

Bio-innovation in Cotton Fabric Scouring - Acid and Neutral Pectinases

Pušić, Tanja; Tarbuk, Anita; Dekanić, Tihana

Source / Izvornik: **Fibres & Textiles in Eastern Europe, 2015, 109, 98 - 103**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:201:364654>

Rights / Prava: [In copyright](#) / [Zaštićeno autorskim pravom.](#)

Download date / Datum preuzimanja: **2024-07-23**



Repository / Repozitorij:

[Faculty of Textile Technology University of Zagreb - Digital Repository](#)



Tanja Pušić,
Anita Tarbuk,
Tihana Dekanić

University of Zagreb,
Faculty of Textile Technology,
Department of Textile Chemistry and Ecology,
Prilaz baruna Filipovića 28a,
HR-10000 Zagreb, Croatia
E-mail: anita.tarbuk@tff.hr,
tpusic@tff.hr,
tihana.dekanic@tff.hr

Bio-innovation in Cotton Fabric Scouring - Acid and Neutral Pectinases

Abstract

Using biotechnology during textile processing has been known for years due to its environmental benefits and special performance of enzymes in comparison with the conventional processing of textiles. This paper deals with the bioscouring of cotton fabric with acid and neutral pectinases in comparison with alkali scouring. Variations in technological procedures, as expressed through pad-roll and exhaustion, were also identified for the bioscouring of cotton fabrics. The varied impacts of alkali, acid, and neutral pectinases on the properties of cotton fabrics throughout the processing technology were evaluated for electrokinetic phenomena, hydrophilicity, mechanical and chemical degradation, inorganic residues, and whiteness.

Key words: cotton fabric, bioscouring, wicking, mechanical damage, chemical damage, whiteness.

Introduction

Raw cotton fibres contain around 95% of pure cellulose balanced by the non-cellulosic impurities of proteins, oils, waxes, pectins, carbohydrates and inorganic materials [1 - 3]. Various treatments should be performed for the removal of natural non-cellulosic materials during the preparation of cellulosic materials for all subsequent finishing processes such as dyeing, printing, and finishing. The selection of a methodology for their removal should be based on proper efficiency and minimum damage to the fibres. Analysis of raw cotton revealed the presence of calcium, magnesium, and iron. Both Ca^{2+} and Mg^{2+} are typically associated with the pectin present in the primary walls of raw cotton fibres, by acting as crosslinking agents. As they are present either in carbonate or hydrocarbonate forms, they should be neutralised by an acid extremely quickly and washed out as CaCl_2 or MgCl_2 afterwards. Metal cations can interfere with dyes, pectin, protein or cellulose, therefore chelating with special compounds should be performed for the prevention of a negative impact on metal cations during the pre-treatment processes [4 - 7]. The aim of conventional alkali scouring performed at high temperatures is the removal of non-cellulosic genetic and added impurities such as waxes, protein substances, pectins, mineral salts and other substances, from cuticles of the cotton fibres. It is well known that sodium hydroxide (NaOH) in the presence of oxygen has the ability to damage the cellulose. The outcome would be the presence of oxycellulose, which causes reduced strength and a certain level of depolymerisation [8 - 21]. A side effect of alkali treatment is surface modification that can lead to further processing problems, e.g.

weak sewabilities of cotton knitted fabrics. The coarse structure of a knitted fabric reduces the mobilities of the stitches when a loop-forming thread is not pushed but pierced [15 - 17]. Alkali processes are also unfavourable due to large energy and water consumption for rinsing and water waste loading. Environmental issues have forced extensive research into the applications of enzymes as they are environmental-friendly and specific in performance, especially since ca. 1990 [22].

The use of enzymes in textile finishing has been carried out since the 20th century (1910) using amylase during starch degradation [11, 19]. According to the key-lock model/enzyme - substrate theory, introduced by Michaelis-Menten in 1913, a substrate diffuses towards the direction of an enzyme, links to it and an enzyme substrate complex is then formed. The final reactive products diffuse from the split products' active centre, thus enabling a new linking of the substrate and catalysis all over again [18 - 20]. According to Roßner, about 75% of organic contaminants from the textile industry come from cotton pre-treatment, which is reason enough for replacing NaOH with biodegradable enzymes [8 - 10, 23 - 27].

Nowadays enzymes applied during textile processing are industrially implemented or in research, such as amylases for the degradation of amylase, applied when desizing; pectinases for the degradation of pectin, applied in bio-scouring and the retting of bast fibres; proteases for the degradation of protein, sericin protein and cellulose protein, applied for the scouring of wool, degumming of silk, stone-washing of denim; cellulases for the degradation of cellulose

and cellulosic substrates, applied for the bio-polishing, defibrillation and stone-washing of denim; hemi-cellulases for degrading hemi-cellulose substrates, applied for the retting of bast fibres; xylanase for degrading lignin substrates, applied for jute processing; catalases for the degrading of hydrogen peroxide, applied for bleaching, dye discolouration and effluent treatment, and glucose oxidase for attacking glucose, acting as a bleaching agent. Enzyme technology, in addition to other benefits, could also offer potential process integration [22].

Protease and lipase have not found extensive application since they showed less activity during the removal of hydrophobic substances [18 - 21]. Therefore research was focused on the application of pectinases [9 - 17, 28 - 34] for the scouring of cotton fabrics.

The scouring of cotton using alkaline pectin lyase isolated by Novozymes, Denmark, labelled as "BioPreparation" or "Bioscouring", resulted in effective and environmental benefits in comparison with the conventional process [9-15, 29 - 33]. Furthermore progress was achieved through applications of neutral and acid pectinases [16, 17, 33, 34]. Enzymes under the trade name BeisoTM (CHT, Germany) were able to remove barrier layers, thus enabling emulsification of the waxes. This resulted in improved hydrophilicity and accessibility of fibres for bleach active compounds or dyestuffs, soft handle, good whiteness and less weight loss. Additionally it was unnecessary to perform neutralisation [16, 17].

The aim of this research is a comparison of efficiency of bio-innovators, acid and

neutral pectinase, and alkali. Therefore, this paper deals with the processing of cotton fabric using alkaline scouring and bioscouring with acid and neutral pectinases in combination with bleaching. The efficiency of pre-treatment conditions was monitored through surface characterisation, sorption ability, whiteness, inorganic content, and mechanical and chemical wear.

Experimental

Material

Plain weave raw cotton fabric of surface mass per unit area of 179 g/m² and yarn linear density of 26 tex was used, with a fabric count of warp 40 cm⁻¹ and weft 30 cm⁻¹.

Pectin splitting enzymes – Beisol HP (CHT/Bezema, Germany) and Beisol PRO (CHT/Bezema, Germany), applicable for discontinuous, semi-continuous and continuous processes, were used for the bioscouring of the raw cotton fabric. Beisol HP is labelled as a highly-effective product that breaks up real pectin, requiring sequestering agents applicable for a temperature range from 20 to 60 °C, whilst having a pH optimum between 1.5 and 5.0. Beisol PRO is a capable product for individual application as well as for integration within a process of enzymatic desizing. It does not require the presence of a sequestering agent, and is efficient within a wide temperature range from 20 to 98 °C and pH of 6.0 - 9.0 as well.

Pre-treatment

The raw cotton fabric was scoured by applying alkali and two individual pectin-splitting enzymes.

Alkali scouring

The raw cotton fabric was alkali scoured for 2 h at 98°C in an autoclave (Scholl) by a pad roll using 3 % NaOH and 2 g/l of the non-ionic surfactant Lavotan TBU (alcanol ethoxylates) from CHT. Afterwards it was rinsed and neutralised until reaching pH 7.

Enzymatic scouring

Enzymatic scouring was performed using two procedures: by a pad-roll in an autoclave (Scholl) and exhaustion in an Ahiba Turbomat (Datacolor, Swiss).

Exhaustion procedure:

Neutral pectinase. The fabric was treated with 2 g/l of neutral pectinase and 1 g/l

of wetting agent Felosan NOG (fatty alcohol ethoxylate) (Bezema, Swiss) at pH 7, at bath ratio 1:45 for 50 min at 60°C.

Acid pectinase. The fabric was treated with 2 g/l of acid pectinase and 1 g/l of wetting agent Felosan NOG at pH 5, at bath ratio 1:45 for 50 min at 90 °C.

Pad-roll procedure:

Neutral pectinase. Bioscouring was performed for 2 h at 60 °C in an autoclave (Scholl, Swiss) by a pad roll using 2 g/l of neutral pectinase and 1 g/l of wetting agent Felosan NOG.

Acid pectinase. Bioscouring was performed for 2 h at 90°C in an autoclave by a pad roll using 2 g/l of neutral pectinase and 1 g/l of wetting agent Felosan NOG. The bioscoured fabrics were neutralised and rinsed until pH 7 was reached.

Bleaching (HP)

Bleaching with hydrogen peroxide (HP) was performed for 3 h at 98 °C in an autoclave by the pad roll process using 20 ml/l of H₂O₂ (35%), 4 g/l NaOH, 5 ml/l Tinoclarit CBB (Ciba, Swiss), an organic stabiliser from Ciba, 15 ml/l of mixture Na₂SiO₃, Na₂Si₂O₅, 10 ml/l Invatex MD, a multi-purpose phosphorus-free anti-wrinkle agent, using a combination of surfactants and complexing/dispersing agent from Ciba, and 0.5 ml/l Fumexol DF (Ciba, Swiss), an antifoaming agent (Ciba).

Labels and treatments are given in *Table 1*.

Test methods

The **Electrokinetic (zeta) potential** was measured by the streaming potential/current method using a Brookhaven-Paar Electrokinetic Analyzer (EKA) (A. Paar, Austria) with a stamp cell and calculated according to the Helmholtz-Smoluchowsky equation [35]:

$$U_p = (\zeta \cdot \varepsilon \cdot \varepsilon_0 \cdot Q \cdot R \cdot \Delta p) / (\eta \cdot L) \Leftrightarrow \zeta = (U_p \cdot \eta \cdot L) / (\varepsilon \cdot \varepsilon_0 \cdot Q \cdot R \cdot \Delta p) \quad (1)$$

where U_p is the streaming potential, ζ the zeta potential, ε_0 the permittivity of the vacuum, ε the dielectric constant, η the dynamic viscosity of the solution, R the electrical resistance, Q the cross-section of the capillary, L the capillary length and Δp is the pressure difference between the inlet and outlet of the capillary system.

Table 1. Labels, treatments and procedures.

Label	Treatment	Agent	Procedure
0	Raw	-	-
1	Alkali scouring	NaOH	Pad roll
2	Bioscouring	Neutral pectinase	Exhaustion
2a			Pad-roll
3		Acid pectinase	Exhaustion
3a			Pad-roll
... -1	Bleaching	H ₂ O ₂	Pad-roll

The zeta potential of the fabrics tested was measured in relation to the pH of the electrolyte solution until the Isoelectric Point (IEP) was achieved and registered as well.

The **Hydrophilicity** of the cotton samples was determined by the drop test, and vertical and horizontal wicking methods by applying water and dyestuff, Benzopurpurin 4B (C.I. 23500, Direct Red 3) (Sigma, USA).

The drop test (AATCC 79-2010 *Absorbency of Bleached Textiles*) allows a drop of water to fall from 1 cm height onto the taut surface of the cotton sample. The time necessary to spread into fabric is measured. The fabric is hydrophilic if the time is < 3 s.

The absorbency of the cotton samples was measured according to the standard vertical wicking test, DIN 53924-1997-03¹). In the vertical wicking test the lower edge of a sample with dimensions of 25.0 by 2.0 cm was placed 1 cm vertically in a vessel with water/dyestuff. The time allowed for the water front to move was set at 15 minutes, and the wicking height was measured in 1, 5 and 15 minutes.

In the horizontal wicking test, according to Chibowski [36], the procedure was like a vertical test but a cotton strip was placed under the small angle (10°) in the closed chamber ousted for planar chromatography. The time allowed for the water front to move was set at 3 minutes, and the wicking length was measured in 0.5, 1 and 3 minutes.

The test methods for **quality control** were performed according to ISO 4312:1989²). In these standard methods for determination of the following characteristics of the test pieces after scouring are specified: intrinsic greying, intrinsic yellowing, increase in organic deposit content, increase in incineration residue, overall decrease in breaking strength, de-

Table 2. Zeta potential of raw and scoured cotton fabrics at pH 10 and IEP.

Fabric	ζ at pH 10	IEP
0	-14.1	2.83
1	-17.5	< 2.5
2	-20.0	
2a	-21.9	
3	-18.0	
3a	-23.1	

crease in breaking strength resulting from chemical degradation of cellulose, determination of the increase (or decrease) in the degree of whiteness and of chemical wear and further a grey scale (colour fastness) and the measurement of reflection. Since scouring and bleaching processes have a major impact on fabric damage, chemical and mechanical wear as well as fabric whiteness were determined. This standard suggests methods defined in different standards for characteristic determination. For that purpose, the breaking force and elongation were measured according to EN ISO 13934-1:1999³⁾ on a MesdanLab Strength Tester (MesdanLab, Italy) and the mechanical wear was calculated according to:

$$\cdot 100 (F_0 - F) / F_0 \cdot 100, \text{ in } \% \quad (2)$$

where U_m is the mechanical wear (damage), in %, F_0 the breaking force of untreated, raw fabric, in N, and F is the breaking force of the treated fabric, in N.

The *degree of polymerisation* (DP) was measured according to DIN 54270-2-1977-08⁴⁾ and calculated according to the Schultz-Blanschke equation. From the limit viscosity limit, the chemical

wear (chemical degradation of cellulose) was calculated according to:

$$U_c = (\log(\frac{2000}{[\eta]} - \frac{2000}{[\eta]_0} + 1)) / \log 2 \quad (3)$$

Where U_c is the chemical wear (damage), $[\eta]_0$ limit viscosity of untreated fabric, in cm^3/g , and $[\eta]$ is the limit viscosity of treated fabric, in cm^3/g .

Ash content (increase in incineration residue). Weighted samples were burnt down in the crucible and put in a furnace at 800°C to calcinate for 1h. After cooling in a desiccator, they were weighted again and the ash content calculated according to:

$$A = (m_1 - m_2) / m_0 \times 100, \text{ in } \% \quad (4)$$

where A is the ash content, in %, m_0 the mass of the test fabric in a dry state, in g, m_1 the mass of the empty crucible, in g, and m_2 is the mass of the ash and crucible after calcination, in g.

The **degree of whiteness** (W_{CIE}) was calculated from spectral characteristics measured on a remission spectrophotometer - SF 600 PLUS CT (Datacolor, Swiss), according to DIN 6167:1980-15).

Results and discussion

Raw cotton possesses a hydrophobic nature due to its impurities, which should be removed in order to achieve an absorbency of cotton materials necessary for further textile processing. Pectin is composed of one linear substance of polygalacturonic acid. In reality pectin is composed of homologous pectin: po-

lygalacturon acid but also a heterologous part, the rhamnogalacturonan, which is bound to the rest of the rhamnosyl residue irregularly with arabinan, galactan, and many other compounds, mostly polysaccharides [6]. The pectin on cellulose fibres is a complex mix of different substances from pectin, cellulose, protein etc. including Ca, Mg and Fe, which forms an interlaced net structure difficult to solve in water [5, 6]. Pectin keeps back cotton fats and waxes because of the net structure. It is important to degrade the pectin net structure in order to obtain bioscoured cotton with a good hydrophilic effect. Complete degradation is unnecessary because the fragments of the complex structure are soluble in water and can be washed off. Therefore the outer layer of the cell should be destabilised by degradation of the pectins using pectinases and a non-ionic surfactant to such a degree that the fats and waxes can be emulsified. Furthermore the pectinase has to be inert in the presence of sequestering agents so that they hydrolyse the metal ions during enzymatic degradation out of the pectin structure.

It is for that reason that in this paper cotton fabrics were scoured with alkali and bioscoured with neutral and acid pectinases by applying pad-roll and exhaustion procedures. These pre-treatments removed hydrophobic substances, resulting in a change in the surface charge that was characterised by the zeta potential. It is important to consider that the zeta potential depends on the polymer nature, impurities, and finishing agents added. It is not a material constant but it provides information about the nature and dissociations of the functional groups, the hydrophilicity or hydrophobicity of the fibre surface, as well as the ions or water sorption [35, 37 - 41]. The electrokinetic (zeta) potential of alkali and bioscoured cotton fabrics was measured as a function of the pH of the electrolyte solution. The results are presented in **Table 2** and **Figure 1**.

Cotton fibres immersed in a neutral aqueous medium, as most textile fibres, show negative values for the zeta potential. The zeta potential became more negative by increasing the pH. The reason for the negative surface charge of cotton is the presence of existing hydroxyl or carboxyl groups. In the case of raw (untreated) cotton, hydroxyl groups exist but they are covered by non-cellulosic impurities. Alkali scouring degrades and

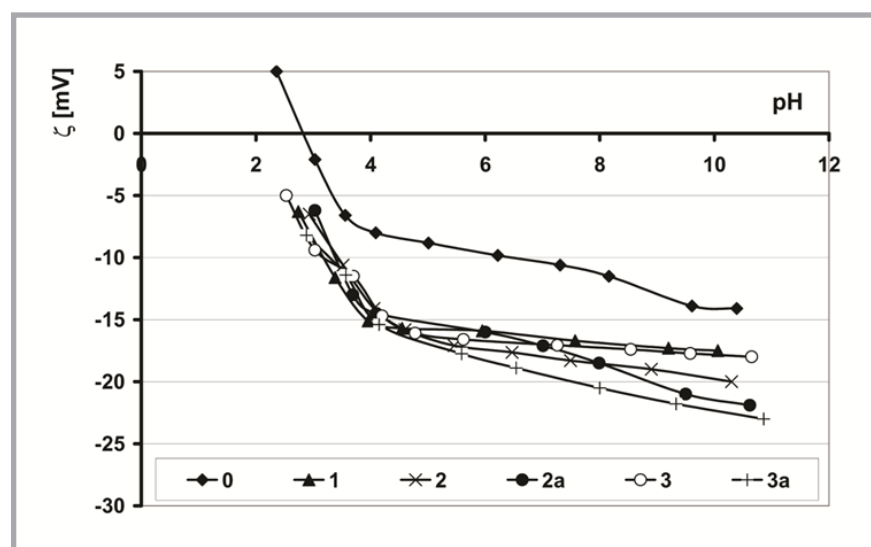


Figure 1. Zeta potential of raw and scoured cotton fabrics in relation to the pH of the electrolyte solution 0.001 M KCl.

removes practically all non-cellulose compounds except waxes. The surface becomes more available for the dissociation or adsorption of ions from the bulk solution. Therefore the raw cotton fabric (0) had a less negative zeta potential within the whole pH region than the scoured ones. Bleaching processes with HP cause the formation of new surface groups (-CO, -CHO and -COOH), resulting in a lower zeta potential [39 - 41]. It is clear that the zeta potential of fabrics treated with neutral and acid pectinase (2 and 3) were more negative, indicating a higher degree of purity and hydrophilicity compared to alkali scoured cotton (1), regardless of the procedure applied. The results showed that the fabrics treated with pectinases by the pad-roll procedure possessed a more negative zeta potential than those treated by exhaustion, thus indicating a better cleaning effect and less damage of cotton cellulose.

The Isoelectric Point (IEP), which is a numeric pH value where the electrokinetic potential equals zero, was identified for the raw cotton fabric only. The IEP of the scoured bioscoured fabrics were approximated because the ionic strength below pH 3.5 was too low, thus producing unreliable results [35].

The results of hydrophilicity determined according to the drop, vertical wicking, and horizontal wicking tests, according to Chibowski, are shown in **Tables 3 - 5**.

The results of the drop test (**Table 3**) confirmed the hydrophobic nature of raw cotton fabric (0) and the better than expected absorbencies of the scoured cotton fabrics. The hydrophilicity of the bioscoured cotton fabric was improved but was still less than that of the alkali scoured fabric, which showed instantaneous penetration. These results indicated that high absorbency is not the only property for achieving a sufficient uptake of dyestuff and finishing agents. In this case, high cotton absorbency can be an indication of fibre damage, which was strongly confirmed by the cellulose degree of polymerisation (DP). Bioscoured cotton fabric with neutral (2) and acid pectinase (3) in the process of exhaustion showed immediate penetration and excellent hydrophilicity as well. Its application by means of the pad-roll procedure resulted in slower penetration but of still less than 5s. All the bleached fabrics showed immediate penetration of water drops with excellent hydrophilicity.

The results of wicking according to the horizontal test shown in **Table 4** indicate that raw cotton fabric (0) is completely hydrophobic. The rate of water penetration to differently scoured cotton fabrics is noticeable. Water penetration is faster on bioscoured cotton fabric than on the alkali one (1). Variation in the procedure, through exhaustion and the pad-roll, showed a small impact on the water penetration rate. Bleached cotton fabrics showed similar water penetration. The fastest penetration was shown by cotton fabric bioscoured with acid pectinase by means of exhaustion and bleached afterwards (3-1). The exhaustion procedure of bioscouring resulted in better penetration of the Benzopurpurin 4B solution than by the pad-roll procedure. The fastest dyestuff penetration was achieved on cotton fabric bioscoured with acid pectinase by means of exhaustion (3). The fastest penetration of dyestuff at the initial intervals was shown by the cotton fabric bleached with acid pectinase after bioscouring, whilst subsequently the best dyestuff penetration was achieved on cotton fabric bleached after bioscouring with

Table 3. Absorbency of raw, scoured and bleached cotton fabrics according to the drop test.

Fabric	Drop Test AATCC 79 – 2010 t, s
0	> 90 min
1	0
2	0
2a	5
3	0
3a	2
1-1	0
2-1	0
2a-1	0
3-1	0
3a-1	0

neutral pectinase by the pad-roll procedure. Dyestuff penetration for bleaching cotton fabrics is slower than water penetration, which implied the presence of hydrophobic and electrostatic repulsed interactions between the dyestuffs and more negative surfaces of the bleached fabrics.

The wicking behaviour of cotton fabrics evaluated by vertical and horizontal tests

Table 4. Water and dyestuff absorbency of raw, scoured and bleached cotton fabrics according to the horizontal wicking test.

Fabric	Horizontal wicking height acc. Chibowski, cm					
	water			dyestuff		
	10 s	1 min	3 min	10 s	1 min	3 min
0	0	0	0	0	0	0
1	3.1	6.20	8.75	2.75	5.25	6.85
2	3.25	6.95	10.45	2.85	6.45	9.80
2a	2.35	6.40	9.45	2.20	5.40	8.25
3	3.80	7.00	10.10	3.05	6.95	10.4
3a	2.25	6.85	9.95	2.25	5.15	7.65
1-1	3.05	6.25	9.05	3.10	5.25	6.55
2-1	2.75	5.90	9.10	3.10	5.70	8.35
2a-1	2.75	6.00	8.85	2.35	5.35	7.60
3-1	3.75	7.05	10.15	3.75	6.80	8.40
3a-1	2.35	5.95	9.40	3.15	5.80	7.60

Table 5. Water and dyestuff absorbency of raw, scoured and bleached cotton fabrics according to the vertical wicking test.

Fabric	Vertical wicking height acc. DIN 53942, cm					
	water			dyestuff		
	1 min	5 min	15 min	1 min	5 min	15 min
0	0	0	0	0	0	0
1	3	6	9.2	2	3.5	4.3
2	3.5	6.4	10.1	2.5	5.9	9.2
2a	3.6	6	9.1	4	4.8	6.9
3	3.1	6	9.2	2.8	5.8	8.9
3a	3.9	6.2	9.5	2.5	5.5	7.4
1-1	2.4	5.3	8.5	3.3	3.5	4.4
2-1	3.5	6.3	9.6	2.7	5	6.1
2a-1	3.3	5.5	8.9	3	4.5	5.5
3-1	4.5	6.9	10.1	3.4	4.5	6
3a-1	3.9	5.2	7.4	2.2	3.9	5.5

Table 6. Ash content in raw and scoured cotton fabrics.

Fabric	Ash content, %
0	0.29
1	0.24
2	0.25
2a	0.29
3	0.14
3a	0.22

was similar (Table 5) but less prominent, showing that water penetration in bleached cotton fabrics indicated greater differences between pre-treatments. Better results were shown by cotton fabrics bioscoured with neutral and acid pectinases by means of exhaustion. Dyestuff penetration was much better for the bioscoured than for the alkali scoured cotton fabric, which was inconsistent with previous interpretations for repulsive interactions between dyestuff anions and negative surface charges.

The influence of pre-treatment procedures often damages the cotton cellulose. Therefore the fabric quality was determined from the ash content, breaking force, degree of polymerisation, and whiteness according to ISO 4312:1989.

Table 7. Breaking force (F), elongation at break (ϵ), and mechanical damage (U_m) of cotton fabrics.

Fabric	F , N	CV, %	ϵ , %	CV, %	U_m , %
0	796	5.4	21.37	0.62	0.00
1	703	11.8	29.33	0.63	11.68
2	698	40.1	30.33	1.05	12.31
2a	772	38.3	30.27	0.92	3.02
3	741	22.3	31.67	0.06	6.91
3a	778	32.6	31.76	0.56	2.26
1-1	691	51.1	31.67	0.35	13.19
2-1	669	37.8	31.46	0.21	15.95
2a-1	698	52.1	30.85	1.11	12.31
3-1	660	10.1	29.43	0.74	17.09
3a-1	675	35.9	30.21	1.41	15.20

Table 8. Limit viscosity [η], degree of polymerisation (DP) and chemical damage of cotton fabrics.

Fabric	$[\eta]$	CV [%]	DP	U_c	U_c [%]
0	1329.83	0.116	2965.51	0	0
1	959.17	0.396	2138.94	0.3341	33.41
2	1092.23	0.479	2435.68	0.1975	19.75
2a	1221.23	0.083	2723.34	0.0840	8.40
3	1123.86	0.111	2506.20	0.1681	16.81
3a	1228.91	0.330	2740.46	0.0778	7.78
1-1	615.24	0.114	1371.98	0.8346	83.46
2-1	813.23	0.113	1813.51	0.5144	51.44
2a-1	1031.65	0.276	2300.59	0.2569	25.69
3-1	880.35	0.082	1963.17	0.4269	42.69
3a-1	1059.92	0.116	2363.62	0.2287	22.87

The chemical and mechanical damage to the cotton cellulose fabrics were used as indirect indicators of fabric quality, in which mechanical damage (U_m) corresponded to a reduction in the breaking load (Equation 2), whilst chemical damage (U_c) was calculated according to Equation 3. The results are expressed in Tables 6 - 8, and shown in Figure 2.

The efficiency of impurity elimination is usually analysed by hydrophilic behaviour and weight loss. As calcium and magnesium ions are directly connected to the polygalacturonic polymers, the ash either consists of deposits of mineral salts as such, or mineral salts that have undergone certain chemical modifications as a result of calcination. The amount of mineral ash (ash content) is an accurate index of the presence of mineral deposits and can be an indirect measurement of scouring efficiency. In this case it was determined by the raw and scoured cotton fabrics (Table 6). The values obtained indicated small differences, but it can still be pointed out that the lowest value was possessed by the cotton fabric bioscoured with acid pectinase, with the most effective being bioscouring performed by means of exhaustion.

There was a small difference in the breaking force of alkali fabrics as compared to bioscoured ones. It is noticeable that fabrics treated by a pad-roll are less damaged (U_m) due to mild mechanical agitation during processing. In the case presented the bleaching of all the scoured cotton fabrics resulted in a significant decrease in the breaking force as a result of degradation and the presence of oxycellulose. The results showing the degree of polymerisation (DP) between the pre-treatments and procedures were much more noticeable. It was evident that the bioscoured fabrics, regardless of the pectinase or procedure applied, had a higher degree of polymerisation than the alkali scoured ones. The degree of polymerisation of the cotton cellulose was in correlation with the breaking force and elongation. The bleaching of the alkali scoured cotton fabric (1-1) caused significant damage to the cotton cellulose according to the lowest value of DP. The pad-roll procedure again resulted in lower degradation of the cotton cellulose than exhaustion.

Whiteness is a very important criterion for assessing the effects achieved in bleaching, and it has been related to the process of scouring. The aim of scouring and bleaching is to achieve hydrophilic and minimal damage to the cotton fabric with satisfactory whiteness. It is evident from the results for whiteness (W_{CIE}) presented in Figure 2 that the removal of genetic and added impurities such as waxes, protein substances, pectin, and others during alkali scouring, enhanced whiteness. Bioscouring degraded only the pectine, therefore the whiteness of the bioscoured cotton was less enhanced than the whiteness of the alkali scoured one. Bleaching with HP removed pigments, resulting in improved whiteness. It should be pointed out that the whiteness of the bioscoured fabrics by the pad-roll procedure was less enhanced by almost 10 units (samples 2a-1 and 3a-1) than the those bioscoured by means of exhaustion (2-1 & 3-1).

Conclusions

The bioscouring of cotton fabrics with acid and neutral pectinases was applied by exhaustion and pad-roll procedures in comparison with alkali scouring. The electrokinetic phenomena, hydrophilicity, chemical and mechanical damage, ash content and whiteness were applied for characterising the pre-treated fabrics.

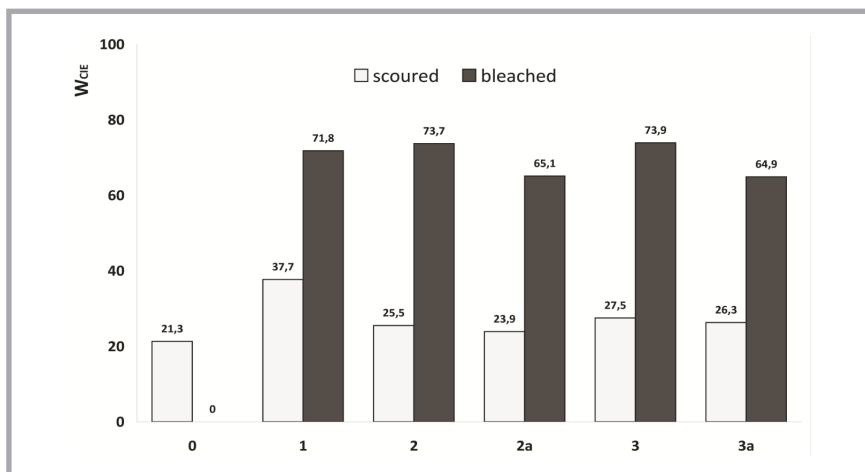


Figure 2. Whiteness according to CIE (W_{CIE}) of cotton fabrics bleached with HP.

When considering the hydrophilicity and whiteness, the best results are achieved when bioscouring by the exhaustion procedure. When considering the surface charge, the available groups and chemical and mechanical damage to the fabrics, the best results were achieved for bioscouring by a pad-roll regardless of pectinase usage.

Therefore the effects of bioscouring achieved with acid and neutral pectinases proved to be much better than alkali scouring. The application procedures should therefore be selected by considering what effect should be achieved.

From an ecological point of view the use of neutral pectinase was of benefit as there was no need for neutralisation of the wastewaters.

References

- Küttler H, Wulfhorst B. *Chemical Fibers International* 1989; 39: E133-E155.
- Kozłowski R. *Handbook of natural fibres: Types, properties and factors affecting breeding and cultivation*. Ed. Woodhead Publishing in Association with The Textile Institute, Series in Textiles No. 118, Cambridge-Philadelphia-New Delhi, 2012.
- Kozłowski R. *Handbook of natural fibres: Processing and applications*. Ed. Woodhead Publishing in Association with The Textile Institute, Series in Textiles No. 119, Cambridge-Philadelphia-New Delhi, 2012.
- Gamble GR. *AATCC Review* 2011; 11, 5: 74-79.
- Dochia M, Stanescu MD, Constantin C. *Fibres & Textiles in Eastern Europe* 2013; 21, 3: 22-25.
- Biscaro Pedrolli D, Costa Monteiro A, Gomes E, Cano Carmona E. *The Open Biotechnology Journal* 2009; 3: 9-18.
- Yang H, Li Q, Niu L, Zhang Y. *Biore-sources* 2012; 7, 3: 4171-4178.
- Bach E, Schollmeyer E. *Textilveredlung* 1992; 27, 3: 220-225.
- Jordanov I, Mangovska B. *Tekstil* 2001; 50, 10: 501-508.
- Zulić D, Grancarić AM. *Tekstil* 2002; 51, 3: 128-132.
- Hardin IR, Li Y. *Textile Chemists and Colorists* 1997; 66(8), 71-76.
- Hardin IR, Li Y. *Textile Chemists and Colorists* 1998; 67, 9: 23-29.
- Hsieh YL, Hartzell M. *Textile Research Journal* 1998; 68, 4: 233-241.
- Grancarić AM, Pušić T, Lesić-Domšić B, Plantić Lj. *Tekstil* 2001; 50, 2: 55-62.
- Grancarić AM, Pušić T, Tarbuk A. *Journal of Natural Fibers* 2006; 3, 2/3: 189-197.
- Grancarić AM, Ujević D, Tarbuk A, Brlobašić Šajatović B. *Tekstil* 2009; 58, 11: 537-545.
- Grancarić AM, Tarbuk A, Marković L. *Book of Proc. 2nd SEM*, Ed. University of Zagreb, Zagreb, Croatia, 2007, 221-226.
- Bischof-Vukušić S, Soljačić I, Katović D. *Tekstil* 1994; 43, 3: 136-143.
- Eriksson KE, Cavaco-Paulo A. *Enzyme applications in fiber processing*. Ed. A. C. S., Michigan, 1998.
- Etters JN, Annis PA. *Americam Dyestuff Reporter* 1998; 87, 5: 18-23.
- Peran J, Pušić T. *Tekstil* 2013; 62, 7-8: 329-337.
- Aehle W., *Enzymes in Industry: Production and Applications*. 3rd ed, Wile-VCH, Verlag GmbH&Co. KGaA, Weinheim, 2007.
- Forte Tavčer P. *Waste Water - Treatment and Reutilization*. Ed. FS. García Einschlag, Chapter 20, In Tech, 2011.
- Nierstrasz VA, Warmoeskerken MMCG. *Textile Processing with Enzymes*. (Eds. Cavaco-Paulo A, Gúbitz G. Ed. Woodhead Publishing Ltd, Cambridge, England, 2003: 129-131.
- Saravanan D, Sivasaravanan S, Sudharsan Prabhu M, et al. *J. Appl. Polym. Sci.* 2012; 123: 2445-2451.
- Eren HA, Anis P, Davulcu A. *Textile Res. J.*, 2009; 79, 12: 1091-1098.
- Forte-Tavčer P. *Biocatalysis and Bio-transformation* 2012; 30, 2: 20-26.
- Yachmenev VG, Bertoniere NR, Blanchard EJ. *Journal of Chemical Technology and Biotechnology* 2002; 77, 5: 559-567.
- Etters JN. *TCC & ADR* 1999; 1, 3: 33-36.
- Preša P, Forte Tavčer P. *Tekstilec* 2007; 50, 1-3: 16-34.
- Rajendran R, Sundaram SK, Radhai R, Rajapriya P, Pak P. *J. Biol. Sci.* 2011; 14, 9: 519-525.
- Tzanov T, Calafell M, Guebitz G, Cavaco-Paulo A. *Enzyme Microb. Technol.* 2001; 29, 6: 357-362.
- Jordanov I, Mangovska B, Forte Tavčer P. *Tekstil* 2010; 59, 10: 439-446.
- Calafell M, Garriga P. *Enzyme and Microbial Technology* 2004; 34, 3-4: 326-331.
- Grancarić AM, Tarbuk A, Pušić T. *Coloration Technology* 2005; 121, 4: 221-227.
- Grancarić AM, Chibowski E, Tarbuk A. *Tekstil* 2008; 57, 1-2: 29-39.
- Grancarić AM, Pusic T, Soljacic I, Biscan J. *Polimeri* 2002; 23, 6: 121-128.
- Luxbacher T, Bukšek H, Petrinić I, Pušić T. *Tekstil* 2009; 58, 8: 401-409.
- Stana-Kleinschek K, Ribitsch V. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* 1998; 140: 127-138.
- Pusic T, Grancarić AM, Soljacic I, Ribitsch V. *Journal of the Society of Dyers and Colourists* 1999; 115, 4: 121-124.
- Grancarić AM, Ristić N, Tarbuk A, Ristić I. *Electrokinetic Phenomena of Cationised Cotton and its Dyeability with Reactive Dyes. Fibres & Textiles in Eastern Europe* 2013; 21, 6, 102: 106-110.

Received 10.02.2014 Reviewed 25.04.2014