Characterization and treatment of rush fibers towards eco-construction reinforcement

Wassef Ounaies

Civil engineering Department, College of Engineering, Jouf University
P.O.Box 2014, Al-Jouf, Skaka, Kingdom of Saudia Arabia.

Abstract. The rush fiber could constitute a potential source of reinforcement of organic matrix, polyester resins or epoxy components, or mineral, cement mortar or lime or gypsum or natural earth. For this reason, we were interested in our research work on the extraction and processing of this plant. To remedy the problem of dimensional variation and fragility of raw earth molded, reinforcement approaches rush plant fibers chemically treated by alkalization have been adopted. This article aims to present a study on which we characterize and process rush fibers in order to reinforce eco-construction. For both economic and ecological considerations we have chosen to use a variety of fibers that we obtained by chemical extraction with hot alkalization (8% NaOH), which have less efficient characteristics but sufficient to be used as reinforcements for the earth mortar. We started from the principle that any land could be valid for construction, even if its initial properties were not quite suitable for the construction method (adobe, rammed earth, compressed blocks, etc.), with the application of grain size correction and / or stabilization by aerial or hydraulic binders or by reinforcement with rush plant fibers. The optimization study of the process for extracting rush fibers led us to obtaining fibers with very high characteristics

Key words: 1.rush fiber, 2.chemical composition, 3.treatment, 4.eco-construction reinforcement

1. Introduction

The rush fiber could constitute a potential source of reinforcement of organic matrix, polyester resins or epoxy components, or mineral, cement mortar or lime or gypsum or natural earth. For this reason, we are interested in our research work in the extraction and processing of this plant; we proceed to the mechanical extraction of the rush plant.

The Rush plant belongs to the Joncaceae family [1,2,3], of which there are about 200 species that grow in wetlands such as around lagoons, lakes and rivers [1,2]. It is currently used to make mats, rugs, baskets, fans and baskets. The rush used in our study (Figure 1) comes from the Amroun region in the governorate of Nabeul in north-eastern Tunisia, and the rush stem has an average length of about 125 cm.

Figure 1: The rush plant (Nabeul - Tunisia)

1. Morphological characterization ("SEM" scanning electron microscope)

The rush plant is composed of a multitude of contiguous radiating stems as shown in figure 1. Each of its stems is made up of cellulosic fibers located on the periphery and others trapped inside the stem and separated by empty honeycomb cells as observed on the images (Figures 3 and 4) of the SEM observations that we made. The rush rod with its diameter of approximately 3300 μm cannot be used as it is as a reinforcement in composites of eco-construction. Lignin and hemicelluloses honeycomb cells should be removed to extract cellulosic fiber cluster peripheral and internal called ultimate fibers [4] which have a diameter of about 300 μm as observed in figure 19.

Figure 2: The scanning electron microscope with the sputtering apparatus used

To evaluate and see the natural rush stem and also the influence of the different treatments on the defibration of the rush fibers, their surface condition and their diameter, we used a scanning electron microscope (SEM) of the JEOL JSM 5400 type (Figure 2). Observations were made on natural rod, bundles of fibers and on isolated fibers coated with a thin layer of gold in a JEOL JFC 1100 sputtering apparatus (Figure 2) and scanning electron micrographs of the fibers were recorded.
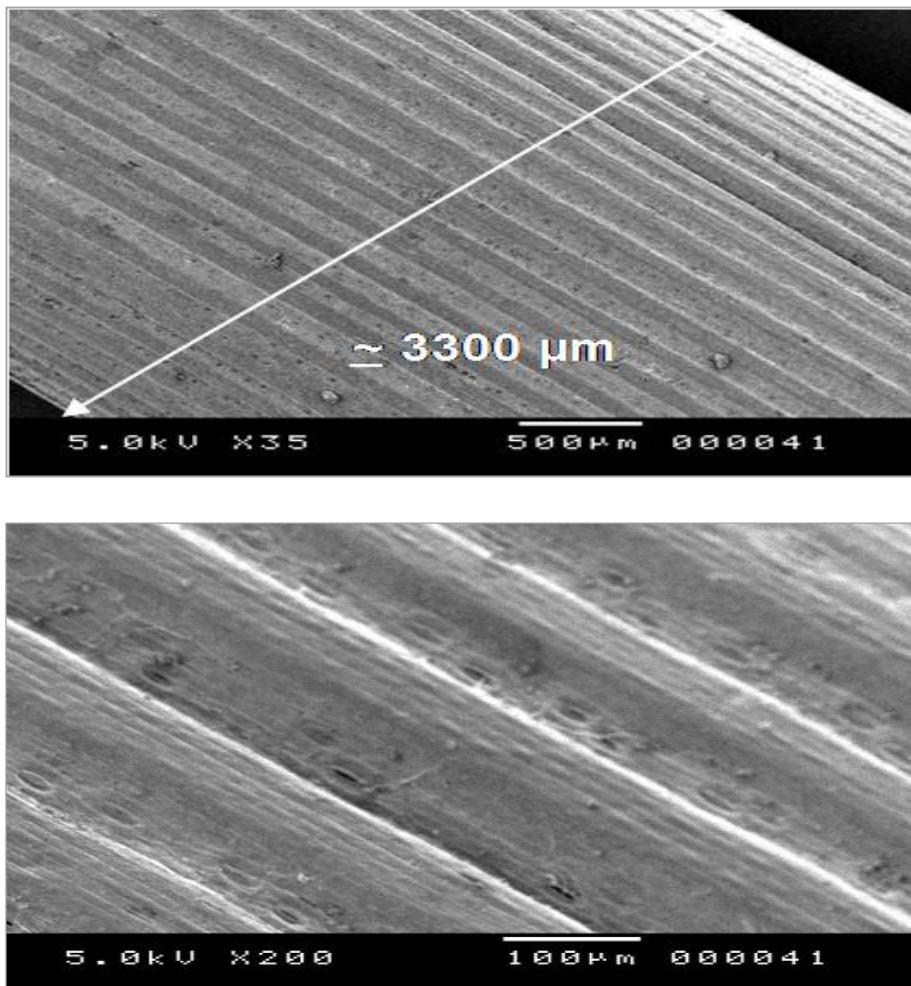
Figure 3: Rod of Reed observed with SEM respectively with a magnification 35 and 200 times
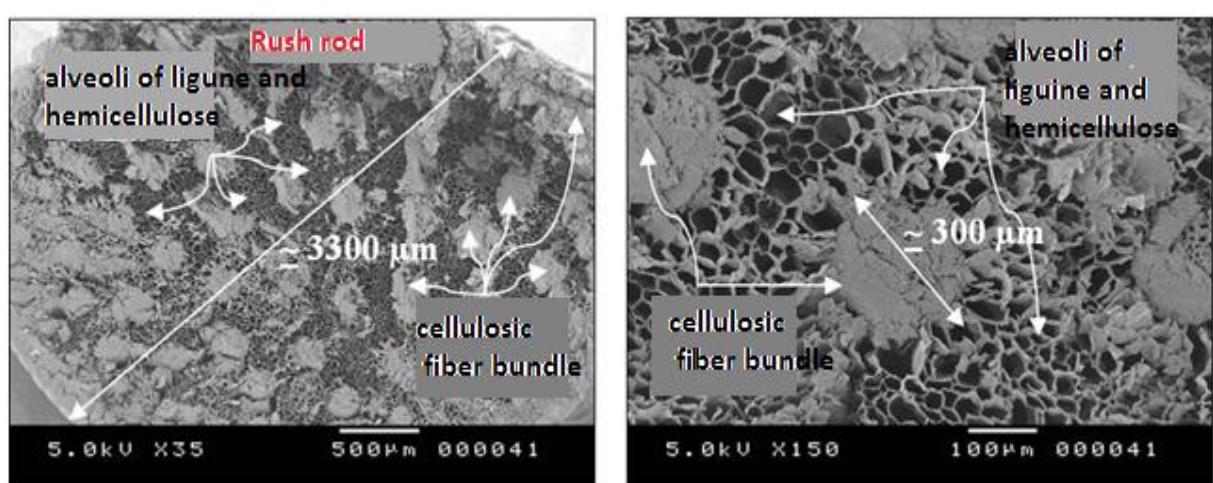

Figure 4: Cross section of a rush stem observed with SEM respectively with 35 and 150 times   magnification

1.1 Determination of fiber diameter

The apparent diameter of the treated fibers was measured by a Leica MD500 digital microscope (Figure 5). Due to

the variability of the fiber cross section, measurements of one hundred diameters (at least) were made along the longitudinal axis of each fiber and the average value was reported along with the variability of the data. The test was repeated at least 10 times.

Figure 5: Apparatus for measuring the apparent diameter of the treated fibers.

1.2 Determination of the absolute density of fibers

The density of the fibers was measured according to the French standard NF T 20 053 [33]. These measurements were carried out on three samples of each type of fiber.

1.3 Determination of the tensile strength of fibers

The singular fibers are separated manually from the different bundles of treated or natural fibers. They are subjected to a tensile test using a Lloyd LRX machine (Figure 6) at constant displacement rate and for a test period of 20 ± 3 s as specified in ASTM C 1557.
Due to the limited length of the fiber, a 50 mm interjaw length had to be chosen for this test. This test was applied on ten samples of fibers of each type of treatment and carried out under standard conditions: 20 ± 2 °C and 65% ± 2% RH.

Figure 6: Tensile test apparatus

1.4 Determination of the chemical composition of the rush fiber

Plant fibers consist mainly of cellulose, hemicellulose, lignin, pectin and waxes. The chemical composition of plant fiber varies from plant to plant, and depends on the species, the age of the plant, the climatic conditions, the

composition of the soil and the extraction method used [5 , 6,7,8].

In our case study, the chemical composition of the raw material of the rush plant and of the fibers treated by various treatment processes was determined by the protocols drawn up by the TAPPI standards (Technical Association of the Pulp and Paper Industry).

In the following an overview on the method of determination of each component:

1.4 Ash rate

To determine the ash content, a given mass (m_0) the vegetable organic raw material is calcined in an oven at 525 ± 25 ° C for 4 hours according to the T211 om-07 protocol [9]. The percentage of ash is the ratio multiplied by 100 of the mass of the sample after calcination to the initial mass.

1.4.1 Total lignin level

The rate of Total lignin is in fact the sum of the rate of soluble lignin determined by the protocol (TAPPI, um 250-91) [34,35] and which generally presents the minority part, and the insoluble lignin also called rate of lignin of Klason determined by the protocol (T222 om-06) [9].
 A quantity of rush stems is exposed to the action of a 72% sulfuric acid solution for 2 hours at 25 ° C. The mixture is then diluted to 3%, then brought to the boil and kept under boiling in the solution for 4 h. The residue is washed and then dried. Klason's lignin level is the ratio of the mass of the sample after treatment and the initial mass multiplied by 100. Soluble lignin is measured by the absorbance of the filtrate at a wavelength equal to 205 nm, at l using a UV-visible spectrophotometer [10].

1.4.1 Holocellulose level

The holocellulose content is determined according to the method of Wise et al. (1946) [11]. Where a given mass of rush fibers is immersed in 160 ml of water. Then 1.5 g of sodium chlorite and 0.5 ml of glacial acetic acid are added; the whole is brought to the boil and kept under boiling and stirring for 1 hour. The same protocol is repeated (addition of the same quantities of sodium chlorite and glacial acetic acid, reflux for 1 hour) until the residues of the rod observed are perfectly white. The level of holocellulose corresponds to the mass of the dry residue obtained divided by the initial mass of material [10].

1.4.2 α -cellulose level

It is determined according to the protocol (T203 cm-99) [10,12]. Where a given amount of holocellulose (m_0) is immersed in 35 ml of a 17.5% NaOH solution of caustic soda. Five minutes later, 40 ml of another sodium hydroxide solution (17.5%) are added four times over a period of 40 min. Then 75 ml of water is added to the mixture and the reaction is carried out under boiling for 30 min. Immediately afterwards, the fibers are washed to remove the soda which remains on them and the fiber sample is dried (m_1).
The level of α -cellulose corresponds to the mass of the dry residue which is expressed by the following formula:

$$\text{Rate } \alpha\text{-cellulose} = 100 \frac{(m_0 - m_1)}{m_0}$$

All tests were repeated at least three times and the difference between the different values was within 5% experimental error.

For the natural rush plant studied, the chemical composition is 29% lignin, 40% cellulose, 21% hemicellulose. By

comparison with that of other plant fibers (Table 1), we essentially observe that the rush fiber is rich in cellulose and poor in lignin. This finding leads us to suppose that its extraction by chemical treatment will be easier than that of other plant fibers.

Table 1: Comparison of the chemical composition of different types of plant fibers

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref
Untreated rush fiber (this study)	**40**	**21**	**29**	
Alfa	45	24	24	[13]
Bagasse	55	17	25	[6]
Bamboo	26 - 43	30	21 - 31	[14]
Kenaf	31 - 39	21	16	[15]
Date palm	46	18	20	[16]

1.5 Determination of the bonds and chemical groups of the rush fiber by infrared spectroscopy with Fourier transform

Fourier transform infrared spectroscopy (SIRTF) is an important analytical technique used in this work to determine the structures and chemical compositions of fibers extracted from the rush plant. The properties of the fibers obtained during the various treatments were analyzed due to the chemical treatments carried out. An IR spectrum was recorded at room temperature using a Nicolet FT-IR 200 spectrometer, equipped with a diamond crystal and having a wide spectral range between 4000 and 400 cm-1 (Figure 7).
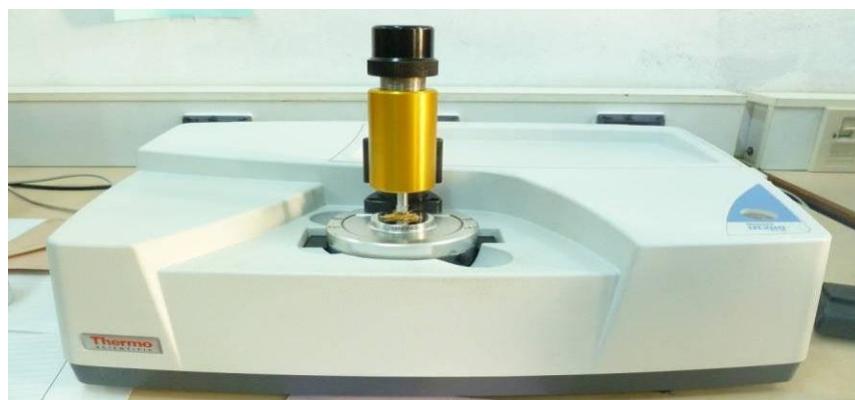

Figure 7: Fourier transform infrared spectroscopy apparatus

1.6   Determination of the crystallographic properties of the rush fiber by X-ray diffraction

The Jonc fibers were characterized by X-ray diffraction, under standard conditions using an X-ray diffractometer (D8 Advance, Brucker AXS, Germany), with a voltage of 40kV and 30mA, Cu Ka radiation (1.5418 Å) at a sweeping rate of 2 ° / min, and an angle range 2θ, between 2 ° and 40 °. Thus, the crystallinity of the treated fibers was obtained by X-ray diffraction. The results indicate the influence of the chemical treatment on the crystalline properties and the crystallographic planes of cellulose. The crystallinity index CrI was determined using the method described by Segal et al. (1959) [17].

1.7 Optimization of the processes for extracting plant fibers from Rush

1.7.1   The pretreatments

Before any extraction process, the plant stems must go through a pre-treatment. Among these processes we can mention:

1.7.1.2 Mechanical brushing

Mechanical brushing involves moving the wire brush (wire comb) in the longitudinal direction of the rods to force them to separate. And so the diameter of the rods is reduced and the samples will be more homogeneous. Samples extracted from mechanically brushed rods are thinner and less rigid than those from unbrushed rods, which makes it easier for chemicals to be more reactive because more surface area is available for the same amount of material. in the step following the preprocessing to defibrillate the rods and give better delignification by removing non-cellulosic products [4].

2.7.1.2 Soaking

Soaking is immersion in a liquid (Figure 8). The soaked material is the vegetable fiber and the liquid is for example salt water. The main role of soaking in the fiber pre-treatment phase is to remove waxes, sand and dust that are on the surface of the rods. Thanks to this elimination, the stems will be more "open" to subsequent treatments during the extraction step [4,18]. The history of the use of salt water in the pretreatment goes back to the old treatments of the producers of some vegetable fibers such as alfa for example. They put them in sea water to soak them [4,18]. Soaking in salt water can be done at room temperature or at high temperature which allows soaking to be done more quickly. The concentration of salt should be close to that in seawater whose salinity varies between 27g / l to 38 g / l [4,18]. The longer the soak is, the better the condition of the fibers is to allow sufficient time for the waxes to dissolve in salt water. In the literature the following conditions are mentioned: 12 h at 80 ° C or 24 h at 60 ° C [4,18].

Figure 8: Process of soaking alfa fibers for example in salt water [4].

1.7.2 Lignocellulosic fiber extraction process

1.7.2.1. Extraction of fibers by physical methods

These methods act on the surface state of the plant fiber by: its cleaning and purification, its modification of its structural properties [21]. To do so, several methods are applied, the most used of which are:

- **Autoclave treatment**

This process was developed by the company CERES B. V (Wageningen, The Netherlands) for the treatment of flax fibers. This treatment is characterized by its simplicity, it is inexpensive and not dangerous for the environment which could eventually replace the chemical treatments currently applied. It consists of vaporizing the non-woven flax fiber at a temperature above 130 ° C for 30 min in an autoclave. This first step is followed by a drying step, then by a heating step at a temperature above 150 ° C for 2 h [18,22].

- **Cold plasma treatment**

It is one of the physical treatments used to improve the interfacial properties of the pair: natural fiber / polymer matrix. This treatment does not require the use of solvent and its duration is short compared to other treatments. It is characterized by its modification of the surface of the fibers by altering or removing weakly attached surface layers without affecting their intrinsic properties. The cold plasma treatment procedure involves putting the non-woven fibers in a reactor, where the pressure is 10-4 Pa. The plasma gas used in this kind of physical treatment is helium He [18,19,20] .

- **Corona treatment**

Corona treatment is one of the most interesting methods for the oxidation of the fiber surface. This technique is based on the use of a low frequency high voltage generator (typically 15 kV, 50 Hz) between two electrodes. The samples are placed between the electrodes and processed for 15 min. The air is ionized and the electrons are accelerated and the surface energy of the cellulosic fibers is increased. For higher and higher power levels improvements in the mechanical properties of cellulose / polypropylene composites are observed [21, 23].

- **Gamma ray treatment**

Gamma radiation is electromagnetic in nature, and the surfaces treated by this radiation can radically change the behavior of the fiber surface. And it is thanks to the implantation of ions, of photons coming from a beam produced by an accelerator, this type of physical treatment can give new characteristics to the material modified by an energy transfer [21].

- **Ultraviolet radiation treatment**

This technique is beginning to interest many scientists with a view to using it in the physical treatment of plant fibers reinforcing composite materials. It oxidizes the surface of the fibers and is just as effective as conventional oxidation treatments with chromic and nitric acids. As with the corona treatment, the UV treatment increases the polarity of the fibers and improves their mechanical properties. However, excessive UV treatment time can lead to degradation of the fiber surface [21].

- **Laser treatment**

The treatment consists of bombarding the surface of the untreated fiber with a coherent laser beam produced either with a gas or a gas mixture (KrF: krypton hexafluoride, XeCl: xenon chloride, CO2 + N2 + He), or with a solid (aluminum garnet and neodymium yttrium: YAG-Nd). Compared to other methods of surface, laser treatment is very expensive but it remains the most precise [21].

1.7.2.2. Fiber treatments by mechanical methods

The most widely used mechanical treatment processes for plant fibers are:

- **Scutching**

This technique consists first of all in exerting a mechanical action (breaking it) on the wood to separate it from the stems (Figure 9). It is mainly used in cases of flax and hemp, where the stems are taken by their ends and inserted into the pond (manual lever instrument) if the operation is manual. The stems are beaten to remove the wood, and this operation is repeated until the fibers are as flexible as possible [4].
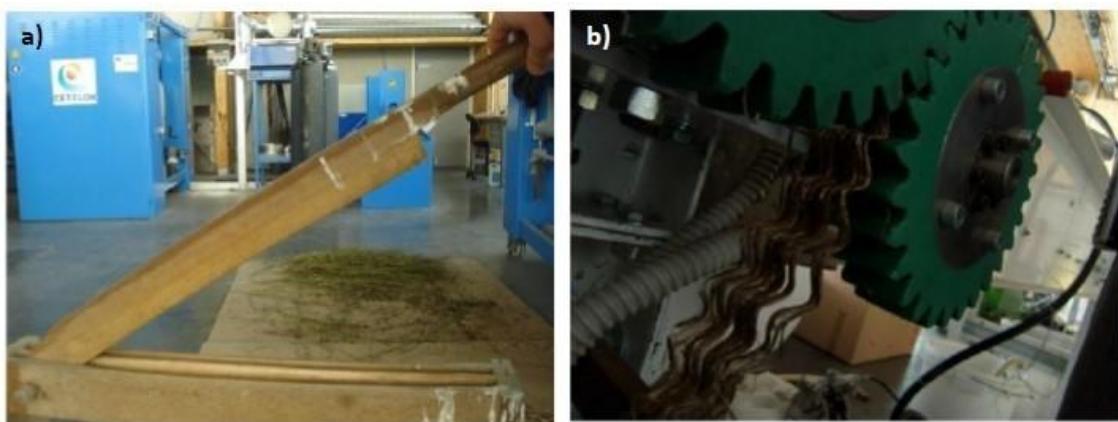
Figure 9: Mechanical extraction by trellis [4]

(a): manual trellis; (b): mechanical trellis.

- **By deflection**

The fiber deflection extraction is done by combined scraping and threshing using a scraper which grates the leaves of the plant and releases the fibers [4].

- **By rolling**

In this technique, the rods are cut into pieces, and then crushed in a press or by rolling or by a combination of the two treatments. This process is repeated separated as much as possible [4].

1.7.2.3. Fiber treatments by chemical methods: The Kraft process

The Kraft process or alkaline process was patented by Carl Ferdinand Dahl in 1884, it is the most widely used industrially for cooking wood, with about 80% of the world production of pulp. This process uses as cooking reagents allowing the delignification of plant fibers a mixture of sodium hydroxide (NaOH) (and / or) sodium sulphide (Na2S) also called white liquor. The chemical treatment of plant fibers is carried out at temperatures between 150 ° C and 170 ° C. The purpose of these reagents in the aqueous phase is to dissolve the lignin and a fraction of the hemicelluloses of the wood. After cooking, the so-called "black" liquor is enriched with dissolved organic matter from the wood and is strongly alkaline [4, 24].

1.7.2.4. **Fiber treatments by biological methods**:

- **By retting ashore**

It is a natural process which consists in spreading the fibers after their harvest in a ventilated space in order to benefit from the combined action of the sun and the rain during a period which extends from 6 to 8 weeks depending on the weather, this which will promote the development of microorganisms capable of dissociating non-cellulosic elements from the fibrous part of the plant by eliminating the bonds which bind them together. Despite the effectiveness of this method, it has several handicaps which lie in its entire dependence on weather conditions, the slightest problem such as excess humidity or lack of it can directly affect the quality of the fibers obtained [4].

- **By water retting**

The retting of flax and hemp was very widespread in northern Europe (France, Belgium, Netherlands), it was traditionally carried out in rivers before it was banned at the beginning of the 20th century for environmental reasons, due to the bacterial decomposition of boots soaked at the bottom of rivers. In fact, in this process, bundles of 5 to 7 kg of plant fibers were immersed in water for several days when an action of bacteria occurred, and as soon as the fibers were detached over the entire length, the plant came out of water to be dried [4].

- **By microbial action**

Three groups of microbial agents are used in this process which are capable of degrading the non-cellulosic components present in the stems or leaves of plants, namely bacteria, protozoa and fungi [4].

1.7.3 **Post-processing**

The post-treatment covers the following phases: calendering, drying and separation of the fibers.

1.7.3.1. **Fiber calendering**

After the extraction process, the fibers are always gathered and glued to each other in bundles which requires them to be individualized and parallelized.
And for this purpose, the fibers are passed through a calendar with two counter-rotating rubber rollers where their spacing is adjusted so as to extract the excess water present in the fibers and to break them and facilitate the separation of any non-m present in the structure[4].

1.7.3.2. **Combing**

In order to make them parallel and individualized, the fibers which have undergone calendering pass through a mechanical comb for the removal of debris and the division of the bundles [4].

1.7.3.3. **Drying**

Drying is the operation which anticipates the characterization tests of these fibers obtained. It can be done in the open air [4].

1.8 **Study of the extraction of rush fibers**

1.8.1 **Mechanical extraction**

In the first place, we opted to proceed by a mechanical extraction using a machine composed of rotating crushing rollers (Figure 10) whose purpose is the shelling and defibration of the rod rod to obtain elementary fibers by

separation of the bundles. best fibers from the generally woody heart. The result was not convincing with this mechanical process and the defibration did not allow the cellulosic fibers to be perfectly separated from the other compounds of hemicellulose and of lignin. The rod fibers obtained after this mechanical treatment had an average length of approximately 250 mm, an average diameter of approximately 280 μm, a density of the order of 0.71 g / cm3, a tensile strength of 31 MPa and a modulus of elasticity of 0.7 GPa. These

values are not very satisfactory in comparison with those of other plant fibers mentioned in Table 2, especially with regard to the density which is very low and the diameter which is very high compared to other plant fibers such as Alfa, Kenaf or Bagasse whose average density is around 1.30 g / cm3 and whose average diameter is around 60μm (Table 2).

Figure 10: Mechanical extraction process of rush fibers.

Likewise for the tensile strength and the modulus of elasticity which are very low compared to other plant fibers whose average tensile strength is of the order of 190 MPa and whose average modulus of elasticity is order of 18 GPa (Table 2). This confirms that the defibrillation was not optimal and that it is necessary to replace the mechanical treatment of husking and defibrillation by a chemical treatment of elimination of lignin and hemicellulose and of effective separation of the lignin and hemicellulose. cellulosic fibers.

1.8.2   Chemical extraction

1.8.3   In Our case study and in what follows, we opted for the alkaline chemical treatment (Kraft process) of the plant fibers of rush because this process and until now is the most used in the extraction and delignification of vegetable fibers.

In order to be able to use the plant fibers of Rush as reinforcement in the construction material that we wish to make, it is imperative to subject them to a treatment which would allow them to be extracted from the stems of the natural plant. We started with a mechanical extraction but it was not satisfactory (Figure 25), which prompted us to study the possibilities of extraction by the most famous chemical method, which is extraction by alkalization. This method has been applied in depth to our knowledge for the first time to the rush plant, in order to obtain better mechanical characteristics (tensile strength and elastic modulus) and better surface morphology.

By examining the previous Table 1, we decided to carry out the alkalization with two low concentrations of NaOH (4% and 8%), in the presence or not of sodium dithionite Na2S2O4 (alkalinizing agent) and with or without the sodium hypochlorite NaOCl agent for delignification and chlorine bleaching of the plant fiber of its woody compounds [25,26,27] and according to two methods of cold and hot treatment by analogy with the treatment detailed in the work of M. Dallel [4].

The chemical treatment of fiber extraction for which we have opted is that of alkalization which is a process commonly used for obtaining elementary fibers by defibrillation of the fiber bundles and the elimination of non-cellulosic compounds such as hemicellulose and lignin [28]. The alkalization process is essentially based on the use of caustic soda NaOH which acts by delignification of plant fibers. The degree of alkalization can be increased with the use of other delignifying chemicals such as sodium dithionite Na2S2O4 and sodium hypochlorite NaOCl.

1.8.4   Chemicals used for alkalization

2.8.3.1 Caustic soda NaOH

The caustic soda solution used in our study is a strong alkaline product that is often used as a chemical reagent in various applications. Its molar mass is 40.00 g / mol and its density is 2.13 g.cm-3. The concentrations used in this study are 4% and 8% of the mass of the water.

2.8.3.2   Sodium dithionite (Na2S2O4)

Sodium dithionite or sodium hydrosulfite Na2S2O4, is a white crystalline powder with a faint sulfurous odor. It is easily soluble in water and sodium hydroxide solutions. Its density is 2.19 g / cm^3 and its molar mass is 174.107 g / mol. In this case study, we used alkaline solutions of 1.5% sodium dithionite to bleach and delignify the rush fibers. Sodium dithionite (Na2S2O4) is known as a reducing agent, especially for the lignin content [26].

2.8.3.3   Sodium hypochlorite NaOCl

The sodium hypochlorite NaOCl used in this study contains 38 g / l (3.8%) or 38000 ppm of active chlorine. It is used in our study as a by-product to delignify the fibers obtained by alkaline treatment, by removal of lignin and other non-cellulosic compounds [27].

2.8.4 Chemical extraction processes

2.8.4.1 The cold chemical extraction process

This process is based on cold alkalization with sodium hydroxide NaOH at concentrations of 4 and 8% for ecological and economic reasons. After having cut the cane stems into pieces of approximate length of 10 ± 1cm (Figure 11), and by analogy with the process for treating the alfa fibers in [4], these pieces are put in a beaker filled with aqueous solution. NaOH at concentrations of 4% or 8% by mass of water for 48 h at room temperature. Subsequently, the treated fibers are rinsed with tap water and then they are dried at room temperature.

Figure 11: The rush fibers cut and used in the extraction.

2.8.4.2 The hot chemical extraction process

The hot process of chemical extraction, consists of carrying out an alkalization at 98 ° C ± 2 ° C for 2 hours for the 4% NaOH concentration and 1 hour for the 8% NaOH concentration, with the use of four treatment variants:
- Treatment with caustic soda NaOH;

- Treatment with caustic soda NaOH and sodium dithionite $Na_2S_2O_4$;

- Treatment with caustic soda NaOH followed by a treatment for one hour in sodium hypochlorite NaOCl;

- Treatment with caustic soda NaOH and sodium dithionite $Na_2S_2O_4$ followed by a one hour treatment in sodium hypochlorite NaOCl.

For each treatment, the rush stems are cut into pieces approximately 10 ± 1cm long, they are placed in a beaker filled, depending on the treatment case, with aqueous NaOH solution, or with [NaOH + $Na_2S_2O_4$] or [NaOH + NaOCl] or [NaOH + $Na_2S_2O_4$ + NaOCl]. The concentration of NaOH is variable with 4% and 8% of the mass of water used for the treatment, that of $Na_2S_2O_4$ is set at 1.5% by weight of the fibers and that of NaOCl is equal to 40% per liter of water. After each of these treatments at hot at 98 ° C. ± 2 ° C. for 1 hour or 2 hours as the case may be, the treated fibers are rinsed with tap water and then they are dried at room temperature.

Figure 12: Hot alkalization process of rush fibers

Figure 13: Process for bleaching rush fibers with bleach processed

Figure 14: States of rush fibers treated after alkaline treatment and bleaching

Figure 15: The fibers obtained after the extraction process.

2.8.5 Yield of production of rush fibers

The fibers obtained after each chemical treatment consist of individual cellulose cells which are held together in the form of a bundle by non-cellulosic substances such as lignin and pectin. Lignin is the main binding material in fibers since most of the pectin will be removed during alkaline processing. The conditions used in this study to obtain fiber (4% and 8% sodium hydroxide, 100 ° C for 60 and 120 minutes) are expected to remove most of the pectin as it will be removed by 0.4% boiling sodium hydroxide [29]. The yield of the production of the fibers obtained depends on the conditions of extraction of fibers such as the concentration of caustic soda, the treatment time, the temperature and the ratio (fibers / alkaline solution) used. In our study, the production yield of chemically treated rush fibers varies depending on the treatment applied and the concentration of sodium hydroxide: for example, and as indicated in figures 30 and 31, the yields in the case of a cold alkaline treatment with 4% and 8% of NaOH are respectively 50% and 40% by weight of the fibers. In the case of an alkaline hot treatment, the production yield decreased to 38% and 36% respectively with 4% and 8% NaOH. Then at 35% and 33% with 4% and 8% NaOH combined with NaOCl. This value reaches 37% and 35% with Na2S2O4 combined with NaOH combined at 4% and 8%. Finally, it can reach 32% and 28% with 4% and 8% of NaOH combined simultaneously with NaOCl and Na2S2O4. For this, let us note the treatments carried out as follows in order to be able to understand the histogram below which recapitulates the yields of rush fibers treated from the various chemical treatments:

no.	Treatment	Symbol
1	Crude fiber	T0
2	Mechanical processing	Tguy
3	4% cold NaOH	T1
4	8% cold NaOH	T2
5	4% hot NaOH	T3
6	8% hot NaOH	T4
7	4% hot NaOH + NaOCl	T5
8	8% hot NaOH + NaOCl	T6
9	4% hot NaOH + Na2S2O4	T7
10	8% hot NaOH + Na2S2O4	T8
11	4% hot NaOH + Na2S2O4 + NaOCl	T9
12	8% hot NaOH + Na2S2O4 + NaOCl	T10

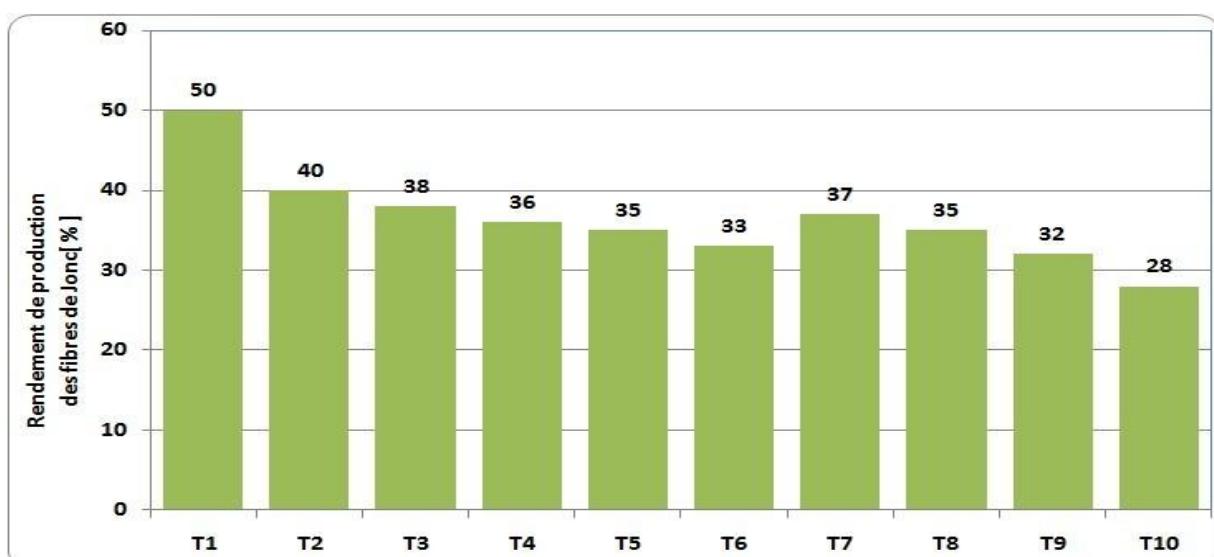*Table 2: Symbols of the various treatments applied to the rush plant.*

Figure 16: The production yield of rush fibers for each type of treatment

In addition to the fiber yield, the degree of removal of non-cellulose substances plays a major role in determining the structure and properties of the treated fibers.

2. Variation of the physical properties of treated rush fibers: effect on the diameter and density of the fiber

The rush rods used here as raw material have an average diameter of 3300 μm and a density of approximately 0.385 g.cm-3. The comparison between these values and those of other plant fibers such as alfa, bagasse, bamboo, kenaf and date palm, subjected to alkaline chemical treatments (Table 2) shows a significant difference in their diameter and mass. volume of the ultimate fibers. Therefore, in order to use rush fibers as reinforcement in composites, it is first necessary to know their characteristics.

The experimental results obtained from the physical and mechanical properties of various plant fibers or synthetic fibers presented in Table 2 provide an idea of the density ranges, diameter and length that the rush fiber should have after its treatment by a mechanical or chemical process in order to be comparable to other fibers often used as reinforcing material in composites. For this reason, we started first with a mechanical treatment with a machine made up of rotary crushing rollers which aims to take off and extract the fiber from the rush. Then we get individual fibers by separating the bundles of fibers from the generally woody heart. It should be mentioned that the mechanical extraction process led to a random effect and produced incomplete separation of the cellulosic fibers. Therefore, the results were not convincing. For this reason, we started first with a mechanical treatment with a machine made up of rotary crushing rollers which aims to take off and extract the fiber from the rush. Then we get individual fibers by separating the bundles of fibers from the generally woody heart. It should be mentioned that the mechanical extraction process led to a random effect and produced incomplete separation of the cellulosic fibers. Therefore, the results were not convincing. Rush fibers For this reason, we started first with a mechanical treatment with a machine made up of rotary crushing rollers which aims to take off and extract the fiber from the rush. Then we get individual fibers by separating the bundles of fibers from the generally woody heart. It should be mentioned that the mechanical extraction process led to a random effect and produced incomplete separation of the cellulosic fibers. Therefore, the results were not convincing. Rush fibers It should be mentioned that the mechanical extraction process led to a random effect and produced incomplete separation of the cellulosic fibers. Therefore, the results were not convincing. Rush fibers It should be mentioned that the mechanical extraction process led to a random effect and produced incomplete separation of the cellulosic fibers. Therefore, the results were not convincing. Rush fibers obtained after this treatment have an average length of approximately 250 mm, an average diameter of approximately 280 μm and a density of approximately 0.71 g.cm-3.

These results are not satisfactory, especially with regard to the very low density and the very large diameter compared to other plant fibers such as Alfa, Kenaf and / or Bagasse having an average density: 1.30 g .cm-3; An average diameter: 60 μm (Table 2). It would therefore be necessary to change the treatment to a chemical method in order to remove the components of lignin and hemicellulose and to ensure effective separation of the cellulosic fibers. The rush rod having a diameter of approximately 3300 microns cannot be used directly in its raw state as a composite reinforcing material. First of all, the removal of lignin and hemicellulose substances to obtain ultimate cellulose fibers has been optimized. The ultimate cellulosic fibers have a diameter of about 300 microns as shown in Figure 19. The diameter has decreased from an initial value of 300 μm (for untreated fiber) to a value in the range [45 μm; 110 μm] for a 4% NaOH solution. This last value also belongs to the range [40μm; 90μm] for the 8% NaOH solution (Figure 17). Thanks to the chemical treatment by alkalization process, it was possible to obtain a rod fiber of 60 μm in diameter. This is a satisfactory result, which corresponds well to what was calculated for other plant fibers commonly used in composite materials (Table 2). It can also be noticed that the diameter of the fiber decreases in the heat treatment (Figure 32). The hot treatment with only 4% NaOH made it possible to reduce the diameter to 60 ± 16 microns while for 8% of NaOH, or with a pretreatment with Na2S2O4 and / or with a post-treatment with NaOCl slightly decreased the diameter to reach 40 ± 4 microns.

It should be noted that the experimental values mentioned in this chapter result from an average of three values from the same sample.
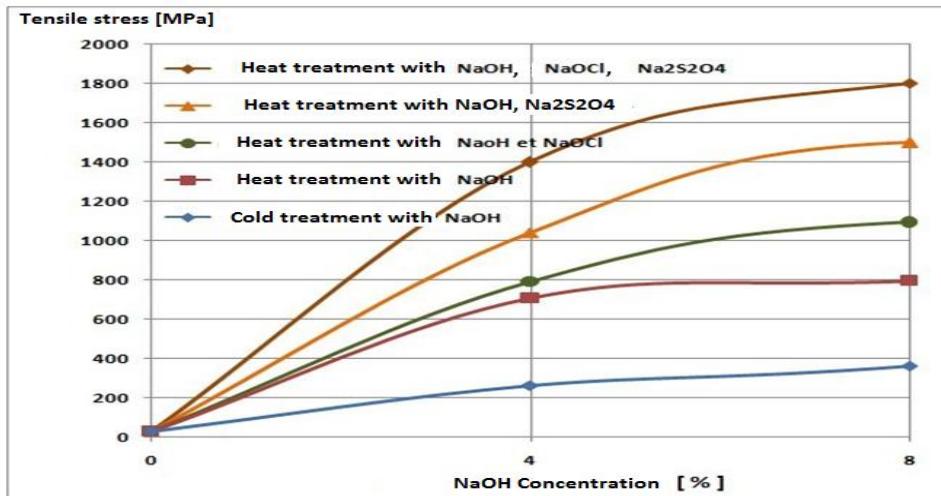
Figure 17: Variation in fiber diameter after each type of chemical treatment.

Due to the mechanical treatment and various chemical treatments applied to the rush plant, the density of the fibers has increased dramatically, as shown in Figure 17. It reflects the expected results of defibrillation, delignification and Cellulose extraction was performed without damaging the ultimate cellulose fibers [30]. In fact, the density has increased from 0.385 g.cm-3 (for untreated fibers) to 0.71 g.cm-3 (for mechanically treated fibers). After the chemical treatment by alkalization, the density was able to reach superior results, namely 0.925 g.cm-3 for the cold treatment with 4% NaOH to reach a maximum of 1.25 g.cm-3 after the hot treatment with 8% NaOH combined with Na2S2O4 and NaOCl. However, it would be important to verify the effects of the reduction in diameter and the increase in density of the rush fiber, in particular on its morphology, surface condition, crystallinity, tensile strength and elastic modulus . These different functionalities will be developed in the following sections. The mechanical treatment and the various chemical treatments applied to the rush fiber have made it possible to considerably increase its density shown in figure 33, thus reflecting the expected result of defibrillation, delignification an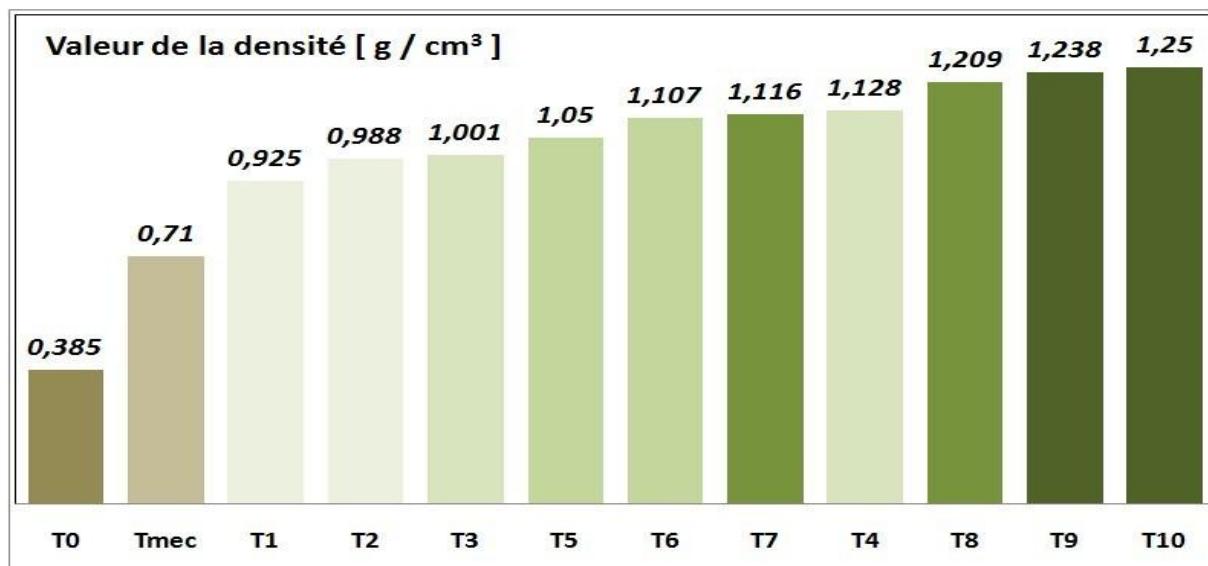d isolation of the cellulosic component. been achieved. its tensile strength and elastic modulus. These different functionalities will be developed in the following sections. The mechanical treatment and the various chemical treatments applied to the rush fiber have made it possible to considerably increase its density shown in figure 33, thus reflecting the expected result of defibrillation, delignification and isolation of the cellulosic component. been achieved. its tensile strength and elastic modulus. These different functionalities will be developed in the following sections. The mechanical treatment and the various chemical treatments applied to the rush fiber have made it possible to considerably increase its density shown in figure 33, thus reflecting the expected result of defibrillation, delignification and isolation of the cellulosic component been achieved.

Figure 33: Variation in density of rush fibers after chemical treatments

2.1 The chemical composition and morphology of the treated fibers

The study of the chemical composition revealed that by treating the fibers of Rush with a solution of 4% of cold NaOH, the groups of cellulosic fibers are surrounded by compounds of lignin (26.85%), hemicelluloses (22.05%) and non-cellulosic compounds and undergo only slight defibrillation (Figures 18.a and 18.b).
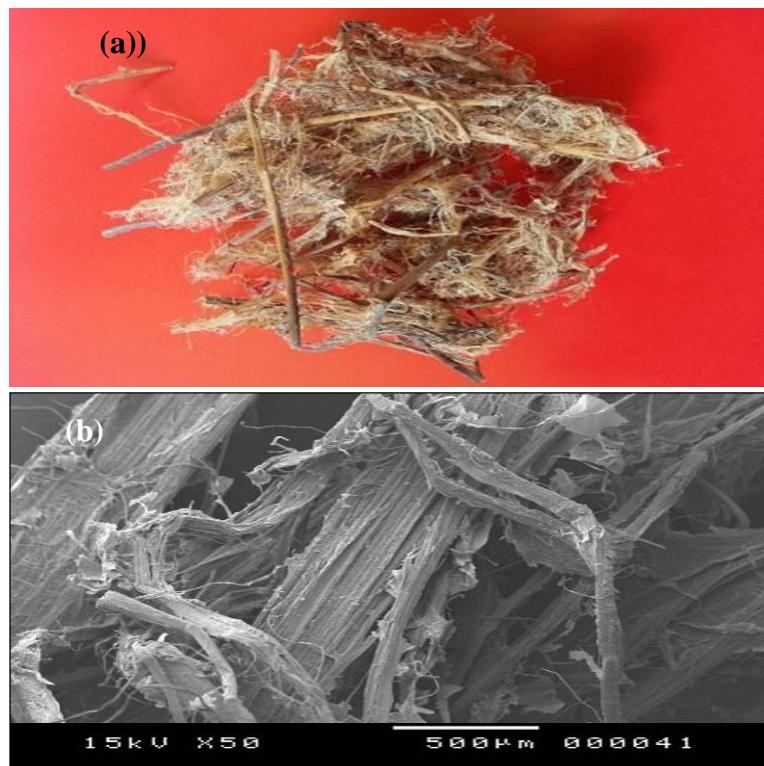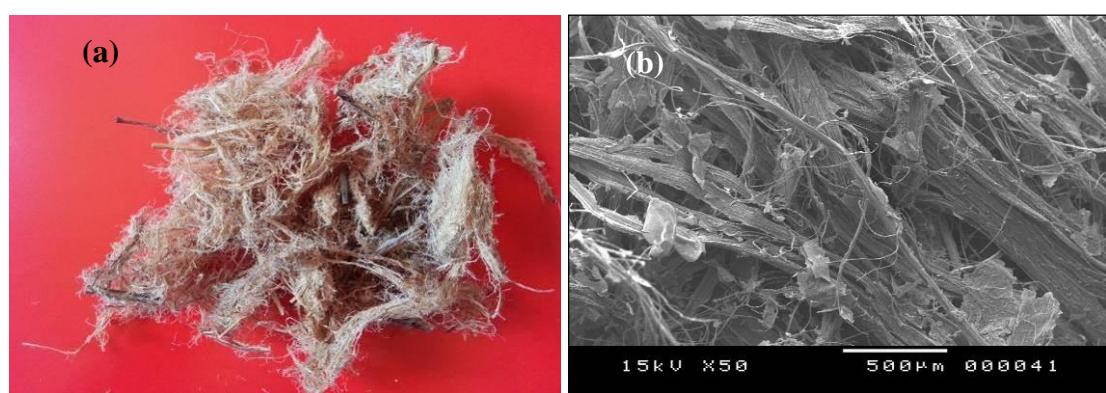

Figure 18: Condition of fibers treated with cold 4% NaOH

With the increase in the concentration of NaOH to 8% and with the same cold treatment process, there is a beginning of elimination of the alveoli of lignin and hemicellulose. Some groups of cellulosic fibers are released and as shown in Figures 19.a and 19.b a slight defibrillation is observed. And the process of delignification begins with the removal of cells of lignin and non-cellulosic compounds . Certain groups of cellulosic fibers are released.
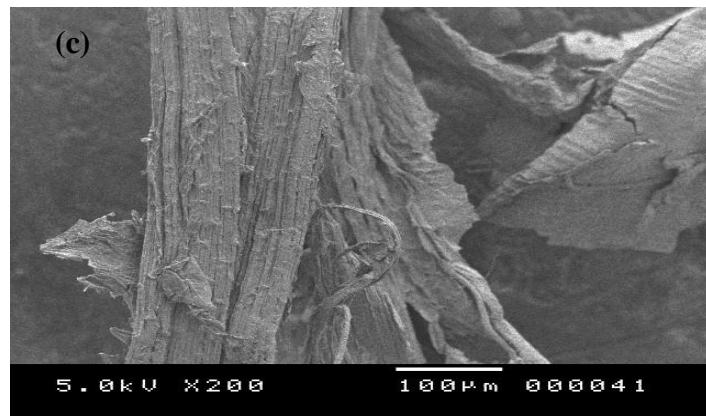
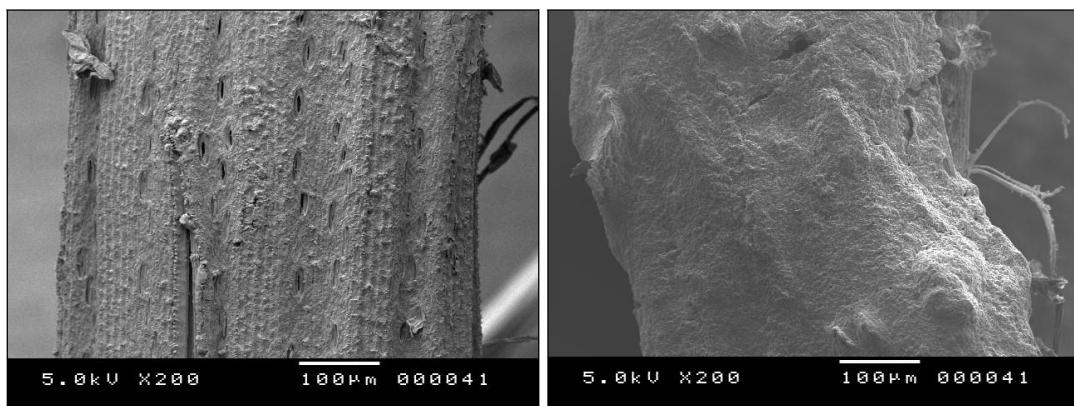*Figure 19: Condition of fibers treated with 8% NaOH cold*

Figure 20: Surface condition with 4% and 8% cold NaOH respectively

In addition, we observe in figure 20, the presence on the surface of a membrane of lignin and hemicellulose which continue to envelop the groups of cellulosic fibers both with a concentration of 4% of NaOH and that of 8%. .
While with the heat treatment process one can see the removal of a large part of non-cellulosic materials such as lignin (16.25% with 4% NaOH and 11.56% with 8% NaOH) and hemicellulose (23.60% with 4% NaOH and 26.08% with 8% NaOH) with the release of the groups of cellulose fibers (Figures 21 and 22).
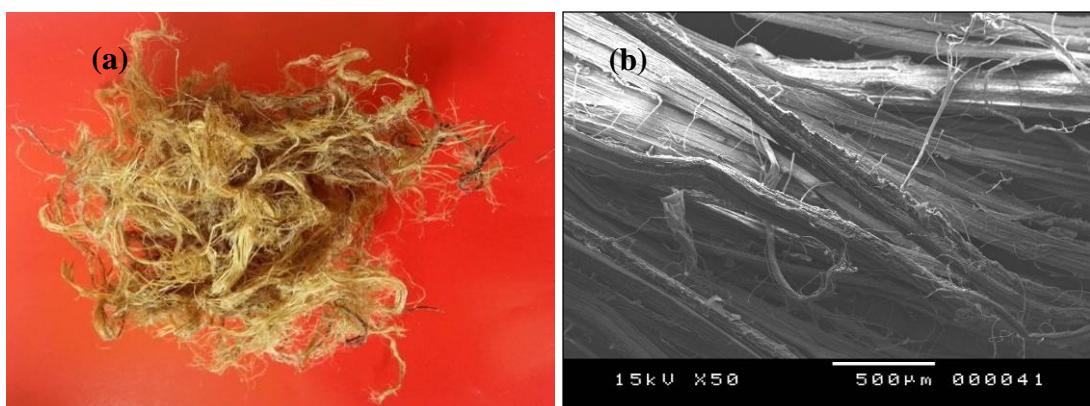
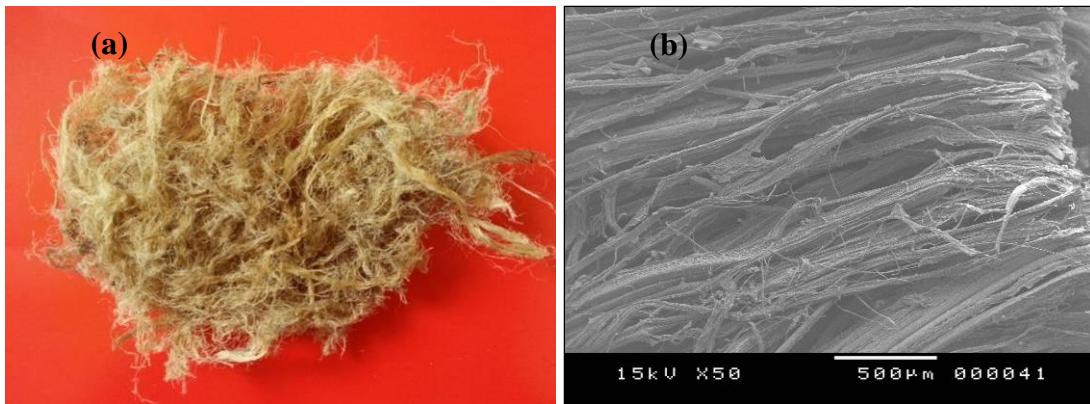*Figure 21: Condition of fibers treated with 4% hot NaOH.*

Figure 22: Condition of fibers treated with 8% hot NaOH

With the hot treatment with NaOH, we observe a more significant decrease in the diameter of the cellulosic fiber cluster (Figures 16 and 23).
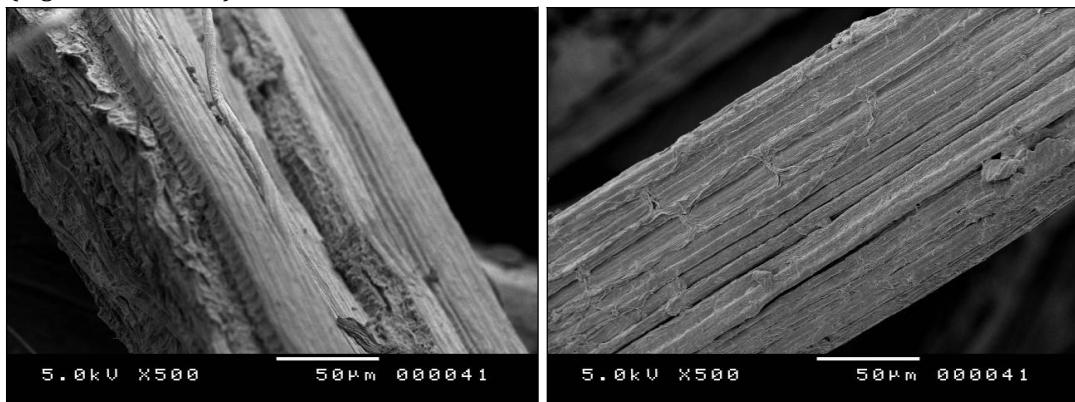

Figure 23: Surface condition with 4% and 8% hot NaOH respectively

We also see the disappearance of the lignin and hemicellulose membrane. The cellulosic fiber groups become more apparent with nevertheless the presence of some traces of elements of lignin and hemicellulose, as observed in figure 23.

With the hot treatment with NaOH in the presence of sodium dithionite Na2S2O4 we observe with the concentration at 4% of NaOH, a significant decrease in diameter as observed in FIGS. 24 and 25. For the concentration at 8% NaOH, the addition of Na2S2O4 does not bring any further reduction in diameter compared to that of 4% of NaOH with the Na2S2O4.

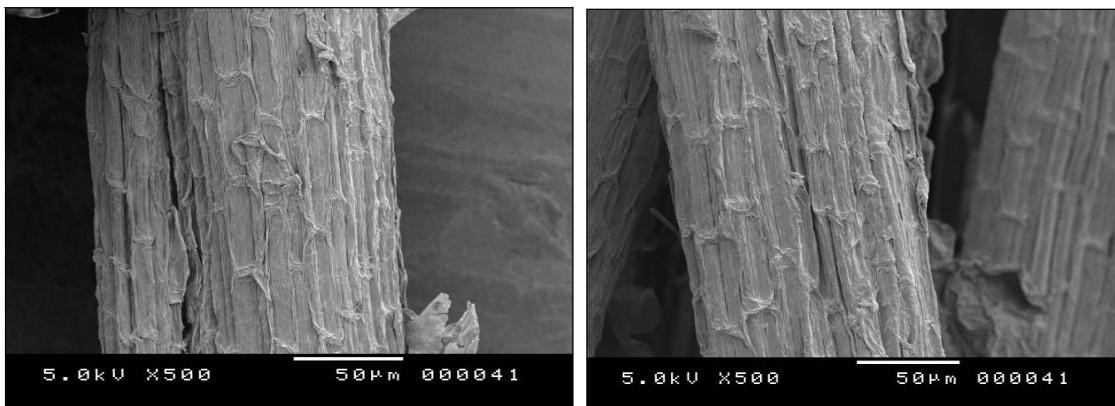*Figure 24: Condition of fibers treated with 4% and 8% NaOH hot with $Na_2S_2O_4$.*

Figure 25: Surface condition with 4% and 8% hot NaOH respectively with $Na_2S_2O_4$.

It seems that the cellulosic fibers are still surrounded by hemicelluloses (20.92% with 4% NaOH and 20.69% with 8% NaOH) and a large amount of lignin (13.01% with 4% NaOH and 9.04% with 8% NaOH).

With the hot treatment with NaOH in the presence of sodium hypochlorite NaOCl we observe with the concentration at 4% of NaOH an important decrease in diameter observed in figures 26 and 27. For the concentration at 8% of NaOH, the addition of NaOCl does not bring any further reduction in diameter compared to that of 4% NaOH with NaOCl.

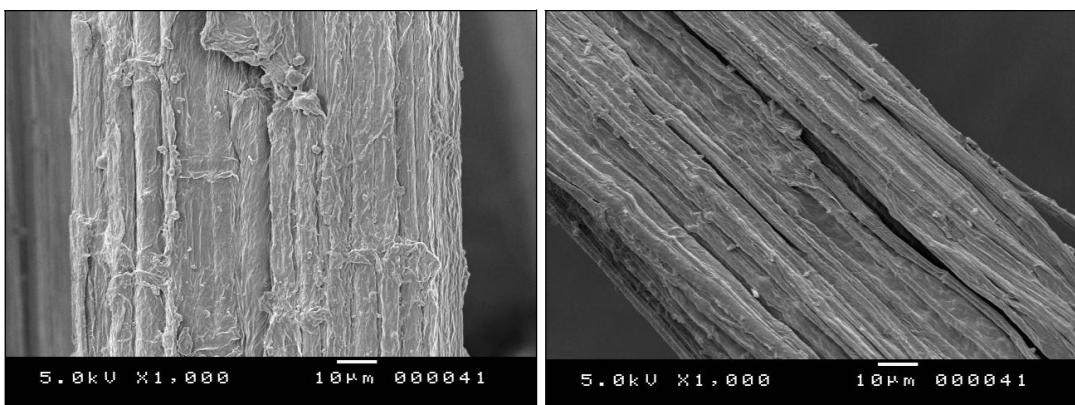*Figure 26: Condition of fibers treated with 4% and 8% NaOH hot with NaOCl.*

Figure 27: Surface condition treated with 4% and 8% NaOH hot with NaOCl.

Regarding the surface condition with the concentration of 4% NaOH we note that the membrane of lignin and hemicellulose although persistent, it envelops the groups of cellulose fibers less. With the concentration of 8% of NaOH we notice that the membrane of lignin and hemicellulose has almost completely disappeared and that the groups of cellulosic fibers become quite apparent. Furthermore, we observe a phenomenon of bleaching of the color of the groups of cellulosic fibers which indicates to us that in the presence of sodium hypochlorite NaOCl, the lignin and the hemicellulose have indeed been eliminated and the cellulosic fibers have indeed been delignified.

With the hot treatment with NaOH in the presence of sodium dithionite $Na_2S_2O_4$ and sodium hypochlorite NaOCl we note both with the concentration at 4% of NaOH and with that at 8%, a very significant decrease in diameter as observed in Figures 28 and 29.

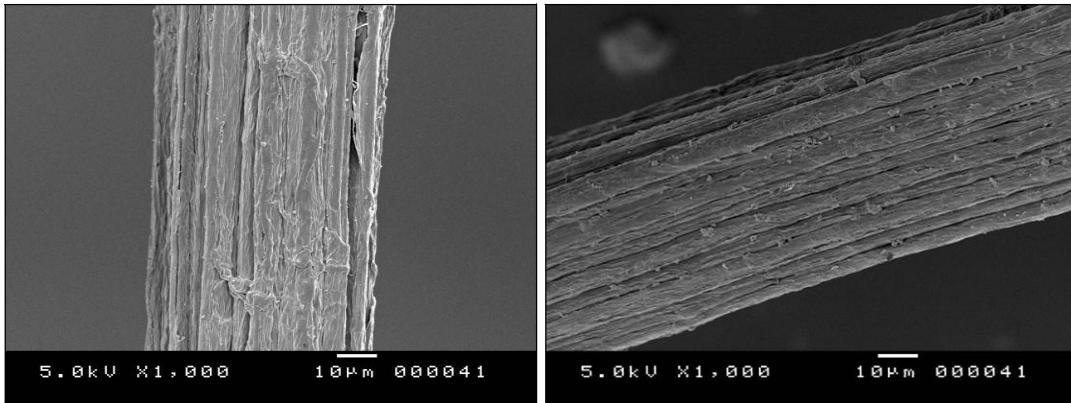*Figure 28: Condition of fibers treated with 4% and 8% NaOH hot with Na$_2$S$_2$O$_4$ and NaOCl.*

Figure 29: Surface condition of fibers treated with 4% and 8% NaOH hot with Na$_2$S$_2$O$_4$ and NaOCl

It will of course remain to check the condition of the cellulosic fibers obtained from the mineralogical and mechanical points of view.

2.2 Fourier transform infrared spectrometry (SIRTF) analysis of treated fibers

Figures 30 and 31 show the results of the SIRTF analysis of rush fibers treated with concentrations of 4 and 8% NaOH in cold or hot mode, in the presence or absence of sodium dithionite Na2S2O4 and hypochlorite of sodium NaOCl.
.
We can see from Figures 30 and 31 that:

- **The chemical treatment with sodium hydroxide NaOH in hot mode, followed by a post treatment with sodium hypochlorite NaOCl constitutes a more aggressive treatment for the delignification and elimination of lignin and hemicellulose, but also seems to be aggressive. with respect to cellulosic fibers.**
- **This is not the case for the chemical treatment with sodium hydroxide NaOH in hot mode, in the presence of sodium dithionite Na2S2O4 constitutes a selective treatment which ensures the delignification and elimination of lignin and hemicellulose, while sparing cellulosic fibers.**
- **When the sodium hypochlorite NaOCl, added after treatment with sodium hydroxide NaOH, is preceded by the pretreatment with sodium dithionite Na2S2O4, it acts only on the lignin and the hemicellulose without attacking the cellulosic fibers.**
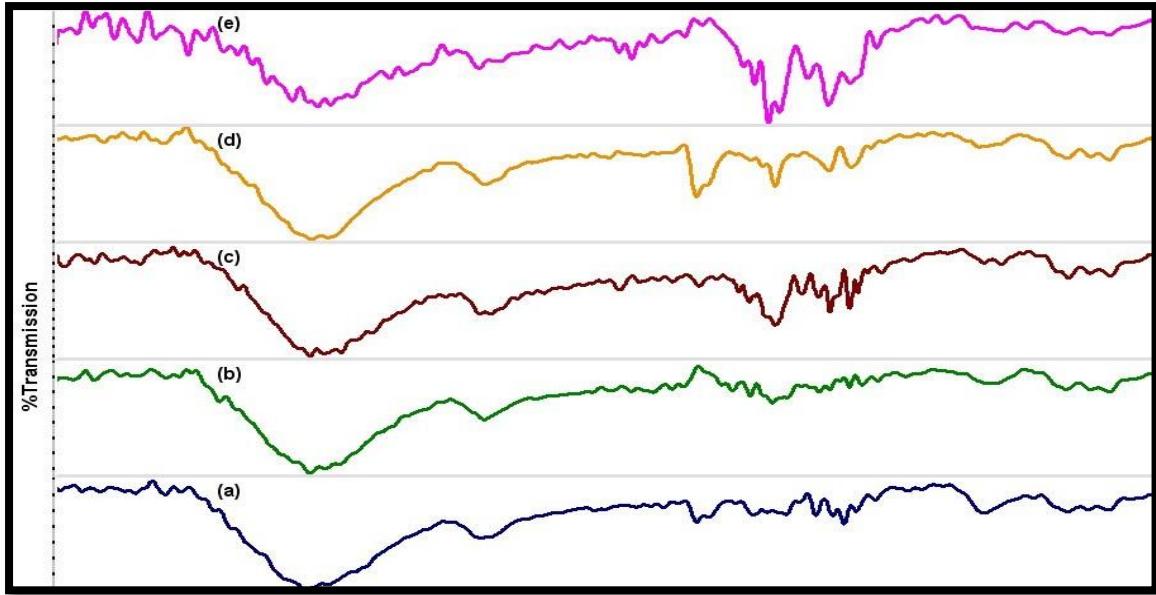
Figure 30: Variation of the FTIR spectra of rush fibers treated with 4% NaOH.

(a): cold treatment; (b): heat treatment; (c): heat treatment with NaOCl;
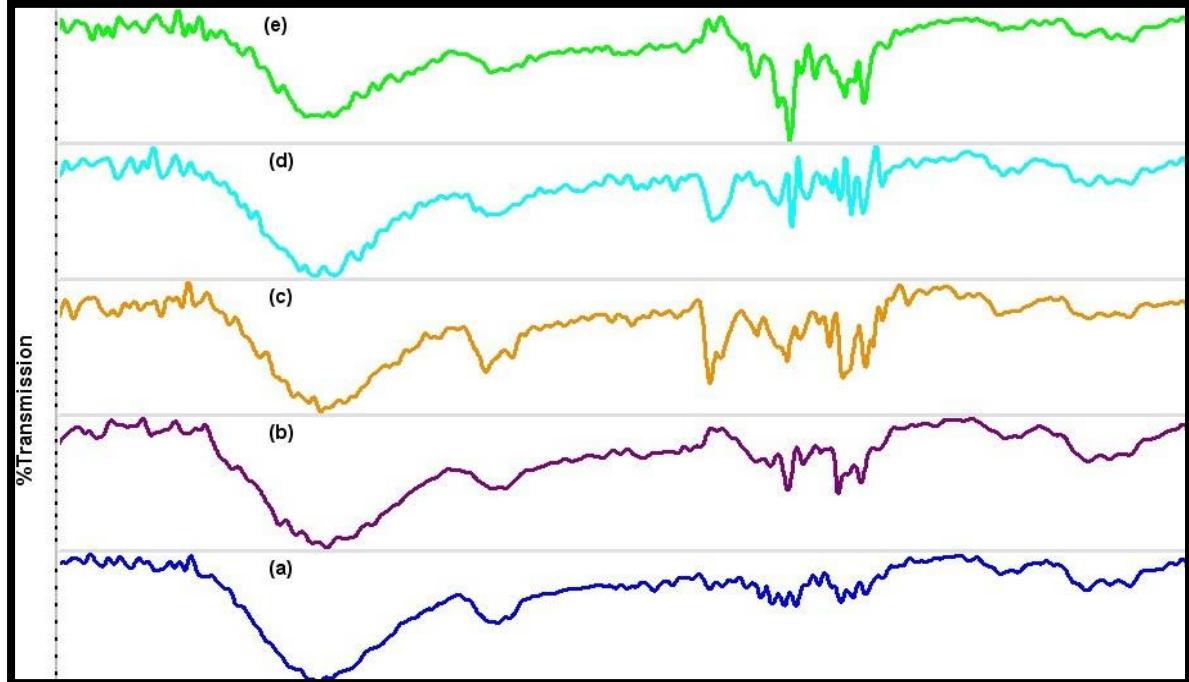**(d): heat treatment with Na2S2O4; (e): hot treatment with Na2S2O4 and NaOCl.**

Figure 31: Variation of FTIR spectra of rush fibers treated with 8% NaOH

(a): cold treatment; (b): heat treatment; (c): heat treatment with NaOCl;
(d): heat treatment with Na2S2O4; (e): hot treatment with Na2S2O4 and NaOCl.

2.3 X-ray diffraction analysis (XRD)

To see the effectiveness of the chemical treatment in the delignification adopted in our case study, we determined and compared the crystallinity of chemically treated fibers with untreated rush fibers. From figures 32 and 33 we see that the spectra of untreated rush fibers and fibers treated by different hot chemical treatments show three main peaks at 2 theta equal to 16.0, 22.5 and 34.8. These peaks are attributed to the crystal structure of Iβ cellulose of chemical formula: (C6H10O5) n according to the DRX software library.
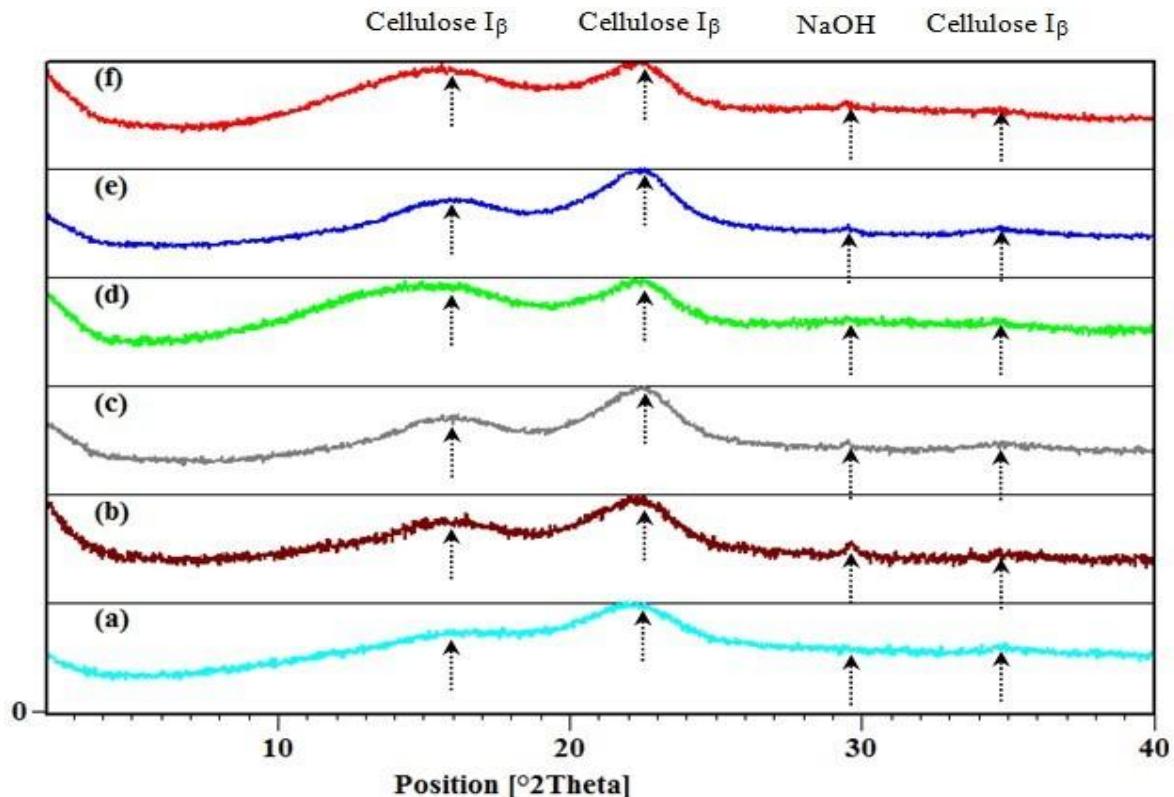

Figure 32: XRD diffractograms of rush fibers treated with 4% NaOH.

(a): Untreated fiber; (b): cold treatment with 4% NaOH; (c): hot treatment with 4% NaOH.
(d): hot treatment with 4% NaOH and NaOCl; (e): hot treatment with 4% NaOH and Na2S2O4
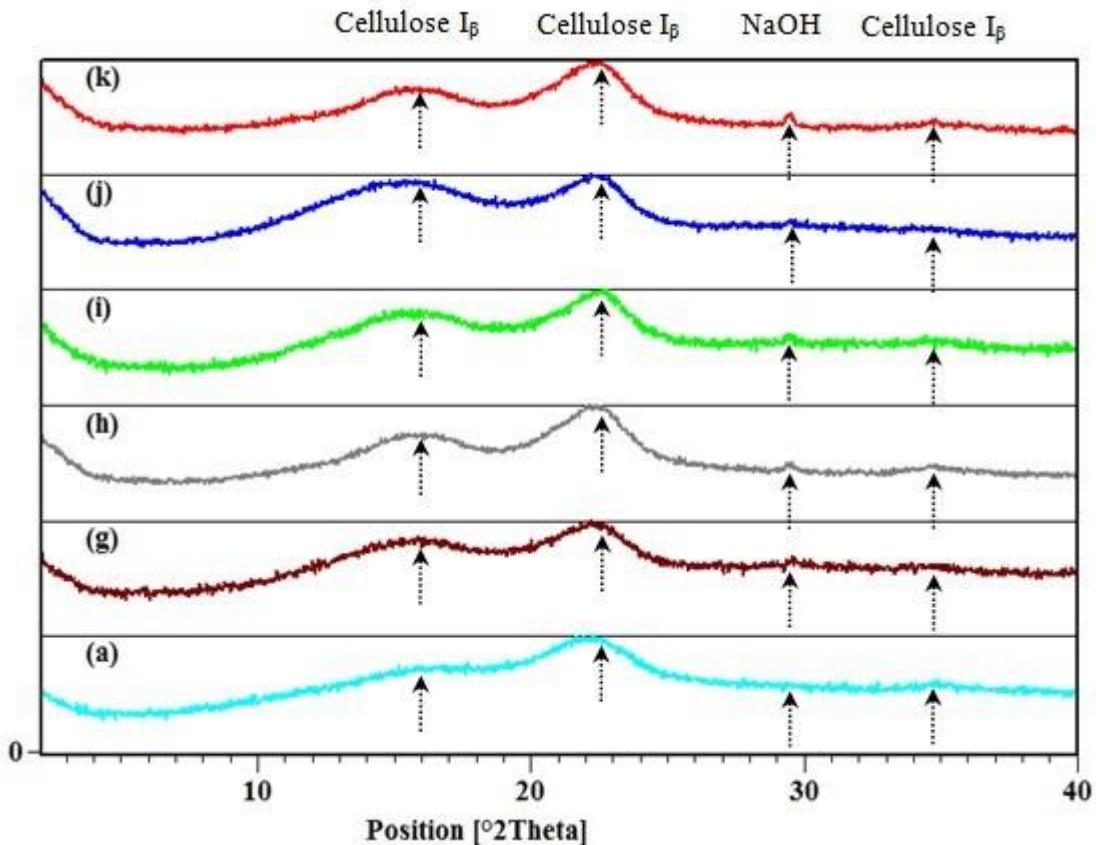**(f): hot treatment with 4% NaOH and Na2S2O4 and NaOCl**

Figure 33: XRD diffractograms of rush fibers treated with 8% NaOH

(a) : Untreated fiber; (g): cold treatment with 8% NaOH; (h): hot treatment with 8% NaOH.
(i) : hot treatment with 8% NaOH and NaOCl; (j): hot treatment with 8% NaOH and $Na_2S_2O_4$
(k): heat treatment with 8% NaOH and $Na_2S_2O_4$ and NaOCl

.

2.4 Mechanical performance of treated fibers

2.4.1 Variation of tensile strength σ_t

Before starting the chemical treatment, the final tensile strength of the fiber obtained by mechanical defibrillation of the rod of Jonc was 31 ± 8 MPa. Different modes of chemical treatments (including heat treatment) considerably increased the tensile strength value of the rush fibers (figure 34).
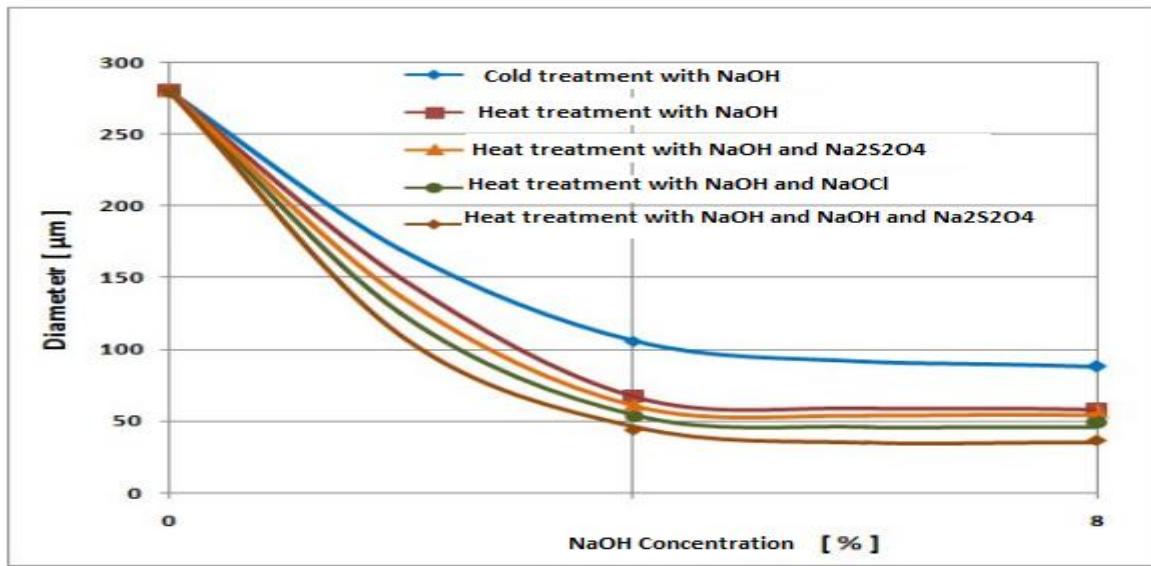
Figure 34: Variation of the tensile strength of the rush fiber after the chemical treatment

The hot treatment with sodium hydroxide NaOH alone for concentrations of 4% and 8% increased the tensile strength to 730 ± 68 MPa and 800 ± 48 MPa respectively. The post treatment with NaOCl made it pass respectively to 800 ± 20MPa and to 1100 ± 40MPa. Pretreatment with Na2S2O4 made it reach respectively 1050 ± 50MPa and 1500 ± 45MPa. The combined treatment of pre-treatment with Na2S2O4 and post-treatment with NaOCl made it possible to further increase the tensile strength of the rush fiber to 1400 ± 90MPa and 1800 ± 60MPa respectively.

2.4.2   *Effect of chemical treatment on Young's modulus of rush fibers*

Regarding the effect of the treatment on the elastic modulus, it can be noted that the fiber obtained by mechanical defibrillation of the Rod rod had a very low elastic modulus (0.7 ± 0.1 GPa). The modes of chemical treatments applied in our study (including hot treatment) considerably increased the value of the elastic modulus of the Rush fiber and therefore provided its composites with a high specific rigidity and resistance.

Hot treatment with 4% and 8% NaOH increased the modulus of elasticity to 41 ± 2GPa and 46 ± 3GPa, respectively. As regards the post-treatment with NaOCl, it further increased this modulus of elasticity up to 47 ± 2GPa and 62 ± 3.5GPa for respectively 4 and 8% of hot NaOH. During the pretreatment with Na2S2O4, these values reached 62 ± 1.5GPa and 70 ± 2GPa respectively. The combination of the pretreatment with Na2S2O4 and the post-treatment with NaOCl generated a further increase in the elastic modulus of the rod fibers up to 103 ± 2GPa and 122 ± 4GPa, respectively.

5. Conclusion

Mechanical extraction of the rush plant yielded an average fiber diameter (280 µm), an average density (0.71 g.cm-3), an average tensile strength (31 MPa) and a average elastic modulus (0.7 GPa). The hot alkaline treatment resulted in the delignification of the fibers by removing the lignin and hemicellulose compounds enveloping the cellulosic fiber groups. Therefore, this treatment allowed to perform a better extraction better than that with mechanical dehulling. Under this heat treatment and with 8% NaOH, Na2S2O4 and NaOCl, the insulation of the fibers was the most effective with a diameter reduced to a value of 40µm, the density of the fibers increased to 1.25 g.cm -3, the tensile strength reached 1800 MPa, and the modulus of elasticity increased to 122 GPa.

REFERENCES

[1] H. Saâd, "Development of biocomposites based on plant fibers and ecological glues", Doctoral thesis, University of Pau and Pays de l'Adour, 2013.

[2] S. Hamza, H. Saad, B. Charrier, N. Ayed, and F. Charrier-El Bouhtoury, "Physico-chemical characterization of Tunisian plant fibers and its utilization as reinforcement for plaster based composites," Ind. Crops Prod., Vol. 49, pp. 357–365, 2013.

[3] H. Ribeiro, CMR Almeida, AP Mucha, C. Teixeira, and AA Bordalo, "Influence of natural rhizosediments characteristics on hydrocarbons degradation potential of microorganisms associated to Juncus maritimus roots," Int. Biodeterior. Biodegrad., Vol. 84, pp. 86–96, 2013.

[4] M. Dallel, "Evaluation of the textile potential of Alfa fibers (Stipa Tenacissima L.): Physico-chemical characterization of the fiber in the yarn", Doctoral thesis, University of Haute Alsace, 2012.

[5] O. Faruk, AK Bledzki, HP Fink, and M. Sain, "Biocomposites reinforced with natural fibers: 2000-2010," Prog. Polym. Sci., Vol. 37, no. 11, pp. 1552–1596, 2012.

[6] R. Khiari, MF Mhenni, MN Belgacem, and E. Mauret, "Chemical composition and pulping of date palm rachis and Posidonia oceanica - A comparison with other wood and non-wood fiber sources," Bioresour. Technol., Vol. 101, no. 2, pp. 775–780, 2010.

[7] R. Khiari, Z. Marrakchi, MN Belgacem, E. Mauret, and F. Mhenni, "New lignocellulosic fibers-reinforced composite materials: A stepforward in the valorisation of the Posidonia oceanica balls," Compos. Sci. Technol., Vol. 71, no. 16, pp. 1867–1872, 2011.

[8] S. Mansouri, R. Khiari, N. Bendouissa, S. Saadallah, F. Mhenni, and E. Mauret, "Chemical composition and pulp characterization of Tunisian vine stems," Ind. Crops Prod., Vol. 36, no. 1, pp. 22–27, 2012.

[9] F. Bettaieb, R. Khiari, ML Hassan, MN Belgacem, J. Bras, A. Dufresne, MF Mhenni, "Preparation and characterization of new cellulose nanocrystals from marine biomass Posidonia oceanica," Ind. Crops Prod., Vol. 72, pp. 175–182, 2015.

[10] R. Khiari, "Valorization of agricultural and marine waste: application in the fields of textiles, paper and composites", Doctoral thesis, Université Monastir, 2010.

[11] LE Wise, M. Murphy, AA D'Addieco, "Chlorite holocellulose: its fractionation and bearing on summative wood analysis and on studies on the hemicellulose", Pap. Trad. J., vol. 122, no. 2, pp. 35–43, 1946.

[12] JEG Van Dam, MJA Van Den Oever, W. Teunissen, ERP Keijsers, and AG Peralta, "Process for production of high density / high performance binderless boards from whole coconut husk Part 1: Lignin as intrinsic thermosetting binder resin," flight. 19, pp. 207-216, 2004.

[13] S. Ben Brahim and R. Ben Cheikh, "Influence of fiber orientation and volume fraction on the tensile properties of unidirectional Alfa-polyester composite," Compos. Sci. Technol., Vol. 67, no. 1, pp. 140–147, 2007.

[14] V. Fiore, T. Scalici, and A. Valenza, "Characterization of a new natural fiber from Arundo donax L. as potential reinforcement of polymer composites," Carbohydr. Polym., Vol. 106, no. 1, pp. 77–83, 2014.

[15] AK Bledzki, P. Franciszczak, Z. Osman, and M. Elbadawi, "Polypropylene biocomposites reinforced with softwood, abaca, jute, and kenaf fibers," Ind. Crops Prod., Vol. 70, pp. 91–99, 2015.

[16] A. Al-Khanbashi, K. Al-Kaabi, A. Hammami, "Date Palm Fibers as Polymeric Matrix Reinforcement: Fiber

Characterization," Polym. Compos., Vol. 26, pp 486-497, 2005.

[17] L. Segal, JJ Creely, AE Martin, CM Conrad, "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," Text. Res. J., vol. 29, no. 10, pp 786–794, 1959.

[18] F. Béttaieb Ep Khiari, "Valorisation of Tunisian cellulosic waste", Doctoral thesis, Monastir University, 2015.

[19] A. SBIAI, "Composite materials with an epoxy matrix loaded with date palm fibers: effect of tempo oxidation on fibers", Doctoral thesis, National Institute of Applied Sciences of Lyon, 2011.

[20] S. Marais, F. Gouanvé, A. Bonnesoeur, J. Grenet, F. Poncin-Epaillard, C. Morvan, M. Me´tayer, "Unsaturated polyester composites reinforced with flax fibers: Effect of cold plasma and autoclave treatments on mechanical and permeation properties, "Compos. Part A Appl. Sci. Manuf., Vol. 36, no. 7, pp. 975–986, 2005.

[21] M. Ragoubi, "Contribution to improving the interfacial compatibility of natural fibers / thermoplastic matrix via treatment under crown discharge", Doctoral thesis, Université Henri Poincaré Nancy 1, 2010.

[22] A. Stamboulis, CA Baillie, and T. Peijs, "Effects of environmental conditions on mechanical and physical properties of flax fibers," Compos. Part A Appl. Sci. Manuf., Vol. 32, no. 8, pp. 1105–1115, 2001.

[23] M. Ragoubi, D. Bienaimé, S. Molina, B. George, and A. Merlin, "Impact of corona treated hemp fibers onto mechanical properties of polypropylene composites made thereof," Ind. Crops Prod., Vol. 31, no. 2, pp. 344–349, 2010.

[24] F. Fehri, "Valorization of plants from the Kasserine region (Tunisia) in the paper industry", PhD thesis, University of Sfax, 2015.

[25] N. Mechi, "Synthesis of a composite material from phosphogypsum reinforced by Tunisian cellulosic fibers", Doctoral thesis, Monastir University, 2016.

[26] M. El-Sakhawy, "Effect of bleaching sequence on paper aging," Polym. Degrad. Stab., Vol. 87, no. 3, pp. 419–423, 2005.

[27] KL Tovar-Carrillo, K. Nakasone, S. Sugita, M. Tagaya, and T. Kobayashi, "Effects of sodium hypochlorite on Agave tequilana Weber bagasse fibers used to elaborate cyto and biocompatible hydrogel films," Mater. Sci. Eng. C, vol. 42, pp. 808–815, 2014.

[28] L. Boopathi, PS Sampath, K. Mylsamy, "Investigation of physical, chemical and mechanical properties of raw and alkali treated Borassus fruit fiber," Compos. Part B: Eng., Vol. 43, no. 8, pp. 3044–3052, 2012.

[29] N. Reddy and Y. Yang, "Structure and properties of high quality natural cellulose fibers from cornstalks," Polymer, vol. 46, no. 15, pp. 5494–5500, 2005.

[30] SH Aziz and MP Ansell, "The effect of alkalization and fiber alignment on the mechanical and thermal properties of kenaf and hemp bast fiber composites: Part 1 - polyester resin matrix," Compos. Sci. Technol., Vol. 64, no. 9, pp. 1219–1230, 2004.

[31] A. Bezazi, A. Belaadi, M. Bourchak, F. Scarpa, K. Boba, "Novel extraction techniques, chemical and mechanical characterization of Agave americana L. natural fibers", Compos. Part B-Engineering, vol. 66, pp. 194–203, 2014.

[32] O. Faruk, AK Bledzki, HP Fink, and M. Sain, "Biocomposites reinforced with natural fibers: 2000-2010," Prog. Polym. Sci., Vol. 37, no. 11, pp. 1552–1596, 2012.

[33] J. Mounir, WBM Slah, and B. Mohamed, "Characterization of mechanical extracted alfa fibers," Int. J. Fiber Text. Res., Vol. 4, no. 1, pp. 1–4, 2014.

[34] RJA Gosselink, MHB Snijder, A. Kranenbarg, ERP Keijsers, E. De Jong, and LL Stigsson, "Characterization and

application of NovaFiber lignin," Ind. Crops Prod, vol. 20, pp. 191–203, 2004.

[35] A. Ashori and A. Nourbakhsh, "Studies on Iranian cultivated paulownia - a potential source of fibrous raw material for paper industry," Eur. J. Wood Prod., Vol. 67, no. 3, pp. 323–327, 2009.