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Conception of hydrofiber wound dressing from cellulose of esparto

K.Messaoud-Boureghda[1]*, M.Z.Messaoud-Boureghda[2], F.Halouane[3]

[1]Laboratoire des Matériaux Minéraux et Composites, Faculté des Sciences de l'Ingénieur U.M.B.Boumerdes, (ALGERIA)

[2]Département du génie de l'environnement (ALGERIA)

[3]Département de Biologie, Faculté des sciences, Boumerdes, (ALGERIA)

E-mail : kboureghda@yahoo.fr

ABSTRACT

The first synthesis of a cellulose derivative goes back to a little more than a century with the development of industrial production of nitrocellulose, which has promoted the development of ethers and esters of cellulose. The carboxymethylcellulose is a derivative occupies an important place in the industry processing and enjoys a wide field of food and pharmaceutical usage; The hydrophilic character of its fibers and their adsorption capacity fact that either at the base of drug composition and design of a wide range of tissue dressings. These dressings are used to treat the wounds of several natures; they are constituted of supports to which has been added to the fibrous layer carboxymethylcellulose whose role is to suck the molecules produced by the bacteria and wound exudate. In this sense we set the target to conceive a wound dressing using the cellulose contained in stems of the esparto, annual vegetal, widely used in Algeria; To do this, two types of extraction were carried out: one, by alkaline delignification in the presence of temperature, followed by a bleaching with hypochlorite and alkaline purification; the other by direct extraction with organic solvent (acetone) using the Kurchner. Method; The cellulose extracted is subsequently quenched in a solution of 30% sodium hydroxide dried to obtain an akali-cellulose and treated it in an excess of mono chloro acetic acid (MCA), thereby to prepare for the CMC, main component of our wound dressing hydrofibre. The different characterization results (identification, humidity, purity tests, degree of substitution, etc.) showed that the CMC obtained is comparable to that which are commercially available and could then meet our goal.

KEYWORDS

Wound dressing;
Hydrofibre;
Cellulose;
Cellulose- derivatives;
Carboxymethylcellulose;
Cellulosic membranes.

INTRODUCTION

Unlike to common belief, a wound heals faster and better in a humid environment than in dry. This is therefore not appropriate to wound to let it dry air because the cicatrization under the scab is slower, it is best served with dressings application of plasters responds to various stages of cicatrization of a wound[1]. In our study efforts are made to take an active interest on dressings it would be possible fashioned from a derivative cellulose from the vegetable "alfa-Stipa tenacissima L" While the countenance of pure cellulose 25 to 30% in esparto,

is less than that of cotton which can reach 94%[2-3], but that does in no way discourage the initiatives, respect of the market value of the two materials.

Of formula $(C_6H_{10}O_5)_n$, cellulose has degree of polymerization up value of 14 000[4].

Main component of the plants, cellulose is the most abundant organic matter on the Earth (more than 50% of the biomass)[5]. This polysaccharide exists naturally and shows an almost unlimited resources of renewable raw materials[6]. Cotton is the most important source[7]. The rest of vegetables, such as the esparto, the cellulose is 35 to 45%[2] to dependency the species, age and different other factors. This polymer, and particularly derivatives thereof, are defined as material of future, par excellence Resulting from renewable energy sources and allowing to obtain biodegradable products, they would allow create new materials (and so new procedures) and protecting environment: most worry of this century. Also, it would stimulate the industries in various domains: the paper mill, packaging, healthcare (plasters, prosthesis), construction (composite) or carrying (air)[8].

Important industrial raw material, cellulose used: either in the form of crude fiber in the manufacture of pulp or, upon transformation into the chemical industry, for the manufacture of artificial fibers (cellulose acetate, viscose, rayon[9] and various derivatives (celluloid, cellophane, etc.) or explosives such as cellulose nitrate, nitrocellulose. Deputy microcrystalline formit may serve as a binder or for the manufacture of transparent rolling papers. it also used in the design of thermal and acoustic insulation (in the form of panels). For any use of cellulose derivatives and the property really important relates its solubility. This solubility affects its behavior in heterogeneous media Cellulose is insoluble in water but the presence of hydroxylated functions give him a hydrophilic character nature from which hydro colloid[10]. however, we can solubilize in acids, bases or inorganic complexes (Schweitzer liquor)[11]. The CMC is obtained from pure cellulose that we have prepared using the following steps:

1. Preparation of the plant[13],
2. Determination of the total amount of cellulose according to the Kushner and Hofer method[14]
3. Délignification and pulping the esparto
4. Determination of the amount of pure cellulose,[14]
5. Determination of degree of polymerization and comparison with that of the cotton cellulose,
6. Obtaining carboxymethylcellulose by the Lilienfred and Bayer method[15]
7. Characterization of ether obtained. Then, we clean, until neutral pH and pass the product, through a plan plastic screen which has very small mesh sizes, so as to enable the manufacture of a fibrous membrane.

MATERIALS AND METHODS

The esparto used comes from Djelfa, semi-arid steppe of Algeria. The test specimens consist of samples taken from differents bundles of esparto grass. This material is 2 years old, picked in July 2009; this vegetal, grows generally,in the natural state (without any contribution forestry) on a soil depth of 13 to 25 cm, limestone (up has 60%)[16], to 80% sandy, with a rainfall of 250mm 300mm[17]. The stems of esparto are cut into twigs and stored in the laboratory room for 24 hours in order for conditioning the vegetal before the determination of its chemical composition.

Chemical analysis of the esparto

Elemental composition

Determining the capacity in cellulose must go through a chemical analysis of the vegetal which we summarize in the following table:

TABLE 1 : Chemical composition of esparto

Desig nation	Mois ture	Rate Of cellulose	Lignins H_2SO_4	Ash	Extra ctives	Water solubles substances	Hémi-Cellu loses
Content %	10	42,85	18	3,2	2,98	1,95	18

The mineral content and the extracts are measured according to TAPPI method-T.12m -59. The ratio of lignin by the method of SHORGER[9] and the rate of cellulose according to the method of Kushner and Hofer[14]. For the quantification of extractives, the vegetal was treated using a soxhlet with a acetone solution. The achievement of 42.85% of total cellulose (based on dry weight) situated the esparto well behind the linen and cotton whose capacity can reach 94 to 99%[18].

Determination of the amount of cellulose α

42.85% is the total amount of cellulose in the veg-

etal; we treat this part, with a solution of sodium hydroxide at 17, 5%, for the remove fraction of "α"; Then the filtrate was treated with dilute acetic acid to assess the celluloses "β" which is less important for us relatively to its degree of polymerization; By subtraction is obtained the capacity degraded cellulose fibrils which is designated by "γ" Cellulose α is the ordered part of the polymer and whose constitution is similar to that of crystalline cotton cellulose; this fraction is being used in pharmaceutical preparations[19]. One of important feature is the D we determine it by the viscosimetric method.

Evaluation of the degree of polymerization

Theoretically, For cotton, the number of glucopyranose units is approximately 15,000, whereas the cellulose of wood and annual plants, it can reach 10000. In our work we referred with the characteristics of cotton of Sidi Ameur (M'sila) or the degree of viscosimetric polymerization determined in the laboratory is 980. For the tests, we took the previously purified cellulose and performed by the conventional method using the Brokfield viscometer and repeat the same operations that were conducted on samples of cotton quoted above; the results are summarized in the following table:

TABLE 2 : Viscosities and degrees of polymerization of cellulose

Caractéristics → Material ↓	Kinematic viscosity	Relative viscosity	Degree of polymerization
Esparto	8,42	3,008	360
Coton	2,3	0,809	985

Delignification process

To evaluate the mechanical strength of cellulose fibers which would serve to the design of the fibrous membrane, we carried out a chemical delignification in the presence of temperature. We use for this purpose a laboratory autoclave, and for cooking, a solution of sodium hydroxide (NaOH) at 25%. The rods of esparto are hairy and covered on waxes; That could hinder delignification; For this mechanical brushing is performed and a pretreatment within a brine of 30 g / l, with the aim to improve the penetration of cooking chemicals and their reactions with the fibers by swelling and minimize the consumption. The firings are carried according to the parameters that summarized as follows: (TABLE 3).

TABLE 3 : Parameters of delignification

Concentration Of the cooking liquor %	Temperature Level (°C)	Cooking time (mn)	Level (mn)	Hydro module H=L/V
25	150	105	60	5

3 tests firings are conducted under the same conditions, which leads to the production of pulp with the physicochemical characteristics following averages:

TABLE 4 : Physicochemical characteristics of pulp

Yield pulp %	Kappa number	Cellulose %	Minerals %	Whiteness	Unburnt %
55,84	22,33	42,81	2,31	72	1,12

The cellulose obtained has a degree of whiteness equal to 72 °C[20]. This implies the presence of incrusting substances and for obtaining a purified cellulose we treated the pulp with a solution of sodium hydroxide (NaOH) at 8% concentration and we have performed a two bleaching stages with sodium hypochlorite (NaOCl), the residue is collected, weighed and dried in an oven at 105 °C until constant weight is achieved yield: 24%.

Determination of the mechanical strength

The mechanical properties of the fibers are of great importance when it comes to setting the field to use. In our case, the polymer must be transformed, to be used in the design of a dressing, it must meet both good strength, good absorbency and especially flexibility. To measure the strength of the fiber we proceeded to making handsheets dough with a weight equal to 70 g/m2 of pure cellulose, for this, the fibers are energetically dispersed in water at a concentration of suspension equal to 3.5% filtered then pressed by a roll of 10 Kg and dried in air for 72 hours (in a conditioned room). This handsheet was transformed into paper strips 200mm long and 15mm wide and used as test piece for trials on a dynamometer. We note then the tensile strength, which is the tension force to which the strip is broken and we deduce the elongation which characterizes the property of extensibility 2.8% for our fiber against an elongation of 5% on cotton of Sidi Amer outcome realized in a characterization have been the subject of an congres presented at the International Symposium on Wood Sciences held in Montpellier October 24, 2004. The

mechanical strength is fairly good.

Measurement of the degree of polymerization

The same procedure is adopted for the characterization of pulp obtained by cooking as that by Kurschner extraction; the results are summarized in the following table:

TABLE 5 : Mechanical properties of cellulose

Designation	Breaking length (m)	Kinematic Viscosity	Relative viscosity	Degree of polymerization
Value	2390	9,04	3,008	395

The parameters are somewhat better than on the celluloses obtained by organic solvent extraction, this can be explained by degradation of the polymer due to reactions of acid (HNO3) at elevated temperature. The feature values, would logically encourage the use of cotton cellulose, but reasoning with an economic character recovery, we would choose the esparto because it is abundant in Algeria and its area of use is restricted to the manufacture of pulp, anarchic fodder and some crafts.

Preparation of carboxymethylcellulose

The principal aim of our work is in reality to get a cellulose derivative for preparing a hydrofiber wound dressing, for use on exuding wounds[21]. The main component of these dressings is the fibrous membrane consisting of carboxymethylcellulose (CMC)[22]; The CMC is the most important cellulose derivative; Its general formula [C6H7O2 (OH) x (OCH2COONa)] y_n

where n is the degree of polymerisation, y = degree of substitution, x = 1.50 to 2.80 y = 1.50 to 0.2; (x + y = 3.0), we represent the CMC as the configuration below (Figure 1).

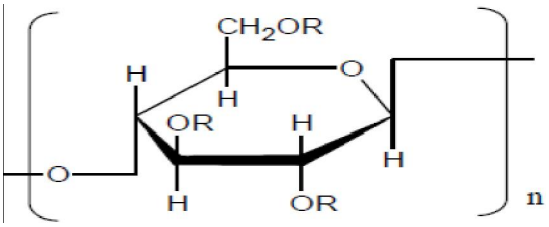


Figure 1: Formula of CMC. (Image N°SIN 466 CAS [9004-32-4] (OIV- Oeno 366 - 2009).

It is a cellulosic derivative containing carboxymethyl groups (-CH 2-COOH) linked to some of the hydroxyl groups of the glucose monomer of the main chain polymer[23]. The degree of substitution of these groups depends on the method of preparation, but remains generally in the range from 0.6 to 0.95 per monomer unit derived[24]. This derivative is generally in the form of granules, powder or fine fibers odorless, white to yellowish; Its field of application is wide and varied (cosmetics, pharmaceutical, food, and other). At our level it would be used as the main element in the design of hydro fiber dressings for to care for the bedsores and wounds, especially caused by burns as internal fibrous membrane which is in direct contact with the wound.

Synthesis of CMC in the laboratory

To prepare the carboxméthylcellulose, we used the portion of á cellulose fibers obtained from alkaline cooking. The synthesis was carried out according to the following protocol:

Alkalization of the cellulose: Soaking within a sodium hydroxide solution at concentrations ranging from 5 to 50%), b). Wringing and elimination of excess hydroxide, followed by drying[25], c). Etherification with monochloro acetic acid in the presence of isopropanol or water[26], d). Filtration and neutralization with acetic acid, e). Purification with alcohol (methanol) and drying of the residue (because it contains up to 40% glycolates f). Characterization of the CMC obtained.

Preparation of the alkali cellulose

The main step within the process of synthesis is the reaction of alkali cellulose obtaining, which drives the modification of the crystalline structure of cellulose and increases the affinity of the fibers by chemical swelling[14]; Also is it necessary that the length of the fibers, in the pulp is homogeneously as possible, because of different lengths provoke different reaction rates. At our level, the fibers have been separated (open), cut greater or lesser uniformly, treated for five hours in sodium hydroxide solutions at concentrations ranging from 5 to 50%; the process is achieved according to the reaction:

$$[C_6H_7O_2(OH)_3]_n + n\ NaOH \longrightarrow [C_6H_7O_2(OH)_2\ ONa]n + n\ H_2O \quad (1)$$

which can be performed with or without solvents[5]. Isopropanol is the appropriate solvent, but We can also

use distilled water;The reaction is exothermic and liberates, nearly 41.5 kcal per mole. After each operation we eliminate the excess of hydroxide by filtration and pressing. The results of absorption of alkali by the fibers are shown in the table and graph below (TABLE 6, Figure 2).

TABLE 6 : Amount of NaOH absorbed

Concentration of NaOH %	Amount of NaOH absorbed
0	0
5	0 ,12
10	0,22
15	0,35
20	0,45
25	0,55
30	0,6
35	0,65
40	0,68
45	0,7
50	0,71

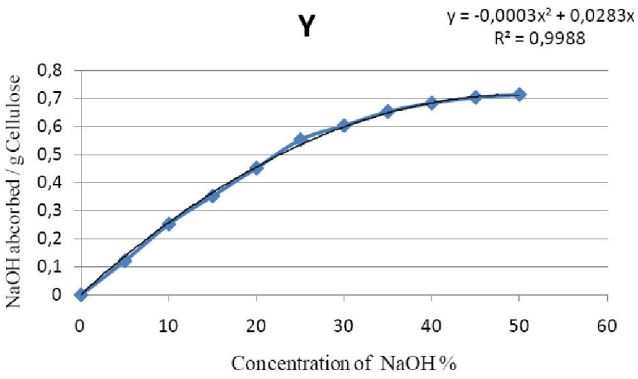


Figure 2 : Absorption of NaOH by cellulose fibers

The test specimens of alkali cellulose thus obtained are treated with solutions of monochloroacetic acid (99.8%) at concentrations of 35, 40 and 45%. For each test the mixture is vigorously stirred on a hot plate provided with magnetic stirrer at a temperature maintained at 70-75 °C for four hours as the solvent we used distilled water, according the following reaction:

$$[C_6H_7O_2(OH)_2ON_a] + nClCH\ COONa \longrightarrow [C_6H_7O_2(OH)_2OCH\ COONa] + nNaCl \quad (2)$$

(with distillated water as solvent)

The CMC gel is subsequently filtered and separated from the solvent and the pH adjusted to 7 after which the product was purified with methanol and dried at 70 °C for one hour[26-29].

Characterization of the CMC obtained

Solubility

Twoo grams of CMC synthesized are mixed with 100ml of distilled water and mixed strongly, we obtain a viscous colloidal solution but no dissolution No reaction with 96% ethanol; These properties allow us to identify the product.

Sodium chloride

The CMC synthesized A sample of is weighed and placed in a 250 ml beaker to which we add 50 ml of water and 5 ml of H2O2 (30%), then we place the beaker in a water bath, stirring to reach a fluid solution. After 20 min (no dissolution is reached), we add 5 ml of H2O2 and continue the heating until complete dissolution. We cool the beaker and add to 100 ml of water and 10 ml of HNO_3 and we place it on a magnetic stirrer for 10 min. We determine the title with $AgNO_3$ 0.1 N; The capacity of sodium chloride is then given in% as follows:

$$C = (AN \times 584, 5) / [G \times (100 - B)] \quad (3)$$

where: C= is the percentage of NaCl, A = volume of AgNO3 solution added (ml); *N* =normality of AgNO3; G = weight of used sample (g), *B* = moisture, determined (in%).

Sodium glycolate

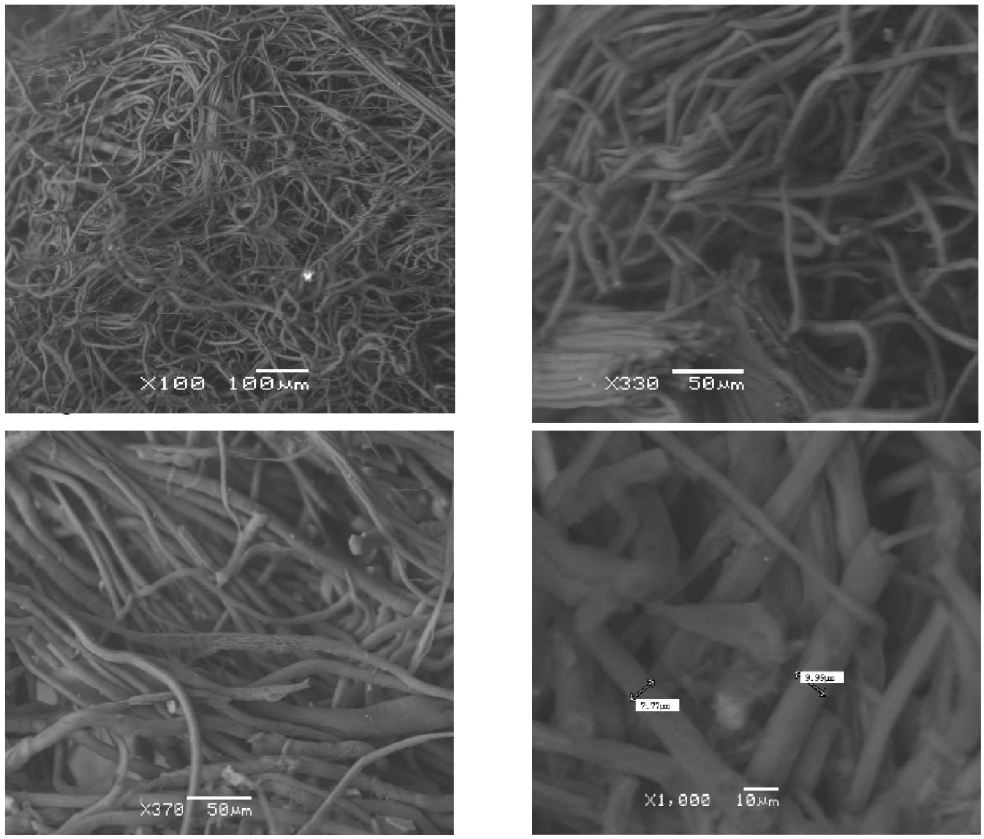
A sample of carboxymethyl cellulose is dissolved into acetic acid (50%), precipitated with acetone in the presence of sodium chloride and filtered. The filtrate containing the sodium glycolate (as glycolic acid) is treated with dihydroxynaphthalene to remove the acetone. The resulting color is measured at 540 nm with a spectrophotometer calibrated using solutions of known concentrations.

Degree of substitution

The degree of substitution (DS) has a maximum value of 3. The substitution of the hydroxyl groups by the carboxy-methyl takes place theoretically at C-2 of the glucose molecule[27,30]. The DS of CMC was determined by the standard method ASTM D 1439[31]. The DS achieved would be less than 0.4 because the CMC swells, but is insoluble in water[32].

A scanning electron microscope (SEM) was used

to characterize the appearance of the dry fibers of samples synthesized. (Figure 3 : a, b, c, d)



a, b, c, d : Carboxymethylcellulose dried fibers magnified under the SEM

Figure 3 : Representations of microscopical dried fibers of CMC synthesized

In comparison to the appearance of the fibers of samples taken at the laboratory level Convatec of Lille (Euro-Pharmat - Lille - 09, 10 & 11 October 2012), our test pieces come in a very adequate appearance. We can clearly see that the entanglement of fibers promises a real opportunity to stay and trap the molecules of exudates, when putting the membrane in contact with the wound.

CONCLUSION

With much caution one might conclude that the result is positive, the syntheses were carried out successfully and the sample realized with the alkali-cellulose obtained with the solution of NaOH (30%), in presence of acetic acid (MCA 40%), has the highest DS. The CMC obtained exhibits a good enough average of brilliance and solubility in water solubility that could be improved by repeating the process of transformation of cellulose, especially since we must consider the variations in properties resulting from different needed treatments; We could also improve the value of the degree of polymerization and the capacity of the pure cellulose of esparto. That would allow us be fixed on the effectiveness and the yield of the process; So, if it was to use this vegetal for obtaining a product of a such importance, we can to propose to improve the conditions of vegetation by a forestry contribution.

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