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BIOTREATMENT OPTIMIZATION FOR A CELLULOSIC/LIGNOCELLULOSIC BLENDED FABRIC

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Abstract: *The paper presents a study on the optimization of the bioscouring treatment of 60 % of cotton + 40 % of flax blended material by using a commercial enzymatic product called Beisol PRO, Denimcol Wash RGN (detergent) from Bezema Company, Switzerland and sodium citrate (complexing agent) from Sigma Aldrich.*
The bioscouring treatment is imposed by the specific natural structure of the fabrics. Both cotton and flax have different organic and mineral compounds which need to be removed during the specific pretreatments applied in textile industry. In this case was chosen an alternative of the classic alkaline treatment. The alternatives propose is an eco-friendly one due to the fact that the temperature use is lower comparative with the classical one (55 °C, respect to 90 °C) and the waste waters pH is in the neutral range.
For treatment optimization, a mathematical model of the 2^nd order was created by a central, rotatable second order compound program with two independent variables: enzyme concentration and treatment time. Based on the values obtained for the weight loss of the treated samples, the mathematical model obtained was analyzed from the technological and graphic point of view, and the optimum parameters for the bioscouring treatment with commercial product Beisol PRO have been set. The best results were obtained in case of 2.1% of enzymatic product and 39 min. of exposure.

Key words: *cotton/flax material, commercial enzyme, biotreatment optimization, weight loss*

1. INTRODUCTION

Cotton and flax fibers contain different percentages of morphological attendants (pectin, hemicellulose, extractable substances, waxes, etc.), which have to be removed through classical or enzymatic methods so that the material becomes hydrophilic [1]. For the enzymatic treatment, a mixture of different types of pectinases could be experienced. By using those in textile chemical finishing is increased the pectin degradation by hydrolysis and demethylation. Those reactions lead to the enlargement of the contact surface as well as to the increas of the molecular diffusion rate [2].

The intensification of the finishing processes of textile under enzyme's action leads to time chemicals reduction. The bioscoring has also implications in different related sectors. For example, the enzyme synthesis could be done using low-cost raw materials (different waste products), the chemical, energy and waster consumption is lower. The treatment is safer for the personal and has an eco-friendly charactheristic [3]. From technical poit of view during the enzymatic treatment the fibres are less damaged and the strength is higer compared with the alkaline treatment. The fibers structural changes occurred during the classical treatment influence the dyes bounding process, causing the decrease of the molecules chemical linked to the fabrics.

2. EXPERIMENTAL PART

For bioscouring treatments were used woven fabric samples of *60 % of Cotton/40 % of Flax* with width 120 ± 3 cm and weight 220 ± 10 g/m^2. The treatments conditions were: 1-3 % (o.w.f. – over weight fiber), enzymatic commercial product Beisol PRO; 2 g/L sodium citrate - complexing agent and 0.5 % Denimcol Wash RGN – surfactant in 0.1 molar sodium phosphate/disodium phosphate of pH 8 buffer solution. The treatments were done in an Elmasonic X-tra basic 2500 bath from Elma Company, Germany at 1:20 fabric to liquid ratio, temperature of 55 ^{0}C and 15 to 55 min. as treatment time [4]. Before and after bioscouring, the samples were prepared as described in [5]. The mass loss was determined by using gravimetric method and calculated using the Eq. 1: [6].

$$\% \text{ mass loss} = (W1\text{-}W2)\ x100/W1 \quad \textbf{(1)}$$

After a series of preliminary determinations to achieve a minimum number of experiments a central, rotatable second order compound program based on a matrix with 13 experiments and two independent variables was used [7]. The variation limits and the experimental plan are presented in Table 1 and Table 2.

Table 1: *The variation limits of independent variables*

Code value / Real value	-1.414	-1	0	1	+1.414
x - enzyme concentration [% o.w.f.]	1.0	1.3	2.0	2.7	3.0
y - time [minutes]	15	21	35	49	55

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

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

3. RESULTS AND DISCUSSIONS

Experimental matrix and the measured values of the response function Y are presented in Table 3.

3.1 Mathematical model interpretation obtained

In order to assess more accurately the influence of enzyme concentration and treatment time on the mass loss, a mathematical modeling of the process was made using a central compound rotatable program with two independent variables: *x* - concentration of enzyme (1-3 % o.w.f.) and *y*

– treatment time (15 - 55 minutes). As a goal-function, the mass loss (%) denoted by Y was chosen. The program has the following mathematical expression:

$$Y = b_0x_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 \quad \textbf{(2)}$$

For the experimental data a program in MathCAD professional and Excel was used, and a regression equation was obtained [7]. The regression equation and coefficients are presented in Table 4. The regression equations obtained after eliminating insignificant coefficients are given by Eq. 3:

$$Y= F(x.y) = 1.758 + (0.106)x +(0.218)y +(-0.348)x^2 + (-0.398)y^2 + (0.000)xy \quad \textbf{(3)}$$

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

Exp. no.	Independent variables				Answers
	x		*y*		*Y*
	x (cod.)	*x* (real) Enzyme (% o.w.f.)	*y* (cod.)	*y* (real) Time, min.	*Y = f(x,y)* Mass loss, %
1.	-1	1.30	-1	21.00	0.89
2.	1	2.70	-1	21.00	0.85
3.	-1	1.30	1	49.00	0.83
4.	1	2.70	1	49.00	0.76
5.	-1.414	1.00	0	35.00	0.90
6.	1.414	3.00	0	35.00	1.58
7.	0	2.00	-1.414	15.00	0.47
8.	0	2.00	1.414	55.00	1.81
9.	0	2.00	0	35.00	2.03
10.	0	2.00	0	35.00	1.91
11.	0	2.00	0	35.00	1.44
12.	0	2.00	0	35.00	1.75
13.	0	2.00	0	35.00	1.66

The significance of the regression equation coefficients was tested using Student test. This test compares the average of a random variable with the average standard deviation. For the center of the program, where all independent variables have the value of zero, the dispersion "s" is calculated. Test values, the degree of coefficients significance and dispersion value are shown in Table 4.

Table 4: *Regression equations coefficients, the dispersion and the verification of the regression equation coefficients significance 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 $t_c>t_t$-term is significant)		
b0	1.758288	S= 0.401712	tc0	169.1637	Significant
b1	0.10644		tc1	16.38484	Significant
b2	0.218095		tc2	33.57245	Significant
b11	-0.34779		tc11	-46.5374	Significant
b22	-0.39781		tc22	-53.2312	Significant
b12	-0.0075		tc12	-0.57726	Insignificant

Verification of model adequacy and percentage deviations was done using the Fisher test. The values obtained are shown in Table 5. The degree of mathematical model's consistency was verified using F'c statistics. Initially, the mean square of residuals "PMrez" and the dispersion of reproducibility $S0^2$ were calculated. The Ratio $Fc = PMrez/S0^2$ was compared to the critical value $F'_c = F_{v1,\ v2,\ \alpha} = F_{5;5;0.01} = 6.59$. The Fisher-Snedecor test was used to check for the deviation of the survey data from the mean value. The calculated value Fc = 16.00524 is greater than the critical table value $F_c = F_{\alpha\ ,\ v1,\ v2} = F_{0.05;\ 12.4} = 5.91$ indicating that deviations are due to experimental errors. The quality of the approximation of the mathematical model expressed by the standard error shows the scattering of the experimental values around the regression equation being 40.17 %. The correlation coefficients are: rx1x2 = -0.00406, rx1y = 0.1778164 and rx2z = 0.3639383. The significance of the simple correlation coefficients was verified using the Student test. The calculated values are: tc x1y = 0.602782, tc x2y = 1.3060111, tc x1x2 = -0.0134759. The calculated value $t_{x1x2} = -0.0134759$ is smaller 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 a correlation between the independent variables. The multiplying factors of 0.660489 shows that the influence of the two independent variables on the result is 66.04%, the rest being due to other factors. The obtained models can be geometrically viewed as hyper surfaces in the three-dimensional space of the independent variables. The extreme points of the hyper surfaces and their exact location or at least knowledge of the shape of the surface in the area adjacent to the extreme are searched. These surfaces can be cut by planes of type y = ct resulting the response contours. The interpretation of the answer and the search for the extreme are more difficult, and it is preferable to bring the surface into a more accessible form of analysis by canonical transformation. Moving to the canonical form of the regression equation, the new center of the axes has the coordinates: x = 0.152, y = 0.274 and the value of the dependent variable in the center of the response surface is: $y_c = 1.796$. By calculating the coefficients of the canonical form, equation 4 was obtained:

$$y = 1.796 - 0.398\, z_1^2 - 0.348\, z_2^2 \qquad \textbf{(4)}$$

Table 5: *Adequacy of the calculation model*

No	Y2 meas	Y2 calc.	(Y2meas. – Y2calc.)^2	Deviation "A"	Average square of residuals "PMrez"	Dispersion of reproduce bility "$S0^2$"	Ratio $Fc = PMrez/S0^2$	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.	0.89	0.6806	0,04382	23.5221	0.23043	0.0519	4.433	Fc= 4.433952 <6.59 Appropri-ate model	Fc= 2.945414 >2.69 Appropri - ate model
2.	0.85	0.9085	0.00342	-6.8862					
3.	0.83	1.1318	0.09110	-36.366					
4.	0.76	1.3297	0.32458	-74.963					
5.	0.90	0.9124	0.00015	-1.3796					
6.	1.58	1.2134	0.13437	23.2006					
7.	0.47	0.6545	0.03404	-39.258					
8.	1.81	1.2712	0.29020	29.7629					
9.	2.03	1.7582	0.07382	13.3848					
10.	1.91	1.7582	0.02301	7.9430					
11.	1.44	1.7582	0.10130	-22.103					
12.	1.75	1.7582	6.86E-05	-0.4735					
13.	1.66	1.7582	0.00966	-5.9209					

Fig. 1 presents the plot which shows the dependence of the goal-function on the two independent variables (x and y). The response surfaces of the regression equations is an elliptical paraboloid, the coefficients of the canonical equation having the same sign. The negative sign corresponds to a maximum in the center of the surface.

In **Fig. 2** are presented the contour curves for various mass loss values ranging from 0.47 to 2.03. On the response surface from **Fig. 2**, which is of the elliptical type, we can observe a stationary point of coordinates x = 0.152 and y = 0.274. These coded coordinates correspond to an enzyme concentration of 2.1% and a treatment time of 39 minutes. The value of the goal function at this point is Y = 1.796.

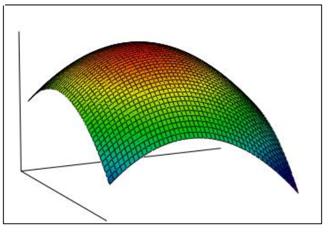

Fig.1: *The dependence of the function Y = f (x, y) on the two independent variables x and y*

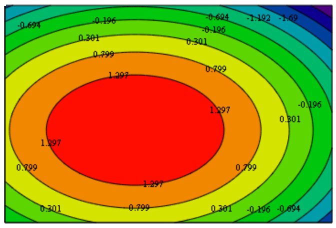

Fig. 2: *Contour curves for various values of Y = f (x, y)*

3.2 The technological interpretation of the mathematical model obtained

From the goal function expression analysis:

$$Y= F(x.y) \quad = 1.758 + (0.106)x +(0.218)y +(-0.348)x^2 + (-0.398)y^2 + (0.000)xy \qquad \textbf{(5)}$$

the following were found:

- the influence of the two independent parameters x and y on the dependent variable Y is manifested in the same way. Both the variables directly affect the resultant Y: the increase of x and y leads to the Y increase; the influence of variable x on Y is 5 % and of 12 %; the existence of the square shape for both parameters indicates that the response surface, defined by the obtained mathematical model, is well formed, reinforcing the hypothesis regarding the influence of the two parameters on the resultant; the ratio between the coefficients of the quadratic terms and the free term quantifies the variation velocity of Y by variation of x is influenced by 19 % and the variable y influences by 22 %.

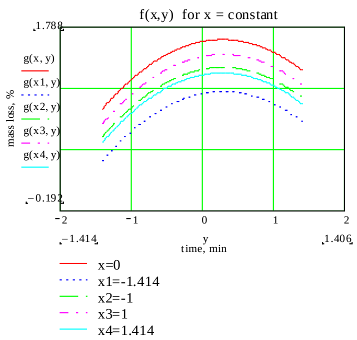

Fig. 3: *The dependence of the function Y = f (x, y) on all significant values of y, for x = const.*

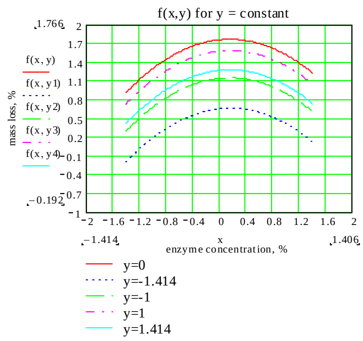

Fig.4: *The dependence of the function Y = f (x, y) on all significant values of x for y = const.*

Fig. 3 presents the dependence of the goal function by one of the two independent variables for all values of the parameters, while the second is constant. For x constant the graph of weight loss variation over time for the interval [-1.414, 0.274] (15-39 min.) indicates an increase in mass loss with maximum at 39 min. which shows a great influence of this parameter. For [0.274 +1.414] interval (39-55 minutes) by increasing time, the mass loss decreases.

Fig. 4 shows the dependence of the goal function by one of the two independent variables for all significant values of the parameters, while the second one is constant. From the graph analysis it can be seen how the enzyme concentration influences the mass loss, and how the curves have the same allure. For the [-1.414, 0.152] interval the mass loss increases with the increasing of enzyme concentration and for the [0.152 + 1.414] interval the mass loss decreases with the increasing of enzyme concentration. From a technological point of view, an experiment with small values for y variable (15-39 minutes) shows an increase in mass loss with the increasing enzyme concentration while for high values of y (39 - 55 minutes) there is a decrease in mass loss with the increasing enzyme concentration.

4. CONCLUSION

The treatment time, temperature and enzyme concentration are reduced with the improvement of the energy balance and costs obtaining textile fabrics with superior qualitative indices. The influence of enzyme concentration and treatment time on the mass loss of bioscoured material was well studied. By analyzing technologically and graphically the mathematical model, the optimal working parameters were determined: enzyme concentration - 2.1 % and treatment time - 39 minutes.

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