Interaction of the Anionic Polyelectrolytes with Crystal Violet of the Dyeing Process of Melana Fibres

Statistic modelling and optimization

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In this paper, data on Melana-type polyacrylonitrile fibres dyeing with Crystal violet (CV) - triphenylmethane dye- in the presence of maleic acid copolymers with vinyl acetate (NaM-VA) or styrene (NaM-S) are presented. Mathematical models of the studied dyeing processes have been developed and the necessary information on their significant factors is produced by means of experiment planning methods, known as Design of Experiment (DoE) or Experimental design. Optimal correlations between the application conditions and the colour differences obtained on Melana-type fibre have also been studied.

Keywords: Melana fiber, Maleic copolymers, Crystal violet dye, Color differences, Statistic modeling, Optimization process

The large afinity of the cationic dyes for the acrylic fibers is the result of the electrostatic interactions and hydrophobic interactions between the fibre and the dye, which results in non-uniform dyeing for acrylic fibres [1, 2].

There are numerous studies concerning processes of dyeing with anionic dyes using cationic retarders, but there are only few references in literature concerning textiles dyeing with cationic dyes that makes use of retarder based on anionic polyelectrolytes [3- 8].

The partners used in this study were selected taking into account the medical and biomedical properties.

There are many data in the literature regarding the applications of maleic copolymers in medical or pharmaceutical field. Most of them can be classified as [9]: i) maleic copolymers with *per se* activity, ii) drug polymer systems (conjugates), iii) drug formulations.

The last two groups belong to the topic of controlled delivery systems. Another more recent application of maleic copolymers is in the fabrication of biomaterials or in tissue engineering [10, 11]. Generally, lower molar mass and narrow molar mass distribution are required in order to provide at the same time suitable biological activity and reduced toxicity. The medical and pharmaceutical applications of maleic copolymers are also favoured by several properties such as: biocompatibility, water solubility, generally well-defined structure, the possibility to vary the hydrophilic/hydrophobic balance by the proper choice of the comonomer or by further chemical reactions on the copolymer. In addition, their chemistry is convenient: the copolymer synthesis is relatively easy and the monomers are cheap; the maleic anhydride cycle is versatile, allowing mild reactions with various partners (drugs, proteins, enzymes). The CV was used until now to dye inks, or in cytology, animal and plant histology, microbiology as antibacterial agent and not only [12-16]. All the dyed acrylic fibres show efficacy toward *Escherichia coli* and *Staphylococcus aureus* [17-18].

Experimental part

Materials and methods

The dye: Crystal violet: CV (Merk, Dearmstadt, Germany), were used as received. The dye structure is presented in figure 1.
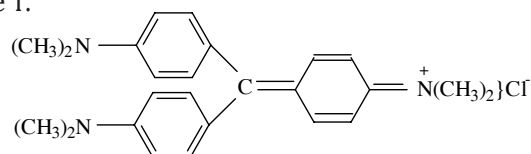

Fig. 1. Chemical structure of the CV dye

Polyelectrolytes

The utilized polyelectrolytes are copolymers of the maleic acid with styrene, and the copolymer of the maleic acid with vinyl acetate, both as sodium salts. The two polyelectrolytes were obtained from copolymers of the maleic anhydride with vinyl acetate or styrene, synthesized in laboratory according to our own method or methods described in literature with $Mv = 70000$ for NaM-VA and $Mv = 95000$ corresponded to NaM-S [19, 20]. The polyelectrolyte structures are illustrated in figure 2.
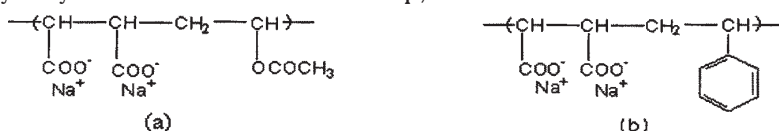

Fig. 2. Chemical structures of the copolymers NaM-VA (a) and NaM-S (b)

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Melana fibre

The Melana fibre is a polyacrylonitrile fibre based on a ternary polymer (acrylonitrile, vinyl acetate, α-methylstyrene) obtained through a radical polymerization reaction initiated in the redox system with potassium persulphate- natrium metabisulphite, its schematic structure being presented in figure 3 [1, 2, 4, 17].
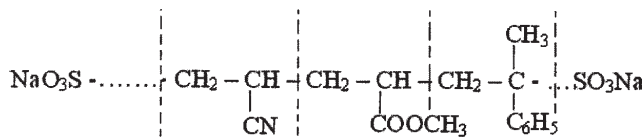
Fig. 3. Schematic structure of Melana fibre

Dyeing method

The dyeing was performed with a dyeing device Mesdan Lab with 6 dyeing positions. The dyeing (by six dyeing of one gram for each colour position) of Melana fibres was performed in aqueous solutions (distilled water), with CV, in the presence of the polyelectrolytes NaM-VA or NaM-S at dye and polyelectrolyte concentrations of: 0.5, 1.0, 1.5, 2.0 and 2.5%, the float having a pH of $5.5 \div 6.2$ adjusted with acetic acid 10% and a hydromodule of 1:50. Practically, to the aqueous solution of the dye, one adds polyelectrolyte in different concentrations and some drops of acetic acid to adjust the pH. The dyeing flask is magnetically stirred 5 min for homogenization, and then the solution stays still for 30 min, after which the Melana fibres (1g) are added. The solution is stirred again for 5 min, and then the dyeing flask follows a thermal regime. The dye liquor is heated up to 80ºC, being then maintained at this temperature for about 10 min. The heating continues up to temperatures of 90, 95 or 100ºC at a heating rate of 1ºC/min, keeping this temperature constant for 75 min, after which the dyeing solution is cooled slowly. The dyed Melana is washed intensely for 5 min with cold water and 5 min with warm water and then dried at room temperature. Besides the dyeing performed in the presence of the two polyelectrolytes, witness (standard) dyeing of Melana was also performed with CV, in the presence and absence respectively of the two polyelectrolytes at 90ºC for 75 min.

Colour differences have been measured with a portable Datacolor 2002 spectrophotometer type Check Plus [4]. We resorted to the measurement of color differences ΔE and implicitly of the color intensity respectively by measuring the color components L*, a* and b*:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

where ΔL* indicate any brightness difference and is marked with "+" if the sample that reproduces is lighter (brighter) than the witness, and with "–"if it is darker than the witness.

The values of Δa* and Δb* indicate the sample positions on the chromatic diagram, namely a* represents chromatic variation/deviation to red for positive values and to green for negative values. Similarly, for the b* coordinate, the positive values indicate yellow colors and the negative ones- blue colors, the chromatic intensity being higher the higher is the numerical value [4].

In order to obtain the mathematical model of the studied processes and the necessary information on the significant factors, an experiment planning is carried out, known as Experimental design or Design of Experiment (DoE) [21]. The data collected according to the experimental program are used to estimate the model coefficients. These represent the relation between the response y (ΔE) and the factors x_1, x_2,…..x_n. The principle of the estimation (approximation) method is represented by the multiple linear regressions (RLM) [4]. Experimental design is a branch of the mathematical statistics and includes the mathematical tools used to establish the number of experiments, the conditions of realization and the methods to estimate the experimental results [21-23]. The adequate experimentation project is chosen in terms of the type of the necessary dependence. The central rotable composed programs are the most indicated for the type of problem approached in this study. We mean to obtain minimum dispersions, equal in all the experimental points. The experimental points must be situated at approximately equal distances to the program centre, in order to realize equal dispersions. The central rotable composed program for four independent variables contains 31 experiments [4]:

- 16 experiments corresponding to the program 2^4;
- 7 experiments situated on the axes of coordinates at distances $\alpha = \pm 1$;
- 7 experiments in the program centre.

In the present case we performed 31 dyeings for each of the 2 systems.

Optimization Method: In this case the Method of descending simplex is used (initiated by Spendley, Hext and Himsworth [1962] and improved later by Nelder and Mead [1965]) [4]. This differs from other deterministic minimization methods because it does not explicitly need one dimensional optimization algorithms. The method presents the evaluation principles only for functions, not for the derivatives, being a 0th order method [24, 25].

Based on experimental results and theoretical appreciations concerning the Melana fibres dyeing process with cationic dyestuffs in the presence of anionic polyelec-trolytes, the colour modifications ye (Δ E) were chosen as optimization criterion [26]. The factors (independent variables) with significant influence on the process have been established, namely x_1- dyestuff concentration (%), x_2 – polyelectrolyte concentration (%), x_3 – dyeing time (min) and x_4 – dyeing temperature (ºC) [4].

Within the statistical modelling, the determination field of the experiment centre and the variation step have been established for each factor apart, taking into account the restrictions for the technological and technical realization of the process. The data are illustrated in table 1.

Results and discussions

The data collected according to the experimental program are used to estimate the model coefficients. This represents the relationship between the responses ye (Δ E) and the factors x_1, x_2, x_3 and x_4. The principle of the estimation (approximation) method is represented by the multiple linear regressions RLM.

Factor	UM	Coded factor	$x_{min} \rightarrow$ x_{max}	x_{io}	-2	-1	0	1	2	Step
Dye conc.	%	x_1	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Polyelec.conc.	%	x_2	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Dyeing time	min	x_3	30→120	75	30	52.5	75	97.5	120	22.5
Dyeing temperature	ºC	x_4	80→100	90	80	85	90	95	100	5

Table 1
FIELDS AND STEPS OF VARIATION FOR INDEPENDENT VARIABLE

Based on the results provided by the MODDE program, it has been considered that the equation which expresses the best ye (x_1, x_2, x_3, x_4) has the form:

$$ye = bo + b_1x_1 + b_2x_1 + b_3x_3 + b_4x_4 + b_{11}x_{12} + b_{22}x_{22}$$
$$+ b_{33}x_{32} + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3$$
$$+ b_{24}x_2x_4 + b_{34}x_3x_4$$

After this, a statistic model was elaborated through a central rotable composed program for four independent variables. Based on the experimental program and experimental results produced through automated processing on an IBM-PC computer, the response functions for CV dye are presented bellow [4].

The tinctorial Melana fibers dyed with CV in NaM-VA presence

Based on the results of the performed experiments, we have obtained for the tinctorial system (Melana CV, NaM-VA) the following mathematical model:

$$y = 15.6057 + 3.31667\,x_1 + 1.42917\,x_2 + 8.55083\,x_4 +$$
$$+ 1.77649\,x_1^2 + 2.21774\,x_2^2 + 2.08024\,x_3^2 - 3.5525\,x_3x_4$$

After examining the coefficients of the mathematical model within the field of the established factors, the following information was obtained:

- colour difference *ye* (ΔE) increases with increasing concentration of the dyestuff CV (x_1), and the polyeletrolyte NaM-VA (x_2), and the dyeing temperature (x_4).
- *ye* increases with the increase of the values of x_1^2, x_2^2, x_3^2 and decreases with the increase of x_3x_4.

The previous results concerning the Melana fibres dyeing with CV in the presence of NaM-VA have shown that ΔE increases from 21.11 to 28.59 (AN) with increasing concentration of NaM-VA (0→2.5%) and from 2.39 to 30.63 (AN) when the dyeing temperature increases within the interval 80÷100°C [4, 27-37].

The tinctorial Melana fibers dyed with CV in NaM-S presence

Based on the results of the performed experiments, we have obtained for the tinctorial system (Melana CV, NaM-S) the following mathematical model:

$$y = 35.6786 + 7.5125\,x_1 + 2.675\,x_2 + 3.2275\,x_3 +$$
$$+ 11.64\,x_4 + 2.19411\,x_1^2 + 3.94286\,x_2^2 - 0.0433911\,x_3^2$$
$$+ 1.94\,x_1x_3 - 2.6525\,x_1x_4 + 2.9675\,x_2x_3 +$$
$$+ 1.0875\,x_2x_4 + 2.9075\,x_3x_4$$

After examining the coefficients of the mathematical model within the field of the established factors, the following information was obtained:

- colour difference *ye* (ΔE) increases with increasing concentration of the dyes CV (x_1), and the polyeletrolyte NaM-S (x_2), and the dyeing time (x_3) and it decreases with increasing dyeing temperature (x_4).
- ye decreases with the increase of the values of x_1x_4 and x_3^2 and increases with the increase of the values of x_1^2, x_2^2, x_1x_3, x_2x_3, x_2x_4, x_3x_4.

The results obtained for the two above analyzed systems can be explained by the fact that the affinity of cationic dyes with acrylic fibers is very high due to electrostatic attraction and to hydrophobic interactions between the fiber and the dye, which represents a big difficulty in obtaining uniform dyeing on acrylic fibers. The absorption of cationic dyes is accomplished after an Langmuir-type isotherm with saturation limit. Starting from the modified equation of

Langmuir isotherm and using the classical Donnan or modified Donnan models, numerous authors have shown that the dyeing of acrylic fibers with cationic dyes can be explained by an ionic and hydrophobic exchange between the fibre and the dye. The dyeing of the polyacrylnitrile fibers with cationic dyes occurs in three stages [1]:
-absorption of dye cation on the external fiber surface;
-dye diffusion inside the fibre;
-formation of electrovalences between dye cations and fibre anions.

The first and the third stages occur at very high velocities, the velocity of the second stage being decisive for the entire dyeing process.

The factors governing the first stage are: temperature, dye liquor stirring and fibre electric potential [4].

Around the acryl fiber a limit static layer of float is formed, its thickness varying inversely proportional with the velocity of float passing by the fiber; the dye molecules must cross this layer first and then they rich the fiber surface. Once at the fibre surface, the cationic dye diffuses inside the fibre, making possible the dye depletion in the float; this can be explained by the fact that the spots left free on the external fiber surface (by inward diffusion) remain vacant and can be easily occupied by other dye molecules from the float. The diffusion stage is the slowest, determining the dyeing velocity. Both dye diffusion and dyeing velocity are influenced by the temperature.
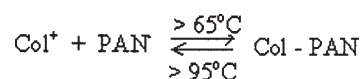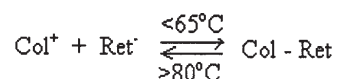
At the beginning of dyeing, when the dye concentration in the bath is high, the absorption rate is also high, but when the balance is reached, the dye concentration in the float is much smaller. This is true irrespective of the initial dye concentration in the float (small under 1%, or big over 1%). At initial large concentrations, the depletion rate is no longer influenced by the dye concentration in the float [4, 38].

The depletion rate changes depending on the dye concentration in the float similar to the variation of the concentration in the fibre in terms of the dye concentration in solution. The modification of the dye concentration at the fiber surface determines the variation in the same direction and of the same importance of the gradient concentration (dc/dx) responsible for dye raising rate on the fiber.

The high dye sorption rate represents the main cause of the dyeing non-uniformities; this peculiarity, together with the impossibility of conventional dyes to migrate represent the real cause of the difficulty to obtain a uniform dyeing [4].

In order to obtain uniform dyeing, it is necessary to control very carefully the temperature rising rate after exceeding the vitrifying temperature. When this is not possible, one must resort to the utilization of balancing and retarder agents.

The mechanism of dyes bonding to the PAN fibre in retarder presence can be schematically represented as follows [4]:

$$Col^+ + Ret^- \underset{>80°C}{\overset{<65°C}{\rightleftarrows}} Col-Ret$$

$$Col^+ + PAN^- \underset{>95°C}{\overset{>65°C}{\rightleftarrows}} Col-PAN$$

where Col^+ – dyes cation; Ret^- – retarder (polyelectrolyte) anion; PAN^- - free anionic groups from the ends of polyacrylonitrile macromolecular chains.

The anionic retarders interact with dyes, forming a compound with a smaller diffusion velocity inside the
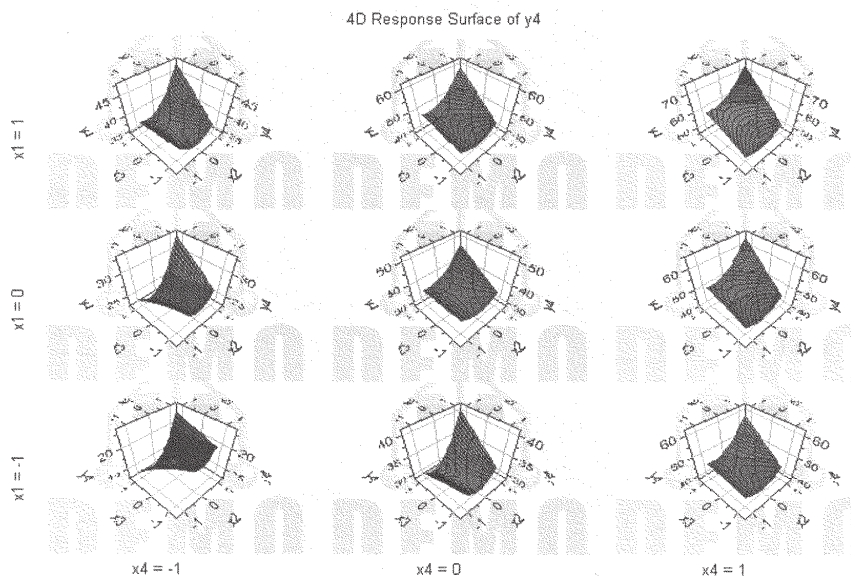
4D Response Surface of y4

Fig.4. Response surfaces for Melana fibre dyed with CV in the presence of NaM-S
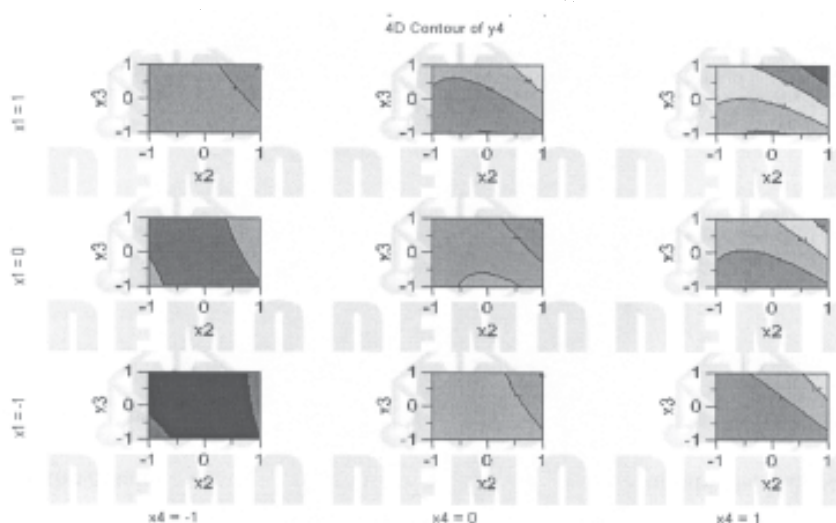

4D Contour of y4

Fig. 5. Level curves for Melana fibre dyed with CV in the presence of NaM-S

solution, therefore a slower sorption. În this cases NaM-S or NaM-VA polyelectrolytes present a retardation effect irrespective of their concentration in the processes of Melana dyeing with CV [4, 5, 7].

Mathematical models presented here were subsequently used to predict the studied processes and to determine the processing conditions necessary for optimal governing. In order to predict the influence of the independent variables on ΔE and their interactions, 222 response surfaces and 207 level curves were mapped out for the two studied systems [4]. Each time two factors were maintained constant (x_1, x_2 coded, equal to -1, 0 or 1), the other three being modified (figs. 4 and 5).

In the present case, we expose for illustration the response surfaces and the level curves for Melana fibre dyed with CV in the presence of NaM-S when the concentration of the dye (x_1) and polyelectrolyte (x_2), as well as the dyeing duration (x_3) change, while the dyeing temperature (x_4) is kept constant [4]. The obtained response surfaces are of the types of ascending ridge, oblong saddle or, elliptic valley, while the level curves are constantly hyperbolas, ellipses or parabolas with saddle points for some systems, that can be displaced toward them (ΔE) maximum value, and maximum or minimum points in certain cases [4].

Optimization of the process of Melana dyeing with CV in NaM-VA or NaM-S presence

The problem of optimization discussed here is a problem maximization of colour difference ye (ΔE), its solution being obtained in the MODDE application with descending simplex [4, 30-39].

Optimization of the process of Melana fibres dyeing with CV in NaM-VA presence

The optimization of the process of Melana fibres dyeing with CV in NaM-VA presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 2.

Under these conditions, the optimum value of the colour difference is of $ye_1 = 44.7141$ and the optimum values of the deciding variables are: $x_1 = 0.5$ g/L, $x_2 = 0.5$ g/L, $x_3 = 120$ min, $x_4 = 85.02555°C$ corresponding to the coded values -2; -2; 2 and -0.0511 respectively.

Finally, experimental verification of the found optimum values was performed. With this aim in view, the decisive variables were established at the obtained values. After the experiment, the measured value of *ye* was 43.85, which confirm the estimated optimum.

No.	x_1	x_2	x_3	x_4	y_3	iter	log(D)
1	-2	-1.9385	1.9999	0.7138	43.2058	10	-1.8116
2	-2	-2	2	1.5489	43.2105	8	-1.8193
3	**-2**	**-2**	**2**	**-0.0511**	**44.7141**	**6**	**-10**
4	-1.828	-1.9936	1.9558	0.9837	42.2255	27	-0.9006
5	-1.921	-2	2	0.3489	43.784	6	-10

No.	x_1	x_2	x_3	x_4	y_4	iter	log(D)
1	2	-1.9999	0.4492	0.6501	72.6752	188	-0.342
2	-0.721	1.9252	1.9959	1.7842	104.754	185	-10
3	-1.9642	1.999	1.3823	1.9996	103.654	255	-10
4	2	0	2	2	98.9929	0	-10
5	**-0.7219**	**1.9996**	**1.9804**	**1.9999**	**111.344**	**305**	**-10**
6	1.9683	-1.4823	1.3023	1.8284	82.6931	27	-10
7	1.8	1	1	1	84.3638	0	-10
8	0.9013	1.9777	0.7165	1.8342	90.4966	85	-10

Optimization of the process of Melana fibres dyeing with CV in NaM-S presence

The optimization of the process of Melana fibres dyeing with CV in NaM-S presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 3.

Under these conditions, the optimum value of the colour difference is of $ye_1 = 111.344$ and the optimum values of the deciding variables are: $x_1 = 1.36095$ g/L, $x_2 = 2.4998$ g/L, $x_3 = 119.559$ min, $x_4 = 99.9995°C$ corresponding to the coded values -0.7219; 1.9996; 1.9804 and 1.9999 respectively.

Finally, experimental verification of the found optimum values was performed. With this aim in view, the decisive variables were established at the obtained values. After the experiment, the measured value of ye was 108.25, which confirms the estimated optimum.

Conclusions

By examining the coefficients of the mathematical model in the value range of the considered factors for the two systems, one can notice that for the (Melana, CV, NaM-VA) system ΔE increases mainly with the increase of the dye and polyelectrolyte concentrations and dyeing temperature. These results agree with those presented in previous works.

The response surfaces are of ascending ridge, oblong saddle or elliptical valley types, while the level curves are hyperbolas, parabolas or ellipses, with the saddle point for some systems which can be displaced toward the maximum value of ye (ΔE), as well as maximum or minimum points in certain cases. There are also situations where straight lines appear which indicates the insignificant influence of some parameters on the target function.

The optimization of the processes of Melana fibres dyeing with CV in the presence of NaM-VA or NaM-S was performed without starting values, when these are implicitly generated by the MODDE application. It was found out that the ΔE values measured during the experiments performed for the two systems are close to the ΔE optimum estimated values.

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