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DYEING OF COTTON MATERIALS AFTER BIOSCOURING AND ENZYMATIC BLEACHING TREATMENTS

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Abstract: *The research aim was to determine the pretreatment (scouring and bleaching) method's influence on 100 % cotton materials dyeing. Before bleaching treatments, the fabrics' non-cellulosic attendants were removed during a pectinolytic treatment and classic alkaline treatment. The general idea of the investigation was maintained in all stages approached, so in addition to the alkaline treatment, an enzymatic treatment was performed (bioscouring) where the classical chelating agent, EDTA, was replaced with sodium citrate. Further, the fabrics were bleached using hydrogen peroxide or a green one, enzymatic, with laccase. A commercial reactive dye was used to colour the cotton samples. The efficiency of the treatment was determined by following the dye fixation degree through soaping.*
The weight loss, hydrophilicity, tensile strength, elongation at break and colorimetric measurements were used to analyse the treated samples. The higher weight loss values of ~ 5% were found for the alkaline scoured sample and alkaline scoured sample followed by hydrogen peroxide bleaching which also showed the lowest value for tensile strength (259.90 N). Hydrophilicity was less than 3 seconds for all treatments. The 100% dye fixation degree was obtained for the bioscoured sample and bleached with H_2O_2.
Even if the eco-friendly treatments proposed as an alternative for classical scouring and bleaching lead to similar or lower results, some of their advantages should be considered: environmentally friendly, lower costs, a lower fibre damage degree, etc. All these procedures use a lower temperature, respectively, fewer quantities of reagents and are not significantly aggressive with the environment.

Key words: *eco-friendly treatments, laccase, dyed cotton fabrics, colorimetric measurements, dye fixation*

1. INTRODUCTION

The textile industry proved to be feasible for the new world tendency in reducing environmental damaging factors. Many studies underline the possibility of using eco-friendly treatments for different purposes as desizing [1], bioscouring [2], or bleaching [3]. The technological steps could be considered separately [1-3] or integrated [4], regarding the enzymatic procedure.

Regardless of the phase, the use of the biotechnologies represents an ecological alternative to the classical approaches. The characteristic parameters of the treated fabrics (wettability, whiteness degree, tensile strength and elongation at break, etc.) are comparable or improved compared with standard methods [5].

Our present investigation had as a primary objective of the comparative evaluation of cotton fabric dyeing behaviour after enzymatic and classical, scouring and bleaching treatments. To ensure the higher ecological approach the samples were bioscoured. The reaction bath formula was modified, also in respect to the complexing agent. In this regard, EDTA was replaced with a citrate salt, considered a greener chelator [6] for Ca^{2+} ions released during the pectic hydrolysis. The cotton fabrics were subjected to bleaching after removing the non-cellulosic attendants (waxes, pectins, organic acids, etc.) during the scouring/bioscouring treatment. The natural yellow-brown colour of the fibre being known is a preparatory step before dyeing. It also improves the hydrophilicity of the material simultaneously with increasing whiteness degree [5]. Currently are used different methods to conduct this procedure. The most used treatment is based on hydrogen peroxide due to its satisfactory results obtained. Over time, different bleaching formulas based on synthetic or enzymatic reagents have been proposed. Although, some non-enzymatic formulas are considered economically efficient [7] they retain their degree of toxicity to the environment. To obtain a whitening effect, the used treatments must be based on oxidative reactions. Under these conditions' oxidases can be successfully used. Good results have been obtained in the case of laccase biocomposites [8]. Looking at efficiency, economic and environmental perspective, promising results at the pilot scale have been obtained using a mixt classic- green system, hydrogen peroxide-laccase in ultrasound media [9].

Another possibility to decrease the harmful potential of classical cotton bleaching treatment consists of the use of different activators. In the case of N-[4-(triethylammoniomethyl) benzoyl]butyrolactam chloride, the reaction temperature needed was almost half (50 °C) compared with the one normally used (90°) [10]. This approach contributes to energy saving.

2. EXPERIMENTAL PART

2.1 Materials

The samples consisted of cotton fabric with 150 ± 3 cm width, 200 ± 10 g/m^2 weight, 100% cotton yarn with Ne 25/2 warp and 100% cotton yarn with Ne 25/1 weft.

The mixture of pectinases, Beisol PRO, the surfactant Denimcol Wash RGN, commercial reactive dye Bezaktiv Rot S-3B and Denimcol LAC-LRE were provided by CHT Bezema. Sulfolen 148 (S-148, alkyl polyglicol ether) and the anionic washing agent Cotoblanc HTD-N were provided by Rotta Company. Sodium citrate, sodium hydroxide, sodium carbonate, sodium bisulfite, sodium silicate, hydrogen peroxide, sodium chloride were purchased from Sigma-Aldrich.

2.2 Methods

2.3.1 Samples pretreatment

To remove the dust and physically linked attendants the samples were first washed at 100 °C in an AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company-USA. The procedure was followed by drying, conditioning and mass determination as described in the international standards.

2.3.2 The bioscouring/scouring treatment

The pectin hydrolysis was developed in an ultrasound (45 KHz) assisted media at 1:20 liquor to fabric ratio. 2 % (concentration over fibre) of Beisol PRO biocatalyst was used for 35

minutes at 55 °C to remove the pectin from the cotton fibre. In the bath reaction were added also a surfactant Denimcol Wash RGN 0.5 % and sodium citrate 2 g/L as a chelating agent. The scouring treatment was performed for 1h at 100 °C using 1 g/L sodium bisulfite, 2 g/L sodium silicate, 5 g/L sodium carbonate, 10 g/L sodium hydroxide and 2 g/L of wetting agent Sulfolen 148 (S-148, alkyl polyglicol ether). All the samples were then washed with hot (70 °C) and cold water and dried at room temperature.

2.3.3 The bleaching treatments

The cotton samples were bleached using a c*lassical procedure* and an *enzymatic* one. In the first case, the reagents mixture consisted of 3 mL/L hydrogen peroxide (30 %), 1 g/L NaOH and 4.5 mL/L sodium silicate. The fabrics were kept 40 min at 95°C. In the enzymatic procedure 3 % o.w.f. (over fibre) commercial laccase (Denimcol LAC-LRE) was used. It is a suitable enzyme for the bleaching of cellulosic materials. The conditions indicated in the technical data sheet from the manufacturer were used: temperature 60 ^{0}C for 40 min. In both cases, the fabric to liquid ratio was 1:10.

2.3.4 The dyeing treatment

Dyeing of the cotton samples was made with a commercial reactive dye Bezaktiv Rot S-3B-2 % (o.w.f.), 1.5 mL/L NaOH 32.5 %, 15 g/L Na_2CO_3 and 80 g/L NaCl. The treatment was carried out by all-in procedure in a JULABO water bath at 60 ^{o}C for 90 minutes at a bath ratio of 1:40. The dyeing treatment was followed by three successive washing steps with distilled water and a washing step in a soap solution of 2 mL/L Cotoblanc HTD-N, anionic washing agent and 1 g/L Na_2CO_3 at 90°C for 15 min. The samples were further rinsed again with distilled water and air-dried at ambient temperature [11].

2.3.5 The weight loss, hydrophilicity and tensile strength

The samples were kept in a standard atmosphere (65 ± 2% humidity at 21 ± 1°C) to achieve the humidity equilibrium before the weight loss, hydrophilicity and mechanical properties determinations. The mass loss of the cotton samples was gravimetric determined. The tests were dried at 105°C in an oven (Caloris Group, Romania). The parameter was determined using the equation (1):

$$\% \text{ weight loss} = (W1-W2)\ x100/W1 \quad \textbf{(1)}$$

where: W1-W2 are the weights of dried samples fabric before and after the treatments.

The standardized AATTCC Test Method 79-2007 was used for hydrophilicity determination. The mechanical properties were investigated based on the method described previously [12] using a 5KT testing machine (Tinius Olsen-United States) with a Horizon software interface running on a connected PC.

2.3.6 The colorimetric measurements

The dyeing efficiency was measured using a Datacolor 500 spectrophotometer. The colour strength [K/S] was determined after the samples' colouring and after the soaping procedure. The %R reflectance was measured at the maximum wavelength (500 nm). The K/S was calculated at the batch wavelength of maximum absorbance according to the equations (2) and (3):

$$K/S = [\{(1-R)_2 / 2R\}] \quad \textbf{(2)}$$

$$\text{Colour Strength} = [(K/S)_{\text{Batch}} / (K/S)_{\text{Standard}}] \times 100 \quad \textbf{(3)}$$

where: R-reflectance measured at 500 nm;
K/S $_{Batch}$-colour strength of the dyed treated sample;
K/S $_{Standard}$-colour strength of the standard.

3. RESULTS AND DISCUSSIONS

The characteristic parameters of the cotton samples after all the applied pretreatments (classical scouring, enzymatic scouring, classical bleaching and enzymatic bleaching) are presented in Table 1.

Table 1: *Characteristic parameters of the 100% cotton samples after all the applied pretreatments*

Samples	Weight loss (%)	Hydrophilicity (s)	Whiteness degree R (%)	Tensile strength (N)	Elongation at break (%)
B	1.3	3	55.88	295.71	21.60
BL	0.34	1.8	57.20	294.40	21.70
BHP	1.54	1.1	70.65	283.40.	21.40
AS	5.0	1	72.90	270.05	24.30
AL	1.89	<1	73.14	269.80	25.20
AHP	4.66	<1	83.30	259.90	19.70

B-bioscoured sample; BL-bioscoured laccase bleached sample; BHP-bioscoured hydrogen peroxide bleached sample; AS-alkaline scoured sample; AL-alkaline scoured-laccase bleached sample; AHP-alkaline scoured hydrogen peroxide bleached sample.

The data presented in Table 1 show a higher weight loss in the case of the samples classical bleached. Comparing the mass decrease degree between the laccase treated samples and the hydrogen peroxide one, the difference registered is only 0.7 %. These results open the possibility to use the enzymatic treatment due to its higher biodegradability. The sample's wettability values are comparable in the case of the whitened specimens independent of the conditions considered. Levels lower than 3 seconds are appreciated as being good. The tensile strength and elongation at break of the treated cotton samples differ depending on the treatment conditions. In the case of the enzymatically treated samples, the mechanical characteristics have higher values after both bioscouring and bleaching treatments. The alkaline scoured samples have lower tensile strength, the minimum value recorded being for the sample alkaline treated and bleached with hydrogen peroxide. The situation may be determined by the fact that this was the most aggressive treatment [13].

The dyed sampled colorimetric characteristics are presented in Figures 1 and 2.

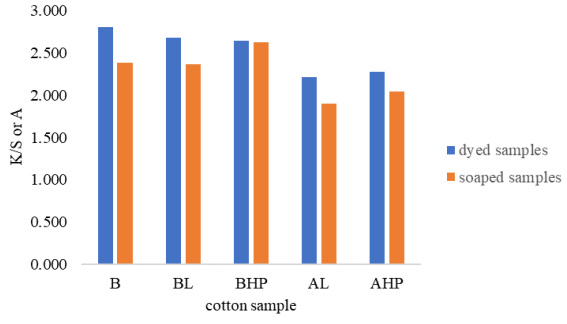

Fig. 1*: Cotton samples colour strength at the wavelength of maximum absorbance*

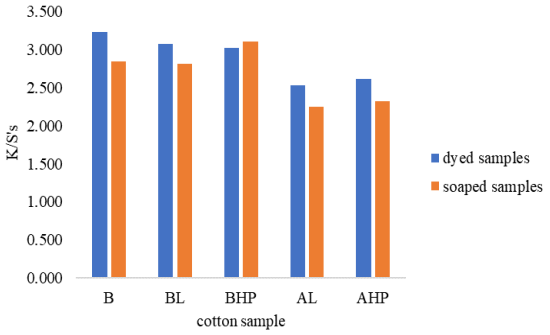

Fig. 2*: Cotton samples colour strength at the dominant wavelength*

The measured reflectance values for the dyed cotton samples were used to calculate colour strength [K/S]. The values varied between 13.413 (B) and 17.825 (AL). The differences between the enzymatic bleached (BL) sample and the classical (AL) one is not significative being of approximative 14%. As expected, the %R increased values were obtained for the alkaline scoured samples, cases in which also the whiteness degree was higher.

As shown in Figures 1 and 2, the calculated colour strength registers a slight decrease in the case of the alkaline scoured samples, the difference being almost 22% compared with the bioscoured one. This indicates the formation of several reactive groups during the pectinolytic treatment, which further influences the cotton-dye covalent link formation. The trend remains the same also after the soaping procedure.

The dye fixation degree after the soaping procedure is presented in Table 2.

Table 2: *Dye fixation degree parameters of the 100% cotton samples after dyeing and soaping*

Samples	Fixation degree calculated with K/S or A at Wl. of Max. Abs. [%]	Fixation degree calculated with Batch K/S's [%]
B	84.827	87.810
BL	88.294	91.491
BHP	99.098	100.001
AL	85.861	88.767
AHP	89.789	88.958

The dye fixation values were calculated using data from Datacolour software (K/S or A at Wl. of Max. Abs. and Batch K/S's). As presented in Table 2, the maximum value was obtained for the cotton sample bioscoured and classical bleached. The differences between the various samples are relatively low, varying with approximative 5%, independent of the bleaching or scouring treatment. The results can be explained by the formation of approximately the same number of cellulose hydroxylic ionic groups which covalently bind the dye [1]. In this situation the enzymatic treatments successfully could be recommended, their impact on the environment being lower compared with the classical ones.

4. CONCLUSIONS

A comparative evaluation of 100% cotton fabric's dyeing behaviour after enzymatic and alkaline scouring followed by enzymatic and classical bleaching treatments was performed. The samples analysis after scouring, bleaching and dyeing were performed based on evaluation of different characteristics: physic, mechanic and colorimetric parameters. All three mentioned treatments were made using enzymatic and classical conditions. The higher weight loss values were obtained in the case of alkaline scoured sample and alkaline scoured sample followed by hydrogen peroxide bleaching. This weight loss also led to lower values for the tensile strength of the fabric. Better results were observed in the case of all enzymatic treatments with lower weight loss values, better tensile strength and comparable values for hydrophilicity. The measured reflectance values for the dyed cotton samples varied between 13.413 (B) and 17.825 (AL), the differences between the enzymatic bleached sample (BL) and the classical (AL) one being of approximative 14%. Fixation degree values of the dyed samples after the soaping procedure were between 87.810% and 100%, the higher value being for BHP sample. The results obtained recommend the enzymatic conditions for scouring followed by hydrogen peroxide bleaching, the procedure being less aggressive, the environmental and economic impact being lower in these cases.

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