ASPECTS REGARDING NATURAL DYEING OF ENZYMATICALLY PRE-TREATED CELLULOSIC BLENDED YARNS

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The objective of this study was to investigate the effects of preliminary enzyme treatments and natural dyeing on the characteristics of yarns made from fibrous blends of cotton and enzymatically cottonized hemp. To attain the cottonized hemp fibres, enzyme and ultrasound treatments were simultaneously applied. The cottonization of technical hemp fibres was performed to remove lignin and pectin from the middle lamella in order to obtain small bundles of elementary fibres, with similar features as those of cotton. To investigate the impact of enzyme processes on the characteristics of hemp fibres, physical-mechanical and physical-chemical investigations, including RAMAN spectroscopy and AFM were used. The cottonized hemp and cotton fibres were used to make yarns that were subsequently pre-treated with pectinase, thereafter a natural dyeing with *Allium Cepa* extract was applied. The enzyme pre-treatment was followed by a treatment with tannic acid and pre-mordanting with potassium or iron alum. To determine the efficiency of the enzyme pre-treatment process on natural dyeing, colour measurements and dyeing fastness to washing, light, acid and alkaline perspiration were carried out.

Keywords: enzymatic pre-treatments, natural dyeing, *Allium Cepa*

INTRODUCTION

Among natural fibres, pluricellular cellulose fibres (flax, hemp, ramia, jute) are distinguished from the monocellular ones (cotton) by complexity of the chemical structure, the more accentuated crystal architecture and the presence of the middle lamella with a role of cementing the constituent elementary cells (Asandei and Grigoriu, 1983). In the case of bast fibrous plants, fibres shall develop in bundles that can be subsequently released from the cellular tissue by means of refining and individualization treatments: retting, scutching, carding, cottonization, thus obtaining fibres that can be spun individually or in blends with other natural or synthetic fibres (Thygesen *et al.*, 2011).

In the area of innobilation processes, the development and application of various enzyme systems play an important role, as they are a feasible and easy alternative to the conventional processes in the textile industry and represent new ways to solve the environment-related problems (Kozlowski *et al.*, 2006). Enzyme pre-treatments of textile materials could improve the dyeing process performances through dye uptake increase.

In this sense, this study presents an investigation of the impact of enzyme pre-treatment processes over dyeing behavior and physical-mechanical and physical–chemical characteristics of blended yarns of 70% cotton-30% cottonized hemp. Laccase enzyme treatment was conducted to obtain cottonized hemp fibres and ultrasonication was used in order to accelerate the enzymatic process. In order to ensure a reduced residual content of impurities and an adequate hydrophilicity for the subsequent dyeing in good conditions with natural dyes, the cotton yarns with cottonized hemp content were subjected to enzyme pre-treatment with pectinase.

EXPERIMENTAL PART

Materials

Technical hemp fibres and cotton fibres were used as raw materials for achieving blended yarns. Cottonization enzyme treatment of hemp fibres was performed with laccase Denimcol LAC-LRE (Bezema AG), under pilot conditions, on installations belonging to SC FIRI VIGONIA SA. For the enzyme pre-treatment of cotton/cottonized hemp blended yarns, BioPrep 3000L (Novozymes) pectinase was used. Natural dye extracted from *Allium Cepa* in aqueous solution was used for the dyeing process. Mordanting was carried out with potassium alum and iron alum supplied by Sigma Aldrich and, respectively, with tannic acid supplied by Consors Romania.

Cottonization of Hemp Fibres

The cottonisation of technical hemp fibres was conducted in two stages, the first one consisting in the treatment at 40°C, for 50 minutes, with a chelating agent-EDTA (5g/L), in an alkaline bath with NaOH (pH=11). The second stage consisted in the fibre treatment in a ultrasonic bath at 70°C, for 30 minutes, with 1% laccase in the presence of a mediator (HOBT), at pH=4.5. After the rinsing, squeezing and drying operations, the cottonized hemp fibres were processed on blow room in view of their mechanical cleaning and pre-individualization, being followed by mixing bed formation with cotton fibres and the other operations prior to spinning. Spinning was conducted on an OE unconventional spinning machine, the obtained yarn having a composition of 70% cotton/30% hemp. These yarns were subjected to subsequent enzyme pre-treatment, pre-mordanting and natural dyeing.

Preliminary Treatments

Treatments were conducted on Ugolini laboratory equipment. Classical pre-treatment (P_1) was performed according to the classical alkaline procedure at boiling temperature. Enzymatic pre-treatment with pectinase (P_2) was conducted with 0.2 g/L BioPrep 3000 L at 55°C, for 30 minutes, the pH of the solution being set at 8 with sodium carbonate. Pre-mordanting with metal salts was carried out at concentration of 5% (owf) at 80°C (Hm 1:30), for 45 minutes. The yarns thus treated were washed with hot and cold water, squeezed and dried. Prior to mordanting, a treatment with 4% concentration (owf) tannic acid at 60°C was carried out for 4 h, the samples being afterwards rinsed, squeezed and freely dried.

Natural Dyeing Process

The *Allium Cepa* infusion was prepared by boiling for 45 minutes 20 g of dried onion peels in 1000 mL of distilled water. The resulted mix was stored for 24 hours and afterwards filtered. The dyeing was carried out at 95°C, for 60 minutes, followed by rinsing at 60°C, soaping, hot and cold rinsings, squeezing and drying.

Methods

To highlight the influence of enzyme treatment on the integrity of the hemp fibre as well as to determine the content of residual non-cellulose impurities on the fibre after cottonisation, the following characteristics were determined: average degree of polymerization (SR ISO 5351-1:1999), waxes content (SR 7690:1993), hydropectin content, pectic substances, hemicellulose and lignin (Rusanovschi and Dragnea, 1981). The cottonized hemp fibers were analyzed using a combined AFM-Raman equipment: NTEGRA Probe NanoLaboratory AFM (NT-MDT, Russia)-inVia Raman Microscope (Renishaw, Wotton-under-Edge, Gloucestershire, United Kingdom). The AFM investigations were carried out in a semi-contact mode using NSG30/Au probes from NT-MDT, Russia, and the Raman spectra were recorded at λ = 785 nm. The efficiency of the preliminary treatments performed with pectinase over natural dyeing, in terms of colour difference attributes and colour fastness, was determined through colour measurements (ISO 105 J03: 2001) and colour fastness to washing (SR EN ISO 105-C 10: 2010), acid and alkaline perspiration (SR EN ISO 105-E 04:2013) and light (SR EN ISO 105-B02:03).

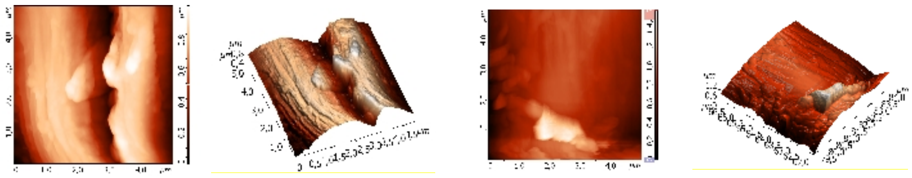
RESULTS AND DISCUSSIONS

The analysis of the characteristics obtained for the hemp fibres cottonized with EDTA/laccase (Table 1) reveals a decrease of impurities content in the fibre, compared with the control raw fibres (untreated), the lignin content decreasing by over 60% and the pectin content by over 40%. The enzymatic cottonization treatment applied has determined a decrease of the average degree of polymerization compared to the control sample without affecting the macromolecular chain integrity of cellulose from hemp fibre.

Table 1. Physical–chemical characteristics of the enzymatically cottonized hemp fibres

Determined characteristics	Untreated	EDTA/laccase
Lignin content (%)	7.6	2.63
Waxes and fats content, (%)	2.4	1
Hydropectin content, (%)	2.03	1.5
Hemicellulose content, (%)	17.72	18.25
Pectin content, (%)	4.15	2.48
GMP	2631	2323

The morphologic structure of the hemp fibers has been revealed by performing AFM investigations and this is presented in Figure 1. The surface of untreated fibers is rough and not well delineated compared with smoother surface of treated hemp fibers. For the treated hemp fibers the cellulose fibrils are visible due to removal of waxes, fats, pectins, hemicelluloses, and probably exhibiting the primary cell wall (Le Troedec *et al.*, 2011).



a. b. c. d.

Figure 1. Topography: a. - 2D of raw hemp fibres, b.- 3D of the raw hemp fibres' surface, c.- 2D of laccase treated hemp fibres, d.- 3D of the surface of laccase treated hemp fibres

Raman spectra exhibited band positions similar with those reported in literature (Figure 2) (Kavkler and Demsar, 2011; Osterberg *et al.*, 2006). For both untreated and treated hemp fibers the bands atributed to cellulose were observed (1095, 1120, 2900 cm^{-1}). The Raman data confirmed that the enzyme treatment of the hemp fibers did not alter crystallinity type I of the cellulose and successfully removed lignin and pectins.

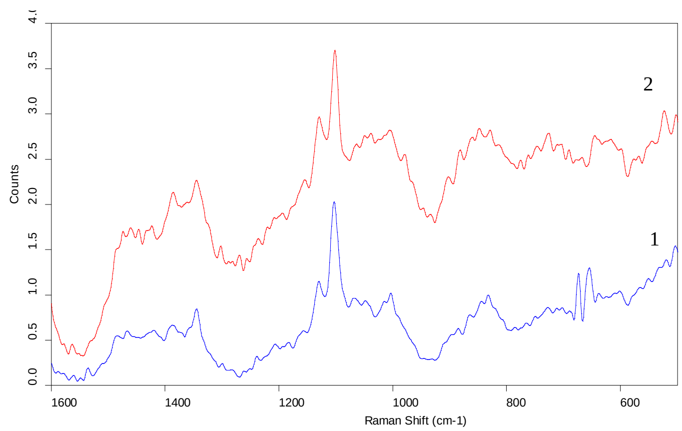


Figure 2. Raman spectra recorded for untreated hemp fibers (1), and laccase treated hemp fibers (2)

Table 2. Physical-mechanical characteristics of blended yarns before and after dyeing

Variant code	Physical–mechanical characteristics			
	Yarn count (Nm)	Tensile strength (N)	Breaking elongation (%)	Breaking length (km)
Raw yarn - untreated	17.2/1	4.49	10.65	7.70
P_1-Potassium alum + Dyeing	16.4/1	3.93	11.31	6.45
P_2-Potassium alum + Dyeing	15.8/1	3.99	10.80	6.30

The enzyme pre-treatment of blended yarns made of cotton and cottonized hemp, followed by mordanting and natural dyeing, leads to a decrease by 11.13 % of the breaking strength and respectively by 18.18 % of the breaking elongation, in comparison with the untreated sample yarns (Table 2). The classical variant of alkaline pre-treatment, followed by mordanting and natural dyeing has a similar behaviour, leading to a decrease by 12.47 % of the breaking strength and, respectively, by 16.23 % of the breaking elongation. These decreases of strength characteristics are normal in the case of cellulosic yarns subjected to wet-thermal finishing treatments. It has also been noticed that the treatments applied do not influence in a negative manner the breaking elongation, the values being similar to those obtained for the raw yarn.

Table 3. Colour difference of blended yarns dyed with *Allium Cepa*

Variant code	X	Y	Z	Colour difference				
				DL*	DC*	DH*	DE*	Mark
P_1 + Potassium alum	17.11	15.21	4.76	REFERENCE				
P_2 + Potassium alum	17.85	16.07	5.13	1.15	-0.16	0.95	1.50	4

In the case of a similar dyeing process, preliminary treatments carried out in a differentiated manner (classically or enzymatically), have influenced the initial whiteness degree (or yellowness degree) of the sample and implicitly led to a total colour difference after dyeing of 1.5 between the enzymatically and classically treated samples (Table 3). The positive value for DL* (lightness difference) reflects a lighter colour for yarns subjected to enzyme preliminary treatment compared to the control sample subjected to classical treatment. The negative value obtained for DC* (difference in chroma) indicates a more unsaturated colour of the sample subjected to preliminary enzymatic treatment, compared to the classically treated control sample.

Table 4. Colour fastness of blended yarns dyed with *Allium Cepa*

Code	Colour fastness												
	Washing				Acid perspiration				Alkaline perspiration				Light
	Colour change	Colour staining			Colour change	Colour staining			Colour change	Colour staining			50ºC, RH 45% 84 h
		CO	PA	WO		CO	PA	WO		CO	PA	WO	
Tannic acid + Potassium alum + Dyeing													
P_1	3-4	3	4	4	4-5	4-5	5	5	4-5	5	4-5	5	3-4
P_2	3-4	3	4	4	4-5	5	5	5	4-5	5	5	5	3
Potassium alum + Dyeing													
P_1	3-4	3	4	4	4-5	4-5	5	5	4-5	4-5	5	5	3-4
P_2	3	3	4	4	4-5	4-5	5	5	4-5	4-5	5	5	2-3
Tannic acid + Iron alum + Dyeing													
P_1	4	4	4-5	4-5	4-5	4-5	5	5	4-5	4-5	5	5	5
P_2	4	4	4-5	4-5	4-5	5	5	5	4-5	5	5	5	5
Iron alum + Dyeing													
P_1	4	4	4-5	4-5	4-5	4-5	5	5	4-5	4-5	5	5	5-6
P_2	3-4	3-4	4-5	4-5	4-5	5	5	5	4-5	4-5	5	5	5-6

Observations: Evaluation on the grey scale: *5- very good; 4/4-5-good; 3/3-4- moderate; 2/2-3-low; 1/1-2- very low;* ***Evaluation on the blue scale:*** *8- exceptional; 7-excellent; 6-very good; 5-good; 4-acceptable; 3- moderate; 2-low; 1- very low.*

Analyzing the data from Table 4 it is noticed that, irrespective of the pre-treatment method applied for cellulose fibres hydrophylization (classical or enzymatic variant), the colour fastnesses to washing and to light of the yarns variants pre-mordanted with/without tannic acid-potassium alum are in general moderate, while the colour fastnesses to acid or alkaline perspiration are good and very good. The pre-mordanting treatments with iron alum improve the colour fastness to light, the marks obtained being higher with 1½-2½ tones compared to the samples pre-mordanted with potassium alum. Furthermore, in the case of pre-mordanting with iron alum better values for washing fastness are obtained, the ratings obtained both for colour change and for colour staining being higher by ½-1 tones compared to the variant subjected to potassium alum pre-mordanting.

CONCLUSIONS

Following the cottonization of hemp fibres with EDTA/laccase, in ultrasonic bath, the successful removal of lignin and pectin from the fibres surface was observed, the enzyme treatment being an efficient alternative to the classical chemical cottonization treatment. Starting from the enzymatically cottonized hemp fibres, it was possible to make spun yarns in blend with cotton by unconventional OE spinning technology. The preliminary treatment of the blended yarn with an enzyme from the pectate lyase class has provided adequate hydrophilization of the cellulose fibres in fibrous blend, leading to even dyeing performed with natural dye extracted from *Allium Cepa*. The pre-mordanting with iron alum provides better values for fastness to washing and to light, compared to the pre-mordanting with potassium alum.

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