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PART I. STUDY REGARDING THE OPTIMIZATION OF THE BIOSCOURING TREATMENT IN ULTRASOUND ON 60 % COTTON + 40 % COTTONISED FLAX MATERIALS

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Abstract: *In the past years the commercial products for the bioscouring treatment were usually dedicated only for 100 % cotton or only for 100% lignocelluloses fabrics. The development of hemp/cotton or flax/cotton mixtures fabrics leds to the necessity of finding of the most apropiate products that could be used for different enzymatic treatments on these types of fabrics.The usage of the commercial product SERA ZYME C-PE for bioscouring treatment in ultrasound conditions on 60 % cotton + 40 % cottonised flax was studied in this work. The optimization of the Bioscouring treatment in ultrasound on 60 % cotton + 40 % hemp materials using the same commercial product was previous published. In order to assess more accurately the influence of some process parameters of the bioscouring treatment in a mathematical modeling of the process was made and a central compound rotatable program with two independent variable: x_1 - the concentration of enzyme (%) and x_2 - treatment time (minutes) was used. The independent variable considered was y_1 – the weight loss. The aim of this study was to investigate the behaviour of cottonised flax/cotton mixtures for the same conditions of bioscouring treatment used as for hemp/cotton mixtures.*

Key words: *cotton, cottonised flax, enzymes, bioscouring treatment with ultrasound, weight loss*.

1. INTRODUCTION

The aim of the removal of the impurities present in the cellulosic materials is to obtain a good absorbency or wettability of the materials necessary for further dyeing and finishing processes. This treatment is referred to as scouring when conventional alkaline processes are followed. And the treatment is referred to as bioscouring when environmentally friendly enzymes are used. The conventional treatment is carried out at higher temperatures with alkalis, which has the disadvantages such as high energy consumption and polluted wastewaters [1]. The bioscouring treatment unlike the classical alkaline treatment is more environmentally friendly by less energy consumption and preserves the fiber's structure and strength by using specific enzymes to remove

non-cellulosic impurities [2, 3]. For the enzymatic treatment the commercial product SERA ZYME C-PE [4], based on 5-15 % Pectate Lyase (E.C.4.2.2.2) in phosphate buffer solution of 0.1 Molar monosodium/disodium phosphate (pH = 7.5) was used. All the experiments were carried out in ultrasound. The producer instructions for usage of SERA ZYME C-PE for 100 % cotton fabrics is to carried out the process less then 20 minutes at 1g/L enzyme concentration [4]. Considering that the lignocellulosic materials shows higher non-cellulosic impurities content we appreciated that the treatment conditions (time and enzyme concentration) for such blended fabrics should be slightly higher than for 100 % cotton fabrics. In this respect the bioscouring treatment for 60 % cotton/40 % cottonised flax blended fabrics was performed in ultrasound with a variable concentration of enzyme (1-3 %) and a larger range for the treatment time (20-60 min.). By measuring the weight loss, the optimum working parameters for the Bioscouring treatment in ultrasound were determined.

2. EXPERIMANTAL PART

Plain woven of 60 % cotton + 40 % cottonised flax composition was used. The woven material has the width 120 ± 3 cm, weight 220 ± 10 g/m^2, warp sett 200 ± 10 fibers/10cm, weft sett 170 ± 10 fibers/10 cm. The treatment was performed in ultrasound in a multi-frequency ultrasonic cleaning unit; model TI-H-10 from Elma Schmidbauer GmbH, Germany. The energy of sonication applied was 200 W (ultrasonic power effective) and 800 W (ultrasonic peak performance max). For the bioscouring treatment a variable concentration between 1-3 % of comercial enzyme was used, 2 mL/L HEPTOL NWS which is a sequestrant agent with binding role for the metal ions in water with high hardness, regardless of temperature; 2 mL/L SULFOLEN 148 a wetting and scouring agent; 10 % of the fleet of treatment was pH = 7.5 buffer solution of 0.1 Molar (sodium phosphate/disodium phosphate,); liquid to fabric ratio - H 10:1, at temperature T = 55 ^{0}C and time - t = (20-60) minutes [5]. After a series of preliminary determinations, to achieve a minimum number of experiments, these were conducted using a central, rotatable second order compound program with two independent variables [6, 7]. The variation limits and experimental plan are presented in Tables 1 and 2.

Table 1: *The variation limits of independent variables*

Value. code / Real value	-1,414	-1	0	1	+1,414
x - enzyme concentration	1	1,7	2	2,7	3
y - time (minutes)	20	34	40	54	60

Table 2: *The experimental plan with two independent variables*

Exp. No.	x	y
1.	-1	-1
2.	1	-1
3.	-1	1
4.	1	1
5.	-1.414	0
6.	1,414	0
7.	0	-1,414
8.	0	1,414
9.	0	0
10.	0	0
11.	0	0
12.	0	0
13.	0	0

3. RESULTS AND DISCUSSIONS

Experimental matrix and the measured values of the response function are shown in Table 3:

Table 3: *Experimental matrix and the measured values of the response function*

No.	Independent variables				Answers
	x		y		x
	x (cod.)	X - Enzyme concentratio [%]	y (cod.)	y Time [min.]	(Y) Weight loss [%]
1.	-1	1.70	-1	34.00	3.04
2.	1	2.70	-1	34.00	1.59
3.	-1	1.70	1	54.00	2.85
4.	1	2.70	1	54.00	1.25
5.	-1.414	1.00	0	40.00	3.55
6.	1.414	3.00	0	40.00	1.11
7.	0	2.00	-1.414	20.00	2.06
8.	0	2.00	1.414	60.00	2.18
9.	0	2.00	0	40.00	4.03
10.	0	2.00	0	40.00	2.57
11.	0	2.00	0	40.00	1.40
12.	0	2.00	0	40.00	1.39
13.	0	2.00	0	40.00	1.89

3.1. Mathematical model interpretation obtained

In order to assess more accurately the influence of some process parameters of the Bioscouring treatment in US of 40 % flax + 60 % cotton blended fabric - the concentration of enzyme (%) and treatment time (minutes) – on the weight loss, a mathematical modeling of the process was made, using a central compound rotatable program with two independent variables**.** The two chosen independent variables are: x - the concentration of enzyme [%] and y - time (minutes). As goal-function the weight loss (%) (denoted by Y) was chosen. Enzyme concentration varies between 1-3 % and the treatment time between 20 - 60 minutes. The second order central compound rotatable program has the following mathematical expression:

$$Y = b_0 + b_1x + b_2y + b_{12}xy + b_{11}x^2 + b_{22}y^2 \quad \textbf{(1)}$$

For the experimental data a program in Mathcad Professional and Excel was used, and a regression equation was obtained [6, 7, 8, 9]. Coefficients of the regression equation are presented in Table 4.

Table 4: *Regression equation coefficients, dispersion and the verification of the significance of the dispersion equation coefficients using the Student test*

Regression equation coefficients		Calculated dispersion "S"	The coefficients significance using Student test $t_T=t_{\alpha,\nu} = t_{0,05;6} = 2,132$; (If tc> t_T-term is significant)		
b0	2.256538	S=0.021251	tc0	9.281732	significant
b1	-0.81252		tc1	-5.34737	significant
b2	-0.04504		tc2	-0.29642	nesignificant
b11	0.027727		tc11	0.158621	nesignificant
b22	-0.07733		tc22	-0.44236	nesignificant
b12	-0.0375		tc12	-0.1234	nesignificant

The regression equation obtained after eliminating insignificant coefficients is:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(2)}$$

3.1.1. Verification of the coefficients significance

Verifying the significance of coefficients is important because it can confirm or invalidate the created model. The Student test compares the average of a random variable with mean standard deviation. For the central part of the program, in which all independent variables have zero code value the dispersion "S" is calculated. The dispersion value was shown in Table 4. The significance of the regression equation coefficients was tested using Student test with critical table value for the test $t_{\alpha,\nu} = t_{0,05;6} = 2,132$. The test values and the significance of the coefficients were presented in Table 4.

3.1.2 Verification of the model adequacy

The appropriate model was verified using Fisher test and percentage deviation.The deviations values are shown in Table 5. To verify the model adequacy and its ability to express the studied phenomenon mathematical, the Y_{calc} values were calculated and the deviation "A" between the measured and calculated values was established according to Table 5. It can be observed that some of the individual deviations do not fit within the limits imposed by ± 10 %, which indicates a poor adequacy of the model.

Table 5: *Adequacy calculation model*

No.	Y meas	Ycalc.	(Ymas. – Ycalc.)^2	Deviation "A"	Average square of residuals "PMrez"	Dispersion of reproducibility "S_0^{2}"	Ratio Fc = PMrez / S_0^2	Statistics Fc<F'c $F'_c = F_{v1, v2, \alpha} = F_{5;5;0,01} = 6,59$	Fisher test Fc>Ft $Ft=F_{v1, v2, \alpha} = F_{12;12;0,05} = 2,69$
1.	3.04	3.02	0.0001	0.427					
2.	1.59	1.47	0.0127	7.109				Fc=	Fc=
3.	2.85	3.01	0.0262	-5.681				0.017482	2.082723
4.	1.25	1.31	0.0038	-4.950					
5.	3.55	3.46	0.0079	2.510					
6.	1.11	1.16	0.0028	-4.781					
7.	2.06	2.16	0.0111	-5.127	4.9473	1.21558	0.01748	0.017482 <6,59	2.082723 <2,69
8.	2.18	2.03	0.0200	6.502					
9.	4.03	2.25	3.1451	44.006				Appropriate model	In-appropriate model
10.	2.57	2.25	0.0982	12.196					
11.	1.40	2.25	0.7336	-61.181					
12.	1.39	2.25	0.7508	-62.340					
13.	1.89	2.25	0.1343	19.393					

The degree of concordance of the mathematical model was verified using F'_c statistics. Initially the average square of residuals PM_{rez} and the reproducibility of dispersion S_0^2 were calculated, obtaining the values shown in Table 5. The ratio $Fc = PMrez/S_0^2$ was compared with the critical value $F'_c = F_{v1, v2, \alpha} = F_{5;5;0,01} = 6,59$. To verify deviation of the survey data from the mean value the Fisher-Snedecor test was used. $F_c = 2.119134$ calculated value is lower than the critical value $F_c = F_{\alpha, v1, v2} = F_{0,05; 12, 4} = 5,91$ which indicates that the deviations appear due to the independent variables. The quality of approximation of the mathematical model expressed by the standard error shows the scattering of the experimental values around the regression equation: 84.06 %. The correlation coefficient has the value: $r_{x1x2} = -0.02032$, $r_{x1y} = -0.7756628$ and $r_{x2z} = -0.0429969$. The significance of the simple correlation coefficients is checked using the Student test. The calculated values are: $tc_{x1y} = -4.07604$, $tc_{x2y} = -0.1427366$, $tc_{x1x2} = -0.067393$. The calculated values are lower than the critical table value $t_{\alpha, v} = t_{0,05; 11} = 2,201$ for t_{x1y} and t_{x2y} which indicates that there is no any relationship between variables, $t_{x1x2} = -0.3752093$ so there is some correlation between independent variables The multiple determination coefficient 0.519859 shows that the influence of the two independent variables on the outcome is 51,98 %, the rest being caused by other factors. The response interpretation and search of extremes are more difficult and it preferred to bring the surface into a form more accessible for the analysis using canonical transformation. Allowing a much easier localization of the extreme, the canonical transformation can be seen as an optimization method. The canonical analysis transforms the regression equation in a more simple form and interprets the resulting expression using geometric concepts:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(3)}$$

In this case we have a first degree equation.

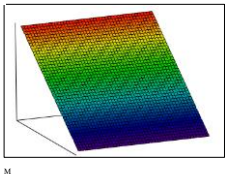

Fig. 1: *The dependence of the goal-function on the independent variables:*

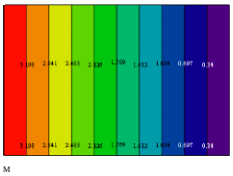

Fig. 2: *Contour curves for various values of Y (weight loss)*

Figure 1 presents the plot which shows the dependence of the goal-function on the two independent variables. The response surface of the regression equation is a plane surface. The constant level curves obtained by cutting the response surface with constant level plans presented in Figure 2 allows the evaluation of the dependent variable *Y*, according to the conditions imposed by the independent variables *x* and *y*. The figure presents contour curves for various values of weight loss, 1.11 to 4.03 between

3.2 Interpretation of the obtained mathematical model technology

By analyzing the expression of the obtained goal function:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(4)}$$

These can be seen: the influence of the two independent parameters, *x* (enzyme concentration) and *y* (treatment time) on the dependent variable *Y* (weight loss) manifests in different way. Only *x* variable (enzyme concentration) influences directly the outcome *Y* (weight loss): the deacreasing of *x* (enzyme concentration) conducts to the increasing of *Y* (weight loss); the influence of variable *x* (enzyme concentration), on *Y* (weight loss) is 31.5 %; the influence of variable y (treatment time), on *Y* (weight loss) is 0 %; the absence of quadratic form for both parameters indicates that the response surface defined by the obtained mathematical model, is not well formed, reinforcing the hypothesis regarding the influence of only one parameter on the outcome.

Figure 3 shows the dependence of the goal-function on one of the two independent variables for all significant values of the parameters, given that the second independent variable is constant. It can be observed how, for a constant value of enzyme concentration, the graph representing the variation of weight loss versus time, indicates for the interval [–1414, 1,414], (between 20–60 minutes) a constant weight loss, which indicates a zero influence of this parameter on the weight loss.

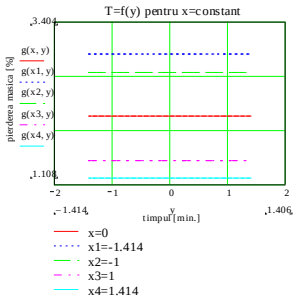

Fig. 3: *The dependence of the goal-function on all significant values of y parameters for x = constant*

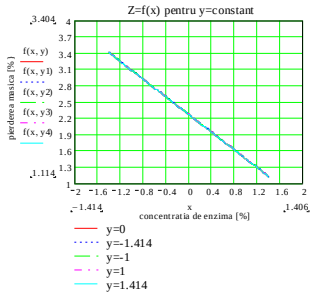

Fig. 4: *The dependence of the goal-function on all significant values of x parameters for y = constant*

Figure 4 shows the dependence of the goal-function of one of the two variables for all significant values of the parameters, given that the second one is constant. From the graph it can be

observed that conducting the experiment with values for variable y between 20–60 minutes will result a linear decrease of weight loss in the same time with the increasing of the enzymes concentration.

4. CONCLUSIONS

It was found that the chosen range of the treatmet parameters (time and concentration) does not influence the process because the enzymatic reaction occurs in less than 20 minutes (as recommended by the producer for 100 % cotton materials). It appears that the behaviour of the 40 % cottonised flax + 60 % cotton fabrics are different from the 40 % hemp + 60 % cotton fabrics [1]. The behaviour of the 40 % cottonised flax + 60 % cotton fabrics is simmilar with 100 % cotton fabrics which can be explained by the fact that previous cottonisation method applied to flax fibers led to fibers with similar characteristics to cotton ones.

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