



Optimized extraction of cellulose nanocrystals from pristine and carded hemp fibres

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ABSTRACT

The extraction of cellulose nanocrystals (CNC) from Carmagnola hemp fibres has been carried out. Before CNC extraction, the effectiveness of two pre-treatment methods, an alkaline chemical and a pectinase enzymatic treatment, applied on the pristine and carded hemp fibres, were compared. Carding allowed removal of most impurities from the fibres, while it had only a modest effect on their structure. After chemical treatment, hemicellulose was removed, more efficiently in carded hemp, and X-ray diffraction suggests an increase in the size of cellulose crystallites. Carded hemp fibres, after interaction with pectinase, show the total decomposition of pectin and hemicellulose. On the basis of these results, carded hemp was selected as start material for CNC extraction and the acid hydrolysis for CNC synthesis was applied on carded hemp after both chemical and enzymatic procedures. The yield of the different hydrolysis methods remains approximately at the same level (around 19%): on the other side, a carding procedure, combined with an alkaline treatment to hemp fibres, represents an optimized process for CNC extraction by acid hydrolysis.

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1. Introduction

In recent years, the reintroduction of hemp, which was basically wiped out of the market due to the consequences of antidrug legislation, is taking place in a number of countries, including Italy, as an effect of the development of hemp varieties with limited content of the psychotropic agent delta-tetrahydrocannabinol (THC). However, the value of THC as a medicine for the treatment of multiple sclerosis suggest separating high THC content varieties for medical purposes, from low THC content ones, aimed at various industrial applications (Croxford et al., 2008). These include, among others, the production of textiles, fatty oils and wood replacement chips while the conversion of hemp seed oil into biodiesel has been lately proposed (Li et al., 2010). In the specific case of Italy, one recently developed very low (less than 0.1%) THC variety is named Carmagnola, from the place it originates in Piedmont; this variety already underwent complete chemical analysis, which suggested that in this variety of hemp polysaccharides form about 70% of

total weight, namely 44% alpha-cellulose and 25% hemicellulose (Gandolfi et al., 2013).

Of course, the development of a productive system involves also the presence of waste by-products and in the case of hemp, this refers particularly to “hemp wool”, usually a bundle of quite short fibres and hemp shives as the inner wooden core of the plant. Lower quality fibres no longer than 30–40 cm are used for the fabrication of hemp wool; when such fibres are mixed with a binder they form layers used for thermal insulation in buildings (Collet et al., 2011). Lower quality fibres are usually excluded from a textile use due to their poor resistance to torque, leading to ineffective draping in fabrics and to scarce friction in strands for ropes, but are nonetheless materials that involve non-negligible labour and costs in their extraction from the plants. More specifically, once cut from the plant, hemp stalks are subjected to retting, i.e., pectin removal, which is normally achieved by open exposure to the environment for a few weeks. During retting, the stalks are turned several times: after retting is completed, they are beaten and crushed (scutched) for ease separation of the fibres from the wooden stalk. The obtained fibres are then cleaned and carded to the desired core content and fineness. In particular, carding is basically a combing operation aimed at obtaining a sliver, therefore disentangling fibres and breaking up locks and unorganized clumps

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of fibre, finally aligning them unidirectionally. All the subsequent processes concern the fabrication of textiles: in other words, after carding, the fibres are ready for operations, such as roving, winding and weaving, which may involve also the application of treatments to improve the mechanical performance of the fibres.

It needs to be noted that most of the above operations are basically tailored on the objective to allow the production of textiles, which is the highest profile product for hemp fibres. Whenever the aim of fibre extraction is not the production of a textile yarn, the question may arise whether the extraction process can be simplified or not. This has been attempted on hemp retting simplification by steam explosion, when the purpose was the production of thermal insulation panels. In the case of the present study, aimed at the production of cellulose nanocrystals (CNC) from low quality hemp fibres, which are therefore not suitable for textile use, the question is whether carding would be still necessary for the purpose. Another open question, regarding plant fibre extraction, is the need to remove non-structural matter, which is mainly formed by pectin and hemicellulose, to expose the cellulose domains of the fibres. This is normally carried out using chemical treatments, the most frequent of which is alkalisation with sodium hydroxide, which derives its origin from the textile industry practice, starting with cotton fibres (Li et al., 2007). Alkali treatment, though effective, has proved to be quite aggressive on a number of fibres, leading to the removal of an excessive amount of material from the fibres and possibly to their embrittlement. An alternative, which has been proposed and applied initially on flax fibres (Akin et al., 2001) and also on other stem extracted fibres, such as hemp and nettle, is the enzymatic treatment through the use of pectinase to remove pectin from the fibre. On hemp fibres, on which a number of research reports are available (Ouajai and Shanks, 2005; Pakarinen et al., 2012), the removal of pectin showed a strong correlation with enzymatic hydrolysis, so that the detachment of single fibre cells within the bast fibre bundle, caused by the partial removal of pectin, increased the availability of the substrate cell wall surface area (Pakarinen et al., 2012).

The extraction of CNC from plant fibres is often performed through acid hydrolysis using sulphuric acid to remove the amorphous cellulose and form highly crystalline cellulose. CNC are typically rigid rod-shaped monocrystalline cellulose domains of 1–100 nm in diameter and from tens to hundreds of nanometers in length, with morphological and structural characteristics, including entanglement and geometrical dispersion, depending on the species, cultivar and agronomical factors, such as plant maturity, characteristics of the soil and fertilisers used. The yield of the extraction process, defined as the quantity of nanocellulose obtained from a given weight of macrofibre, depends on both the crystallinity of the specific plant fibre and on the procedure adopted for extraction. Nanocellulose extraction through hydrolysis of hemp yarns and use of obtained CNC as coupling agent to reinforce hemp fibres has been proposed in Dai et al. (2013).

The method adopted in this research has been applied originally on sisal fibres by Morán et al. (2008) and already employed for incorporation of okra bahmia (*Abelmoschus esculentus*) fibres in a PVA matrix (Fortunati et al., 2013a), from phormium fibres (Fortunati et al., 2013b,c) and from Belinka flax fibres (Fortunati et al., 2013c). The extraction method involves a first chemical treatment leading to the production of holocellulose by the gradual removal of lignin, while the subsequent sulphuric acid hydrolysis process allowed obtaining cellulose nanocrystals in an aqueous suspension. The same method is applied again in this work, starting either from carded or non-carded hemp fibres and applying either chemical or enzymatic treatment on hemp fibres of the Carmagnola variety, to show the effect of the carding process on the properties of CNC.

2. Experimental

2.1. Materials

Hemp (Carmagnola) pristine fibres (p-Hemp) were obtained from Assocanapa in Carmagnola, Piedmont, Italy.

The reagents, toluene, ethanol, acetic acid, sodium chlorite, sodium bisulphate, sulphuric acid and the buffer solution were supplied by Sigma–Aldrich.

The enzymes selected for this work were Pectinex® supplied by Sigma–Aldrich. Pectinex® is prepared using a selected strain of *Aspergillus aculeatus*.

2.2. Carding process

A carding treatment was applied to the p-Hemp fibres. Carding is a mechanical process normally used in the industrial field to disentangle and clean the fibre to produce a continuous sliver suitable for subsequent processing. The main purpose of this work was to analyze the effect of carding process on the pre-treatment efficiency and cellulose nanocrystal extraction yield: chemical, morphological and thermal analyses were therefore conducted on pristine and carded hemp fibres.

The microstructure, dimension and appearance of pristine (p-Hemp) and carded hemp (c-Hemp) were investigated by means of field emission scanning electron microscope (FESEM, Supra 25-Zeiss). The fibres were swollen in distilled water before FESEM observation. A 1 wt% aqueous solution of fibres was stirred for 4 h at room temperature. The solution was then subjected to 1 h sonication over 2 h in 10 min intervals, in order to loosen up the fibres. Few drops of the suspension were cast onto silicon substrate, vacuum dried for 2 h and gold sputtered before the analysis. FESEM images of the fibres were analyzed by the NIS-Elements BR (Nikon) software in order to determine the average diameters of the start materials. One hundred measurements were performed in order to obtain a reliable result.

Fourier infrared (FT-IR) spectra of p-Hemp and c-Hemp fibres were recorded using a Jasco FT-IR 615 spectrometer in the 400–4000 cm⁻¹ range, in transmission mode. The fibres were analyzed using KBr discs made by using pulverized fibres and dust of KBr.

Thermogravimetric measurements (TGA) of p-Hemp and c-Hemp fibres were performed by using a Seiko Exstar 6300 analyzer, in order to evaluate the effect of the carding process on the thermal behaviour of hemp fibres. Heating scans from 30 to 600 °C at 10 °C min⁻¹ in nitrogen atmosphere were performed for each sample.

2.3. Chemical pre-treatment

Pristine hemp fibres and carded hemp fibres were pre-treated before cellulose nanocrystals extraction. The fibres were washed with distilled water several times and dried in an oven at 80 °C for 24 h. Then, they were chopped to an approximate length of 5–10 mm. Finally, a de-waxing step was carried out, boiling in a mixture of toluene/ethanol (2:1, v/v) for 30 min and dried. Subsequently, for cellulose extraction, hemp fibres were firstly treated with 0.7% (w/v) of sodium chlorite NaClO₂; the fibres (liquor ratio 1:50) were boiled for 2 h and the solution pH was lowered to about 4 by means of acetic acid for the bleaching. Then, a treatment with sodium bisulphate solution at 5% (w/v) was carried out and, at the end of this preliminary chemical process, holocellulose (α-cellulose + hemicellulose) was obtained by the gradual removal of lignin. The holocellulose was treated with 17.5% (w/v) NaOH solution, filtered and washed with distilled water. The obtained

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