Study on the Response Surface Modelling by Central Composite Design and Optimization of paper Nanocoating

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By the superficial grafting of monochlorotriazinyl- β-cyclodextrin (MCT-β-CD) on a special paper (Japanese veil), hosting nanocavities are generated, which can include certain guest chemicals for special protection effects (antibacterial nanocoatings, deodorants, UV protector etc). The original results obtained in the experimental research have been used for the statistic modelling of the grafting process. The regression equations determined through orthogonal Central Composite Design (CCD) represent the objective functions necessary for maximizing optimization. The canonical analysis of the obtained response surfaces was carried out. In order to obtain the optimum grafting conditions, the Lagrange multipliers method was used. Eventually the maximum grafting degree was established, adequate for the stage of subsequently including the guests to attenuate the destructive effects of the environment factors on the heritage documents written on paper support.

Keywords: Central Composite Design, Response Surface Methodology, grafting, nanomaterials

The heritage documents from libraries and archives are subjected to the influence of environment conditions (temperature, humidity, light, microorganisms, polluting agents, dirt, etc), which lead to ageing phenomena-yellowing, loss of resistance). There are several means and methods to prevent the damaging action produced by these factors [1].

The researches undertaken while drafting this work join the more general world preoccupations for the development and diversification of highly performing advanced materials by using new compounds adequate for the production of protective nanocoatings for paper.

For the paper treatment with CDs there are a few literature reports [2, 3].

That is why a deeper study of the chemical modifications of a cellulose paper substrate chosen as model (Japanese veil) frequently used in the conservation of the archive documents and other heritage objects (painted supports, for example). For this modification, a reactive derivative was used, namely monochlorazinyl- β-cyclodextrin (MCT-β-CD).

For further application in the field of heritage documents conservation, the superficial grafting of MCT- β-CD on papers has provided hosting nanocavities that can include guest chemicals (e.g. cinammic, urea or ketonic derivatives) for specific protective effects (antibacterial, deodouring, UV protective, antistatic finishes etc.) [4 - 6].

The FT-IR-ATR and SEM studies have proved that the paper samples were successfully functionalized with the reactive product monochlorotriazinyl – β - cyclodextrin. Our results have indicated that the included components (ferulic acid, allantoin and Michler's ketone) are efficiently hosted in the CD cavities and the paper surface properties are significantly modified by the chemical treatment in the desired direction of antimicrobial protection [6- 8].

Until now, the technique and the compounds which we have studied had been neither used for the preservation of the heritage objects, nor described in specialized literature. Therefore, the objectives of these studies consisted necessarily in the mathematical modelling and the optimization of the grafting process of the reactive derivative monochlorotriazinyl –β– cyclodextrin on cellulosic paper substrates.

Theoretical studies have recommended the Response Surface Methodology and Process Optimization Using Designed Experiments. This work presents a study on the response surface modelling and grafting optimization of a reactive derivative (monochlorotriazinyl-β-cyclodextrin) on the cellulosic paper supports. As experimental design is employed an rotatable Central Composite Design (CCD) [9-12].

The obtained regression equations constituted the objective functions with three decission variables each. At first, the canonical analysis of the obtained response surfaces was carried out, then the Lagrange multipliers method was used [13]. The obtained results provided the operation parameters necessary for getting the maximum grafting degree for the monochlorotriazinyl- β-cyclodextrin reactive derivative on the Japanese veil substrate.

The completely original study presented here represents a complex approach of the problem of paper grafting, with solid conclusions which could be used in practice for the restoration and preservation of the heritate objects on paper (cellulose) substrate, constituting a highly performing, modern and useful working tool.

Experimental part

Materials

As *grafting substrate*, a Japanese veil (with a thick of 25 microns and an areal density of 15 g/m^2) from CTS Europe Co., was used.

Chemically modified cyclodextrin (monochlorotriazinyl – β -cyclodextrin with degree of substitution of 0.46 per anhydrous glucose unit, as host) was purchased from Wacker Chemie Gmbh, Germany).

Sodium carbonate (Na_2CO_3, as analytical reagent grade) was obtained from Sigma Chemical Co (Bucharest, Romania).

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Design variable	UM	Actual values of coded levels				
		- α	-1	0	1	+ α
MCT-β-CD Conc. (z_1)	g/L	50	80.41	125	169.59	200
Na_2CO_3 Conc. (z_2)	g/L	20	36.22	60	83.78	100
Curing temperature (z_3)	^0C	100	110.14	125	139.86	150

Table 1
THE LEVELS OF DESIGN VARIABLES AND THEIR ACTUAL VALUES USED IN EXPERIMENTAL DESIGN

Methods

Experimental Design

Grafting of (MCT –β–CD) to the paper substrate was realized according to a modified procedure to treat linen fibres [4, 6, 7].

This study was performed with the use of an experimental design method. According to the central composite design (*CCD*), a total of 20 experiments was generated including a 2^3 of the two level factorial design, central points, star points and 6 replicates at the center point [14, 15]. The value of α (star point) is 1.682. The number 3 represents the independent variables used in this study, consisting of the concentrations of MCT-β-CD and Na_2CO_3, and the curing temperature.

Paper samples were dipped (impregnation method) or brushed (brushing method) with solutions of MCT and NaOH / Na_2CO_3 in different concentrations (tables 1 and 2).

After the paper drying, the samples were cured in an oven at different temperatures (table 2) for 3 periods, namely 5, 10 and 15 min. After that, the paper samples were washed under running water for 5 min and then with distilled water to remove non-reacted substances and

Run	Input variables			Responses					
	x_1	x_2	x_3	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
1	-1	-1	-1	4.39	5.45	4.04	2.24	7.16	5.73
2	1	-1	-1	1.09	7.054	4.21	0.41	0.86	7.4
3	-1	1	-1	9.87	6.21	10.46	6.84	6.43	7.57
4	1	1	-1	9.83	0.96	9.86	6.04	1.39	7.54
5	-1	-1	1	8.7	9.13	9.39	9.65	10.25	9.16
6	1	-1	1	8.6	7.98	8.73	1.61	8.04	8.86
7	-1	1	1	6.16	9.35	9.81	9.94	8.94	8.97
8	1	1	1	9.89	2.15	7.82	4.06	6.95	8.13
9	-1.682	0	0	9.3	7.54	9.04	8.67	8.27	7.3
10	1.682	0	0	9.11	1.01	7.25	1.26	1.4	7.49
11	0	-1.682	0	2.62	7.92	2.06	2.97	7.96	8.71
12	0	1.682	0	7.54	3.15	9	7.73	6.83	9.72
13	0	0	-1.682	6.9	7.14	7.68	1.51	1.5	5.26
14	0	0	1.682	8.53	9.35	10.51	6.85	9.85	9.11
15	0	0	0	5.38	4.12	5.37	4.65	5.36	5.91
16	0	0	0	5.23	4.02	4.2	5.37	5.19	6.26
17	0	0	0	5.67	6	5.95	4.84	5.22	6.03
18	0	0	0	5.34	3.75	5.59	5.66	6.03	5.63
19	0	0	0	4.14	4.48	6.16	4.96	5.05	5.03
20	0	0	0	5.25	5.8	5.56	7.86	5.36	5.75

Y_1, Y_2 and Y_3 are the objective functions for the impregnation procedure at fixation durations of 5, 10 and 15 min, and Y_4, Y_5 and Y_6 are the objective functions for the brushing procedure at fixation durations of de 5, 10 and 15 min

Table 2
ROTATABLE CENTRAL COMPOSITE DESIGN, INPUT VARIABLES AND RESPONSES

again dried in vacuum at 80°C for 24 h. Finally, the samples were conditioned at 20±2°C and 65% relative humnidity.

The quantity of MCT – β –CD bonded to the papers was estimated gravimetrically as the difference between the samples weights before and after the above mentioned curing process.

In developing the regression equations, the test variables were coded according to the equation:

$$x_j = (z_j - z_{0j}) / \Delta_j \qquad (1)$$

where x_j is the coded value of the independent variable, z_j is the real value of the independent variable, z_{0j} is the value of the independent variable on the centre point and Δ_j is the step change value.

The levels of independent variables and experimental design matrix based on *CCD* are shown in tables 1 and 2.

The response surface methodology (*RSM*) was used to analyze the experimental design. The response variables were fitted by a second order model to correlate the response variables with the independent variables [12, 16]. The Multi Linear Regression (MLR) [17] method used is based on finding the regression model that minimizes the residual sum of squares of the response. The general form of the second degree polynomial equation is :

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i \cdot x_i + \sum_{i=1}^{3} \beta_{ii} \cdot x_i^2 + \sum_{i=1}^{3} \sum_{j>i}^{3} \beta_{ij} \cdot x_i \cdot x_j + e \qquad (2)$$

where β_o, β_i, β_{ii} and β_{ij} are regression coefficients (β_o is a constant term, β_i is a linear effect term, β_{ii} is a squared term and B_{ij} is an interaction effect term), *Y* is the predicted response value and *e* is the random error .

The *RSM* model coefficients for each response are computed according to the matrix equation:

$$\bar{\beta} = \left(\bar{X}' \cdot \bar{X}\right)^{-1} \cdot \bar{X}' \cdot \bar{Y} \qquad (3)$$

with $\bar{\beta}$- the vector of regression coefficients, $\bar{X}$ - matrix of the independent variables and $\bar{Y}$ -vector of responses.

The analysis of variance (*ANOVA*) [18] is the statistical analysis used to check the significance of the equation with the experimental data. This analysis included the Fisher's *F*-test (overall model significance), its associated probability $p(F)$, correlation coefficient R, determination coefficient R^2 which measures the goodness of fit of the regression model. The Student's *t*-value for the estimated coefficient and associated probabilities $p(t)$ are also included. For each variable, the quadratic models were represented as surface and contour plots. The best combinations was determined from these. *MODDE* software (*trial version*) was employed for design, regression analysis, and plotting.

Optimization

The optimization of the objective function $Y(x_1, x_2, x_3)$ implies the determination of the grafting degree for the Japanese veil. The problem can be formulated as a problem of maximizing the objective function accompanied by inequality type restrictions:

$$max\{Y(x_1, x_2, x_3)\} \qquad (4)$$

$$g_j(x_1, x_2, x_3) \le 0 \quad j = 1 \ldots \ell \qquad (5)$$

The solution (maximum) of the problem can be found inside or on the border of the admissible domain, defined by the relations (5). Two categories of methods can be used to solve this type of problem, namely methods that ignore the inequalities and methods based on inequalities transformation.

Approaching the solution identification through methods that ignore the inequality restrictions is carried out according to the following algorithm:

- the objective function is treated as a non-restriction function;
- check if the determined stationary points are within the admissible domain, i.e. if they verify the restriction system;
- if the stationary points are within the admissible domain, the solution of the problems with inequality restrictions is identical with the solution of the non-restriction problem;
- if the stationary points do not belong to the admissible domain, the searched optimum can be found on the restrictions imposed border. In this case, the solution identification can be done by imposing at the border to be satisfied the inequalities which are not satisfied, by transforming them in equality restrictions. After that, the problem is solved by restarting with the first stage of the algorithm, also including in the calculations the equality restrictions thus obtained.

To solve the problem (4), the coordinates of the stationary point are determined by solving the equations system:

$$\begin{cases} \dfrac{\partial Y}{\partial x_1} = 0 \\ \dfrac{\partial Y}{\partial x_2} = 0 \\ \dfrac{\partial Y}{\partial x_3} = 0 \end{cases} \qquad (6)$$

In order to establish the nature of the stationary point, the *Hessian* determinant is calculated for this point:

$$Hessian = \begin{vmatrix} \dfrac{\partial^2 Y}{\partial x_1^2} & \dfrac{\partial^2 Y}{\partial x_1 \partial x_2} & \dfrac{\partial^2 Y}{\partial x_1 \partial x_3} \\ \dfrac{\partial^2 Y}{\partial x_1 \partial x_2} & \dfrac{\partial^2 Y}{\partial x_2^2} & \dfrac{\partial^2 Y}{\partial x_2 \partial x_3} \\ \dfrac{\partial^2 Y}{\partial x_1 \partial x_3} & \dfrac{\partial^2 Y}{\partial x_2 \partial x_3} & \dfrac{\partial^2 Y}{\partial x_3^2} \end{vmatrix}_{\bar{x}=\bar{x}_s} \qquad (7)$$

The main minors of theHessian determinant are:

$$\Delta_1 = \left| \dfrac{\partial^2 Y}{\partial x_1^2} \right| \qquad (8)$$

$$\Delta_2 = \begin{vmatrix} \dfrac{\partial^2 Y}{\partial x_1^2} & \dfrac{\partial^2 Y}{\partial x_1 \partial x_2} \\ \dfrac{\partial^2 Y}{\partial x_1 \partial x_2} & \dfrac{\partial^2 Y}{\partial x_2^2} \end{vmatrix} \qquad (9)$$

$$\Delta_3 = |Hessian| \qquad (10)$$

If, following the analysis of these minor values, it is established that the stationary point represents a minimax point this situation is verified by means of the standard canonic equation of the empiric model.

The canonic transformation of the quadratic equation [18,19] consists in choosing a new coordinate system (with its origin in the stationary point) through which the equation gets a shape whose geometric interpretation allows to assess the optimum domain. This transformation is accomplished by a translation of the system of coordinate axes and a rotation of the axes. The canonical form of the quadratic equation (for *n=3*) is:

$$Y - Y_s = \omega_{11} \cdot \chi_1^2 + \omega_{22} \cdot \chi_2^2 + \omega_{33} \cdot \chi_3^2 \quad (11)$$

where:

Y is the value of the objective function in the stationary point (Y_s = 38.462);

ω_{11}, ω_{22}, ω_{33} - the coeficients of the regression equation in the canonic form;

χ_{11}, χ_{22}, χ_{33} - the factors values in the new coordinate system of axes (canonic axes). The coefficients of the regression equation in the canonical form are calculated by solving the characteristic determinant:

$$det(B - \omega \cdot E) = 0 \quad (12)$$

with B the matrix of the interaction coefficients from the regression equation, $b_{ij} = b_{ji}$ and E- the unitary matrix.

The method based on inequalities transformation introduces a variable ecart (the *Valentine transformation*) in every inequality type restriction, through which this becomes an equality type restriction, and the optimization problem becomes:

$$max\{Y(x_1, x_2, x_3)\} \quad (13)$$

$$g_j(x_1, x_2, x_3) + x_j^2 = 0 \quad j = 4\ldots6 \quad (14)$$

Under the specified conditions, one can use the method of Lagrange multipliers to solve the optimization problem (13).

For this modified problem, the *Lagrange* function is built under the form:

$$L(x_1, x_2, x_3, x_4, x_5 x_6, \lambda_1, \lambda_2 \lambda_3) = \\ = Y(x_1, x_2, x_3) + \sum_{j=4}^{6} \lambda_j \cdot [g_j(x_1, x_2 x_3) + x_j^2] \quad (15)$$

The identification of the solution can be done analitically, by solving the system resulted from cancelling the partial derivatives of the objective functions in terms of the decision variables:

$$\begin{cases} \frac{\partial L}{\partial x_1} = 0 \\ \frac{\partial L}{\partial x_2} = 0 \\ \frac{\partial L}{\partial x_3} = 0 \\ \frac{\partial L}{\partial x_4} = 0 \\ \frac{\partial L}{\partial x_5} = 0 \\ \frac{\partial L}{\partial x_6} = 0 \\ \frac{\partial L}{\partial \lambda_1} = 0 \\ \frac{\partial L}{\partial \lambda_2} = 0 \\ \frac{\partial L}{\partial \lambda_3} = 0 \end{cases} \quad (16)$$

To solve the set of equations (16), it is necessary to know the values of the Lagrange multipliers. The solution of this set is found through numerical methods. An iterative method is used, through which various values are assigned to Lagrange multiplier. For maximizing problems, it is recommended to chose the value of the λ multiplier so that to exceed the value of the highest canonical coefficient, while for the minimizing problems the value of λ must be smaller than the smallest canonical coefficient.

Results and discussion

To determine the polynomial regression equations through *RSM*, the experimental data showed in table 2 were used.

The mathematical modelling of the grafting process of the reactive derivative monochlortriazinyl -β- cyclodextrin on Japanese veil substrate was carried out through non-orthogonal second order complex central rotating program of the 2^3 type. The mathematical model quantifies the influence of three independent variables: the MCT-β-CD concentration (x_1), the Na_2CO_3 catalizator concentration (x_2), and the temperature of fixation (x_3) on the grafting degree (Y) – the objective function.

The obtained regression equations are presented in table 3.

The values of determination coefficients R^2 (table 3) suggest that the responses models may be accounted for 94.728 to 99.28% variations of the totals. The values of adjusted determination coefficients R_{adj} (from 0.8998 to 0.9883) were also high enough. These results indicate that the second order polynomial models (eq. 2) were highly significant and adequate to represent the actual relationships between the responses and the independent variables [18].

The corresponding analysis of variance (*ANOVA*) is given in table 4. The *F*-value is a measure of the variation of the mean data. Generally, if the model was a good prediction of the experimental results and the estimated factor effects were real, then the calculated *F* value should be several times greater than the tabulated *F* value ($F_{0.05;316}$ = 8.69[9]). In this case, the *ANOVA* of the regression model proved that the models are highly significant based on the calculated *F* values (table 4) and a very low probability *P* values (table 4).

The student *t*-distribution and the corresponding *p*-values, along with the second order polynomial coefficients for each response were calculated. The *p*-value serves as a tool for checking the significance of each of the coefficients. The variables with low probability levels contribute to the model, whereas the others can be neglected and eliminated from the model.

The three dimensional (*3D*) response surface plots were employed to determine the variables and the optimum levels, which significantly affected the grafting degree. The response surface plots were shown in figures 1 for Y_3, which illustrated the relationship between the response and the experimental data. Figure 1 suggests that the grafting degree was predominantly affected by the action of x_2.

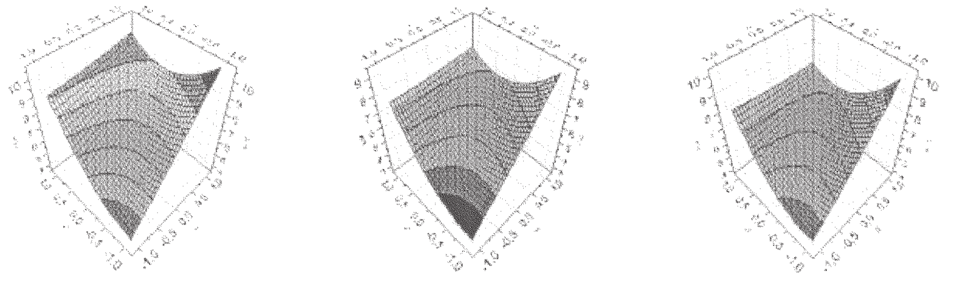
By interpreting the geometric correspondences of the response surfaces, the influence of the factors on the response functions can be established. As one can see from figure 1 for Y_3, one can state that the variable x_1 has a diminished negative influence on Y_3, x_2 has a marked positive influence, and x_3 has a medium positive influence on the response Y_3. These results show that the grafting degree is subject to the contradicting influences of three factors, namely: the MCT-β-CD concentration (x_1) diminishes the grafting degree, the catalyst Na_2CO_3 concentration (x_2) consistently increases it, while the temperature of fixation (x_3) has a positive influence, yet smaller than x_2.

Table 3
REGRESSION EQUATIONS

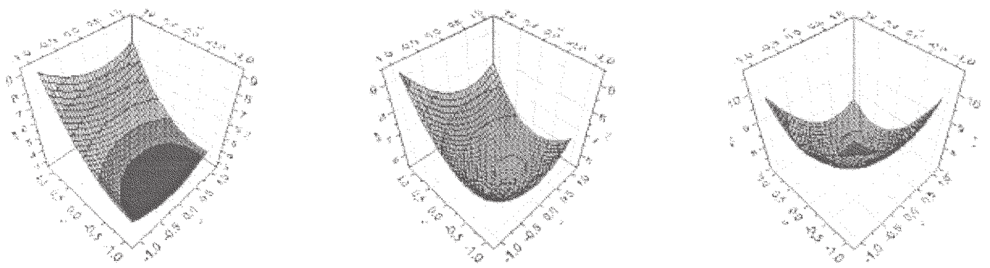
No.	R^2	$R^2_{Adj.}$	Q^2	SDY	RSD	N	Model validity	Reproductibility
1	$Y_1 = 5.17309 + 1.5555x_2 + 0.798906x_3 + 1.39564x_1^2 + 0.868974x_3^2 + 0.88625x_1x_2 + 0.87125x_1x_3 - 1.93375x_2x_3$							
	0.979182	0.960446	0.910863	2.54951	0.507048	20	0.859849	0.957111
2	$Y_2 = 4.56573 - 1.68466x_1 - 1.39089x_2 + 0.92422x_3 + 1.28714x_3^2 - 1.60925x_1x_2 - 0.58425x_1x_3 - 0.0307495x_2x_3$							
	0.965214	0.926079	0.872607	2.74301	0.745779	20	0.97273	0.865867
3	$Y_3 = 5.46131 - 0.445942x_1 + 1.70249x_2 + 0.874201x_3 + 1.01287x_1^2 + 1.34866x_3^2 - 1.57x_2x_3$							
	0.964811	0.933142	0.8578	2.46433	0.637202	20	0.885454	0.922545
4	$Y_5 = 5.54833 - 2.12426x_1 + 1.5358x_2 + 1.37001x_3 - 1.41125x_1x_3 - 0.93625x_2x_3$							
	0.94728	0.899833	0.877783	2.85245	0.902777	20	0.991608	0.827333
5	$Y_5 = 5.36036 - 1.98381x_1 - 0.32952x_2 + 2.37107x_3 + 0.768656x_2^2 + 0.8924995x_1x_3 - 0.275x_2x_3$							
	0.992803	0.986326	0.968373	2.80679	0.32821	20	0.865947	0.984943
6	$Y_6 = 5.77291 + 0.977849x_3 + 0.977849x_1^2 + 1.18826x_2^2 + 0.470721x_3^2 - 0.3475x_1x_2 - 0.362499x_2x_3$							
	0.964754	0.933032	0.856472	1.49131	0.385923	20	0.898893	0.919524

Table 4
ANOVA FOR JAPANESE VEIL GRAFTING

Response		Sum of squares	Degree of freedom	Mean square	F_{value}	P	SD
Y_1	Total corrected	123.5	19	6.49999			2.54951
	Regression	12.9929	9	13.4365	52.2625	0.000	3.66559
	Residual	2.57097	10	0.257097			0.507048
Y_2	Total corrected	127.909	17	7.52408			2.74301
	Regression	123.46	9	13.7178	24.664	0.000	3.70375
	Residual	4.44949	8	0.556186			0.745779
Y_3	Total corrected	115.385	19	6.07292			2.46433
	Regression	111.325	9	12.3695	30.4647	0.000	3.51702
	Residual	4.06027	10	0.406027			0.637202
Y_4	Total corrected	154.592	19	8.13645			2.85245
	Regression	146.442	9	16.2714	19.9647	0.000	4.03378
	Residual	8.15007	10	0.815007			0.902777
Y_5	Total corrected	149.683	19	7.87807			2.80679
	Regression	148.606	9	16.5118	153.281	0.000	4.06347
	Residual	1.07722	10	0.107722			0.32821
Y_6	Total corrected	42.2557	19	2.22399			1.4913
	Regression	40.7664	9	4.5296	30.4129	0.000	2.12828
	Residual	1.48937	10	0.148937			0.385923



a)



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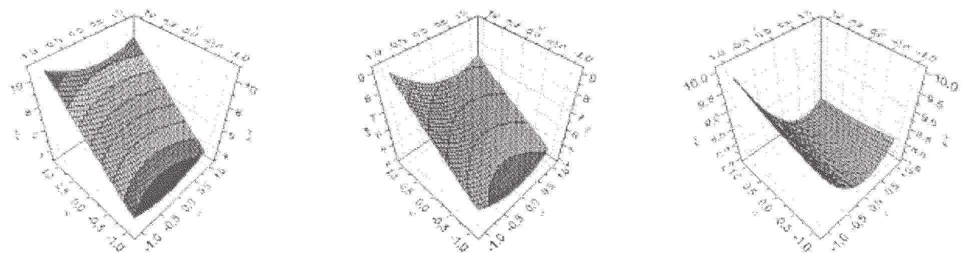

c)

Fig. 1. Response surface plots for Y_3 as a function of (a) $x_1=0$, (b) $x_2=0$, (c) $x_3=0$ (experiment center)

Table 5
RESULTS OF CANONICAL ANALYSIS

Objective function	Stationar point coordinates			Δ_1	Δ_2	Δ_3	Canonical equation	Stationar point type
	x_1	x_2	x_3					
Y_1	-0.432	0.764	0.607	2.7912	-0.785	-14.789	$Y_1 - 6.009 = -0.795\,\chi_1^2 + 1.655\,\chi_2^2 + 1.404\,\chi_3^2$	Minimax
Y_2	-0.854	-0.843	-0.563	0	-2.59	-6.724	$Y_2 - 5.611 = -0.827\,\chi_1^2 + 1.376\,\chi_2^2 + 0.7394\,\chi_3^2$	Minimax
Y_3	0.22	1.682	0.655	2.02	0	-4.993	$Y_3 - 7.697 = 1.013\,\chi_1^2 - 0.361\,\chi_2^2 + 1.709\,\chi_3^2$	Minimax
Y_4	1	0	0	0	0	0	$Y_4 - 3.424 = -0.847\,\chi_1^2 + 0.847\,\chi_3^2$	Minimax
Y_5	-1.682	0.515	1.682	0	0	-1.225	$Y_5 - 9.956 = 0.803\,\chi_1^2 + 0.42\,\chi_2^2 - 0.454\,\chi_3^2$	Minimax
Y_6	-0.402	-0.192	-1.261	1.089	2.59	2.008	$Y_6 - 5.156 = 0.666\,\chi_1^2 + 0.307\,\chi_2^2 + 1.234\,\chi_3^2$	Local Minimum

Optimization

Since the *RSM* results made evident the antagonistic effects on the studied responses, the grafting degrees, an optimization was carried out in the following, using two methods.

Canonical analysis

The canonical analysis belongs to the methods which ignore the inequality restrictions. The obtained canonical equations, the stationary point coordinates, the objective function values in the stationary points and the stationary point nature are presented in table 5. Since the eigenvalues for Y_1 have mixed signs, the stationary point $\overline{x_{Y1,s}} = [-0.432\ 0.764\ 0.607]^T$ is a saddle or minimax point [20]. In the case of Y_6, the canonical coefficients have positive signs and it can be concluded that the stationary point, $\overline{x_{Y6,s}} = [-0.402\ -0.192\ -1.261]^T$, is a minimum point.

To render more evident the situation of the determined stationary points, the response surfaces were plotted [21] for the response functions in canonical form. Figure 2 presents, for exemplification, the diagrams for the function Y_3.

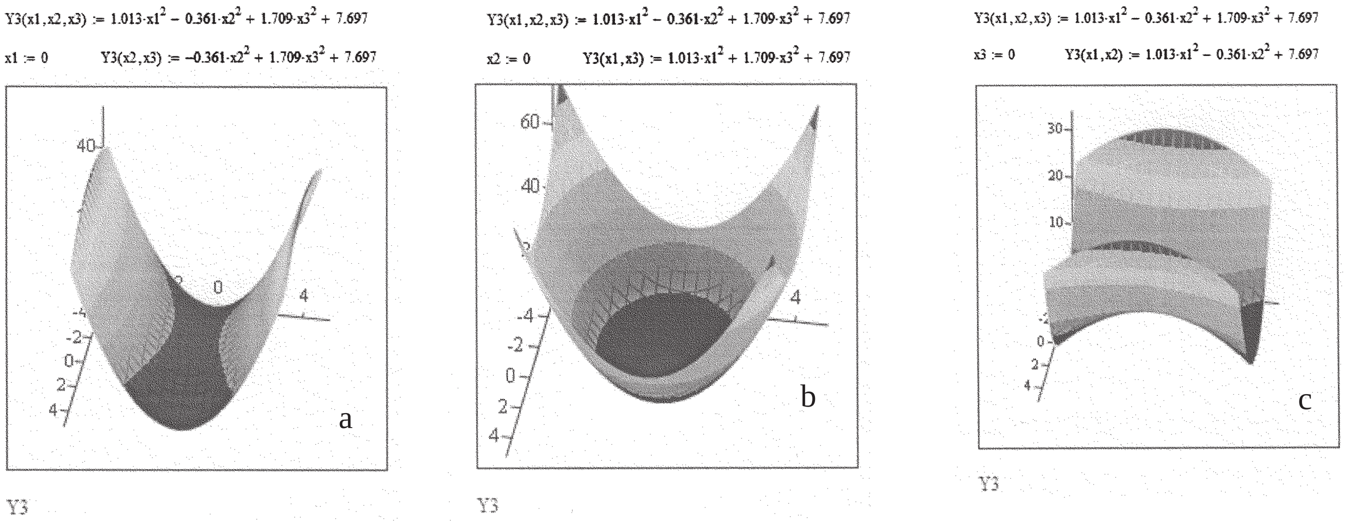

Fig. 2. Lagrange Multiplier Method- obtained results by solving the equations system for Y_3 (a) $x_1=0$, (b) $x_2=0$, (c) $x_3=0$

Table 6
OPTIMAL VALUES OBTAINED BY LAGRANGE MULTIPLIERS METHOD AND BY EXPERIMENTAL WAY

System Type	*Lagrange Multiplier*	*Unrealized Optimum*	*Restrictioned Optimum*	*Experimental Optimum*
Y_1	1.705	x_1=2.306 x_2=0.3 x_3=1.338 Y_1optunreal=18.188	x_1=1.682 x_2=0.3 x_3=1.338 Y_1optres=13.825	18.19
Y_2	1.525	x_1=-0.655 x_2=-0.138 x_3=2.757 Y_2optunreal=19.133	x_1=-0.655 x_2=-0.138 x_3=1.682 Y_2optres=11.562	14.94
Y_3	1.075	x_1=-3.589 x_2=0.633 x_3=0.218 Y_3optunreal=21.022	x_1=-1.682 x_2=0.633 x_3=0.218 Y_3optres=10.193	18.93
Y_4	0.355	x_1=-1.259 x_2=4.983 x_3=-2.392 Y_4optunreal=19.125	x_1=-1.259 x_2=1.682 x_3=-1.682 Y_4optres=5.548	14.99
Y_5	0.94	x_1=-4.827 x_2=-1.764 x_3=-0.772 Y_5optunreal=19.03	x_1=-1.682 x_2=-1.682 x_3=-0.772 Y_5optres=10.397	14.26
Y_6	1.28	x_1=-0.282 x_2=-2.355 x_3=1.192 Y_6optunreal=15.375	x_1=-0.282 x_2=-1.682 x_3=1.192 Y_6optres=11.856	14.43

From figure 2 one can draw the conclusion that the response Y_3 is influenced by the three factors in different ways, and the research for the optimum solution must take into account a compromise between the increase of x_1 and the decrease of x_2.

Optimization by Lagrange multipliers method

The optimization algorithm using the *Lagrange* multipliers has been implemented in an original *Mathcad* software [22]. The obtained sets of equations is solved giving values to λ in the corresponding intervals. The sets of equations is solved for each value. Figure 3 presents one example of the results obtained by this method for Y_3.

The values obtained for the coordinates of the extremum points were analyzed, checking if the point is within the investigated domain (-1.682 to 1.682- codified values), because the statistical models are only valid within this

$Y3(\lambda) := 5.46131 - 0.445942 \cdot F(\lambda)_o + 1.70249 \cdot F(\lambda)_1 + 0.874201 \cdot F(\lambda)_2 + 1.01287 \cdot (F(\lambda)_0)^2 + 1.3486\,(F(\lambda)_2)^2 - 1.57 \cdot F(\lambda)_1 \cdot F(\lambda)_2$

$\lambda := 4.000, 3.955{:}\ -4$

	$\lambda=$	$F(\lambda)_o=$	$F(\lambda)_1=$	$F(\lambda)_2=$	$Y3(\lambda)=$
	0	0	0	0	0
50	1.75	-0.302	-0.017	1.123	8.372
51	1.705	-0.322	4.592	-8.889	6.417
52	1.66	-0.345	0.786	-0.577	7.729
53	1.615	-0.37	0.626	-0.203	6.907
54	1.57	-0.4	0.576	-0.067	6.79
55	1.525	-0.435	0.556	$8\cdot10^{-3}$	6.794
56	1.48	-0.477	0.548	0.051	6.843
57	1.435	-0.528	0.548	0.083	6.922
58	1.39	-0.591	0.551	0.109	7.034
59	1.345	-0.671	0.557	0.129	7.189
60	1.3	-0.777	0.566	0.147	7.409
61	1.255	-0.921	0.576	0.163	7.743
62	1.21	-1.131	0.588	0.178	8.297
63	1.165	-1.466	0.602	0.192	9.351
64	1.12	-2.081	0.616	0.205	1.864
65	1.075	-3.589	0.633	0.218	1.222

Fig. 3. Example of the results obtained by application of Lagrange multipliers method

domain. If the coordinates go beyond the borders of this domain, the minimum is considered as unfeasible. A restricted optimum is defined in these situations, which is obtained by forcing the variables that go beyond the region borders to take values on their limits, namely -1.682 or +1.682. certainly, the two optimum values are different from each other. Finally, the obtained solutions (unfeasible and restricted) are experimentally checked up and interpreted.

When the experimentally obtained optimum is far from the two values calculated as above, the model itself is reanalyzed. If the experimental optimum is close to the unfeasible optimum within the necessary limits, the statistic model is considered as valid also outside the experimentally investigated domain and is accepted accordingly. When the experimental optimum is closer to the feasible one, the conclusion is that the model is accurately describing the studied system.

The results obtained for the six objective functions are presented in table 6.

The experimentally verified results (table 6) show that for the Japanese veil the maximum grafting degree, of 18.93, is obtained for Y_3 and $x_1=1.682$, $x_2=0.633$ and $x_3=0.218$ in coded values, namely the MCT-β-CD concentration of 200g/L, the Na_2CO_3 catalyst concentration of 75.05 g/L and the temperature of fixation of 128.24°.

Conclusions

The works include a complete original study of modelling and optimization on grafting the reactive derivative monochlortriazinyl-β-cyclodextrin on Japanese veil substrate.

The mathematical modelling was carried out through rotable Central Composite Design on large domains of variations for the independent variables: *MCT-β-CD* concentration (x_1), Na_2CO_3 catalyst concentration (x_2), and temperature of fixation (x_3), and quantifies their influence on the grafting degree (Y) – objective function.

The RSM analysis was performed through canonical analysis. Thereafter, for grafting the Japanese veil to MCT-β-CD, the optimum values of the operation parameters were determined through the Lagrange multipliers method. The experimentally verified obtained results confirm the correctness of the model and of the applied optimization techniques.

Nomenclature

B –interaction coefficients matrix;
E – identity matrix;
F-value – Fisher's test, computed value;
F-tab - Fisher's test, tabulated value;
N – number of experimental runs;
Q^2- goodness of fit;
P – Student's *t* test *p* value;
R^2 – determination coefficient;
R^2_{adj} – adjusted determination coefficient;
t- value - Student's t-test;
$\overline{X}$ - matrix of independent variables ;
$\overline{x}$ - vector of coded variables ;
x_1, x_2, x_3 - coded levels of factors (independent or design variables);
$\underline{x}_s$ - vector of coordinates of the stationary point in coded terms;
$\overline{Y}$ - vector of responses;
z_1, z_2, z_3 - actual values of independent variables;
$z_{0,j}$,- value of variable z_j in the center of the domain.

Subscripts
i and j – integer variables

Greek letters
α - axial points of CCD;
$\beta_o, \beta_o, ..., \beta_n$ - regression coefficients;
$\overline{\beta}$ - vector of the regression coefficients;
x_1, x_2, x_3 - canonical axes with the origin located in stationary point;
Δz_j - difference between the maximum level and the center of the domain;
λ_j- *Lagrange* multipliers;
$\overline{\varpi}$ - vector of eigenvalues of *B* matrix

Abbreviations
ANOVA - analysis of variance;
CCD - central composite design;
RSD - residual standard deviation;
RSM - response surface methodology;
SD - standard deviation;
SDY - standard deviation of the response

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