depended on the NaOH concentration, where a significant drop in the crystallinity was observed for concentrations higher than 3.25 M.

ACKNOWLEDGMENTS: We would like to thank Professor Herbert Sixta; the director of the Bioproducts and Biosystems Department at the Aalto University in Finland, Professor Tatiana Budtova from the Center of Materials Forming, Mines Paristech in France, and Professor Abderrazak Smaoui from the Biotechnology Center in Borj Cedria Technopolis. Besides, a special thank you is given to Rita Hatakka and Yibo Ma from the Bioproducts and Biosystems Department at the Aalto University in Finland.

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