ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

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

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Abstract: *The paper presents the optimization of the Bioscouring treatment in ultrasound on 60 % cotton + 40 % hemp materials, using the commercial product SERA ZYME C-PE (Roglyr Eco 183), based on 5-15 % Pectate Lyase (E.C.4.2.2.2). In order to assess more accurately the influence of some process parameters of the BIOSCORING treatment in ultrasound of 40 % hemp + 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 Bioscouring treatment was performed in ultrasound under the following conditions: (1-3 %) SERA ZYME C-PE (ROGLYR ECO 183) – Pectate Lyase; 2 mL/L HEPTOL NWS – sequestrant agent which have a binding role for the metal ions in water with high hardness, regardless of temperature; 2 mL/L SULFOLEN 148 - wetting and scouring agent; 10 % of the fleet of treatment was buffer (0.1 Molar sodium phosphate/disodium phosphate, pH = 7.5); liquid to fabric ratio - H 10:1, at temperature T = 55 ^{0}C and time - t = (20-60) minutes. Using the data obtained by measuring the weight loss, the optimum working parameters for the Bioscouring treatment in ultrasound with commercial enzyme SERA ZYME C-PE (ROGLYR ECO 183) were determined.*

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

1. INTRODUCTION

The Bioscouring treatment consists into eliminating natural attendants of the cotton and hemp fiber (non-cellulosic substances) using pectinases [1, 2]. For the enzymatic procedure the treatment with the commercial product SERA ZYME C-PE (Roglyr Eco 183), 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 experimented. For all the experiments the ultrasound energy was used.

2. EXPERIMANTAL PART

For the research, 60 % cotton + 40 % hemp blended fabrics were used, with the following characteristics: width 120 ± 3 cm, weight 220 ± 10 g/m2, warp sett 200 ± 10 fibers/10cm, weft sett 170 ± 10 fibers/10 cm. The Bioscouring treatment was performed in ultrasound under the following conditions: (1-3 %) SERA ZYME C-PE (ROGLYR ECO 183) – Pectate Lyase; 2 mL/L HEPTOL NWS – sequestrant agent which have a binding role for the metal ions in water with high hardness, regardless of temperature; 2 mL/L SULFOLEN 148 - wetting and scouring agent; 10 % of the fleet of treatment was buffer (0.1 Molar sodium phosphate/disodium phosphate, pH = 7.5); liquid to fabric ratio - H 10:1, at temperature T = 55 ^{0}C and time - t = (20-60) minutes [1]. 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 [3, 4]. 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 (% compared to fiber)	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*

Exp. No.	Independent variables				Answers
	x		y		x
	x (cod.)	x (real) Enzyme concentration [%]	y (cod.)	y (real) Time [minutes]	(Y) Weight loss [%]
1.	-1	1.70	-1	34.00	3.09
2.	1	2.70	-1	34.00	2.98
3.	-1	1.70	1	54.00	3.40
4.	1	2.70	1	54.00	2.46
5.	-1.414	1.00	0	40.00	2.34
6.	1.414	3.00	0	40.00	3.39
7.	0	2.00	-1.414	20.00	2.74
8.	0	2.00	1.414	60.00	3.00
9.	0	2.00	0	40.00	3.11
10.	0	2.00	0	40.00	3.12
11.	0	2.00	0	40.00	2.90
12.	0	2.00	0	40.00	2.97
13.	0	2.00	0	40.00	3.10

3.1. Mathematical model interpretation obtained

In order to assess more accurately the influence of some process parameters of the BIOSCORING treatment in ultrasound of 40 % hemp + 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 [%];

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 [3, 4, 5, 6]. The regression equation coefficients 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"	Verification of 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	3.040693	S=0.217896	tc0	1543.499	significant
b1	0.054338		tc1	44.13198	significant
b2	0.019705		tc2	16.00406	significant
b11	-0.05697		tc11	-40.2236	significant
b22	-0.05447		tc22	-38.4577	significant
b12	-0.2075		tc12	-84.264	significant

The regression equation obtained after eliminating insignificant coefficients is:

$$F(x.y) = 3.040 + (0.054)x + (0.019)y + (-0.056)x^2 + (-0.054)y^2 +(-0.207)xy \quad \textbf{(2)}$$

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.

3.1.2Verification 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.	3.09	2.647	0.19562	14.313				Fc=22.121	Fc= 1.262914
2.	2.98	3.171	0.03662	-6.422					
3.	3.4	3.102	0.08873	8.761					
4.	2.46	2.795	0.11275	-13.649					

5.	2.34	2.849	0.26004	-21.792	0.9109	0.00985	22.121	22.121 >6,59 In-appropriate model	1.262914 <2,69 In-appropriate model
6.	3.39	3.003	0.14929	11.397					
7.	2.74	2.903	0.02686	-5.982					
8.	3	2.959	0.00162	1.345					
9.	3.11	3.040	0.00480	2.228					
10.	3.12	3.040	0.00628	2.541					
11.	2.9	3.040	0.01979	-4.851					
12.	2.97	3.040	0.00499	-2.380					
13.	3.1	3.040	0.00351	1.913					

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 $F'_c = F_{\nu1,\ \nu2,\ \alpha} = F_{5;5;0,01} = 6,59$.

To verify deviation of the survey data from the mean value the Fisher-Snedecor test was used. $F_c = 29.20031$ calculated value is greater than the critical value $F_c = F_{\alpha\ ,\ \nu1,\ \nu2} = F_{0,05\ ;\ 12,\ 4} = 5,91$ which indicates that the deviations appear due to experimental errors.

The approximation quality of the mathematical model expressed by the standard error shows the scattering of the experimental values around the regression equation: 36.07 %.

The correlation coefficient has the value: $r_{x1x2} = -0.11241$, $r_{x1y} = 0.1552379$ and $r_{x2z} = -0.0562956$. The significance of the simple correlation coefficients is checked using the Student test. The calculated values are: $tc_{\ x1y} = 0.521184$, $tc_{\ x2y} = 0.187008$, $tc_{\ x1x2} = -0.3752093$.

The calculated values are lower than the critical table value $t_{\alpha,\ \nu} = t_{0,05;\ 11} = 2,201$ for t_{x1y} and t_{x2y} which indicates that there is a relationship between variables, $t_{x1x2} = -0.3752093$ so there is some correlation between independent variables.

The square of the correlation coefficient $R^2 = R_{xY}$ is called coefficient of determination and expresses that part of the variation of variable Y which can be attributed to variable x.

The multiple determination coefficient 0.20818 shows that the influence of the two independent variables on the outcome is 20.81 %, the rest being caused by other factors.

The obtained models scans are viewed geometric as hyper-surfaces in three-dimensional space of independent variables. The hyper-surface represents the response of the model; because the extreme points (maximum, minimum) of the hyper-surfaces present technological interest their exact location is searched or at least knowledge about the shape of the surface in the extreme field neighboring. The surface can be cut by planes of type *y=ct,* resulting response contours. 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:

$$F(x.y) = 3.040 + (0.054)x + (0.019)y + (-0.056)x^2 + (-0.054)y^2 + (-0.207)xy \qquad \textbf{(3)}$$

The canonical form of regression equation and the new center has the coordinate's axes: $x = -0.062$, $y = -0.294$. Value of the dependent variable in the center of the response surface is: $yc = 3.041$.

The coefficients of the canonical form were calculated and the equation which resulted is:

$$y = 3.041 - 0.158\ z_1^2 + 0.048\ z_2^2 \qquad \textbf{(4)}$$

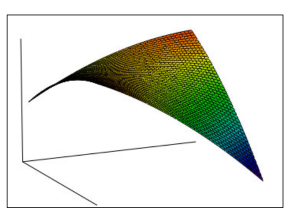

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Fig. 1: *The dependence of the goal-function on the independent variables:*
(x – enzyme concentration and y – treatment time)

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 hyperbolic paraboloid, the canonical equation coefficients having different signs. The metric invariant of changing coordinates is different from 0, so there is a single center, of type "saddle".

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*.

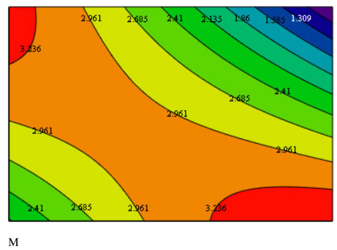

Fig. 2: *Contour curves for various values of Y (weight loss)*

Figure 2 presents contour curves for various values of weight loss, 2.34 to 3.40 between. On the response surface from figure 2 which is type "saddle" form, a stationary point of coordinates $x = -0{,}062$ and $y = 0{,}294$ can be observed. These encoded coordinates are associated with an enzyme concentration of 1.9 % (o.w.f) and a treatment time of 44 minutes. The value of the goal-function at this point is $Y = 3.041$.

3.2 Interpretation of the obtained mathematical model technology

By analyzing the expression of the obtained goal function:

$$F(x.y) = 3.040 + (0.054)x + (0.019)y + (-0.056)x^2 + (-0.054)y^2 + (-0.207)xy \quad \textbf{(5)}$$

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 the same way. Both variables *x* (enzyme concentration) and *y* (treatment time) directly influence the outcome *Y* (weight loss);
- the influence of variable *x* (enzyme concentration), on *Y* (weight loss) is 1.44 %;
- the influence of variable y (treatment time), on *Y* (weight loss) is 0.62 %;
- the existence of quadratic form for both parameters indicates that the response surface defined by the obtained mathematical model, is well formed, reinforcing the hypothesis regarding the influence of both parameters on the outcome;
- the ratio between the coefficients of the quadratic and free term quantifies the speed of *Y* (weight loss) outcome change variation to the variation of the two parameters; variables *x* (enzyme concentration) influences with 1.51 % the outcome function and *y* variable (time of treatment) influences with 1.44 % respectively;
- the influence of the interaction of the two parameters on the dependent variable is 6.80 %.

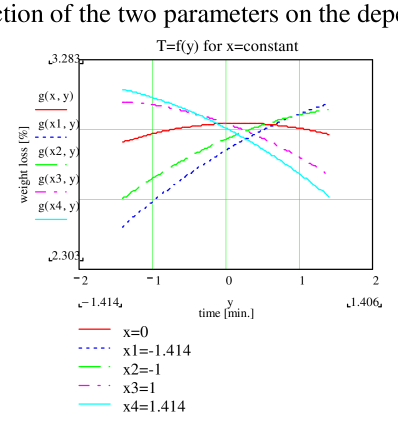

Fig. 3: *The dependence of the goal-function on all significant values of y parameters for x = constant*

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, 0], (between 20–40 minutes) an increasing in weight loss and the existence of a maxim point around 44 minutes, which indicates a big influence of this parameter on the weight loss, and for the interval [1, 1414] (between 54–60 minutes) it can be seen that with time increasing, the weight loss decrease.

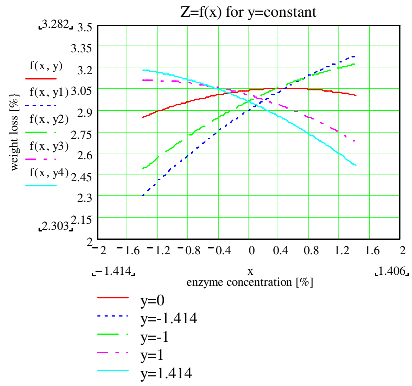

Fig. 4: *The dependence of the goal-function on all significant values of x parameters for y = constant*

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 seen how the enzyme concentration is influencing the weight loss, as the curves have not similar forms. For the interval [–1414, 0] the weight loss increases with the increasing of enzyme concentration, and for the interval [1, 1414] weight loss decreases with the increase of the enzymes concentration. By analyzing the graph it can be observed that conducting the experiment with small values for variable y (for 20–34 minutes) there is an increase in weight loss with the increasing of enzyme concentration. Conducting the experiment with high values for the variable y (for 54–60 minutes) it can be observed a decreasing of the weight loss with the increasing of enzyme concentration.

4. CONCLUSIONS

The optimum parameters established by this optimisation are:
- Enzyme concentration – 1.9 %;
- Treatment time – 44 minutes.

ACKNOWLEDGEMENT

This research work was supported by ‘‘Bast plants - Renewable Strategic Resources for European Economy - BASTEURES’’ project, no. 210/2010 POS-CCE - supported by Structural Founds - “Investment in Your Future”.

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