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EFFICIENCY ASSESSMENT OF THE DIFFERENT SCOURING CONDITIONS OF COTTON MATERIALS BY RUTHENIUM RED DYEING

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***Abstract**: Natural fibres are subjected to scouring treatment in order to remove different impurities like waxes, organic acids, pigments and pectins. Pectines are found in the plant cell walls. From the chemical point of view are polysaccharides. The modern trends in different industrial sectors are based on the utilisation of eco friendly treatments to remove them. In our case, the classical alkaline procedure was substituted by an enzymatic one. On 100 % of cotton samples were applied different bioscouring treatments with a pectinases mixture in different conditions. All the bioscouring treatments were developed in presence of ultrasound (45 KHz). The reaction bath contained a commercial pectinolytic product, a complexing agent and a washing agent. There were used diffent enzyme concentratios and the treatment time was variable. To determine the samples behavior toward the enzymes action, the residual pectin was quantified. Ruthenium red dye was chosen since it is considered to be a specific one for binding pectin presented in the fibres. The measurements were done spectrophotometrically with a Datacolor 500 spectrophotometer and the colour strength ratio [K/S] was obtained by measuring the reflectance at 530 nm. The results obtain in case of each treatment were compared with the one determined for the untreated sample, which was considered to have the highest amount of pectin.*

***Key words:** cotton fabric, pectins, ruthenium red, dyeing, pectinase, ultrasound*

1. INTRODUCTION

As pectin are named a group of compounds closely related from the chemical point of view. They are polysaccharides ensuring primarily the plants cell walls mechanical resistance. The pectin has an anionic structure, which is considered to contribute also to ionic transportation, to influence the walls porosity and its permeability to enzyme [1]. Studies made on the pectine structure showed a complex matrix made of different monosaccharides and types of linkages. The main residue present is considered to be the galacturonic acid which has partially esterified acidic groups. It is considered that between the carboxylic unesterified groups of two pectic chains are formed calcium bridges [1]. As shown in the literature, the pectin carboxylic groups show two different hydrolysis

models. One type of the acidic group is affected by the pectinesterase produced by higher plants, and the other one by microbial enzymes or alkali treatments [2].

In our case, we used a mixture of microbial pectinases to hydrolyse and eliminate the methil groups from the pectin chain present in the cotton fibres. As control method, to determine the efficiency of the bioscouring process the colour strength ratio [K/S] was determined. The samples were treated with ruthenium red dye. It is known that it has the property to particular link the pectin's carboxylic groups internally located. Calcium forms bridges between pectin's different acidic groups linked in the chains. During the treatment, the calcium pectate become red colored due to the fact that the intermolecular reactive clusters are not stericaly affected by the calcium ion [2]. A less colored sample will indicate a higher efficiency of the bioscouring treatment. The ruthenium red method is frequently used now to determine the quantity of residual pectin from natural fibers or fabrics after application of different specific treatments.

The intention to use an eco friendly pretreatment is based on the wold trend to protect the environment by using natural, biodegradable, non aggressive industrial procedure. In many researches are proposed viable solutions to use recycled natural material. Also, some of the synthesis reagents used could be successfully replaced by natural ones. For example, recycled nonwoven cotton treated with a natural amino polisscharide (chitosan) have been obtain good results regarding the antimicrobial properties, the biodegradability of the product an also of the mechanical strength and flexural rigidness index [3]. The chitosan positive influence on reducing the cotton stiffness has been proven not only to the fiber but also to the fabric [4].

The results presented in the literature underline the utility of using the ultrasound in the bioscouring treatments. It was shown that a frequency varying between 40-270 kHz has less influence on enzyme activity [5]. Also the two new approaches for cotton pretreatment, enzymes and ultrasound, could successfully represent an eco alternative to the aggressive alkaline treatment, by decreasing the industrial wastewater quantity and the effluents non degradable chemical charge. The positive influence of the bioscouring treatment developed in an ultrasound media has been observed not only for the cotton fabrics but also in case of the cotton slivers [6].

Recent research underlines the efficiency of the bioscoring treatment on cotton fibers and the possibility of natural dyes recovery using pectinases. This creates the opportunity to decrease pollutants concentration to acceptable level [7].

2. EXPERIMANTAL PART

2.1 Materials

For determinations were used 100 % cotton fabric characterised by: width (150 ± 3 cm), weight (200 ± 10 g/m^2), and warp of 100 % cotton yarn with Nm 25/2 and weft of 100 % cotton yarn with Nm 25/1.

The enzymatic product Beisol PRO was a mixture of pectinase purchase from CHT Bezema Company. Denimcol Wash RGN used as surfactant, was supplied by the same company. Sulfolen 148 (S-148, alkyl polyglicol ether) was provides by Rotta Company. The ruthenium red dye, sodium citrate, sodium hydroxide, sodium carbonate, sodium bisulfite, sodium silicate were purchased from Sigma-Aldrich.

2.2 Methods

2.2.1 Cotton pretreatment before bioscouring

Initialy, the cotton samples were washed with hot water at 100 °C in an AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company-USA. After that, were dried, conditioned and weighing according to the specific international standards.

2.2.2 The bioscouring procedure

The bioscouring procedure was made in ultrasound (45 KHz) bath in the presence of commercial pectinolytic product Beisol PRO. The enzyme concentrations varied between 1-3 % (o.w.f – concentration over fiber), 2 g/L sodium citrate and 0.5 % Denimcol Wash RGN. The reaction was developed at 55 ^{o}C. The exposure time has variable ranging from 15-55 min. and the liquor to fabric ratio was 1:20.

For the alkaline treatment, the exposure time was 1 h at 100 ^{0}C, and a treatment bath consisting of: 10 g/L sodium hydroxide, 5 g/L sodium carbonate, 1 g/L sodium bisulfite, 2 g/L sodium silicate and 2 g/L of wetting agent Sulfolen 148 (S-148, alkyl polyglicol ether) was used.

After applying the above treatments, the cotton samples were washed with hot (70°C) and cold water and dried at room temperature.

2.2.3 The dyeing treatment with Ruthenium red

The dyeing bath was made of: 0.2 g/L ruthenium red dye, 1.0 g/L ammonium chloride, 2.5 ml/L ammonium hydroxide solution (28 %) and 1.0 g/L Denimcol Wash RGN. The nonionic surfactant was used to obtain the dye's uniformly adhesion to the cotton surface [8].

2.2.4 The spectrophotometric analisys

The cotton samples were analyzed using the Datacolor 500 spectrophotometrer. It was measured the colour strength [K/S] of the bioscoured samples after dyeing with ruthenium red. The reflectance (R %) was measured at 530 nm and K/S values were calculated by according to equations (1) and (2):

$$K/S = [\{(1-R)^2 / 2R\}] \quad \textbf{(1)}$$

$$\text{Color Strength} = [(K/S)_{\text{Batch}} / (K/S)_{\text{Standard}}] \times 100 \quad \textbf{(2)}$$

where: R-reflectance measured at 530 nm;

K/S_{Batch} -color strength of the dyed treated sample;

K/S_{Standard}-color strength of the standard.

The pectin amount for enzymatic treated cotton samples was determined comparing it with the control one. The control one had the highest pectin amount (untreated sample). The sample from the alkaline treatment was considered to have the least amount of pectin.

3. RESULTS AND DISCUSSIONS

An effective pretreatment of the material is given by the removing of natural attendants, including pectin. The color strength [K/S] value is a number related to the amount of the dyestuff present in a substrate. For bioscoured cotton samples, it was determined after dyeing with ruthenium red, which in the presence of calcium ions from pectin forms salts giving a color reaction. The [K/S] values were directly calculated by the DataColor Tools software from the reflectance measured at the wavelength of 530 nm. From these data, the percentage of residual pectin could be calculated.

Table 1 and Table 2 show the [K/S] values and the percentage of residual pectin for all types of experimental conditions for the cotton fabric samples.

Table 1: *The color strength [K/S] of the ruthenium red dyed cotton samples treated in different conditions*

Sample	Enzyme [%]	Treatment time [s]	Color strength [K/S] Rhutenium red
1	1.30	21.00	0.4975
2	2.70	21.00	0.4415
3	1.30	49.00	0.4508
4	2.70	49.00	0.3759
5	1.00	35.00	0.2678
6	3.00	35.00	0.2452
7	2.00	15.00	0.6741
8	2.00	55.00	0.3951
9	2.00	35.00	0.3320
10	2.00	35.00	0.3302
11	2.00	35.00	0.3310
12	2.00	35.00	0.3386
13	2.00	35.00	0.3596
Alkaline			0.0012
Control			2.6973

Table 2: *The percentage of residual pectin for cotton samples treated in different conditions*

Sample	Enzyme [%]	Treatment time [s]	Residual pectin [%]
1	1.30	21.00	18.44
2	2.70	21.00	16.37
3	1.30	49.00	16.71
4	2.70	49.00	13.94
5	1.00	35.00	9.93
6	3.00	35.00	9.09
7	2.00	15.00	24.99
8	2.00	55.00	14.65
9	2.00	35.00	12.31
10	2.00	35.00	12.24
11	2.00	35.00	12.27
12	2.00	35.00	12.55
13	2.00	35.00	13.33
Alkaline			0.04
Control			100.00

As a direct result of dyeing with ruthenium red, for the enzymatic treated samples, lower values of the intensity of dyeing [K/S] were obtained compared to the control sample because of the pectin elimination. Considering that the untreated cotton sample (control) has the higher quantity of pectin it showed the biggest color strength of 2.6973 due to the complexation between pectin and ruthenium red dye. The values obtained for enzymatically treated cotton samples decreased by a percentage between 75 % - 33 % compared to the control. For alkaline treatment a ~ 99 % decreasing was obtained. The alkali-treated sample is considered to have 100 % pectin removed; therefore it has the lowest [K/S] value of 0.0012.

All enzymatic treatments shows small amounts of residual pectin, these ranging between 9.09 % for sample 6 (3 % o.w.f. enzyme concentration and 35 minutes as enzyme action time) and 24.99 % for sample 7 (2 % o.w.f. enzyme concentration and 15 minutes as enzyme action time).

The smallest amount of residual pectin is present in the sample treated with 3 % o.w.f. enzyme for 35 minutes, followed by sample 5 (9.93 % o residual pectin) which was treated with 1 % o.w.f. enzyme concentration for 35 minutes.

A higher quantity of residual pectin is presented by samples 1 (1.3 % o.w.f. enzyme concentration and 21 minutes as enzyme action time) and 7 (2 % o.w.f. enzyme concentration and 15 minutes as enzyme action time) with a percentage of 18.44 % and 24.99 %, respectively. A reproducibility of the data can be seen in case of the samples from 9 to 13 (2 % o.w.f. enzyme concentration and 35 minutes as enzyme action time).

The variation of the residual pectin quantity from the treated cotton samples depends on the treatment conditions, which is influenced by both the concentration of the enzyme used and the time of its action.

4. CONCLUSIONS

By using this method of determining the residual pectin content, an assessment of the efficiency of different scouring treatment conditions can be carried out. From the acquired data of [K/S] values and the residual pectin quantities, it can be concluded that the most effective treatment in the case of enzymatically treated one was obtained for the sample treated with 3 % o.w.f. enzyme concentration and 35 minutes as enzyme action time.

A low [K/S] values was registered for all bioscouring conditions, indicating a decrease in the pectin content from the treatead samples. Since ruthenium red is a pectin-specific dye, by measuring the color intensity [K/S] of bioscoured samples after dyeing, its value may be an indicator for pectin removal from the fabric substrate.

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