DEVELOPING A STATISTICAL MODEL OF CI REACTIVE RED 194 DYE EXHAUSTION ON COTTON FABRIC USING DIFFERENT DYEING PARAMETERS

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The exhaustion characteristic features of CI reactive red 194dye on cotton fabricunder differentdyeing conditions wereinvestigated in this study. For this purpose, dye temperature, time intervals, the concentration of dye, salt and soda were selected as dyeing inputs. Dye solutionsamples weredrawn from the dye-bathfrom the beginning to the end of the process at 10 min intervals for determining dye exhaustion. The transmittance of the colored dye bath sample was measured by using the UV-Vis technique. The dyeing results were investigated by statistical analysisusing ANOVA and regression curves.In addition, the times of half dyeing ($t_{1/2}$) were evaluated. The maximum exhaustion conditions were obtained and discussed according to the statistical outputs.

Keywords: exhaustion model, CI reactive red 194, time of half dyeing, cotton

INTRODUCTION

CI reactive red 194 (RR194) dye has two different reactive groups, which are monochlorotriazine and vinylsulfone, in its molecular structure.[1] Highly exhausted reactive dye is ideal for dyeing cotton and other cellulosic fibers.[2] The reactive dye reduces the cost with its significant fixation yield and higher exhaustion efficiency. In addition, the drained and wash liquors after dyeing contain a much smaller quantity of unfixed reactive dye.[3] One of the advantages of heterobifunctional reactive dyes, such as monochlorotriazine/vinylsulfone dye, is the difference in reactivity levels between the two functional groups, which compensates somewhat for the variation in dyeing conditions, such as temperature and pH, and results in the dye being more durable.[4] Sumitomo launched the first complete range of heterobifunctional reactive dyes, which contained both a monochloro-*s*-triazine and a sulfatoethyl sulfone group attached to the same dye molecule. These reactive dyes were named Sumifix Supra.[5]

Scientific investigations on reactive dye exhaustion have been made with different objectives.[6-9] In order to achieve a higher dyeing level, a number of studies have been focused on determining the exhaustion rate of some reactive dyes.[10-18] The kinetics of the alkaline hydrolysis of azo reactive dyes has been studied on monofunctional dyes with one monohalogeno-s-triazine reactive group and bifunctional dyes with two identical monohalogeno-*s*-triazine reactive groups at different temperatures. The hydrolysis rate coefficient of monofunctional dyes is more temperature dependent than that of homobifunctional dyes.[11] Reactive dyes with a less reactive monochloro-*s*-triazine group are more sensitive to temperature variations than reactive dyes with a more reactive monofluoro-*s*-triazine group. The adsorption characteristics of Reactive Blue 222, Reactive Red 195 and Reactive Yellow 145 on cotton fiber were investigated according to the color strength and fixation rate.[12] Their experimental results show that the adsorption of the dyes on cotton is in better agreement with the Langmuir model.[12]In order to optimize color strength and fastness for reactive dyeing, some variations in the dyeing procedure were adopted by using different buffers, Borax+NaOH and compared with soda under identical dyeing conditions.[13] Better exhaustion and fixation properties of Tencel fabrics treated by atmospheric pressure plasma and dyed with Reactive Black 5 dye were reported.[14] Demarchi *et al.* studied chitosan–iron(III) crosslinked with glutaraldehyde (Ch-Fe) as an adsorbent for the textile anionic dye, Reactive Red 120 (RR120) in batch and fixed-bed systems. They calculated the maximum adsorption capacity from the adsorption isotherms, and observed that the adsorption was well fitted to the Langumir–Freudlich isotherm model.[15] The adsorbent material, chitosan, was used for the adsorption of CI Reactive Red 3 and CI Direct Brown 95 dyes from aqueous solutions. Functions of dye contact time, dye concentrations, temperature, pH and sodium chloride concentration were investigated as basic dyeing parameters.[16] Chen *et al*. investigated reusing spent reactive dye baths by replacing water with non-nucleophilic green solvents. They concluded that dye sorption and dye fixation were affected by solvent composition and, compared with conventional aqueous dyeing, the solvent-based process required up to 40% less dye, 97.5% less base, and no inorganic salts.[17] Bertea *et al.* studied about the reuse of waste dye bath containing CI Reactive Blue 19 and CI Reactive Red 243 dyes after an oxidative process.[18] Their experimental study shows that the dyeing and wash-off wastewater can be recycled only at low dye concentration.[18]

A statistical study on multifactor experiments provides a better interpretation and comparison of the results.[19] Various statistical evaluations of the dyeing process have been reported in the literature.[20-22] One of these studies discusses the influence of color on the UPF of cotton fabrics, which are appropriate for summer articles.[22] Through statistical models, the research seeks to relate the level of protection achieved in dyeing with three azo dyes to the factors governing the process, the shade, and the color intensity, as well as their interaction with the initial UPF of the fabrics.[22]

Research on the exhaustion behavior together with the time of half dyeing ($t_{1/2}$) of RR194 on cotton fabrics is limited. For this purpose, in this study we aimed to determine the maximum exhaustion level with optimum dyeing parameters for cotton using RR194, by statistical analyses. We have developed two different linear and quadratic models to describe the exhaustion behavior. The analysis of variance and regression curves are used to evaluate the exhaustion results.

EXPERIMENTAL

Fabric and dye

Knitted cotton fabrics, which were scoured, bleached and free of fluorescent whitening agents, were supplied by Balgüneş Textile Company (Kayseri, Turkey). The weight of the fabric was 150 gm^{-2}. Commercial RR194 dye was used as obtained from the dye manufacturer EksoyChem(Adana, Turkey) without further purification. The dyestuff structure is shown in Figure 1.

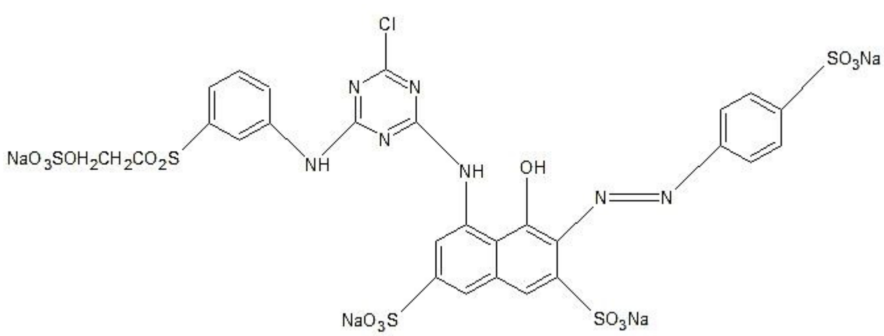

Figure 1: Structure of CI Reactive Red 194 dye

Dyeing and kinetic study

All dyeing processes were carried out using laboratory equipment (Termal HT, Turkey). About 10 g of fabric samples was weighed and a liquor to fabric ratio of 20:1 was used. The various dyeing parameters applied are given below:

- Temperature (°C): 40, 50 and 60;
- Salt concentrations (g/L): 0, 40, 70 and 100;
- Dye concentrations, owf (on weight of fiber): 1, 2 and 3%;
- Soda concentrations (g/L): 20 and 50.

The all-in exhaust dyeing method was used. The dyeing process began at 30 ºC in dye baths containing salt, soda, dye, fabric sample and distilled water. The temperature was raised to the target level in 20 min and held constant for 70 min. The temperature was then decreased to 40 ºC, the samples were rinsed with cold tap water, washed with non-ionic detergent (1 g/L Setalan BNH-Setaschem, Turkey) at boiling temperature, rinsed with hot tap water and then dried under laboratory conditions. The dyeing diagram is given in Figure 2.

Measurement of dye exhaustion

The RR194dye solutions were prepared at different known concentrations and their absorbance values at the wavelength of maximum absorption (533 nm) were recorded by UV-Vis. (PG Inst., PG80). The results were then plotted to make a calibration curve from which the unknown concentrations could be determined by their absorbance values. The absorbance of the unknown dye solution was measured on aPG T80 spectrophotometer on the basis of λ_{max} of the dye. The uptake amount of the RR194 by cotton fabric was calculated after determining the amount of dye in the dye-bath.

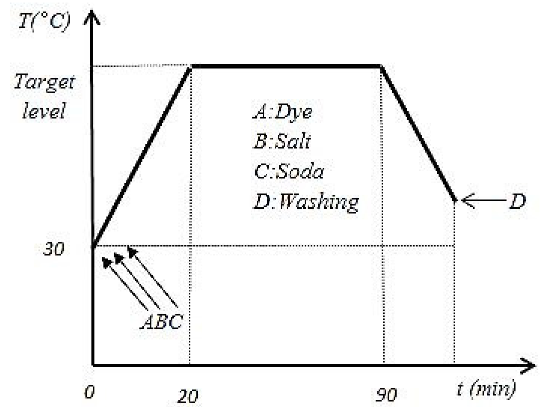

Figure 2: Dyeing diagram

Time of half dyeing (Thd)

The dye exhaustion curve is informative with regard to the time of half dyeing ($t_{1/2}$) and the dyeing equilibrium exhaustion. The time of half dyeing was determined from the regression curves for the exhaustion to reach 50% of its dyeing equilibrium level.

Statistical analysis

Variable parameters, such as dyeing, salt and soda concentrations, temperature and time interval, were determined, whereas the response variable was the exhaustion percent.[23] For this purpose, we used Design Expert software to carry out the general factorial design for this statistical study. In this investigation, we tested 216 types of fabric and conducted a total of 1944 tests by using 3 replications. The statistics for the developed model of exhaustion are summarized in Table 1. Here, the R-squared value (R^2), which represents the explanation rate of the model by the analysis of variance, is found as 96.611%. Also, the standard deviation (STD) of exhaustion is determined as 2.991.

Table 1
Statistic model for dye exhaustion

STD	2.991
Mean	62.564
C.V.*	4.782
R^2	0.9661

*Coefficient of variation

The normal distribution test should be applied in order to start the statistical investigation to see the conformity of residuals to the normal distribution line. In general, probability plotting is a graphical technique for determining whether sample data conform to the hypothesized distribution based on a subjective visual examination of the data. In Figure 3, the exhaustion data are scattered approximately around the normality line and conform to normal distribution.

The Analysis of Variance (ANOVA) was carried out for exhaustion and the results are given in Table 2. Here, "A" represents temperature, "B" is dye concentration, "C" is salt concentration, "D" is soda concentration and "E" is time interval in minutes. The parameters in the ANOVA table with p-values of less than 0.05 are expected to be significant by a 95% confidence interval. The effects of the model terms to the exhaustion are also given in Table 2, which is indicated as "contribution". Here, the primary contribution to the model is maintained by "E" or a time interval of 42.38%. The contribution of "C" or salt concentration is of second importance at 18.26%. The dye concentration "B" and soda concentration "D" are the successive models with contributions of 14.00% and 12.41%, respectively. Other terms in the ANOVA table have relatively low values with respect to these terms. Hence, it can be inferred from Table 2 that salt concentration and time interval have the maximum effect on dye exhaustion. The quadratic regression equation was also developed:

$$\text{Exhaustion} = +69.72+1.04*A-7.42*B+9.34*C+5.71*D+16.34*E-2.40*A^2+0.39*B^2-2.55*C^2-11.7*E^2 + 0.19*A*B +0.13*A*C-0.73*A*D-1.27*A*E+0.52*B*C-0.03*B*D+1.57*B*E-1.54*C*D + 0.09*C*E - 0.3*D*E \quad (1)$$

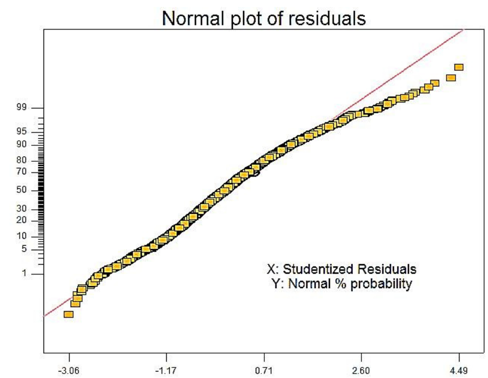

Figure 3:Normality test for dye exhaustion

Table 2
ANOVA for different dyeing parameters using RR194

Source	Sum of squares	Contribution(%)	DF	Mean square	F value	P value	
Model	490981.02		19	25841.11	2886.82	< 0.0001	significant
A	1406.05	0.28	1	1406.05	157.08	< 0.0001	significant
B	71168.32	14.00	1	71168.32	7950.51	< 0.0001	significant
C	92822.98	18.26	1	92822.98	10369.64	< 0.0001	significant
D	63090.21	12.41	1	63090.21	7048.07	< 0.0001	significant
E	215391.86	42.38	1	215391.86	24062.31	< 0.0001	significant
A^2	2572.35	0.51	1	2572.35	287.37	< 0.0001	significant
B^2	140.38	0.03	1	140.38	15.68	< 0.0001	significant
C^2	2652.05	0.52	1	2652.05	296.27	< 0.0001	significant
D^2	0.00	0.00	0				
E^2	35661.67	7.02	1	35661.67	3983.91	< 0.0001	significant
AB	105.47	0.02	1	105.47	11.78	0.0006	
AC	86.14	0.02	1	86.14	9.62	0.0019	
AD	762.48	0.15	1	762.48	85.18	< 0.0001	significant
AE	943.18	0.19	1	943.18	105.37	< 0.0001	significant
BC	265.36	0.05	1	265.36	29.64	< 0.0001	significant
BD	75.63	0.01	1	75.63	8.45	0.0037	
BE	1399.52	0.28	1	1399.52	156.35	< 0.0001	significant
CD	2608.90	0.51	1	2608.90	291.45	< 0.0001	significant
CE	78.32	0.02	1	78.32	8.75	0.0031	
DE	78.32	0.02	1	78.32	8.75	0.0031	
Residual	17222.53	3.39	1924	8.95			
Lack of fit	14616.73	2.88	628	23.28	11.58	< 0.0001	significant
Pure error	2605.80	0.51	1296	2.01			
Cor. Total	508203.55	100	1943				

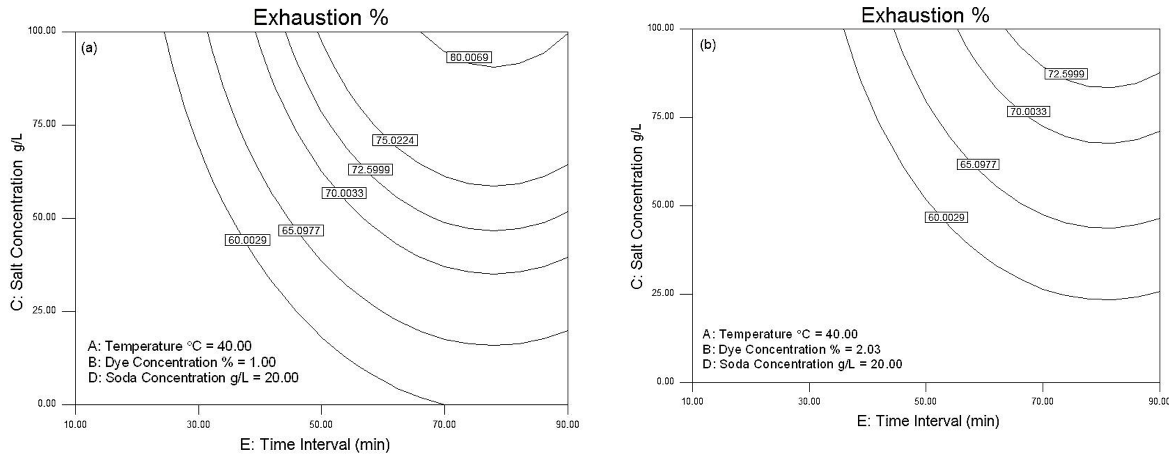

Figure 4: Exhaustion contour lines for different dye concentrations: a) dye concentration 1%; b) dye concentration 2%

The Mean Absolute Percent Error (MAPE-%) value was also determined. The results of the overall 1944 experimental tests were recorded and the actual and predicted values were compared. We concluded that the MAPE-% value was 4.28%. In other words, the regression equation above predicts the exhaustion at 4.28% error in general.

Another simple (linear) exhaustion model was developed in this study, but the R^2 value of this model was 0.874, which indicates that the linear model explains only 87.4% of exhaustion, as compared to 96.6% of exhaustion explained by the quadratic model discussedabove. The regression equation of this linear model is given below as Eq.2. However, in order to obtain more reliable results, we preferred the quadratic equation (1).

$$\text{Exhaustion} = + 28.66 + 0.105*A - 7.4*B + 0.19*C + 0.38*D + 0.41*E \qquad (2)$$

RESULTS AND DISCUSSION

As salt concentration and time interval are important parameters when examining the contribution ratios for the model developed according to the ANOVA table, the corresponding figures were plotted taking this information into consideration (Figures 3-5). In these contour plots, the x-axis stands for the time interval and the y-axis shows the salt concentration. The contour curves indicate identical exhaustion values for different process conditions. In Figures 3-5, the exhaustion values are given in order to show how to obtain the maximum exhaustion, which is 92.31% in this study, under different process conditions.

Figure 4 shows the exhaustion contour curves for varying the dye concentration from 1% (Fig.4a) to 2% (Fig.4b), while the other factors were fixed, as indicated in the figure. Figure 4a should be also used as a reference for comparison with Figures 5 and 6. Increasing dyeing concentration decreases the exhaustion values, as shown in Figure 4. The maximum exhaustion (80.069) is obtained under the following conditions:75 min dyeing time, 90 g/L salt concentration, 40 ºC temperature, 1% dye concentration, and 20 g/L soda concentration (Figure 4a).

The effect of the dyeing temperature can also be noted in Figure5 (in comparison with Fig. 4). When increasing the temperature from 40 ºC to 50 ºC (Figure 4a and Figure 5a), the exhaustion increases. However, further increase in temperature from 50 ºC to 60 ºC decreases the exhaustion. Hence, the optimum temperature for the maximum exhaustion can be determined as about 50 ºC. The maximum exhaustion (84.189%) is reached under the following conditions: about 75 min dyeing time, 85 g/salt concentration, 50 ºC temperature, 1% dye concentration and 20 g/L soda concentration (Figure 5a).

The effect of soda concentration on exhaustion can be observed in Figure 6. By examining Figs.4a, 5a and Figure 6altogether, it can be seen that increasing soda concentration increases exhaustion values. Maximum soda concentration (50g/L) gives the maximum exhaustion. The maximum exhaustion in this study was obtained as indicated in Figure 5b. In this case, the following conditions were determined as the optimum: temperature 50 ºC, minimum dye concentration 1%, maximum soda concentration 50 g/L, 75 min dyeing time and 90 g/L salt concentration, giving the maximum exhaustion of 92.3062.

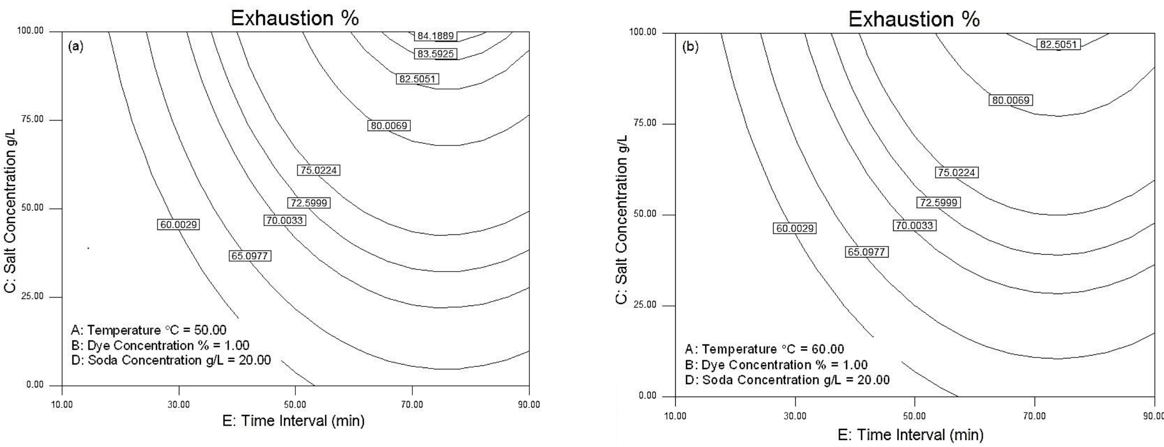

Figure 5: Exhaustion contour lines for different temperatures: a) temperature 50 ºC; b) temperature 60 ºC

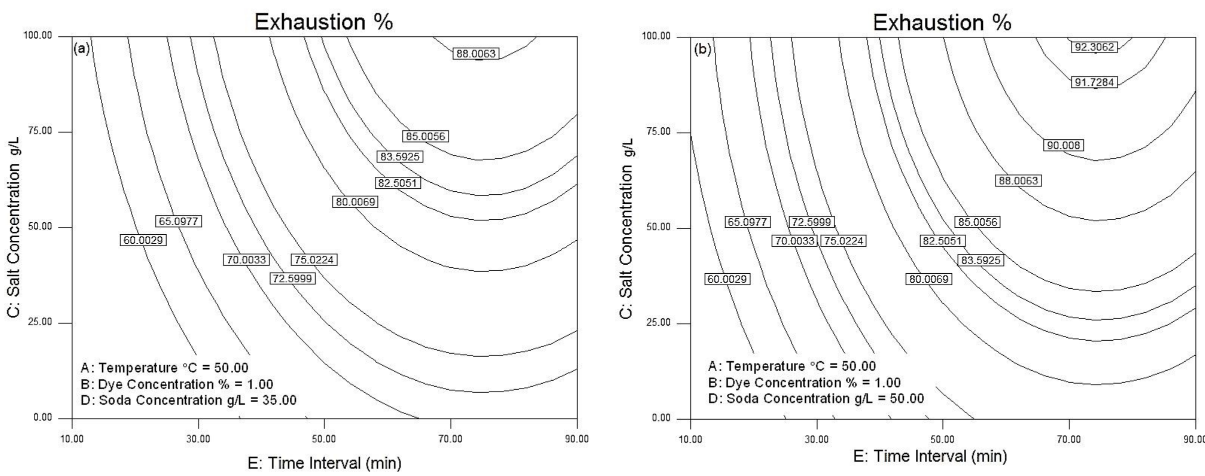

Figure 6: Exhaustion contour lines for different soda concentrations: a) soda concentration 35 g/L; b) soda concentration 50 g/L

The average time of half dyeing (Thd) for different dyeing conditions is presented in Table 3. Considering the dyeing temperatures, it was noted that there was no significant difference between40ºCand50ºC. However, Thd decreased at 60 ºC because the kinetic energy of the dye molecules increased. Because of the reduction in the diffusion of the amount of dye molecules to the fiber with an increasing dyeing concentration in the dye-bath the Thd increased. An increasing salt concentration reduced Thd. This is probably due to the decrease in negative zeta potential on the fiber surface, which causes a decrease in Thd. In addition, a higher salt concentration increased the aggregation of dye in the dye-bath. Since the dye molecules accelerated the reaction between the fiber and dye molecules, an increasing concentration of soda decreased Thd.

Table 3
Time of half dyeing ($t_{1/2}$) in minutes, using RR194

Dye Conc. (%)	Salt Conc. (gL^{-1})	Soda Conc.(gL^{-1})	40 ºC	50 ºC	60 ºC
1%	0	20	13.31	13.51	8.73
		50	9.07	9.17	7.23
	40	20	10.36	10.86	8.8
		50	7.32	7.65	6.44
	70	20	9.64	8.63	7.9
		50	7.06	7.83	6.55
	100	20	8.76	8.68	7.11
		50	6.64	6.71	6.31
2%	0	20	9.94	15.08	11.88
		50	10.44	10.58	8.88
	40	20	10.26	12.83	10.03
		50	9.29	9.87	7.59
	70	20	11.34	11.75	8.92
		50	9.89	8.96	7.56
	100	20	9.99	9.91	8.87
		50	9.42	8.79	7.97
3%	0	20	24.55	23.72	18.12
		50	19.37	16.1	15.66
	40	20	21.58	21.74	15.26
		50	11.07	14.28	13.67
	70	20	14.46	14.37	12.8
		50	11.35	10.1	8.04
	100	20	11.5	12.8	9.31
		50	9.72	10.94	8.72

CONCLUSION

In the present study, the changes in the dye exhaustion level of RR194as a function of the dyeing time were investigated on cotton fabrics by evaluating the dye-bath color density and time of half dyeing. The maximum exhaustion level was found to differ for the cotton fabrics dyed with RR194under different dyeing conditions. In accordance with the selected dyeing conditions, the regression equations for exhaustion were obtained and plotted, and the maximum exhaustion values were calculated for different dyeing parameters under equilibrium conditions. The data provided (as shown in Figs.3, 4, 5) indicate the highest dye exhaustion values and suitable dyeing time, which could be useful to manufacturers. The half dyeing values, which have an implication for the full dyeing time, were also determined for selected dyeing parameters. We developed two regression models, a quadratic one and a linear one. Although the quadratic model was quite complex, it provided more reliable results. The simple linear model had a lower, but acceptable R^2 value. We preferred the quadratic model for the evaluation. However, in order to make a simple calculation, the linear one may be preferred.

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