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Dyeing of Nylon 66 with Disperse Dyes. An Optimization Study

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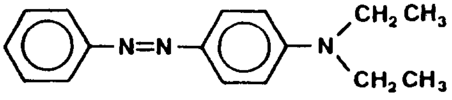
ABSTRACT

The use of chemometric methods in dyeing process optimization is explored. Multivariate strategies of experimental design are applied as they allow for simultaneous variation of all the intervening variables. The computer-assisted Response Surface Method is used to determine the optimum experimental conditions for dyeing nylon 66 with a disperse azo dye.

1 INTRODUCTION

In a previous study[1] we reported the positive effect of small quantities of double-tailed surfactants on the dyeing of polyester with disperse dyes as far as dyebath exhaustion and uniformity of coloration are concerned. The dyeing mechanism of the disperse azo dye **I** on nylon 66 and the effect of



(I)

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dispersant concentration and of various kinds of additives on the dyeing have been studied previously.[2]

The aim of this paper is to explore the applicability of chemometric procedures to the optimization of the dyeing process of nylon 66 with dye **I**. A multivariate approach is used for the experimental design which allows for a simultaneous variation of all the intervening variables. The multivariate Response Surface Method is the technique used for the optimization.

Studies devoted to the optimization of dyeing processes are widely growing under the stimuli of economical and environmental grounds.

1.1 Optimization procedure

Optimizing a process means determining the experimental conditions that give an optimal performance. In this present study the problem can be defined as maximizing the dyebath exhaustion and the dyeing rate.

The search for optimum conditions of a process or optimal properties of a product is usually done by measuring the desired response on varying the causal variables one at a time. This strategy is largely insufficient to explore the experimental domain. Multivariate approaches are needed to evaluate the effects on the response of all the variables as well as the effects of their combined interactions.

Factorial designs[3] can be used successfully to collect the required information, with the minimum number of experiments, since the investigation covers the maximum span in the variable space. The logic of a factorial design is straightforward. The strategy is to locate the experiments in the space of the variables (factors) in such a way that all the information necessary to determine the effects of the variables and of their interactions on the response can be collected. In a full factorial design all k variables are taken into account at two levels, a low and a high level, so that the number of experiments required is 2^k. Response values determined by the experimental design permit the calculation of the main effects and interactions: the data treatment can be done by multiple regression or by simpler procedures such as the Yates algorithm.[3]

When a large number of variables has to be controlled, fractional factorial designs are generally used because they provide the desired information by performing only a fraction of the full factorial design. The number of experiments to be run is 2^{k-m}, where m is the fraction of the experimental design used. The reduction of the experiment number produces confusion between the effect of an individual variable and the interaction of other variables. Nevertheless fractional factorial designs can properly be used to select the most important variables for the process under study.

However, factorial designs are not sufficient to indicate the optimal experimental conditions. Some more experiments are necessary in order to have enough degrees of freedom to make possible the statistical analysis and to evaluate the reproducibility of the process. The best strategy for collecting the required information is to use a 'central composite design', which is a full factorial design with added experiments and replicates located at the central point of the design, and a pair of experiments along the coordinate axes at a distance equal to half of the diagonal of the square or the cube, according to whether the variables are two or three. Accordingly, a central composite design in three variables requires 16–20 experiments and one in two variables 10–14 experiments.

With a central composite design it is possible to build the mathematical model, i.e. to determine a response surface (Fig. 1), the projection of which is called an isoresponse diagram.

The mathematical form of a response surface is a polynomial equation (1) in which the factors are present in their linear and quadratic terms as well as in their bifactorial cross-products:

$$y = b_0 + \sum_i b_i x_i + \sum_i b_{ii} x_i^2 + \sum_{ij} b_{ij} x_i x_j \tag{1}$$

where y is the response, b_0 is the independent term, b_i, b_{ii} and b_{ij} are the coefficients of each monomial, and x represents the variables or factors.

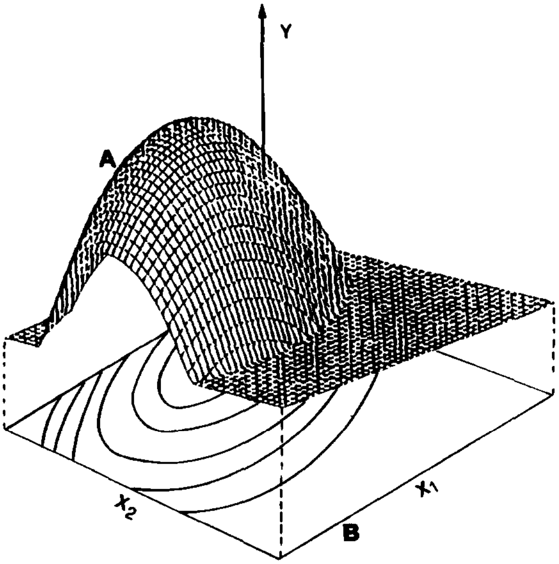

Fig. 1. A, Response surface; B, isoresponse diagram.

The coefficients are usually calculated by multiple regression analysis, as the experimental design is rigorously orthogonal and equally spaced.

In the preliminary part of a study it is often unknown which variables are the most relevant to the response, and the number of experiments required for a central composite design would become impractically large. Consequently, it is preferable to carry out a preliminary study by the strategy of a fractional factorial design, which permits the control of a larger number of variables with fewer experiments. The results of the fractional factorial design can properly be used to select the most important variables to be studied subsequently in the central composite design.

This is the approach used in the present study.

2 EXPERIMENTAL

The commercial dye was recrystallized from ethanol until chromatographic purity (by TLC) was attained. Polyamide 66 fibres were prewashed with a soap solution, well rinsed, dried and stored at constant temperature and humidity before weighing (0·5 g). The dye baths were prepared by dissolving in acetone (10 ml) weighed amounts of dye ($3{\cdot}3 \times 10^{-3}$ g) and dispersant (Ethofor RO 40, ICAI, Turin). The solvent was gently removed to obtain a dense syrup to which buffer solution, additive solution, and water to a final volume of 250 ml were added.

The sorption rate curves were obtained measuring *in continuo* the absorbance of the bath at 420 nm, using the apparatus previously described.[4] For each dye the validity of Lambert–Beer's law has been verified, in the presence of the dispersant, either at room temperature or at the dyeing temperature.

The ratio (dye concentration in the fibre:dye concentration in the bath) at the equilibrium is taken as K_{eq}, as suggested by the previous study.[2]

The Vickerstaff equation[5] (2) has been applied to the sorption rate curves and the constant term k has been used as K_{rate}:

$$\frac{t}{c_t} = \frac{1}{kc_\infty^2} + \frac{1}{c_\infty}t \tag{2}$$

where c_t is the dye concentration in the fibre after time t and c_∞ the dye concentration in the fibre at equilibrium.

The calculations were carried out using an IBM AT personal computer. PLS models were obtained by the SIMCA package and response surface models by the REGFAC program package (both packages developed at the University of Umea, by the research group directed by S. Wold).

3 RESULTS AND DISCUSSION

3.1 Factorial design

Two-level fractional factorial designs have been used to explore the effect of a number of variables on the dyeing process of the disperse azo dye **I** on nylon 66 fibre. The responses (dependent variables) were the following:

(a) dye partition constant, i.e. the ratio dye in the fibre : dye in the bath at the equilibrium, K_{eq};
(b) empirical dyeing rate constant (Vickerstaff's k), K_{rate}.

The independent variables and the corresponding levels are listed in Table 1.

The additives examined were double-tailed cationic and anionic surfactants:

DDDAB	Didodecyldimethylammonium bromide
DDDAC	Didodecyldimethylammonium chloride
DHDAC	Dihexadecyldimethylammonium chloride
DDMHAC	Didodecylmethylhydroxyethylammonium chloride
DHP	Sodium dihexadecyl phosphate
No additive	

Three 2^{4-1} fractional factorial designs were run according to the design matrix of Table 2, to compare the above-listed additives. The experiments were performed in random order, not as they are reported in the Table. The response values obtained in the three designs are listed in Table 3.

Data were analysed by calculating the main effects and the second-order interactions by the Yates algorithm.[3] Numerical values of the effect are not reported here because of the poor comparability of the individual figures owing to the arbitrary splitting into three distinct designs. From the results,

TABLE 1
Independent Variables and Respective Levels in the Fractional Factorial Design

Variable	*Level*	
	(−)	(+)
Temperature (°C)	60	80
Buffer (1×10^{-2} mol litre^{-1})	TRIS[a]	Phosphate
Dispersant concentration (g litre^{-1})[b]	2	1
Additive	A	B

[a] 2-Amino-2-hydroxymethyl-1,3-propanediol.
[b] Ethofor RO 40 (castor oil, degree of ethoxylation 40)

TABLE 2
2^{4-1} Fractional Factorial Design Matrix

Run no.	*Variable*			
	1 *Temperature*	*2* *Buffer*	*3* *Dispersant concn*	*4* *Additive*
1	−	−	−	−
2	+	−	−	+
3	−	+	−	+
4	+	+	−	−
5	−	−	+	+
6	+	−	+	−
7	−	+	+	−
8	+	+	+	+

it can be concluded that K_{eq} is mainly influenced (negatively) by dispersant concentration while K_{rate} is mainly affected (positively) by temperature. The same conclusions can be reached by the direct application of the PLS method[6] to all data collected in the three designs. The model for K_{eq} explains 92% of the variance by one single latent variable mainly due to the dispersant concentration. The model for K_{rate}, although poorer, explains

TABLE 3
Responses for the Three Designs Using Different Additives

Run no.	*Design* *I*		*II*		*III*	
	Responses					
	K_{eq}	K_{rate}	K_{eq}	K_{rate}	K_{eq}	K_{rate}
1	147	16	163	14	145	13
2	119	78	137	74	104	63
3	148	10	158	16	152	14
4	155	25	137	33	134	23
5	286	10	223	12	273	8
6	237	29	212	44	210	21
7	300	9	265	13	280	9
8	231	27	213	35	244	21
Additives						
A	DDDAB		DHDDC		None	
B	DDDAC		DDMEOC		DHDP	

TABLE 4
Central Composite Design in Two Variables: The Design Matrix and the Responses

Run. no.	*Variables*		*Responses*	
	X_1	X_2	K_{eq}	K_{rate}
1	−1	−1	288	15
2	+1	−1	277	36
3	−1	+1	227	19
4	+1	+1	214	30
5	−1·41	0	252	18
6	+1·41	0	226	43
7	0	−1·41	288	29
8	0	+1·41	214	26
9	0	0	237	31
10	0	0	239	29
11	0	0	232	30

over 52% of the variance by one single latent variable; the most relevant contribution to this latent variable is given by the temperature.

3.2 Response surface method

Information from the fractional factorial design was used to run the central composite design with two variables and three centre points reported in Tables 4 and 5. All the experiments were performed in random order, in the presence of additive DDDAC ($2{\cdot}16 \times 10^{-5}$ mol litre^{-1}) with phosphate buffer (1×10^{-2} mol litre^{-1}). We also tried to study as a variable the buffer concentration, but the results showed that only in the range 1×10^{-3}–1×10^{-2} mol litre^{-1} was precipitation of the dye avoided. In the range mentioned above the buffer variation effect was under the limits of the experimental error.

TABLE 5
Experimental Domain and Coding of the Variables

Variables	*Levels*				
	−1·41	*−1*	*0*	*+1*	*+1·41*
X_1: temperature (°C)	73	75	80	85	87
X_2: dispersant concn (g litre^{-1})	0·79	0·85	1·00	1·15	1·21

Response surface models showing Y_1 and Y_2 respectively as functions of the experimental variables X_1 and X_2 were calculated by multiple regression analysis using the REGFAC program package. The polynomial equations (1) obtained are the following:

$$Y_1 = 236 - 7{\cdot}6X_1 - 28{\cdot}6X_2 + 3{\cdot}1X_1^2 + 9{\cdot}1X_2^2 - 0{\cdot}5X_1X_2$$
$$(R^2 = 97{\cdot}7\%;\ \mathrm{S} = 5{\cdot}9;\ P < 0{\cdot}005)$$
$$Y_2 = 30{\cdot}0 + 8{\cdot}4X_1 - 0{\cdot}8X_2 - 0{\cdot}8X_1^2 - 2{\cdot}3X_2^2 - 2{\cdot}5X_1X_2$$
$$(R^2 = 95\%;\ S = 2{\cdot}6;\ P < 0{\cdot}01)$$

The projections of the response surface models both for K_{eq} and K_{rate} are shown in Fig. 2. It can be seen that values of K_{eq} greater than 230 can be obtained only for dispersant concentrations lower than 1 g litre^{-1} (coded value zero). On the other hand, values for K_{rate} greater than 30 can be obtained only for temperatures greater than 80°C (coded value zero).

As actually coded values significantly lower than -1 (0·85 g litre^{-1}) are to be avoided in order to guarantee a stable dispersion of the dye, which is essential to avoid its precipitation on the fibre, the optimum dyeing conditions should be found within the marked area in Fig. 2, which corresponds roughly to 0·85–1 g litre^{-1} of dispersant and temperature ≥ 80°C. Predicted values of the responses in this area are K_{eq} 230–270,

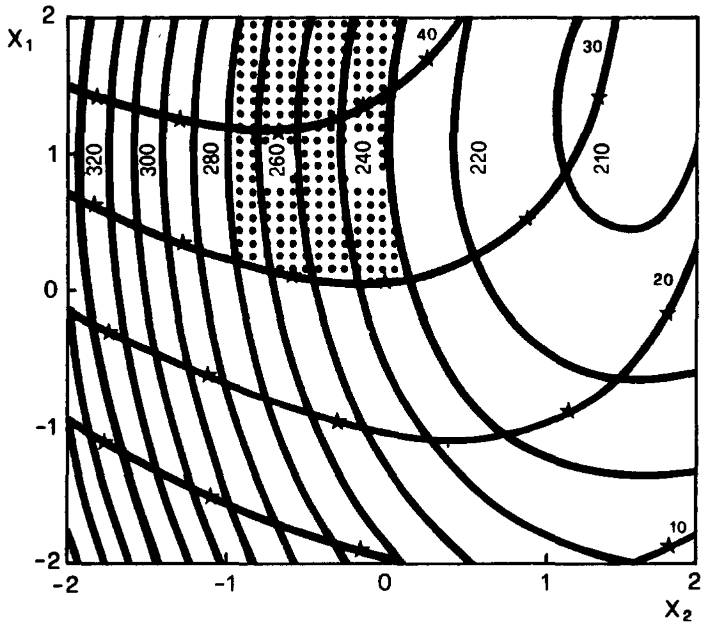

Fig. 2. Isoresponse projections of the models. Solid lines show K_{eq} values. Starred lines show K_{rate} values. The spotted area corresponds to the optimum dyeing conditions.

$K_{rate} \geq 30$. The reliability of the response surface predictions is supported by the experimental values of K_{eq} (287) and K_{rate} (36) obtained at 85°C (coded value 1) and 0·8 g litre^{-1} of dispersant (coded value −1·35) for checking a different chemometric model which will be reported elsewhere.

4 CONCLUSIONS

This preliminary paper indicates the applicability of the computer-assisted Response Surface Method to the optimization of a dyeing process. Multivariate experimental design is essential to control simultaneously all the intervening variables with a minimum number of experiments. The study should be carried out in two steps, the first of which is aimed at detecting the most relevant causal variables and the second at determining the response surface.

The experimental data collected so far showed that low dispersant concentration and high temperatures are the optimum conditions to improve both dyebath exhaustion and dyeing rate.

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