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Calcium Content Indicator of Scouring Efficiency

Abstract
The pectin content of cotton fibers disrupts the uniform dyeing of cotton materials, decreasing their quality. The process of pectin elimination, known as scouring, may be realised by classic alkaline treatment or ecological enzymatic procedures. Pectins are galacturonic based polymers having as monomers: galacturonic acid (mainly as calcium salt) and methyl-galacturonate. The efficiency of pectin elimination is usually evidenced by analyses of the hydrophilicity and weight loss of the scoured material. A solution for accurate evaluation of the scouring degree is measurement of the calcium content due to diminishing of calcium content proportional with pectin removal.

Key words: *scouring, bioscouring, calcium content measurement, hydrophilicity.*

Introduction

Cotton is the most important raw material for the textile industry, comprising over 38% of the fibres consumed [1]. Large cotton use is based on its qualities like softness, comfort ability, ease of dyeing and printing, durability, and even the biodegradability of textile waste based on cotton. The main component of cotton is cellulose, a polysaccharide formed by the 1-4 link of β-D-glucose. In the external cuticle there are also other components. According to literature [2], pectins a family of complex polysaccharides that contain 1-4 linked α-D-galacturonic acid molecules are present as a major component in the cotton cuticle (see ***Figure 1***) [3], esterified with methanol or as calcium salts.

Calcium ions make the pectin chains interact by means of a cross-bridge formation [4, 5]. The OH groups of the carbohydrate molecule coordinate with the calcium ion to reinforce the supramolecular structure [6]. These structures stabilise the pectin polymers, making their removal difficult. The presence of pectin poses technical problems during the wet processing of cotton and cotton blended textile materials [7].

The removal of the non-cellulosic constituent from cotton is called the scouring process, and may be performed in a classical way, by treatment with alkaline solution, which solubilises the pectin or biochemically, by treatment with an enzyme, like a pectatlyase [8 - 13] or with a mixture of enzymes [14 - 17], etc. Besides the specific reagent for pectin removal, the scouring solution contains wetting agents and polydentate ligands like di-sodium salt of ethylenediamine-tetraacetic acid (EDTA) [18] or sodium citrate [8] as calcium complexing agents. The ligands help pectin elimination from the cuticle by destroying calcium bridges through the formation of coordination compounds with calcium ions.

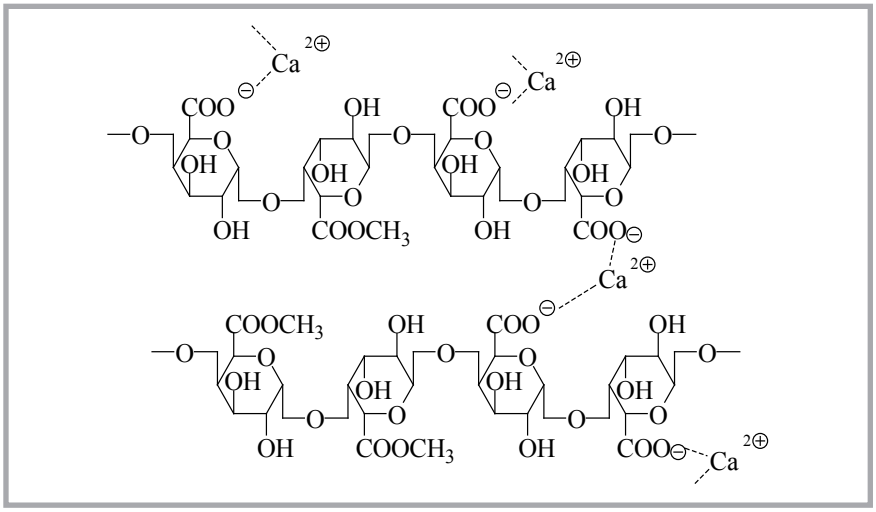

Figure 1. *Pectin structure.*

The usual quantitative measures for pectin removal from a cotton sample are the weight loss, and hydrophilicity of the material, the latter being determined by the drop method [10], sinking test [19, 20], or other procedures [21, 22].

The diminishing of the calcium content could be another way of measuring the pectin elimination, taking into account that calcium ions are directly connected to the polygalacturonic polymers and the diminishing of calcium content is an indicator of pectin removal. Thus the paper presents the results obtained by measuring the calcium content before and after different scouring treatments, comparing the results obtained with those given by determination of the weight loss and hidrophilicity of the scoured materials.

Materials and methods

100% cotton textile material was of knitted jersey structure, with a weight of 120 g/m^2. The reagents were of analytical grade, purchased from Sigma-Aldrich (USA) or Merck (Germany). For bioscouring a commercial product, BioPrep 3000 L, supplied by Novozym,

was employed. The enzyme used was a pectinlyase (E.C. 4.2.2.2). The activity of the enzyme was determined by the method described in literature [23] monitoring the absorbance at 235 nm. The experimental activity was 0.039 U per mg of commercial enzyme.

The non-ionic wetting agents Sandozin NIT (a poly-etoxylated alcohol) and Felosan RGN (mixture of etoxylated fatty alcohols) were supplied by Bezema (Switzerland). The anionic surfactant Sulfolen 148 (polar moiety a sulfate) was supplied by ROTTA Gmbh (Germany).

The di-sodium salt of ethylenediamine-tetraacetic acid (EDTA) was purchased from Sigma-Aldrich.

Enzymatic treatments were performed in a buffered solution of pH 8.8 (optimum for the enzyme), prepared from H_3BO_3, KCl and NaOH of high purity grades, at a ratio necessary for establishing the pH value.

Experimental parts

Pre-treatment of textile material

The knitted cotton was firstly degreased by treatment with a water solution of Na_2CO_3 (5 g/l) and Felosan RG-N (5 ml/l). The liquor-to sample ratio was 1/10 (ml/g), with an incubation time of 1 h, at a temperature 80 - 90 °C. After the treatment, the material was washed and dried.

Bioscouring process

Enzymatic treatments were performed in an alkaline buffer solution prepared from a mixture of H_3BO_3, KCl and NaOH at a ratio leading to pH 8.8. The mixture contained different quantities of enzyme, Sandozin NIT as a wetting agent, and EDTA, for calcium coordinative bounding, (which was or not added - see ***Table 1***). The liquor-to fabric ratio was 15/1 (ml/g). The mixture was kept for one hour at 55 °C. Afterwards the textile material was carefully washed with water at 90 °C and then dried.

Alkaline scouring

The classical scouring process was performed by the immersion of the textile material into a solution of NaOH (5 g/l), Na_2CO_3 (2 g/l), $Na_2S_2O_4$ (2 g/l), $NaHSO_3$ (1 g/l), EDTA (1.25 g/l), Sulfolen 148 (2 g/l) and Felosan RGN (2 g/l). The liquor-textile material ratio was 15/1. The material was kept for 1 h at 98 °C. The knitted cotton was then washed with water and dried. This experiment was performed with four similar knitted cotton samples of 100×100 mm, the average values of the experimental data being taken into consideration for the scoured material properties.

Textile sample weight measurement

The weight of the textile samples was determined using a high performance Sartorium MA 100 thermo balance. Measurements were performed for the initial and after scouring textile samples, in order to calculate the weight loss.

Hydrophilicity of scoured cotton

Circular samples of 3 cm of cotton material were immersed in a 7 cm height column of water in a 600 ml beaker and the time of sinking was determined [24]. The sinking times were measured with a stopwatch for three similar samples, and the arithmetical mean of the results was recorded.

Calcium content determination

For each sample of textile material (named sample henceforth) the following procedure was applied:

1 g of the sample was treated for wet digestion with a mixture of concentrated acids, namely 65% HNO_3 and 70% $HClO_4$ at volume ratio 3/1 and heated until dry. The residue was dissolved into 0.6 N HCl and filtered in a 10 ml vial.

To eliminate interferences in the determination, 0.5% $LaCl_3\ 7\,H_2O$ was added to the control, standard and sample solutions at volume ratio 9/1.

A Unicam 929 AA-Solar System ET-AAS equipped with an Unicam GF-90 graphite furnace and FS-90 autosampler was used. The operational conditions were as follows:

- wavelength: 422.7 nm;
- slit width: 0.5 nm;
- injection volume: 1 µl;
- burner height : 4 mm;
- acetylene flow : 2.5 l/min;
- air flow: 13.5 l/min;
- hollow cathode lamp current: 7 mA.

A Merck standard solution was used to prepare a calibration curve with at least 4 different concentrations of calcium within the analytical range, the correlation coefficient being ≥ 0.990. Periodical checking for accuracy was performed every 20 samples. The concentration of calcium in the sample solutions was determined based on the standard curve prepared. For each sample solution, three replicates were made and the average value calculated.

Results and discussion

The removal of pectin from the cotton cuticle is essential for the good finishing of textile materials. Thus the scouring process is an important component of cotton treatment. The process was performed at the beginning with alkaline solutions, but lately, due to environmental demands, the bio-scouring process has developed. Both alkaline and enzymatic scouring were performed and the efficiency of the different treatments compared based on the measurement of the calcium content before and after the process.

The enzymatic scouring was performed in alkaline conditions due to the optimal pH range indicated for the pectinlyase involved in the process. In the case of bio-scouring different reaction conditions were carried out in order to evidence the importance of enzyme content, as well as the need for wetting and chelating agents. As a wetting agent, Sandozin NIT was chosen considering its biodegradability and stability in working conditions (alkaline). EDTA was used for the elimination of calcium ions by chelate formation with the octahedral structure proposed, as presented in ***Figure 2*** [25].

For the bio-scouring process, different reaction conditions were imposed, with various ratios of enzyme-material expressed as a percentage of cotton weight (% owc – over weight cotton), with different quantities of the wetting

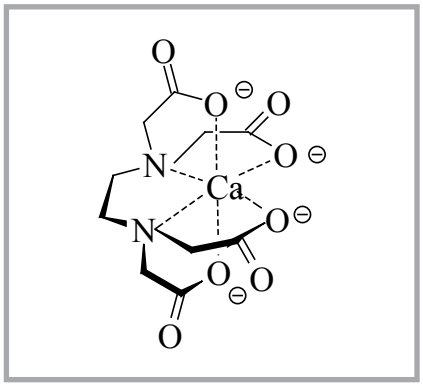

Figure 2. *Calcium EDTA chelate structure.*

Table 1. *Bioscouring process reagents.*

Knitted cotton	Enzyme content, % owc	Sandozin NIT, ml/l	EDTA, g/l
Sample 1	0.68	5	0.5
Sample 2	1.55	5	0
Sample 3	1.55	0	1.25
Sample 4	1.55	5	1.25
Sample 5	1.55	10	1.25
Sample 6	1.55	1.75	2.5
Sample 7	2.41	8	2.0

Table 2. *Properties of scoured cotton samples.*

Sample	Type of scouring	Weight loss, %	Hydrophilicity, s	Calcium content, mg g^{-1}
Sample 0	-	0		0.6525
Sample 1	Bio-scouring	1.52	2.5	0.5169
Sample 2		1.05	3.0	0.6340
Sample 3		1.22	2.5	0.3632
Sample 4		1.50	2.0	0.4153
Sample 5		1.51	3.0	0.3387
Sample 6		1.16	2.0	0.5297
Sample 7		1.86		0.0741
Sample 8	Alkaline scouring	3.00		0.0717

agent and in the presence or not of EDTA. Details concerning the enzymatic scouring are illustrated in ***Table 1***. The scouring process was performed according to the general method described before (see ***Materials and methods***). For each type of experiment, three similar test samples with dimensions of 100 mm × 100 mm were processed.

The experiments varied in the content of enzyme, wetting agent and calcium chelating reagent. Commercial enzyme, with an activity of 0.039 U/mg, was taken from 0.68 to 2.41% of the cotton sample weight. Sandozin NIT was added in the amount of 0 to 10 g per l of the bio-scouring solution. Calcium chelating reagent EDTA was added in the amount of 0 to 2.5 g per l of bio-scouring liquor.

The alkaline scouring was performed as described in the experimental part.

Evaluation of the scouring process was based on the following properties of the knitted cotton: weight loss, hydrophilicity, and calcium content before and after the treatments. The experimental results are presented in ***Table 2***. The weight loss of each sample was calculated based on the known formula (1):

$$\Delta W = 100\,(W_1 - W_2)/W_1 \qquad (1)$$

where:

ΔW – weight loss in %;

W_2 – weight after scouring in g;

W_1 – weight before scouring in g.

The average values of triplicate experiments are presented in ***Table 2***.

Due to the fact that the results obtained by using the drop test may give errors, being influenced by the change in pore radius of fabric samples resulting after different treatments [11], another procedure was applied. The hydrophilicity of the textile materials was measured using the sinking time as described in the experimental part.

The calcium content was determined by the method of Atomic Absorption Spectroscopy as described in the experimental part. All the results obtained are given in ***Table 2***. The bioscoured samples are labelled as in ***Table 1***. In addition, the initial sample of the knitted cotton, labeled as *Sample 0*, and that obtained by alkaline scouring, *Sample 8,* have been added in ***Table 2***.

Analysis of ***Table 2*** data leads to the following assertions:

- Taking in account the connection between the pectin and calcium contents, the diminishing of the calcium content seems to be a correct measure of pectin removal.
- The weight loss does not only reflect pectin elimination, other components could also be included (fats, proteins, etc.), as in sample 1 where ΔW is 1.52% but according to the calcium content and the hydrophilicity value, there is still unresolved pectin.
- The hydrophilicity measurements do not reflect the pectin removal correctly. A good value for the sinking test seems to be not related with higher pectin removal (see sample 4).
- Similar weight loss values do not reflect the same quantity of calcium removal (sample 1, 4 & 5). The same affirmation could be made for similar values of hydrophilicity (sample 4 and 7).
- The wetting agent seems to be not so important in connection with calcium removal by scouring, with different quantities of this agent in the bio-scouring solution giving similar results (sample 3 - 5).
- For the bio-scouring process the presence of EDTA is important; unfortunately it led to poor results concerning textile material properties (sample 2). At the same time applying more chelating agent does not improve the results (sample 6).
- The sample with the highest ratio enzyme/textile material gives similar results with the alkaline scouring process but at a lower weight loss, which means a higher mechanical resistance for the bio-scoured material (sample 6).

Conclusions

Samples of knitted cotton, previously degreased, were scoured in different conditions using the classical alkaline and enzymatic procedures. The efficiency of the scouring process was expressed by the weight loss, hydrophilicity and calcium removal. Based on the experimental results the calcium content proved to be a more accurate measurement of pectin removal by scouring compared with the values for weight loss and hydrophilicity, which are not a true expression of pectin removal.

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