OPTIMIZATION OF ENZYMATIC DESIZING AND SCOURING OF COTTON FABRIC BY RESPONSE SURFACE METHODOLOGY

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The study aimed to estimate the influence of temperature, time, and ultrasound application during desizing and scouring of cotton with α-amylase and pectinase, respectively, on the weight loss, breaking force and color difference between raw and bio-scoured cotton, to obtain purified and hydrophilic cotton, with a simultaneous slight decrease in mechanical properties. Under the optimal conditions, determined by the application of Response Surface Methodology (time – 30 min, temperature – 59.4 °C, with ultrasound treatment), a weight loss of 4.97%, color difference of 3.86, and a breaking force of 730.22N were obtained. The bio-scoured cotton fabric was also characterized in terms of electro-kinetic and sorption properties, chemical composition and morphology of the cotton surface by zeta-potential measurement, wicking and contact angle determination, FTIR and SEM characterization, respectively. The developed enzymatic scouring process leads to obtaining purified, whiter and hydrophilic cotton, with slight changes in mechanical properties, which makes bio-scoured cotton fabric suitable for further wet processing.

Keywords: bio-scouring of cotton, α-amylase and pectinase, ultrasound application, response surface methodology, hydrophility

INTRODUCTION

The excellent physico-chemical characteristics of cotton, such as softness, and its hygroscopicity, *i.e.* good moisture absorption that ensures good thermo-physiological comfort, together with its mechanical properties, have made cotton one of the top-grade raw materials from the group of natural fibers for clothing and technical textile manufacturing. Therewithal, cotton fiber does not release harmful substances over time, and allergies to pure cotton have barely been recorded.[1,2] It is estimated that today the world production and consumption of cotton is 27 million tons of cotton per year.[3]

The seed hairs of cotton plants present the main source of cellulose in almost pure form. The chemical composition of cotton can vary to a lesser extent, depending on the type of seed and growing conditions, but, generally, cotton fibers consist mainly of cellulose (95–97%), while non-cellulosic compounds (pectins, fats and waxes, mineral compounds, proteins, organic acids, *etc*., are present in much smaller quantities, from 3% to 5%, and they are arranged in a layered structure of cotton, which includes the cuticle, primary and secondary layers.[1,4–6] In the middle of the fiber there is a canal (lumen), which is surrounded by a secondary wall rich in cellulose. The secondary wall is wrapped by a concentric primary wall that is formed from cellulose, hemicelluloses and pectin substances that have the role of plant adhesive in the cotton primary wall.[4] A primary wall is surrounded by cuticula – a protective layer

full of waxes, pectin substances, proteins, *etc*. The presence of non-cellulosic substances make cotton fibers less hydrophilic and reduce their reactivity.[1]

In order to remove hydrophobic components and other non-cellulose impurities from cotton fibers, enhance absorbency and facilitate further treatments, it is necessary to perform pretreatments of raw cotton.[7] Besides bleaching, dewaxing, extraction, *etc*., one of the most important pretreatments of cotton is scouring.[8] The typical scouring treatments of cotton include processing with an alkaline solution and an appropriate amount of detergents at high temperatures.[9] The appropriate conditions for alkali scouring generally depend on several factors, such as the type of scouring agent and fabric type, *i.e.* woven or knitted, thick or thin; texturized or non-texturized, color, the extent of impurities present in the fibers, *etc.* The selection of alkali is most important as free alkali can have a deleterious effect on certain fibers. Karmakar,[9] for example, lists the use of the following processing conditions: boiling of cotton fabric with a solution of 10 to 20 g/L (3 to 6% o.w.f.) caustic soda in a kier with a liquor ratio of 3:1); in single stage boiling, a mixture of caustic soda and soda-ash boil (in a ratio of 2:1) is often used. Although after alkaline processing, cellulose has a high absorbency, it becomes harsh.[8,10] Also, since large amounts of energy and water are consumed in these processes, it is important to find alternative ecological and economical processes that do not lead to the formation of large amounts of effluent.[11–13] Having in mind the reduction in the use of pollutant chemicals in cellulose treatments, enzymes are nowadays increasingly used, and their application is becoming a more common step of wet textile processing.[14,15] Enzymatic treatments are nature-friendly, non-toxic, reduce the amount of pollution generated during textile processing, and have low energy consumption, reducing the vast amounts of discharged wastewater.[16–18] Predominant enzymes used in textile processing for removing non-cellulosic components from cellulose fibers are amylase, pectinase, lipase, *etc.*, which may be used alone or combined.[19–21]

During the weaving process, to prevent the warp yarn from breaking, it is common to use starch, which can be easily removed after weaving using alpha-amylase enzymes that break down starch into glucose and water-soluble oligosaccharides.[15,16] Alpha-amylase enzymes differ significantly in terms of optimal conditions for desizing: for most amylase treatments, the optimal temperature is at least 70 °C, and the optimum pH (5.5-7.5),[15] but higher temperatures than 70 °C are preferred. For these purposes, at temperatures even higher than 95 °C, thermostable amylases can be used.[22] The main advantage of using higher temperatures lies in the fact that the same efficiency is achieved but in a shorter time in comparison with the conventional process.[23–25] However, there is a global trend towards reducing temperature, time, and the use of chemicals in the wet-pretreatment of textiles. So, a more efficient process could involve the use of amylase, which works at lower temperatures. Desizing does not need an as high temperature and as much time as the conventional process does. Desizing is done below 70 °C, while conventional caustic desizing is done around 90-105 °C. Higher temperature means higher energy consumption, which, in turn, increases the cost of desizing and is more time-consuming.

Another important enzyme for enhancing the scouring process, originating from the *Bacillus subtilis* bacteria, is pectinase,[26] which degrades the pectin substances and plant cell walls of cellulose fibers,[14] which can be easily washed out in subsequent washing.[27] Fabric breakage, pilling formation, hydrophility and uniformity of dyeing are all controlled by the pectinase-based scouring.[28–30]

Enzymatic effectiveness can be additionally enhanced by the ultrasound application.[12,31–34] The effect of ultrasound enables faster movement of liquid, which results in increased diffusion of the dissolved substance within the pores of the fabric.[35–37] Harifi and coauthors found that the influence of ultrasound on enzyme activity consists in the induction of powerful strike waves that initiate the substantial stirring of the liquid layer at a solid-liquid phase, enhancing the influence of enzymes on textile materials during scouring in those mixed phases.[38]

Response Surface Methodology (RSM) is a set of mathematical and statistical tools designed to optimize mathematical models to best suit experimental data, predict an adequate response, as well as for planning experiments to optimize testing conditions to ensure the desired response as a function of input variables.[39] RSM has tools for evaluating complex systems of many different processes with many parameters, and it is commonly used for the optimization of processes in many areas, especially for research, planning and control of processes.[40–42] There are numerous

examples of RSM applications to optimize different processing processes of textile materials.[31,43–48]

Shanthi and Krishnabai tested the effect of different experimental parameters (pH, enzyme dosage and temperature), on the removal of natural and accidental impurities from two fabrics (cotton and lycra cotton weft knitted fabric), to make them suitable for further processing like dyeing and finishing.[45] To ascertain the optimal experimental conditions, they used the response surface methodology using the Box–Behnken model, and the optimum values were found to be pH 8.5, enzyme dosage 0.4% on weight of fabric and temperature 55 °C. Perincek and Duran studied the desizing and bio-scouring of greige woven linen fabrics with commercial enzymes in one bath with the aid of ultrasound energy.[46] They chose five factors with three levels Box–Behnken response surface experimental design to study and optimize the influence of different process variables: amylase concentration, laccase concentration, pectinase concentration, sonication time and treatment temperature, on the whiteness, lightness, weight loss and hydrophility properties of linen samples. They provided a regression model that presented an excellent explanation of the relationship between the independent variables and the response. Zhu *et al*. investigated different physicochemical properties of pre-wetted cotton yarns and optimized the snailase treatment for raw cotton yarns.[48] Based on single factor design, they studied the effects of snailase treatment on the removal percentage of pectins and cotton waxes, wettability, weight loss in different snailase concentrations and the optimal concentration range was obtained. Also, they employed the Box-Behnken design to determine the optimal condition of snailase treatment for achieving the maximum wettability of cotton yarns.

Based on all the above mentioned, the aim of this work is to develop and optimize a non-polluting and low-cost scouring process of cotton fabric by the RSM application. The influence of different temperatures (55, 75 and 95 °C), time (15, 30 and 45 min), and ultrasound application during desizing of cotton fabric with α-amylase and scouring with pectinase, on the weight loss, breaking force and elongation, color difference between raw and bio-scoured cotton, was estimated and optimized. Optimized conditions for the bio-scouring purification are needed in order to obtain a maximal increase of hydrophilic properties of cotton fabric, with a minimal decrease in mechanical properties and weight loss, with increased wicking properties, which makes bio-scoured cotton fabric suitable for further wet processing.

EXPERIMENTAL

Materials and method

Plain weave raw cotton fabric with a surface mass per unit area of 163.30 g/m^2 and yarn linear density of 40.70 tex, with a fabric count of warp 21.3 cm^{-1} and weft 19.0 cm^{-1}, was used in this research. The research plan is shown in Figure 1. Cotton warp yarns are sized before weaving to increase the strength of the yarn and reduce hairiness. Starch based materials are mostly used as sizing materials, which helps the weaving process by reducing end breakage during interlacing. For efficient dyeing and finishing, these size materials must be removed. The process by which size materials are removed is known as desizing. In the first stage, the commercial enzyme α-amylase – Termamyl, produced by Novozymes, Denmark, with the activity of 120 KNU (one Kilo Novo alpha-amylase Unit (KNU) is the amount of enzyme that breaks down 5.26 g starch per hour in Novozymes' standard method for determination of alpha-amylase) was used for desizing of cotton fabric. After that, the commercial pectinase enzyme Endozym Eclair, manufactured by AEB, Italy, with high pectinlyasic activity (total pectinolytic activity 16800 U/g) was used for bioscouring of cotton fabric.

Two-stage bio-scouring of cotton fabric with α-amylase and pectinase enzymes

The first stage of desizing of cotton fabric was the treatment with a commercial enzyme α-amylase – Termamyl. In the fleet ratio of 1:30, the cotton fabric was soaked in the solution of 2 mL/L of α-amylase and 1 g/L of nonionic agent Leonil FW, and at a mixture pH 5.5. The modification was done at an appropriate temperature (55 °C, 75 °C, 95 °C), for 15, 30 and 45 min, according to the procedure shown in Figure 1. In one case, the modification was done without the presence of ultrasound, in a WNB 22 water bath (Memmert, Germany), while in the other case, the modification was done under the same conditions, but in the presence of ultrasound, *i.e.* in a WUC-A03H ultrasonic bath (Witeg Labortechnik, Germany).

In the second stage of bio-scouring, cotton fabric was treated with pectinase – Endozym Eclair. 8 g/L pectinase was added to the acetate buffer solution, and the pH value was adjusted to 4. In a fleet ratio of 1:30, a sample cotton fabric, previously pretreated with α-amylase, was added to the prepared buffer solution and it was treated for 45 minutes, again, one way without ultrasound, and a second –with ultrasound application (+ US, Fig. 1).

Afterward, the cotton samples were rinsed with hot water (80 °C), with the addition of 1 g/L NaH_2PO_4, then with cold water and distilled water, in the rinsing fleet ratio of 1:50, and then drained and dried at 105 °C to constant weight.

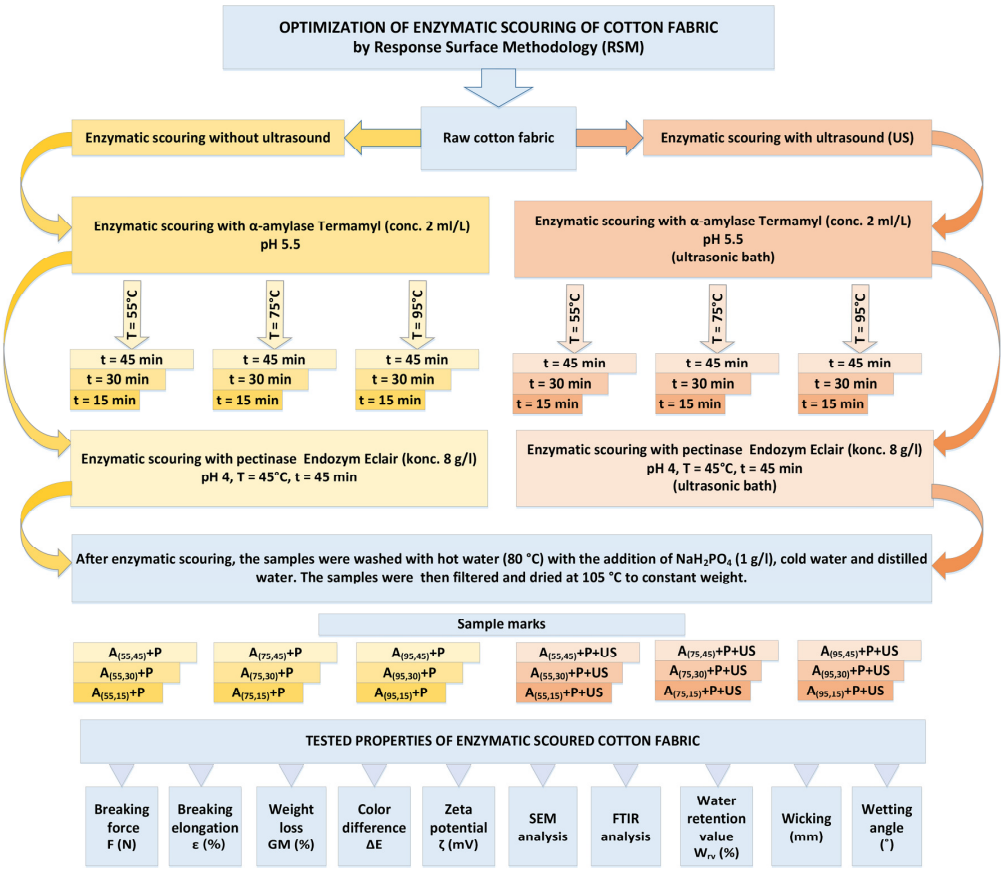

Figure 1: Research plan for two-stage enzymatic scouring and characterization of cotton fabric

Design of experiments and mathematical modeling

The design of experiments, the development and the evaluation of mathematical models were performed using the I-optimal design method and Historical Data method, with the application of the Design-Expert 11 program (Stat-Ease, Inc.). The following variables were used as independent variables: temperature (Factor 1) and presence of ultrasound (Factor 2), and time (Factor 3). The monitored dependent variable (response) was the change of the sample weight (Response 1), breaking force (Response 2), and color difference (Response 3).

The numerical optimization of the developed mathematical models was also carried out with the application of the Design-Expert 11 program (Stat-Ease, Inc.), to determine the optimal temperature, resulting in the minimum reducing breaking force and weight loss as consistent as possible. During optimization, it is necessary to select the limits for every variable and its level of significance, and optimization criteria with a general objective.

Methods of analysis of textile materials

Determination of weight loss after enzymatic treatment

The weight loss, obtained after bio-scouring, was measured using the direct gravimetric method.[49]

Testing of breaking force and elongation

The breaking force and elongation of raw fabric and enzyme-treated fabric were determined according to the standard method.[50]

Determination of CIEL*a*b* color coordinates, color difference (ΔE) and whiteness index

Determination of CIE L*a*b* color coordinates and whiteness index (WI) of the raw and enzymatically scoured cotton fabrics, as well as of the color difference (ΔE) between the samples modified with and without ultrasound application, was performed according to the literature.[51,52]

Zeta potential measurement

The zeta potential of the unmodified and enzymatically scoured cotton samples was measured on a Sur-PASS Electrokinetic Analyzer (Anton Paar GmbH, Austria) by determination of streaming potential, according to the procedure given in the literature.[53,54]

FT-IR ATR characterization spectroscopy

The structural characterization of the raw and enzymatically scoured cotton fabrics was performed by Attenuated Total Reflection (ATR) Fourier Transform Infrared Spectroscopy (FTIR). The spectra were recorder on a Thermo Fisher Scientific Nicolet™ iS™ 10 spectrometer.

SEM analysis of surface morphology

SEM microphotographs of cotton samples, previously sputter-coated with Au alloy, were recorded and observed by a Zeiss ULTRA Plus Scanning Electron Microscope at 10 kV.

Wicking and water retention determination

Wicking, *i.e.* capillary rise measurement, and water retention value were investigated according to the procedure described in the literature[55] and the standard method,[56] respectively.

Determination of wettability

The measurement of the contact angle of a water drop was done to determine the wettability of cotton fabric, according to the literature.[57–59]

RESULTS AND DISCUSSION

The influence of temperature (55, 75 and 95 °C), time (15, 30 and 45 min), and ultrasound application during scouring with α-amylase and pectinase of cotton fabric on weight loss, mechanical properties and the color difference between raw and bio-scoured cotton, are shown in Figures 2 and 3, and Tables 1 and 2.

The severity of the enzymatic treatments can be generally characterized by the determination of weight loss of bio-scoured cotton samples. Under the tested conditions, the weight loss varied moderately and ranged from 3.12% to 7.84% (Fig. 2). The obtained weight loss is probably the result of the water-solubility of impurities from cotton fabrics during bio-scouring. Alfa amylase degrades starch to glucose and water-soluble oligosaccharides,[16] while pectinase depolymerizes the pectin to water-soluble oligomeric carbohydrates.[26] Greater weight loss is obtained in the case of bio-scouring under the highest temperature and with prolongation of treatment time, as well as with ultrasound application. Ultrasound energy is known for its effectiveness and sonication produces two key actions: cavitation and heating.[32] Strong strike waves formed from small cavitation bubbles after falling on the solid phase, initiate the substantial stirring of the liquid layer, enhancing the influence of enzymes on textile materials during scouring, and leading to efficient cleaning of the cotton fibers from impurities.[12] This leads to an increase in the values obtained for weight loss in the case of ultrasound assisted enzymatic scouring of cotton fabric, under the same other conditions (Fig. 2). The obtained results are in accordance with numerous studies that have reported on the effect of ultrasound application during enzymatic purification of cotton fabric.[21,24,31]

The results of the influence of enzymatic scouring of cotton fabric with/without ultrasound application on the breaking force and elongation of cotton fabric show slight changes, *i.e.* a decrease of breaking force, in the range from 744.74 N to 712.16 N, in all bio-scoured cotton samples, while for breaking elongation – an increase from 28.5% to 31.6% was obtained, compared to the breaking force and elongation of the raw cotton fabric (Table 1). The breaking force and elongation of raw cotton fibers are 768.73 N and 23.7%, respectively. Changes in breaking force after enzymatic scouring are more pronounced in the case of ultrasound assisted bio-scouring, under the same other conditions. According to the literature,[38] ultrasounds enhance enzyme activity by inducing powerful strike waves that initiate substantial stirring of the liquid layer at a solid-liquid phase.

The influence of enzymatic scouring of cotton fabric under different conditions on CIE-Lab coordinates and color difference (ΔE) between the raw and the bio-scoured cotton samples are shown in Table 2. In the case of bio-scouring without ultrasound application, the color difference was in the range from 1.45 to 2.56, while in the presence of ultrasound, ΔE ranged from 1.83 to 4.07.

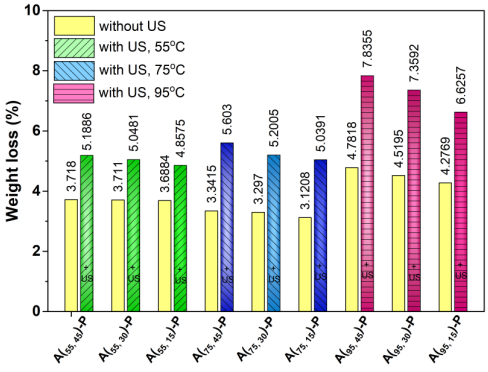

Figure 2: Influence of ultrasound application during enzymatic scouring, under the same other conditions, on weight loss of cotton samples

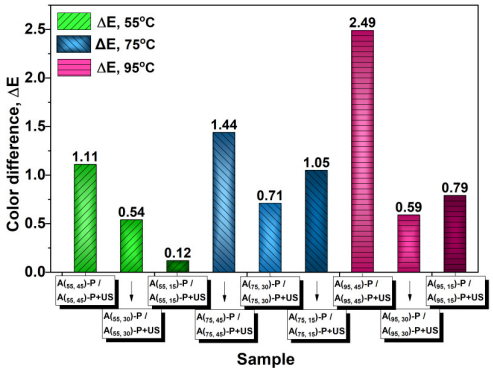

Figure 3: Influence of ultrasound application during enzymatic scouring, under the same other conditions, on color difference (ΔE) of cotton samples

Table 1
Influence of enzymatic scouring of cotton fabric without/with ultrasound assisting on breaking force (F) and elongation (ε) of cotton fabric

Sample code	Enzymatic scouring without ultrasound		Sample code	Ultrasound assisted enzymatic scouring	
	F (N)	ε (%)		F (N)	ε (%)
Raw cotton	768.73	23.7	-	-	-
$A_{(55, 45)}$-P	740.15	29.7	$A_{(55, 45)}$-P + US	728.84	28.5
$A_{(55, 30)}$-P	740.20	29.0	$A_{(55, 30)}$-P + US	729.92	31.2
$A_{(55, 15)}$-P	741.38	30.2	$A_{(55, 15)}$-P + US	731.39	31.8
$A_{(75, 45)}$-P	743.04	30.1	$A_{(75, 45)}$-P + US	725.65	31.1
$A_{(75, 30)}$-P	743.39	29.8	$A_{(75, 30)}$-P + US	728.75	31.0
$A_{(75, 15)}$-P	744.74	31.6	$A_{(75, 15)}$-P + US	729.99	28.7
$A_{(95, 45)}$-P	731.97	29.6	$A_{(95, 45)}$-P + US	708.49	29.6
$A_{(95, 30)}$-P	733.99	28.9	$A_{(95, 30)}$-P + US	712.16	29.8
$A_{(95, 15)}$-P	735.85	30.8	$A_{(95, 15)}$-P + US	717.39	29.2

A – scouring with amylase; 55, 75 and 95 °C – temperature of scouring with amylase; 15, 30 and 45 min – time of scouring with amylase; P – scouring with pectinase; US – ultrasound assisted enzymatic scouring

Table 2
Influence of enzymatic scouring of cotton fabric without/with ultrasound application on CIE-Lab coordinates and color difference (ΔE) between the raw and bio-scoured cotton fabric

Sample code	Bio-scouring without ultrasound				Sample code	Ultrasound assisted bio-scouring			
	L*	a*	b*	ΔE*		L*	a*	b*	ΔE*
Raw cotton	89.58	0.45	13.05	-	Raw cotton	89.58	0.45	13.05	-
$A_{(55, 45)}$-P	88.68	0.86	11.52	1.82	$A_{(55, 45)}$-P + US	87.62	0.96	11.22	2.73
$A_{(55, 30)}$-P	88.39	1.10	12.05	1.68	$A_{(55, 30)}$-P + US	88.02	1.17	12.43	1.83
$A_{(55, 15)}$-P	88.68	0.95	12.04	1.45	$A_{(55, 15)}$-P + US	88.62	1.02	11.97	1.55
$A_{(75, 45)}$-P	87.88	1.35	12.29	2.07	$A_{(75, 45)}$-P + US	87.15	1.01	11.10	3.17
$A_{(75, 30)}$-P	88.26	1.00	12.00	1.77	$A_{(75, 30)}$-P + US	87.66	1.36	11.91	2.41
$A_{(75, 15)}$-P	88.47	1.06	12.15	1.55	$A_{(75, 15)}$-P + US	88.38	1.23	11.12	2.40
$A_{(95, 45)}$-P	88.28	1.34	11.04	2.56	$A_{(95, 45)}$-P + US	85.94	1.77	11.79	4.07
$A_{(95, 30)}$-P	88.91	1.05	10.86	2.37	$A_{(95, 30)}$-P + US	88.38	1.22	10.64	2.80
$A_{(95, 15)}$-P	88.81	1.04	11.43	1.89	$A_{(95, 15)}$-P + US	88.29	1.23	10.86	2.66

A – scouring with amylase; 55, 75 and 95 °C – temperature of scouring with amylase; 15, 30 and 45 min – time of scouring with amylase; P – scouring with pectinase; US – enzymatic scouring with the ultrasound assisting

The influence of ultrasound application during enzymatic scouring is also confirmed by a comparison of color difference between the cotton samples scoured with and without ultrasound,

under the same other scouring conditions (Fig. 3). Higher color difference was determined for the samples scoured for 45 min, while the highest color difference was obtained in the case of scouring under the most severe conditions (95 °C and 45 min). The effectiveness of enzymatic purification of cotton is increased by acoustic cavitation, probably due to the improved transfer of molecules, which leads to the acceleration of the reaction rate, so ultrasound amplifies the performance of enzymes.[31,33,35]

Based on the test results for mass loss, breaking force and breaking elongation, the measured color coordinates (L*a*b*), and the calculated values for color difference (ΔE) between enzymatically scoured samples at different temperatures and processing times, it was concluded that only mass loss and breaking force are affected by temperature in the entire temperature range analyzed. Therefore, it was decided to develop a mathematical model that would describe such influence in the presence and the absence of ultrasound. For the optimization of the enzymatic scouring of cotton fabric, Response Surface Methodology was used.

Development of numerical models

During optimization, it is necessary to select the limitations (the range for every variable and its level of significance) and optimization criteria with the objective. The influence of the temperature and ultrasound presence on the monitored dependent variables (responses R1 and R2) was determined for enzymatic scouring time of 30 and 45 minutes. We found that there was no significant influence of time on R1 and R2.

Table 3 shows the design of experiments with the corresponding results of measurement of the responses. The influence of the temperature and ultrasound presence on the color difference (response R3) was determined for enzymatic scouring time of 15, 30 and 45 minutes. Table 4 shows the design of experiments with the corresponding results of measurement of R3 (ΔE). Table 5 shows the basic data on the analyzed responses R1, R2 and R3.

The relationship between the dependent variables (temperature, time and ultrasound) and the modeled variable (weight loss, breaking force and color difference) was tested by fitting to linear, quadratic, cubic and higher-order equations, where the applied software selected a second-degree polynomial as an optimum model for R1 and R2 responses, and a linear model in the case of R3 response. We have tried to model as a second-degree function which is presented as (1):

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + e$$

where Y_i is the response of interest (R1, R2 and R3); X_i – independent variables (temperature, time and ultrasound); β_0 – constant coefficient; β_1, β_2 – linear coefficients; β_{12}, – coefficient of interaction between the variables; β_{11} and β_{22} – quadratic coefficients, and e is the modeling error.

Table 3
Design of experiments using the I-optimal design option

Run	Factor 1 A: Temperature	Factor 2 B: Ultrasound	Response 1 Weight loss (%)	Response 2 Breaking force (N)
2	55	No	3.711	740.20
5	95	No	4.5195	733.99
6	55	No	3.718	740.15
8	75	No	3.297	743.39
1	75	Yes	5.2005	728.75
3	55	Yes	5.0481	729.92
4	95	Yes	7.3592	712.16
7	55	Yes	5.1886	729.92
9	95	Yes	7.8355	708.49

Table 4
Design of experiments using the Historical Data design method

Factor 1 A: Temperature	Factor 2 B: Ultrasound	Factor 3 C: Time	Response 3 Color difference (ΔE)
55	No	15	1.45
55	No	30	1.68
55	No	45	1.82
75	No	15	1.55
75	No	30	1.77
75	No	45	2.07
95	No	15	1.89
95	No	30	2.37
95	No	45	2.56
55	Yes	15	1.55
55	Yes	30	1.83
55	Yes	45	2.73
75	Yes	15	2.40
75	Yes	30	2.41
75	Yes	45	3.17
95	Yes	15	2.66
95	Yes	30	2.80
95	Yes	45	4.07

Table 5
Response analysis

Response	Name	Observ.	Analysis	Min.	Max.	Mean	Std. Dev.	Ratio	Model
R1	Weight loss, %	9	Poly-nomial	3.297	7.8355	5.10	1.58	2.38	Quadratic
R2	Breaking force, N	9	Poly-nomial	708.49	743.39	729.45	12.18	1.05	Quadratic
R3	ΔE	9	Poly-nomial	1.45	2.56	1.91	0.3677	1.77	Linear
R3 (US)	ΔE	9	Poly-nomial	1.55	4.07	2.62	0.7342	2.63	Linear

The influence that independent variables have on the dependent variable in the proposed mathematical model was determined by applying Fisher's statistical test (F-test) as part of the analysis of variance (ANOVA). ANOVA analysis of the tested mathematical models showed that weight loss and breaking force may be described by a quadratic model, and the obtained models are presented by equations in coded form (2) and (3), and by an equation with actual values of the variables (2a and 2b) and (3a and 3b):

$$R_1 = 4.25 + 0.8290 \cdot A + 1.08 \cdot B + 0.4105 \cdot AB + 0.9967 \cdot A^2 \quad (2)$$

$$Weight\ loss\ (US\ No) = 15.61 - 0.3528 \cdot T + 0.0025 \cdot T^2 \quad (2a)$$

$$Weight\ loss\ (US\ Yes) = 14.70 - 0.3118 \cdot T + 0.0025 \cdot T^2 \quad (2b)$$

$$R_2 = 736.07 - 6.27 \cdot A - 8.39 \cdot B - 3.05 \cdot AB - 7.77 \cdot A^2 \quad (3)$$

$$Breaking\ force\ (US\ No) = 647.23 + 2.7540 \cdot T - 0.0194 \cdot T^2 \quad (3a)$$

$$Breaking\ force\ (US\ Yes) = 653.30 + 2.4494 \cdot T - 0.0194 \cdot T^2 \quad (3b)$$

ANOVA analysis of the tested mathematical models showed that color difference, without and with ultrasound – US, in both cases may be described by linear models. The obtained models are presented by equations in coded form (4) and (5), and by an equation with the actual values of the variables (6) and (7):

$$R_3(US\ No) = 1.91 + 0.3117 \cdot A + 0.2600 \cdot C \quad (4)$$

$$R_3(US\ Yes) = 2.62 + 0.5700 \cdot A + 0.5600 \cdot C \quad (5)$$

$$Color\ difference\ (US\ No) = 0.22 - 0.0156 \cdot T + 0.0173 \cdot t \quad (6)$$

$$Color\ difference\ (US\ Yes) = -0.63 - 0.0285 \cdot T + 0.0373 \cdot t \quad (7)$$

These equations could be used to predict weight loss and breaking force for a given temperature and usage of ultrasound. Usually, input variables are coded in the range of -1 to +1, so this way the relative impact of factors could be identified. In our case, factor A is coded linearly between values -1 to +1, where -1 corresponds to 55, and +1 to 95. In the case of factor B, the coded value of -1 corresponds to the absence of ultrasound (US No), and the coded value +1 corresponds to the presence of ultrasound (US Yes). Factor C is coded linearly between values -1 to +1, where -1 corresponds to 15, and +1 to 45 minutes. The coding method of variables is presented in Table 6.

The results of the analysis show that the developed models are statistically significant. The p-values are below 0.05 and that shows a very high statistically significant influence. High F-values of the models indicate a relatively low probability (0.02%) that it could be an effect of noise in the experiments (Table 7). Those are the members of Equation (2) with the variables A, B, AB and A^2. That means that the specified values may be used for the prediction of the response (weight loss), by simple insertion of the coded values A and B, or, in the case of Equations (3a) or (3b), by inserting the actual temperature values.

The low value of the parameter Lack of Fit (1.05) for the F-value implies that the Lack of Fit is not statistically important compared to the error. The probability is 38.00% that a Lack of Fit F-value is so large due to measurement error. According to Prasad *et al*., (2012)[60] low value of Lack of Fit is an additional parameter that indicates that the model fits. The Model F-value of 101.55 (Table 8) implies the model is significant.

Tabel 6
Coding method of variables

Factor	Name	Type	Min.	Max.	Coded Low	Coded High	Mean	Std. Dev.
A	Temp., °C	Numeric	55.00	95.00	-1 ↔ 55.00	+1 ↔ 95.00	72.78	18.56
B	Ultrasound	Categoric	No	Yes	-1 ↔ No	+1 ↔ Yes	Levels	2
C	Time, min	Numeric	15	45	-1 ↔ 15.00	+1 ↔ 45.00	30.00	12.99

Table 7
Analysis of variance (ANOVA) for a quadratic model in coded form (Eqs. 2)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	19.87	4	4.97	119.20	0.0002	significant
A-Temperature	4.44	1	4.44	106.58	0.0005	
B-Ultrasound	9.80	1	9.80	235.24	0.0001	
AB	1.09	1	1.09	26.13	0.0069	
A^2	1.52	1	1.52	36.41	0.0038	
Residual	0.1667	4	0.0417	-	-	-
Lack of Fit	0.0434	1	0.0434	1.05	0.3800	not significant
Pure Error	0.1233	3	0.0411	-	-	-
Cor. Total	20.03	8	-	-	-	-

Table 8
Analysis of variance (ANOVA) for a quadratic model in coded form (Eqs. 3)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1174.50	4	293.63	101.55	0.0003	significant
A-Temperature	254.16	1	254.16	87.90	0.0007	
B-Ultrasound	590.82	1	590.82	204.34	0.0001	
AB	59.94	1	59.94	20.73	0.0104	
A^2	92.30	1	92.30	31.92	0.0048	
Residual	11.57	4	2.89	-	-	
Lack of Fit	2.99	1	2.99	1.04	0.3820	not significant
Pure Error	8.58	3	2.86	-	-	
Cor. Total	1186.07	8	-	-	-	

Table 9
Analysis of variance (ANOVA) for a quadratic model in coded form (Eq. 4)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.9884	2	0.4942	31.75	0.0006	significant
A-Temperature	0.5828	1	0.5828	37.45	0.0009	
C-Time	0.4056	1	0.4056	26.06	0.0022	
Residual	0.0934	6	0.0156			
Cor. Total	1.08	8				

Table 10
Analysis of variance (ANOVA) for a quadratic model in coded form (Eq. 5)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.83	2	1.92	23.87	0.0014	significant
A-Temperature	1.95	1	1.95	24.30	0.0026	
B-Time	1.88	1	1.88	23.45	0.0029	
Residual	0.4814	6	0.0802			
Cor. Total	4.31	8				

Table 11
Fit statistics of regression models (Eqs. 2 and 3)

	Equation 2	Equation 3		Equation 2	Equation 3
Std. Dev.	0.2041	1.70	R^2	0.9917	0.9902
Mean	5.10	729.45	Adjusted R^2	0.9834	0.9805
C.V. %	4.00	0.2331	Predicted R^2	0.9424	0.9327
			Adeq. Precision	28.8972	26.7198

Table 12
Fit statistics of regression models (Eqs. 4 and 5)

	Equation 4	Equation 5		Equation 4	Equation 5
Std. Dev.	0.1248	0.2833	R^2	0.9137	0.8884
Mean	1.91	2.62	Adjusted R^2	0.8849	0.8512
C.V. %	6.54	10.79	Predicted R^2	0.8142	0.7571
			Adeq. Precision	15.8736	13.8192

Similar analysis (ANOVA) can be carried out for Equation (4) (Table 9) and Equation (5) (Table 10). The Model F-value of 31.75 in Table 9 implies the model is significant. There is only a 0.06% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A and C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Model F-value of 23.87 in Table 10 implies the model is significant. There is only a 0.14% chance that an F-value this large could occur due to noise.

The further validation of the developed models (Eqs. 2 and 3) was carried out by analyzing the fit statistics from Tables 11 and 12 for Equations (4) and (5). Table 11 shows that, apart from extremely high values of the obtained coefficient of determination (R^2), the values of the Adeq. Precision parameter (28.8972 for Eq. 2 and 26.7198 for Eq. 3) are significantly higher than 4, which is considered the acceptance limit for a relation between noise and response. In addition, the very close values of Adjusted R^2 and Predicted R^2, whose difference is less than 0.2, show the presence of the tested correlation between the independent variables and the dependent variable (weight loss).[61] Similar conclusions can be drawn from Table 12. In the case of Equation (4), the Predicted R^2 of 0.8142 is in reasonable agreement with the Adjusted R^2 of 0.8849; *i.e.* the difference is less than 0.2. In the case of Equation (5), the Predicted R^2 of 0.7571 is in reasonable agreement with the Adjusted R^2 of 0.8512; *i.e.* the difference is less than 0.2.

All this indicates that the tested models may be used for determining the corresponding responses (R_1 and R_2) in a designed space (the tested range

of variation in the values of independent variables A and B).

The chart in Figures 4 and 5 shows that weight loss and breaking force changes, both as a function of temperature and as a function of presence (B2 – Yes) or absence of ultrasound (B1 – No). The separate dependence of weight change in the presence (green line) or absence (red line) of ultrasound is clearly visible because there is no overlapping within 95% of statistical significance (± 95% CI Bands). It can also be noticed that weight change has a minimum value (equation of quadratic form) and that the obtained model was further optimized to find the optimal value of temperature for a minimum weight loss. Also, one can notice that breaking force change has a maximum value (equation of quadratic form) and that the obtained model was further optimized to find the optimal value of temperature for a minimum weight loss.

The chart in Figures 6 and 7 shows color difference changes, as a function of both temperature and time. Figure 6 shows those changes in the absence of ultrasound, while Figure 7 shows them with ultrasound presence.

Additional optimization of the created equations was done with the Design-Expert 11 program (Stat-Ease, Inc.), in order to determine the minimum temperature, resulting in the minimum weight loss as consistent as possible. We selected the limits for every variable and its level of significance, and optimization criteria with a general objective (Table 13).

The results of numerical optimization of the developed mathematical models are presented in Figure 8. Consequently to the accepted optimization criteria presented in Table 13, the optimum conditions are the temperature of 59.4 °C and the application of the ultrasound treatment. Under such conditions, the weight loss of the sample after enzymatic treatments is of 4.97%, and the breaking force is 730.22 N. The results present the highest level of desirability of 0.370.

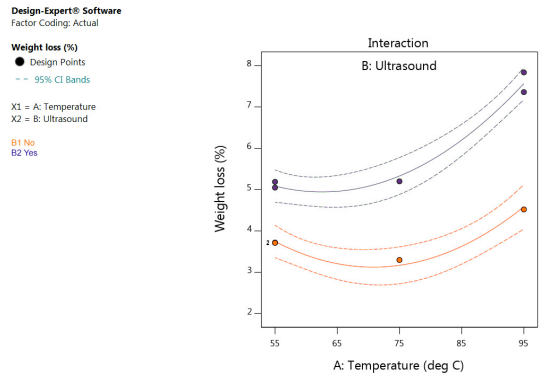

Figure 4: Plot of the developed model of dependence of weight loss on temperature without ultrasound (B1 No) and with ultrasound (B2 Yes); (Responses from runs 2 and 6 are overlapped, and thus represented as one point - 2)

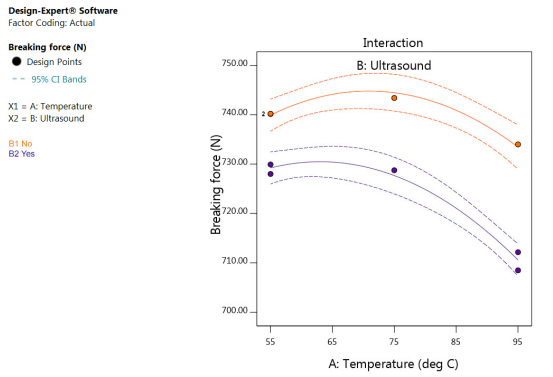

Figure 5: Plot of the developed model of dependence of breaking force on temperature without ultrasound (B1 No) and in the presence of ultrasound (B2 Yes)

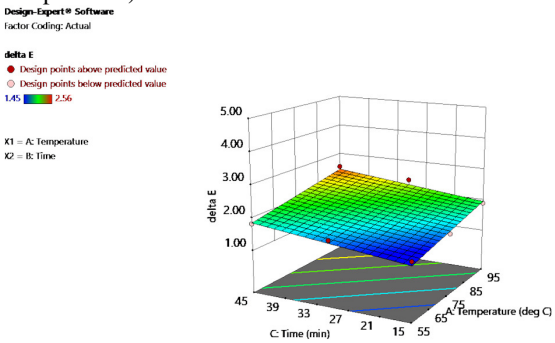

Figure 6: Plot of the developed model of dependence of color difference (ΔE) on temperature and time, without ultrasound

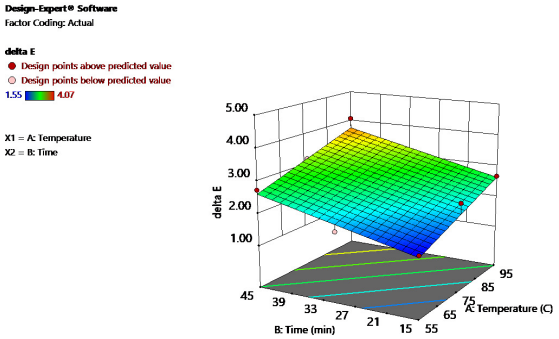

Figure 7: Plot of the developed model of dependence of color difference (ΔE) on temperature and time, with ultrasound

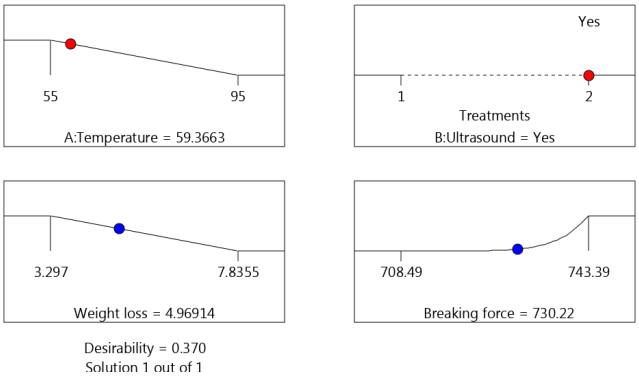

Figure 8: Results of numerical optimization of the developed mathematical model

Table 13
Optimization criteria of regression model

	Optimization objective	Range of numerical values	Level of significance of the objective (from 1 to 5)
Factor A	in range	55-95 °C	5
Factor B	Equal to yes	Yes	Not applicable
Response R_1	none	3.297-7.8355	3
Response R_2	none	708.59-743.39	3

Based on the results of testing breaking force (Table 1) and weight loss (Fig. 2) of enzyme-treated fabric under different treatment conditions, and the achieved color difference (ΔE) in comparison with the raw fabric (Table 2), the color difference between fabric treated with and without the application of ultrasound (Fig. 3), as well as the RSM methodology, we selected the optimum procedure of fabric pretreatment, which was performed for 30 minutes at a temperature of 59.4 °C, with the application of ultrasound (Figs. 4 and 5).

Under the optimal conditions, a weight loss of 4.97%, color difference of 3.86, a water retention value of 32.40%, as well as breaking force and elongation of 730.22 N and 28.6%, respectively, were obtained for bio-scoured cotton fabric.

Characterization of cotton fabric bio-scoured under optimized conditions – Chemical composition, morphology, electro-kinetic and sorption properties

The cotton fabric bio-scoured under the optimum treatment conditions was subjected to the following analyses: FTIR, SEM, zeta potential, capillarity and contact angle, in order to gain an insight into whether the selected conditions for treating cotton fabric with α-amylase and pectinase enzymes were appropriate for subsequent wet treatments of the samples.

FT-IR ATR measurement

The effects of α-amylase and pectinase scouring of cotton fabric were investigated by recording the FT-IR spectra of the raw and enzymatically treated cotton fabric, and their analysis (Fig. 9).

Due to the similar structure of cellulose and starch moiety in the spectrum of cotton fabric, characteristic vibrations of their groups were overlapped and thus not easily recognized in the spectra. The O-H stretching vibration of hydroxyl groups was noticed at 3331 cm^{-1} and 3286 cm^{-1}.[62,63] The region of 2916-2850 cm^{-1} belongs to the C-H stretch vibrations of symmetric and asymmetric methyl and methylene groups of the polysaccharide moiety in cotton fabric. These peaks confirmed the presence of waxes.[63] The absence of peaks for ester groups around 1730 cm^{-1} corresponding to non-cellulosic structure, present in waxes and the ester moiety in pectin, confirms their low content in raw cotton fabric. A band at 1632 cm^{-1} was assigned to the deformation vibrations of the O-H groups. Other bands related to C-H bending and wagging vibration of the methylene and methyl groups, O-H in-plane bending, as well as asymmetric and symmetric vibration of the C-O-C and C-O groups, appear at 1427 cm^{-1}, 1365 cm^{-1}, 1314 cm^{-1} and in the 1204-1028 cm^{-1} region, respectively. Vibration at 896 cm^{-1} originates from the *β*-

glucosidic bond.[63] Small changes in the peak structure/intensity ratio after scouring with enzymes could be observed in the 2916-2850 cm^{-1} region and around 1600 cm^{-1}, as well as in the 1054-1028 cm^{-1} region, while in the rest of the spectra, no observable differences were found. As a result of the purification process by enzymes, in the region 2916-2850 cm^{-1}, the peak at 2916 cm^{-1} disappeared, while lower intensity was noticed at 2897 cm^{-1} and 2850 cm^{-1}, which indicates the decreased presence of waxes after the application of enzymes. The peak at 1622 cm^{-1} in the raw cotton fabric also decreased, and the concomitant shift to 1645 cm^{-1} in enzymatically treated cotton is a result of enzymatic scouring. The intensity of the characteristic vibrations of ether (C-O-C and C-O) groups increased in the spectrum of the bio-scoured cotton fabric. This increase is probably due to different mechanisms in the structure of cotton during enzymatic scouring. Generally, changes in absorption intensity on the fabric surface are an expected result, because, as it is known, the purification process of cotton with α-amylase and pectinase has been successful in removing starch and pectin from cotton, respectively.[18]

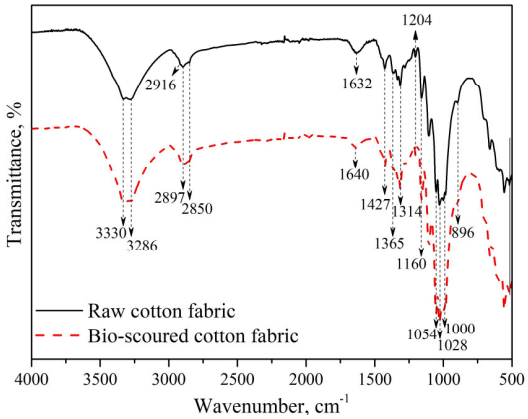

Figure 9: FT-IR spectra of raw and enzymatically scoured cotton fabrics

Surface morphology

During enzymatic scouring, which is a procedure carried out under wet conditions, in addition to removing impurities, the textile materials undergo some structural changes[14,30,37,64–66] that can be monitored by the SEM technique. As may be observed in the SEM microphotograph corresponding to the raw cotton fiber, the surface of the fiber is covered by a thin cuticula and primary wall, which are rich in pectin and other non-cellulose compounds,[1,5] also, the typical parallel ridges and grooves may be seen (Fig. 10a). The surface of the bio-scoured cotton shows more pronounced and unevenly distributed concave grooves (Fig. 10b).

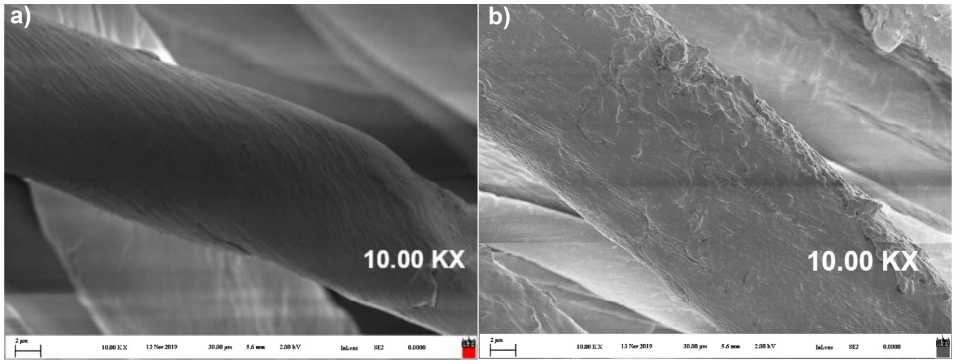

Figure 10: SEM microphotographs of the surface of a) raw and b) enzymatically scoured cotton fabric, under magnification 1000x

Those new characteristics can be ascribed to the effect of pectinase enzyme etching on pectin substances in the thin cuticula and primary wall of cotton.[65]

Potential measurement

During wet treatments of textile materials, the adsorption of chemical compounds from solution onto textile materials surface, as well as their wettability, represents an important phase that influences the success of the processing. Interface phenomena that occurred between the liquid and the solid phase, the aqueous solution and the textile material, lead to changes in the surface free energy and charge of textile materials.[53,67] The changes of the surface charge of cotton fabric caused by enzymatic scouring can be investigated by streaming (zeta) potential determinations, comparing the voltage difference at a range of pH for raw and treated samples.

Both raw and bio-scoured cotton samples displayed negative zeta potential because of the cellulose nature of cotton, *i.e.* the existence of the OH and COOH groups that show a negative surface charge.[27,68] The raw cotton fabric has ζ values close to −13 mV, and an isoelectric point (IEP – pH value where ζ value is equal to zero) at the value of 1.8. Upon enzymatic scouring, however, the cotton fabric ζ values decrease down to −25 mV, indicating a higher degree of purity and hydrophilicity of bio-scoured cotton compared to its raw counterpart (Fig. 11). Obtained increases in the negative of the ζ plateau after enzyme scouring is the result of the degradation and removal of starch and hydrophobic non-cellulose compounds that cover the OH and COOH functional groups of cellulose.[68] The determined weight loss value of 4.97% for cotton fabric scouring with enzymes, obtained as a result of the disintegration of natural pigments, non-cellulosic compounds and impurities in cotton fibers, confirms the removal of non-cellulose compounds from cotton fabric.[27] Also, the inter-fibrillar swelling enlarges the surface area, and zeta potential increases in the negative, because the shear plane is shifting into the liquid phase.[68] At pH values lower than 5, the ζ values continue to increase for both samples. According to the literature, in the case of the enzymatic scouring of cotton, only the complete cleaning of cotton fibers in parallel leads to an increase in the negative values of the ζ plateau, as well as a move of the IEP to lower pH values.[68] Obtaining a higher value for IEP (2.3), after enzymatic treatment, in comparison with IEP of untreated cotton (1.8), in our study, agrees with the literature data,[68] where *inter alia* the enzyme pectinase had been applied for cotton purification. According to the literature,[27] complete degradation is unnecessary because the structure of non-cellulose impurities is destabilized by the degradation of the pectins using pectinases, and the fragments of their complex structure can be washed off. The presents of some waxes in the bio-scoured cotton fabric were confirmed by the FT-IR ATR analysis that is presented above (see Fig. 9).

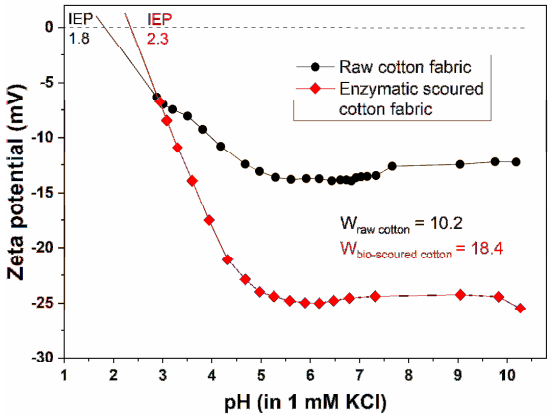

Figure 11: Zeta potential of raw and enzymatically scoured cotton fabrics

It is known that removing the non-cellulose compounds, impurities and natural pigments during cotton bio-scouring leads to changes in color and increases the degree of whiteness of the purified material.[27] On the other hand, since the bio-scouring of the textile materials can be monitored with the ζ-pH function, there is a possibility that changes in the color of the

modified material can be indirectly monitored by the results obtained for streaming potential.[68] According to this, a comparison of the ζ-pH function with the whiteness index (WI) shows that the WI of raw cotton fabric is 10.2, while the sample scoured with enzymes (with increased ζ plateau in the negative) shows a higher whiteness index – of 18.4 (Fig. 11). The results obtained confirm the significant removal the impurities and natural pigments from cotton fabric by the application of two-stage enzyme scouring.

Wicking properties

The changes in chemical composition and surface charge of cotton fabric occurring during enzymatic purification affect the sorption properties of bio-scoured cotton fabric, which have been estimated by wicking, sessile water drop contact angle and water retention measurements. The completely hydrophobic properties of the raw cotton, due to the presence of pectin and waxes in cuticula and its impurities,[1,5] were confirmed by sessile water drop contact angle measurements, with obtained contact angle values of 144.19° (left) and 144.18° (right), as well as by the value zero for wicking height of raw cotton fabric in the warp and weft directions (Fig. 12 a and b).

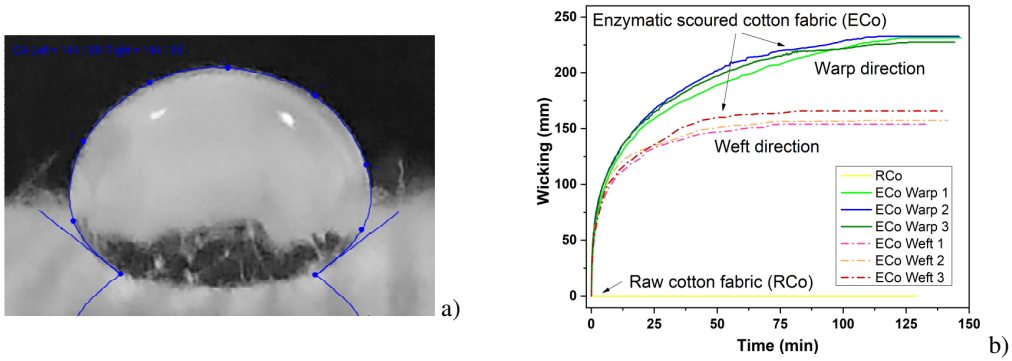

Figure 12: a) Sessile water drop contact angle measurements for raw cotton fabric; b) Wicking measurement for raw and enzymatically scoured cotton fabric in the warp and weft direction

Scouring treatment with amylase and pectinase has an important influence on the wicking properties of modified cotton fabric. During wicking measurement, bio-scoured cotton fabric shows up to 233 mm and 166 mm values for maximum wicking height, in the warp and weft direction, respectively. The wicking properties of bio-scoured cotton fabric are affected by the surface charge, as well as chemical changes that occurred during the enzymatic treatment.[27,34] Enzyme pectinase is suitable for the hydrolysis of pectin and breaks the bond between waxes and other non-cellulosic compounds present in cotton fibers, thereby improving the wicking properties of the bio-scoured cotton fabric.[27] However, the wetting time, during the sessile water drop contact angle measurements of enzymatically scoured cotton fabric, was less than one second, so it was not possible to perform the measurement. Besides the influence on wicking properties, enzymatic scouring significantly increased the water retention value (WRV) of scoured cotton fiber. The WRV of bio-scoured cotton fabric was even 32.40%, which is 9.5 times higher in comparison with the WRV for the raw cotton fabric (3.42%). The increase in wicking ability and water retention value makes cotton fabric available for the dissociation or adsorption of a chemical compound from a solution during further wet treatments, such as natural dyeing with medicinal plant extracts.

CONCLUSION

It can be concluded that RSM was successfully used for the optimization of the two-stage enzymatic scouring of cotton fabric. The application of the I-optimal design method results in the development of a mathematical model based on the second-degree polynomial. The model describes the influence of temperature and ultrasound application during the scouring of cotton samples on weight loss and breaking force. The statistical analysis proved the reliability of the above-mentioned models in the experiments design space. It was established that the influence of temperature can be described by the tested

models with sufficient reliability. The developed mathematical models have been used for the selection of the most appropriate operating conditions: temperature 59.4 °C, time of treatment 30 min, and with ultrasound assistance. Under optimized conditions, the enzymes α-amylase and pectinase not only removed the impurities, but also caused changes in surface charge, which led to obtaining whiter cotton with hydrophilic properties, and a slight decrease in mechanical properties and weight loss. All achieved changes make bio-scoured cotton fabric suitable for various subsequent wet processing. The application of the Historical Data method is a developed model of dependence of color difference (ΔE) on temperature and time, without and with ultrasound application.

The identification of the most appropriate operating conditions for an ecological and economical enzymatic scouring of cotton confirms the scientific value of this research and makes it useful for potential industrial applications.

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REFERENCES

[1] P. J. Wakelyn, "Cotton Fiber Chemistry and Technology", CRC Press, Boca Raton, 2006, https://doi.org/10.1201/9781420045888

[2] P. J. Wakelyn, N. R. Bertoniere, A. D. French, D. P. Thibodeaux and B. A. Triplettet, in "Handbook of Fiber Chemistry", edited by M. Lewin, Taylor and Francis Group, London, 2007, pp. 521–666

[3] OECD-FAO Agricultural Outlook 2021-2030, https://doi.org/10.1787/19428846-en, 2021, accessed on 8 February 2022

[4] T. Heinze, in "Cellulose Structure and Properties", edited by O. Rojas, Springer, Cham, 2015, pp. 1–52, https://doi.org/10.1007/12_2015_319

[5] P. J. Wakelyn, N. R. Bertoniere, A. D. French, D. P. Thibodeaux and B. A. Triplettet, in "Handbook of Fiber Chemistry", edited by M. Lewin, CRC Press, Boca Raton, 2006, pp. 521–666

[6] D. Klemm, B. Heublein, H.-P. Fink and A. Bohn, *Angew. Chem. Int. Ed.*, **44**, 3358 (2005), https://doi.org/10.1002/anie.200460587

[7] S. R. Karmakar, "Chemical Technology in the Pretreatment Processes of Textiles**"**, Elsevier, Amsterdam, The Netherlands, 1999

[8] G. Varadarajan and P. Venkatachalam, *Environ. Chem. Lett.*, **14**, 113 (2016), https://doi.org/10.1007/s10311-015-0533-3

[9] S. R. Karmakar, in "Chemical Technology in the Pre-Treatment Processes of Textiles", edited by S. R. Karmakar, Elsevier, Amsterdam, The Netherlands, 1999, pp. 86–131, https://doi.org/10.1016/S0920-4083(99)80005-X

[10] I. Arslan Alaton, G. Insel, G. Eremektar, F. Germirli Babuna and D. Orhon, *Chemosphere*, **62**, 1549 (2006), https://doi.org/10.1016/j.chemosphere.2005.06.010

[11] P. Senthil Kumar and E. Gunasundari, in "Detox Fashion", edited by S. Muthu, Springer, Singapore, 2018, pp. 37–60, https://doi.org/10.1007/978-981-10-4876-0_2

[12] J. Sheikh and I. Bramhecha, in "The Impact and Prospects of Green Chemistry for Textile Technology", edited by S. Islam and B. Butola, Woodhead Publishing, Sawston, 2019, pp. 135–160, https://doi.org/10.1016/B978-0-08-102491-1.00006-X

[13] S. Saxena, A. S. M. Raja and A. Arputharaj, in "Textiles and Clothing Sustainability", edited by S. Muthu, Springer, Singapore, 2017, pp. 43–79, https://doi.org/10.1007/978-981-10-2185-5_2

[14] S. Kabir and J. Koh, in "Biodegradation Technology of Organic and Inorganic Pollutants", edited by K. Mendes, R. De Sousa and K. Mielke, IntechOpen, London, 2021, p. 494, https://doi.org/10.5772/intechopen.97198

[15] M. Shahid, F. Mohammad, G. Chen, R.-C. Tang and T. Xing, *Green Chem.*, **18**, 2256 (2016), https://doi.org/10.1039/C6GC00201C

[16] D. Saravanan, S. Sivasaravanan, M. Sudharshan Prabhu, N. S. Vasanthi, K. Senthil Raja *et al*., *J. Appl. Polym. Sci.*, **123**, 2445 (2012), https://doi.org/10.1002/app.34838

[17] S. Sarkar, K. Soren, P. Chakraborty and R. Bandopadhyay, in "Advances in Functional Finishing of Textiles", edited by M. Shahid and R. Adivarekar, Springer, Singapore, 2020, pp. 115–127, https://doi.org/10.1007/978-981-15-3669-4_5

[18] R. Araújo, M. Casal and A. Cavaco-Paulo, *Biocatal. Biotransform.*, **26**, 332 (2008), https://doi.org/10.1080/10242420802390457

[19] M. M. Hartzell and Y.-L. Hsieh, *Text. Res. J.*, **68**, 233 (1998), https://doi.org/10.1177/004051759806800401

[20] B. L. Colombi, R. De Cássia Siqueira Curto Valle, J. A. Borges Valle and J. Andreaus, *Clean. Eng. Technol.*, **4**, 100160 (2021), https://doi.org/10.1016/j.clet.2021.100160

[21] A. Niaz, Q. J. Malik, S. Muhammad, T. Shamim and S. Asghar, *Color. Technol.*, **127**, 211 (2011), https://doi.org/10.1111/j.1478-4408.2011.00292.x

[22] A. K. Roy Choudhury, in "Roadmap to Sustainable Textiles and Clothing", edited by S. Muthu, Springer, Singapore, 2014, pp. 203–238, https://doi.org/10.1007/978-981-287-065-0_7
[23] K. Fu, D. Wang, Y. Li and D. Lu, *J. Text. Inst.*, **106**, 1322 (2015), https://doi.org/10.1080/00405000.2014.1000011
[24] M. Rahman, D. Hack-Polay, M. M. Billah and M.N. Un Nabi, *Int. J. Technol. Manag. Sustain. Dev.*, **19**, 87 (2020), https://doi.org/10.1386/tmsd_00017_1
[25] M. T. Hoque, N. Mazumder and M. T. Islam, in "Sustainable Practices in the Textile Industry", edited by L. J. Rather, M. Shabbir and A. Haji, Wiley, 2021, pp. 87–110, https://doi.org/10.1002/9781119818915.ch4
[26] S. Ahlawat, S. S. Dhiman, B. Battan, R. P. Mandhan and J. Sharma, *Process Biochem.*, **44**, 521 (2009), https://doi.org/10.1016/j.procbio.2009.01.003
[27] T. Pušić, A. Tarbuk and T. Dekanić, *Fibres Text. East. Eur.*, **23**, 98 (2015), http://www.fibtex.lodz.pl/article1397.html
[28] T. Tzanov, M. Calafell, G. M. Guebitz and A. Cavaco-Paulo, *Enzyme Microb. Technol.*, **29**, 357 (2001), https://doi.org/10.1016/S0141-0229(01)00388-X
[29] M. Calafell and P. Garriga, *Enzyme Microb. Technol.*, **34**, 326 (2004), https://doi.org/10.1016/j.enzmictec.2003.11.008
[30] M. Joshi, M. Nerurkar, P. Badhe and R. Adivarekar, *J. Mol. Catal. B Enzym.*, **98**, 106 (2013), https://doi.org/10.1016/j.molcatb.2013.10.010
[31] M. Easson, B. Condon, A. Villalpando and S. Chang, *Ultrasonics*, **84**, 223 (2018), https://doi.org/10.1016/j.ultras.2017.11.007
[32] V. G. Yachmenev, E. J. Blanchard and A. H. Lambert, *Ultrasonics*, **42**, 87 (2004), https://doi.org/10.1016/j.ultras.2004.01.011
[33] H. Aksel Eren and B. Erismis, *Color. Technol.*, **129**, 360 (2013), https://doi.org/10.1111/cote.12035
[34] H. Benli and M. İ. Bahtiyari, *Cellulose*, **22**, 867 (2015), https://doi.org/10.1007/s10570-014-0494-x
[35] W. Wang, B. Yu and C. Zhong, *J. Clean. Prod.*, **33**, 179 (2012), https://doi.org/10.1016/j.jclepro.2012.04.010
[36] O. E. Szabó and E. Csiszár, *Carbohyd. Polym.*, **98**, 1483 (2013), https://doi.org/10.1016/j.carbpol.2013.08.017
[37] L. Hao, R. Wang, K. Fang and J. Liu, *Carbohyd. Polym.*, **96**, 474 (2013), https://doi.org/10.1016/j.carbpol.2013.04.003
[38] T. Harifi and M. Montazer, *Ultrason. Sonochem.*, **23**, 1 (2015), https://doi.org/10.1016/j.ultsonch.2014.08.022
[39] W. J. Hill and W. G. Hunter, *Technometrics*, **8**, 571 (1966), https://doi.org/10.2307/1266632
[40] S. Jang, A. Y. Lee, A. R. Lee, G. Choi and H. K. Kim, *Integr. Med. Res.*, **6**, 388 (2017), https://doi.org/10.1016/j.imr.2017.08.003
[41] R. Ghelich, M. R. Jahannama, H. Abdizadeh, F. S. Torknik and M. R. Vaezi, *Compos. Part B Eng.*, **166**, 527 (2019), https://doi.org/10.1016/J.COMPOSITESB.2019.01.094
[42] M. R. Miladinović, O. S. Stamenković, P. T. Banković, A. D. Milutinović-Nikolić, D. M. Jovanović *et al.*, *Energ. Convers. Manag.*, **130**, 25 (2016), https://doi.org/10.1016/j.enconman.2016.10.020
[43] S. Kalantzi, D. Kekos and D. Mamma, *Cellulose*, **26**, 2771 (2019), https://doi.org/10.1007/s10570-019-02272-9
[44] Q. Wang, X.-R. Fan, Z.-Z. Hua and J. Chen, *Biochem. Eng. J.*, **34**, 107 (2007), https://doi.org/10.1016/j.bej.2006.11.004
[45] R. Shanthi and G. Krishnabai, *Carbohyd. Polym.*, **96**, 291 (2013), https://doi.org/10.1016/j.carbpol.2013.03.080
[46] S. Perincek and K. Duran, *J. Clean. Prod.*, **135**, 1179 (2016), https://doi.org/10.1016/j.jclepro.2016.06.193
[47] A. Rehman, Z. A. Raza, R. Masood, M. T. Hussain and N. Ahmad, *Cellulose*, **22**, 2107 (2015), https://doi.org/10.1007/s10570-015-0598-y
[48] B. Zhu, J. Liu and W. Gao, *Appl. Biochem. Biotechnol.*, **182**, 1065 (2017), https://doi.org/10.1007/s12010-016-2382-3
[49] A. I. Koblyakov, "Laboratory Practice in the Study of Textile Materials", Mir Publichers, Moscow, 1989
[50] ISO 13934-1-Textiles, Tensile Properties of Fabrics - Part 1: Determination of Maximum Force and Elongation at Maximum Force Using the Strip Method, International Orgnization for Standardisation-ISO, Switzerland, 2013
[51] J. Schanda, "Colorimetry: Understanding the CIE System", Wiley, New York, 2007
[52] D. Grujić, B. Škipina, D. Cerović, L. Topalić-Trivunović and A. Savić, *Contemp. Mater.*, **12**, (2021), https://doi.org/10.7251/COMEN2101080G
[53] T. Luxbacher, "The ZETA Guide: Principle of the Streaming Potential Technique", Graz, Austria, 2014
[54] J. Z. Milanovic, M. Milosevic, M. Korica, I. Jankovic-Castvan and M. M. Kostic, *Fiber. Polym.*, **22**, 2052 (2021), https://doi.org/10.1007/s12221-021-0450-y
[55] P. M. Milanovic, S. B. Stankovic, M. Novakovic, D. Grujic, M. Kostic *et al.*, *PLoS One*, **15**, e0241665 (2020), https://doi.org/10.1371/journal.pone.0241665
[56] DIN53814, Testing of Textiles; Determination of Water Retention Power of Fibres and Yarn Cuttings, Deutsches Institut fur Normung E.V. (DIN), Germany, 1974
[57] A. F. Stalder, T. Melchior, M. Müller, D. Sage, T. Blu *et al.*, *Colloid. Surfaces A Physicochem. Eng. Asp.*, **364**, 72 (2010), https://doi.org/10.1016/j.colsurfa.2010.04.040
[58] EPFL Biomedical Imaging Group, Free software for high precision contact angle measurement/ImageJ's plugin, EPFL Biomedical Imaging Group, http://bigwww.epfl.ch/demo/dropanalysis/, 2020,

accessed 20 October 2021
[59] L. Putić, J. Stajić-Trošić, V. Ćosović, A. Grujić, J. Milanović *et al*., *J. Text. Inst*., 1 (2022), https://doi.org/10.1080/00405000.2021.2024343
[60] K. N. Prasad, K. W. Kong, R. N. Ramanan, A. Azlan and A. Ismail, *Separ. Sci. Technol*., **47**, 73 (2012), https://doi.org/10.1080/01496395.2011.606257
[61] M. Bimakr, R. A. Rahman, F. S. Taip, N. M. Adzahan, M. Z. I. Sarker *et al*., *Molecules*, **17**, 11748 (2012), https://doi.org/10.3390/molecules171011748
[62] E. K. Choe, M. Lee, K. S. Park and C. Chung, *Text. Res. J*., **89**, 2305 (2019), https://doi.org/10.1177/0040517518790976
[63] C. Chung, M. Lee and E. Choe, *Carbohyd. Polym*., **58**, 417 (2004), https://doi.org/10.1016/j.carbpol.2004.08.005
[64] Q. Wang, X. Fan, W. Gao and J. Chen, *Carbohyd. Res*., **341**, 2170 (2006), https://doi.org/10.1016/j.carres.2006.04.048
[65] E. Csiszar, *Text. Res. J*., **82**, 2030 (2012), https://doi.org/10.1177/0040517512444329
[66] E. Csiszar, Z. Szabo, O. Balogh, E. Fekete and K. Koczka, *Ultrason. Sonochem*., **78**, 105711 (2021), https://doi.org/10.1016/j.ultsonch.2021.105711
[67] A. M. Grancaric, A. Tarbuk and T. Pusic, *Color. Technol*., **121**, 221 (2005), https://doi.org/10.1111/j.1478-4408.2005.tb00277.x
[68] K. Stana-Kleinschek and V. Ribitsch, *Colloid. Surfaces A Physicochem. Eng. Asp*., **140**, 127 (1998), https://doi.org/10.1016/S0927-7757(97)00301-4