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NEW COMBINED BIO-SCOURING AND BIO-BLEACHING PROCESS OF COTTON FABRICS

NOV, ZDRUŽENI POSTOPEK BIOIZKUHAVANJA IN BIOBELJENJA BOMBAŽNIH TKANIN

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A new commercial bio-bleaching process for cellulose fibres was investigated in this study. The process runs enzymatically with arylesterase enzymes (EC 3.1.1.2) and hydrogen peroxide. The enzyme system catalyses the perhydrolysis of propylene glycol diacetate. During the reaction propylene glycol and peracetic acid as a bleaching agent are formed in situ. The main advantage of the bleaching with peracetic acid is that a satisfactory degree of whiteness of a cotton fabric can be obtained at 65 °C at a neutral pH. The bleaching performance of the new bio-bleaching process on a traditionally alkaline-scoured and bio-scoured 100 % cotton fabric and the feasibility of a one-bath bio-scouring/bio-bleaching pre-treatment were investigated. The whiteness degrees, tenacities at maximum loads and water absorbencies of the treated cotton fabrics were compared. The hydrogen peroxide and peracetic acid concentrations, pH and TOC values of the remaining treatment solutions were measured. The research showed that the new bio-bleaching system has a powerful bleaching ability under mild process conditions and that bio-scouring and bio-bleaching can be efficiently combined in a one-bath process.

Keywords: cotton, bio-scouring, bio-bleaching, peracetic acid

V študiji je bil raziskan nov komercialni postopek biobeljenja celuloznih vlaken. Proces poteka encimsko z encimi arilesterazami (EC 3.1.1.2) in vodikovim peroksidom. Med reakcijo se v kopeli tvorita propilen glikol in perocetna kislina kot belilno sredstvo. Poglavitna prednost beljenja s perocetno kislino je zadostna stopnja beline bombažne tkanine, dosežena pri 65 °C v nevtralnem pH. Raziskana je bila belilna sposobnost novega biobelilnega postopka na tradicionalno alkalno izkuhani in bioizkuhani 100 % bombažni tkanini in možnost enokopelnega procesa bioizkuhavanja in biobeljenja. Pri obdelanih bombažnih tkaninah je bila izmerjena stopnja beline, natezna trdnost ob maksimalni obremenitvi in vodovpojnost. Pri odpadnih obdelovalnih kopelih je bila izmerjena koncentracija vodikovega peroksida in perocetne kisline, pH in TOC-vrednost. Raziskava je pokazala, da ima nov biobelilni postopek močno belilno sposobnost v blagih procesnih razmerah in da sta lahko postopka bioizkuhavanja in biobeljenja uspešno združena v enokopelni proces.

Ključne besede: bombaž, bioizkuhavanje, biobeljenje, perocetna kislina

1 INTRODUCTION

The most important natural cellulose fibre is cotton, whose use is constantly increasing. Natural cotton is highly hydrophobic and slightly coloured. To prepare the fibres for further treatment and use, pretreatment processes are needed. With scouring, non-cellulose substances (wax, pectin, proteins, hemicelluloses, etc.) that surround the fibre cellulose core are removed and, as a result, fibres become hydrophilic. With bleaching the natural pigments of cotton fibres are removed and fibres become white. Traditionally, scouring and bleaching processes are conducted at the temperatures up to 120 °C in a very alkaline medium at a pH of 10 to 12. In these treatments large amounts of auxiliary agents are added. Due to the high working temperatures, a lot of energy is consumed. Large amounts of water are used to rinse and neutralise the alkaline-scoured and bleached fabrics. Consequently, the textile industry is considered to be one of the biggest water, energy, and chemical consumers. To comply with the increasingly more rigorous environmental regulations and to save water and energy, biotechnology and several types of enzymes have entered the textile sector. Bio-scouring with enzyme pectinases is an alternative to sodium hydroxide scouring in the removal of non-cellulose substances from the cotton-fibre surface. The process occurs at moderate temperatures in a slightly acidic or alkaline medium which is dependent on the type of pectinases.[1,2]

Some of the alternatives to bleaching with hydrogen peroxide (HP) have been explored in the textile, and pulp and paper industries, i.e., the enzymatic bleaching using peroxidases,[3] laccase/mediator system and glucose oxidases[4–6] and bleaching with the peracids either produced industrially[7] or generated *in situ* from different bleach activators.[8]

A new commercial bio-bleaching product, Gentle Power Bleach from Huntsman, is available on the market. It functions enzymatically with arylesterase enzymes (EC 3.1.1.2) and HP. The enzyme system catalyses the perhydrolysis of propylene glycol diacetate. During the reaction propylene glycol and peracetic acid (PAA) as the bleaching agents are formed in situ. If bio-scouring and bio-bleaching could be combined into one process, large amounts of water, energy, time and auxiliary agents would be saved.

The objective of our work was to investigate the bleaching performance of the new bio-bleaching process on a traditionally alkaline-scoured and bio-scoured 100 % cotton fabric. Secondly, the feasibility of a one-bath process combining bio-scouring and bio-bleaching pre-treatments was investigated. The whiteness degree, tenacity at maximum load and water absorbency of the treated cotton fabrics were evaluated. After the treatments, the pH and TOC (total organic carbon) values of the remaining baths were measured. The quantities of HP and PAA in the remaining bleaching baths were also measured.

2 EXPERIMENTAL WORK

2.1 Materials

Desized cotton fabric, 100 g/m^2, was obtained from Tekstina, Slovenia. Beisol PRO (a commercial pectinase solution), Felosan RG-N (a non-ionic wetting agent), Cotoblanc HTD-N (an anionic wetting and dispersing agent) and Lawotan RWS (a non-ionic wetting agent) were supplied from CHT, Germany. The Gentle Power Bleach chemicals (CLARITE® LTC, INVATEX® LTA, INVAZYME® LTE) were supplied from Huntsman, Switzerland. H_2O_2 35 % (HP) was obtained from Belinka, Slovenia and Stabilizer SIFA from Clariant. NaOH and Na_2CO_3 were purchased from Sigma Aldrich.

2.2 Treatment methods

The desized cotton fabric was treated according to the procedures presented in **Table 1**. Two parallel sets of experiments were undertaken. The treatments were performed in a laboratory dyeing machine DL-6000 Plus from Starlet in the 500 ml bakers at a liquor ratio of 1 : 20. After each treatment the samples were washed in hot water, rinsed twice in cold water and air dried.

Table 1: Abbreviations of the treatments and treated samples with treatment descriptions
Tabela 1: Okrajšava obdelave in obdelanega vzorca z opisom obdelave

Treatment/sample abbreviation	Treatment description
AS	alkaline scouring
TB (AS)	two-bath alkaline scouring and traditional bleaching with HP
BB (AS)	two-bath alkaline scouring and bio-bleaching
BS	bio-scouring
BB (BS)	two-bath bio-scouring and bio-bleaching
BS/BB	one-bath bio-scouring and bio-bleaching
BS/BB+	one-bath bio-scouring and bio-bleaching with an additional final temperature rise

Alkaline scouring (AS) was carried out in a bath containing 2 g/l of Cotoblanc HTD-N and 3 g/l of NaOH at 95 °C for 40 min. Traditional bleaching (TB) was carried out in a bath containing 10 ml/l of H_2O_2 (35 %), 0.1 g/l of Lawotan RWS, 0.5 g/l of Stabilizer SIFA and 4 g/l of NaOH at 90 °C for 60 min. The ingredients and data conditions for bio-treatments are presented in **Tables 2** and **3**.

Table 2: Ingredients of bio-treatments
Tabela 2: Sestavine bioobdelav

Ingredient	Bio-treatment				
	BB (AS)	BS	BB (BS)	BS/ BB	BS/ BB+
1 g/l Felosan RG-N	–	+	+	–	–
2 g/l Beisol PRO	–	+	+	+	+
1.5 g/l CLARITE® LTC	+	–	+	+	+
3 g/l INVATEX® LTA	+	–	+	+	+
6 ml/l H_2O_2 35 %	+	–	+	+	+
1 g/l INVAZYME® LTE	+	–	+	+	+
2 g/l Na_2CO_3	+	–	+	+	+

+ the ingredient is included in the treatment bath
– the ingredient is not included in the treatment bath

Table 3: Data conditions for bio-treatments
Tabela 3: Podatki pogojev bioobdelave

	Bio-treatment conditions				
	BB (AS)	BS	BB (BS)	BS/BB	BS/BB+
Bio-scouring	–	55 °C, 15 min 85 °C, 15 min	55 °C, 15 min 85 °C, 15 min	–	–
Bio-bleaching	65 °C, 60 min	–	65 °C, 60 min	65 °C, 60 min	65 °C, 60 min
Final treatment	–	–	–	–	85 °C, 15 min

– the treatment step was not included

2.3 Analytical methods

Prior to the measurements, samples were conditioned for 24 h at 20 °C and 65 % relative humidity. The pH was measured using a pH meter MA5740 (Iskra, Slovenia). The rates of PAA and HP were measured with iodometric titrations.[5] The degree of whiteness was measured with a spectrophotometer Spectraflash SF600 Plus (Datacolor, Switzerland) using the CIE method, according to EN ISO 105-J02:1997(E). The water absorbency was measured according to DIN 53 924 (the velocity of the soaking water for textile fabrics, the method for determining the wicking height). The measurements of the tenacity at maximum load were performed on a Tensile Tester Model 5567 (Instron, USA). The total organic carbon (TOC) was measured with a TOC-5000A (Shimadzu, Japan) according to ISO 8245.

3 RESULTS AND DISCUSSION

3.1 Concentration of oxidants during the bio-bleaching process

The measurements confirmed that during the bio-bleaching process HP is converted into PAA (**Figure 1**). Almost 0.02 mol/l of PAA was produced and con-

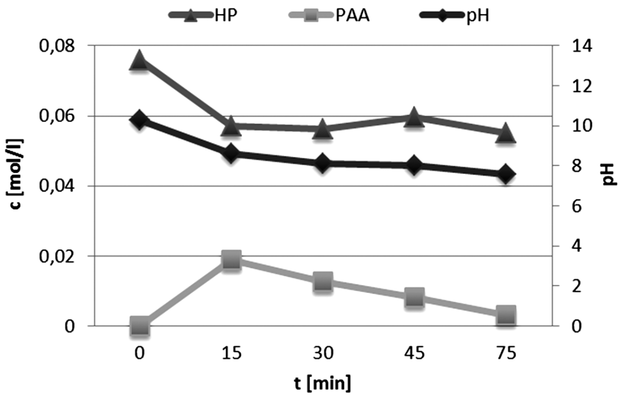

Figure 1: Changes in the concentrations of hydrogen peroxide (HP) and peracetic acid (PAA) and change in the pH during bio-bleaching of an alkaline-scoured sample (during the first 15 min the bath was heated to 65 °C)

Slika 1: Sprememba koncentracije vodikovega peroksida (HP) in perocetne kisline (PAA) ter sprememba pH med biobeljenjem alkalno izkuhanega vzorca (začetnih 15 min je bila kopel ogrevana na 65 °C)

sumed during the bleaching process. During the bleaching with PAA, acetic acid is formed and the pH decreases. For this reason the starting pH was set to be highly alkaline (pH 10.3). During the process the pH decreased to 7.6.

3.2 Fabric analysis

3.2.1 Whiteness

The achieved degrees of whiteness (*W*) are presented in **Table 4**. The alkaline-scoured sample (AS) had a whiteness of 20.7 and the bio-scoured sample (BS) had a whiteness of 10. After the alkaline scouring, the fibres swelled, became smoother and clean of non-cellulose impurities and the degree of whiteness increased. Alkaline scouring is more intensive and removes some of the coloured substances from the fibre that the bio-scouring does not. The whiteness degrees of both samples increased significantly after the bleaching process. The highest whiteness (84.5) was obtained on the HP-bleached and alkaline-scoured sample (TB (AS)). Not much less (81.7) was obtained on the alkaline-scoured and bio-bleached sample (BB (AS)), while the whiteness degrees of bio-scoured and bio-bleached samples were lower: 73.5 on the separately bio-scoured and bio-bleached sample (BB (BS)), 67.8 on the one-bath bio-scoured and bio-bleached sample (BS/BB) and 72.8 on the one-bath bio-scoured and bio-bleached sample with the final temperature rise. As it can be seen in **Figure 1**, a high quantity of HP remains in the bio-bleaching bath. At a pH bellow 10 °C and at 65 °C HP is very stable and does not contribute to the bleaching of the fibres. The rising of the temperature at the end of the bio-bleaching process activated the remaining HP, which further increased the degree of whiteness.

3.2.2 Tenacity at maximum load

There were no significant differences in the tenacity values among all the treated samples in the weft directions whereas the tenacity values in the warp directions were very different. The highest value was measured on the alkaline-scoured sample (AS) and on most of the bio-bleached samples. The high tenacity of the AS sample is a result of the contraction of the fabric exposed to a high process temperature. After the HP bleaching of the alkaline-scoured sample (TB (AS)) the tenacity at maximum load decreased significantly. On the other hand, the tenacity after the bio-bleaching of the alkaline-scoured sample remained similar (BB (AS)). These results confirm that during a bio-bleaching process the fabric does not get damaged.

3.2.3 Water absorbency

The remaining substances influence the water absorbency. All the treated samples revealed very good absorption properties. The highest rising height was measured on the traditionally alkaline-scoured and HP-bleached sample (TB (AS)). The rising height of the bio-scoured samples was a bit lower but the differences among all the treated samples were not significant. All the samples could be considered to be absorbent.

Table 4: Whiteness degree (*W*), tenacity at maximum load (σ_s) and wicking height after 300 s of various sample treatments

Tabela 4: Stopnja beline (*W*), trdnost ob maksimalni obremenitvi (σ_s) in višina kapilarnega dviga v času 300 s različno obdelanih vzorcev

	W	σ_s/ (cN/10^{-6} kg m^{-1})		Wicking height (cm)	
Sample		warp	weft	warp	weft
AS	20.68	26.41	16.09	–	–
TB (AS)	84.51	18.36	13.01	6.27	5.67
BB (AS)	81.68	25.50	13.57	–	–
BS	10.11	22.08	13.20	5.62	4.75
BB (BS)	73.47	19.86	12.87	5.12	4.62
BS/BB	67.84	25.99	14.01	5.00	4.15
BS/BB+	72.77	25.52	15.93	5.10	4.27

3.3 Ecological parameters of the remaining treatment baths

The ecological parameters – the remaining concentrations of HP and PAA, the final pH and TOC values – are presented in **Table 5**. High quantities of the unconsumed HP remained in all the bleaching baths, especially in the traditional one. In all the bio-bleaching baths PAA was detected, but the concentrations were low, meaning the PAA was consumed for the bleaching of the cotton fabric.

Traditional alkaline scouring and bleaching are conducted in an alkaline environment. These baths should be neutralised prior to drainage into the sewage system. During the neutralisation, salts that additionally load wastewaters are produced. The final pH value of the bio-scouring bath was 6 and it was around 7.5 for the bio-bleaching baths. Since none of these treatment processes requires a neutralisation of the fabric, the treatment process can be shorter and less expensive.

Bio-scouring, traditional bleaching and alkaline scouring baths had low TOC values and all the bio-bleaching baths had significantly higher values. A bio-bleaching bath includes more additives than other processes; especially enzymes contribute a lot of organic carbon. On the other hand, enzymatic processes require much less water, energy and time, which compensate for high TOC values from the ecological point of view. Nevertheless, all the treatments exceeded the limit TOC values (60 mg C/l) for direct drainage into the sewage system.

Table 5: Ecological parameters of the remaining treatment baths (concentrations of hydrogen peroxide – HP and peracetic acid – PAA, final pH and TOC values)
Tabela 5: Ekološki parametri odpadnih obdelovalnih kopeli (koncentracija vodikovega peroksida – HP in perocetne kisline – PAA, končni pH in vrednosti TOC)

Treatment	*c* (HP)/ (mol/l)	*c* (PAA)/ (mol/l)	pH	*TOC* /(mg/l)
AS	–	–	11.0	1096
TB (AS)	0.1084	–	11.7	558
BB (AS)	0.0542	0.0032	7.6	2372
BS	–	–	5.7	510
BB (BS)	0.0531	0.0034	7.4	2510
BS/BB	0.0588	0.0042	7.6	2673
BS/BB+	0.0608	0.0012	7.4	2842

4 CONCLUSIONS

The research showed that the new bio-bleaching system with enzymatically gained peracetic acid has a powerful bleaching ability under mild process conditions, i.e., a neutral pH and a temperature of 65 °C. With the new bio-bleaching process the fabrics with a high whiteness degree, good water absorbency and high tenacity at maximum load were obtained having properties comparable to the results of the traditional process. During the bio-bleaching process the cotton fabric did not get damaged as during the traditional pre-treatment. A slightly higher degree of whiteness was obtained on the alkaline-scoured cotton fabric compared to the bio-scoured one. Bio-scouring and bio-bleaching can be efficiently combined in a one-bath process. The final temperature rise of the one-bath process contributes to a higher whiteness degree. This kind of a one-bath process is shorter, consuming less energy and hence being less expensive.

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