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Reviving of Cotton Dyeing by Saxon Blue: Application of Microwave Irradiation to Enhance Dyeing Performances

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Abstract: The present paper illustrates an unconventional but green exhaust dyeing process of cotton, in which the conventional reduction step of the indigo dyeing process is eliminated following the substitution of the insoluble indigo by the soluble indigo carmine. Indigo carmine can meet ecological requirements in terms of chemical consumption reduction, cleaner releases, and biodegradability. However, this dye produces unsatisfactory dyeing quality compared to indigo. In order to enhance dyeing quality, cotton samples were treated with Sera Fast GMX (a cationic agent) before they were dyed with indigo carmine. The influence of dyeing parameters (i.e., indigo carmine concentration, dyeing temperature, dyeing duration, and sodium carbonate concentration) on the evolution of the color strength (*K/S*) was studied. A response surface design was employed to optimize this unconventional dyeing process. The addition of salt to the dye bath appeared to improve both color strength and fastness properties. Finally, the effect of treating cationized cotton samples with microwave radiations was investigated. The results showed that exposure to microwave radiation for 5 min resulted in improvements in dyeing quality.

Keywords: Sustainable dyeing process, Indigo carmine, Modified cotton, Process optimization, Microwave pretreatment

Introduction

The range of available indigoid dyes was considerably enlarged at the beginning of the 20th century. Thereafter, some of these dyes were substituted by other classes of dyes. Currently, only 15 to 20 indigoid dyes are still used. These dyes hold an important position among artificial dyes because they are derived from indigo, which is the most commonly used dye for the purpose of dyeing cotton warp yarns for blue denim articles.

Prior to the dyeing process, this initially insoluble vat dye must be converted to its leuco-soluble form with a certain affinity for cotton. The leuco-soluble form of indigo is conventionally obtained by chemical reduction using sodium dithionite as a reducing agent [1]. The use of this reducing agent has several technical and ecological limitations, such as instability, storage problems, and corrosivity [2]. It is also responsible for various ecological problems due to the production of large amounts of sulfate and sulfite ions derived from the oxidation of sodium dithionite during the reducing process, which increases the cost of industrial wastewater treatment [3,4]. The goal of solving these problems has been the main concern of numerous researchers, and many attempts have been made to replace this harmful reducing agent with more attractive ecological substitutes [5-7]. The following attempts have been documented in the literature::

- Electrochemical reduction: The reduction of indigo by means of an electric current makes the indigo dyeing process cleaner, as the addition of chemical reagents is not required in this method [8-11]. However, this method requires a specific installation and consumes a large amount of electrical energy.
- Chemical reduction: Environmentally unfavorable sodium dithionite can be replaced by several environmentally friendly reducing agents, such as borohydride [12,13] and α hydroxycarbonyls [14-16], leading to a biodegradable product after oxidation. Despite their advantages, these reducing agents are not able to achieve the same dyeing performance as sodium dithionite.

The methods described above have not been deemed satisfactory on an industrial scale. Therefore, sodium dithionite remains the most widely used reducing agent because of its low cost and high dye yields. However, researchers are still in the process of developing a successful concrete application of these reducing agents in industrial processes.

In the present study, the harmful reduction step of the indigo dyeing process was eliminated in the development of a new cleaner process for dyeing cotton, in which the indigo is replaced by Saxon blue (also called indigo carmine), which is a dye of natural origin extracted from the indigo tree. Saxon blue is a blue acid dye [17,18] and contains two sulfonate groups, which facilitate solubility in water (see Figure 1).

Previously, indigo carmine has only been used to dye protein fibers, such as wool and silk [19]. The indigo carmine dyeing process creates beautiful, bright shades that are different from those obtained by the traditional indigo dyeing process [20]. These shades are generally desired by fashion professionals. The use of indigo carmine to dye

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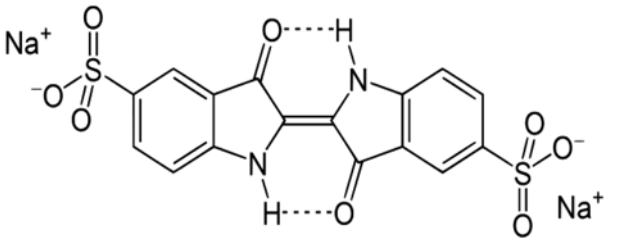

Figure 1. Chemical structure of indigo carmine.

cotton was first investigated by Bergmann [21], who found the performance of this dye unsatisfactory in terms of color strength and fastness properties. This dye has a low affinity for cellulosic fiber because cotton carries a slightly negative charge on its surface in an alkaline medium that repels anionic dyestuff. The use of indigo carmine to dye cotton exhibits many economic and ecological advantages over the conventional dyeing process using indigo, such as easy control over dyeing quality. Further, the elimination of the reduction step minimizes chemical inputs and reduces energy consumption. Also, the wastewaters generated by the residual baths after dyeing with indigo carmine are much cleaner than those generated after dyeing with indigo, as they are free of sodium sulfate and sodium sulfite. The presence of these species makes wastewaters more polluting, more difficult to treat, and very saline. Therefore, this process has the advantage of decreasing the cost of wastewater treatment. Finally, this exhaustion dyeing process with indigo carmine opens the way to success in dyeing garments with blue indigo by machine. The use of machines to dye garments with indigo is very advantageous, but it typically yields dissatisfying results in terms of color yield and level dyeing.

Despite the undeniable benefits of substituting indigo with indigo carmine, no prior studies to our knowledge have aimed to revive and improve the process of dyeing cotton with indigo carmine. In order to increase the substantivity of cotton to indigo carmine, we investigated the development of a cationization process before dyeing with Saxon blue dye in a recent work [22]. In this study, we found that treating cotton samples with a cationic agent improved dyeing quality and fastnesses properties of the samples dyed with indigo carmine.

Moreover, other approaches have been proposed in the literature to impart better shades and color fastness, such as modifications of the fiber surfaces via exposure to microwave and gamma ray radiation. Microwave treatment has proved successful in improving the substantivity of cotton fabrics [23,24]. Microwave radiation has also been shown to uniformly modify textile samples by effectively penetrating inside them and heating them [25,26]. Considering these effects, the influence of microwave heating of cotton fibers on the performance of indigo carmine dye was investigated in the present study.

The present work focused on developing a cleaner process of dyeing cationized cotton samples with indigo carmine. The effects of the main experimental conditions (amount of indigo carmine, dyeing temperature, dyeing duration, and concentration of sodium carbonate) on the performance of the dye were investigated. Moreover, a response surface plan was designed to determine the optimal conditions needed to obtain the best dyeing quality and to model the relationship that links the experimental parameters to the response. Finally, to further improve the obtained dyeing quality, the effect of exposing cationized cotton samples to microwave radiation was investigated.

Experimental

Chemicals and Materials Used

Indigo carmine ($C_{16}H_8N_2Na_2S_2O_8$, Sigma-Aldrich, Switzerland) was the dye used for dyeing cotton fabrics. Sodium carbonate (Na_2CO_3, Shamlab, Syria) and sodium chloride (NaCl, Cotusal, Tunisia) were used during the dyeing process. Sera Fast GMX noted SRF (CPM, Tunisia) was used as a cationic agent. Commercially bleached but unfinished cotton fabric (SITEX, Tunisia) was used for dyeing with the following specifications: mass per area= 270 g/m², warp count=31 yarns/cm, and weft count= 20 yarns/cm.

Cationization Process

The bleached cotton samples were modified using SRF as a cationic agent. The modification of cotton before dyeing with indigo carmine was carried out based on the optimal conditions of the cationization process proposed in our previous work [22]. This method involves treating the samples in a bath containing 6.5 % SRF and 0.15 g/*l* of sodium hydroxide for 43 min at 45 °C. Then,, the treated cotton samples were dried at room temperature.

Radiation Process

The cationized and dried cotton samples were exposed to microwave radiation at a frequency of 750 W for different duration ranging from 1 to 15 min using a commercially available microwave irradiator (Whirlpool, Sweden) designed for food heating with the continuous adjustable power of 350-1000 W.

Exhaustion Dyeing Process

The cationized samples were dyed in a dye bath containing a specific amount of indigo carmine at a pH of 8 and a liquor ratio of 1:50. The dye bath was prepared in a pot and then placed in a laboratory autoclave machine (Ahiba Datacolor International, USA), and the dyeing step was carried out at a temperature of 100 °C for 60 min. Then, the dyed samples were rinsed with tap water and finally dried at

room temperature.

Color Evaluation

The dyed samples were subjected to color measurement by using a Spectroflash SF 300 spectrophotometer with data Master 2.3 software (Datacolor international, USA). The reflectance value of the dyed samples were measured at 620 nm and the color strength (*K/S*) values was assessed by applying Kubelka-Munk equation [27]

$$\frac{K}{S} = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \quad (1)$$

where R is the decimal fraction of the reflectance of the dyed fabric compared to the white standard (100 % reflectance, R=1), R_0 is the decimal fraction of the reflectance of the undyed fabric, K is the absorption coefficient, and S is the scattering coefficient.

Assessment of Fastness Properties

ISO standard methods were used to assess fastness to washing, rubbing and light. The specific tests included ISO 105-C06 (2010) for color fastness to washing, ISO 105-X12 (2001) for color fastness to rubbing, and ISO 105-B02 (2013) for color fastness to light.

In order to evaluate fastnesses to washing, the dyed samples were assembled into multifiber fabrics and placed in an Autowash II (Mesdan, Italy) at 40 °C for 30 min. Then, the degradation of the dried samples was assessed using the gray scale. A Suntest CPS+ machine (Atlas Material Technology, Mount Prospect, IL, USA) was used to measure light fastness. In order to evaluate degradation, exposed samples to Suntest CPS+ machine for 24 h were compared to a Blue Scale treated under the same conditions. Rubbing fastness was measured using a Crockmeter, and solidity was evaluated using the Gray Scale.

Evaluation of Mechanical Properties

The ISO standard 13934:2013 was used to evaluate the mechanical behavior of the dyed samples. Tensile strength tests were carried out using a Lloyd Instruments LR5K testing machine with a 50-mm length of samples between clamps, a 5-N sensor, and a 100-mm/min speed of displacement.

Design of Experiment (DOE)

To minimize the number of experiments, a response surface methodology was designed to study the effects of certain experimental parameters on dyeing quality and to determine the optimal conditions for this dyeing process. Using Minitab software (version 14, State College, PA, USA), the run of experiments was designed by response surface methodology for four factors and three levels. A

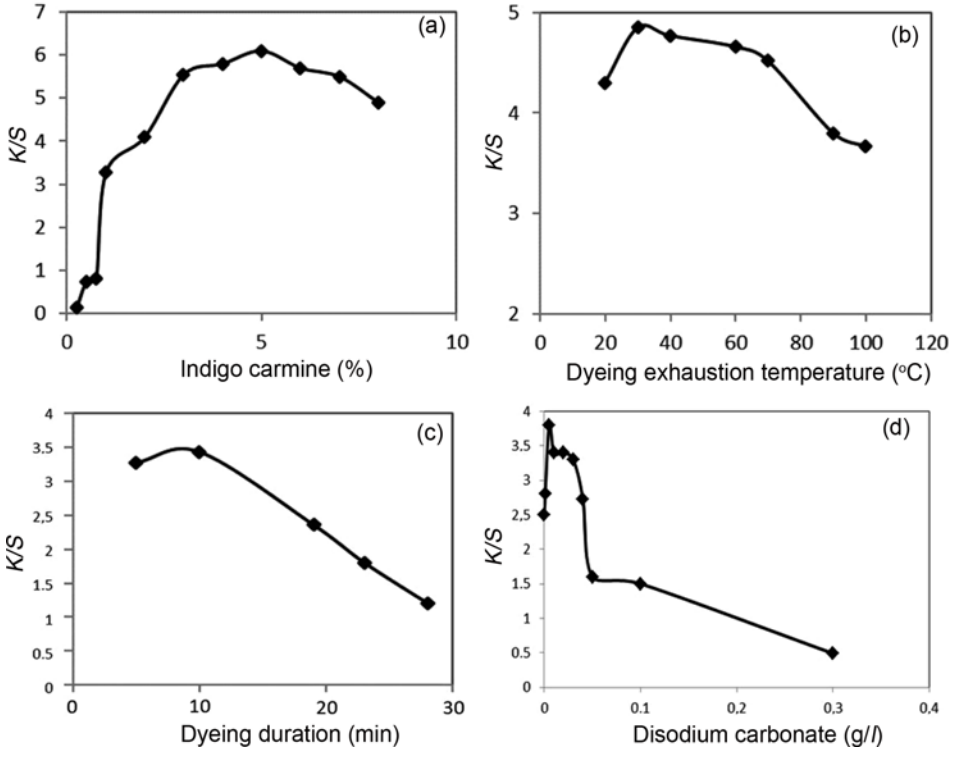

Figure 2. (a) Effect of indigo carmine amount, (b) effect of the dyeing exhaustion temperature, (c) effect of the dyeing duration, and (d) effect of the sodium carbonate concentration on the evolution of the color strength (*K/S*).

comparison of means was conducted using an analysis of variance (ANOVA) with Tukey's post hoc test ($p<0.05$) [28].

Results and Discussion

Factors Affecting the Dyeing Process

Effect of the Amount of Indigo Carmine

To evaluate the effect of the indigo carmine concentration on color strength (*K/S*), cationized cotton was dyed with concentrations of indigo carmine ranging from 0.25 % to 8 %. The dyeing process was carried out at a pH of 8 and a temperature of 100 °C for 60 min. The results of the color strength measurements are plotted in Figure 2(a). A gradual increase in color strength was observed, and the maximum color strength was reached at a dye concentration of 5 %. This increase can be attributed to the fact that cationic sites adsorb more colorant. Above this concentration, the dye parameters gradually decreased, possibly due to the fact that the cationic sites of the support were saturated with anionic dye.

Table 1. Studied variables and their levels for a surface design

Variable	Symbol	Coded variable level		
		-1	0	1
Indigo carmin amount (%)	*col*(%)	2	5	7
Temperature (°C)	*T*(°C)	20	30	60
Sodium carbonate (g/*l*)	*Cs*(g/*l*)	0	0.005	0.01
Duration (min)	*t*(min)	5	10	20

Effect of Dyeing Temperature

The evolution of color strength was studied under exhaustion dyeing temperatures varying from 20 °C to 100 °C for an indigo carmine concentration of 1 %, a pH of 8, and a 60 min dyeing duration. Figure 2(b) shows that the best dyeing quality was obtained at a temperature of 30 °C and that color strength decreased rapidly beyond this temperature. This decrease was expected because indigo

Table 2. Coded actual levels of studied variables and results obtained for a surface design

Run	Coded level of variables				Actual level of variables				*K/S* (experimental)	*K/S* (predicted)
	A	B	C	D	*col* (%)	*T* (°C)	*t* (min)	*Cs* (g/*l*)		
1	1	0	-1	0	7	30	5	0.005	5.15	5.26
2	0	0	-1	1	5	30	5	0.01	4.97	5.34
3	0	1	0	-1	5	60	10	0	5.33	6.15
4	1	1	0	0	7	60	10	0.005	4.88	6.32
5	0	1	1	0	5	60	20	0.005	4	6.99
6	-1	0	0	1	2	30	10	0.01	4.08	5.04
7	1	0	0	1	7	30	10	0.01	5.11	5.90
8	1	-1	0	0	7	20	10	0.005	4.73	5.65
9	-1	0	0	-1	2	30	10	0	4.48	5.11
10	0	0	1	1	5	30	20	0.01	5.21	6.64
11	1	0	0	-1	7	30	10	0	5.36	5.66
12	0	0	0	0	5	30	10	0.005	6.67	7.32
13	0	-1	0	1	5	20	10	0.01	5.05	5.64
14	-1	0	1	0	2	30	20	0.005	4.2	5.61
15	-1	0	-1	0	2	30	5	0.005	4.62	4.83
16	0	1	0	1	5	60	10	0.01	5.47	6.23
17	0	-1	-1	0	5	20	5	0.005	5.63	5.16
18	0	0	0	0	5	30	10	0.005	6.68	7.32
19	0	1	-1	0	5	60	5	0.005	4.6	5.81
20	-1	-1	0	0	2	20	10	0.005	4.54	4.97
21	0	0	-1	-1	5	30	5	0	4.48	5.24
22	0	0	0	0	5	30	10	0.005	6.63	7.32
23	1	0	1	0	7	30	20	0.005	5.53	6.86
24	-1	1	0	0	2	60	10	0.005	4.22	5.50
25	0	-1	1	0	5	20	20	0.005	5.5	6.46
26	0	0	1	-1	5	30	20	0	4.86	6.48
27	0	-1	0	-1	5	20	10	0	4.74	5.51

carmine is similar to indigo, which presents a better affinity for cotton at lower temperatures [29].

Effect of the Dyeing Duration

The effects of dyeing durations ranging from 5 to 28 min on the evolution of color strength were studied at an indigo carmine concentration of 1 %, a pH of 8, and a temperature of 100 °C. Figure 2(c) shows that the maximum color strength was reached at a duration of 10 min. This result may have been due to the fact that many cationic sites were still available on the treated cotton support at this point in the process. As time proceeded, color strength gradually decreased, possibly due to the desorption of the indigo carmine molecules.

Effect of Alkalinity

In this part of the study, the influence of alkalinity of the dyeing bath was investigated for an indigo carmine concentration of 1 %, a dyeing temperature of 100 °C, and a dyeing duration of 60 min. The concentration of sodium carbonate varied from 0 to 3 g/*l*. According to the results reported in Figure 2(d), the obtained curve represented an increase in color strength for alkali concentrations less than 0.005 g/*l*. As this concentration was exceeded, color strength gradually decreased. This result can be explained by the fact that adding a small amount of alkali can ameliorate the adsorption of the dye onto the fiber, while an excessive amount of alkali would be detrimental. This result was expected; in fact, Bertholet *et al.* found that the addition of a significant amount of alkali resulted in pale shades, as the alkali dissolved the blue molecules of the dye [21].

Modeling and Optimization of the Dyeing Process

Response Surface Regression

Regression analysis makes it possible to model certain phenomena by determining mathematical equations that relate the response to the input variables. The analyzed input variables included the concentration of indigo carmine, the temperature of the dyeing process, the dyeing duration, and the concentration of sodium carbonate (Table 1).

The analyzed result was the color strength parameter, which will be called the response hereafter. The experimental plan is presented in Table 2, and the regression analysis led to the following equation:

$$\begin{aligned} K/S = & -4.486 + 1.49\ col(\%) + 0.222\ T(^{o}\mathrm{C}) + 0.434\ t(\mathrm{min}) \\ & + 305.682\ Cs(\mathrm{g}/l) - 0.168\ col^{2}(\%) - 0.0026\ T^{2}(^{o}\mathrm{C}) \\ & - 0.016\ t^{2}(\mathrm{min}) - 32519.214\ Cs^{2}(\mathrm{g}/l) + 0.0007\ col(\%) \\ & \times T(^{o}\mathrm{C}) + 6.294\ col(\%) \times Cs(\mathrm{g}/l) - 0.002\ T(^{o}\mathrm{C}) \times t(\mathrm{min}) \\ & - 0.126\ T(^{o}\mathrm{C}) \times Cs(\mathrm{g}/l) + 0.366\ t(\mathrm{min}) \times Cs(\mathrm{g}/l) \end{aligned} \quad (2)$$

R^2 (predicted)=83.7 %

where *col*(%) is the percentage of indigo carmine, *T*(°C) is the dyeing temperature, *t*(min) is the dyeing duration, *Cs*(*g/l*) is the concentration of sodium carbonate, and R^2 is the squared multiple correlation coefficient.

R^2 is a percentage indicating the adequacy of the data with a statistical model. In fact, a model with perfect predictability has an R^2 equal to 1, and a model with no predictive capability has an R^2 equal to 0. The R^2 of the present model was 0.83; therefore, the procured model had good predictability. The regression model was assessed based on the p-value obtained for each parameter in each model. According to Table 3, a significant linear effect was found for *col*, *T*, *t*, and *Cs* ($p<0.01$), and a significant squared effect was found for col^2, T^2, t^2, and Cs^2.

Analysis of Variance (ANOVA)

The ANOVA was based on the law of total variance,

Table 3. Estimated regression coefficients for the color strength parameter (*K/S*)

Term	Coef. (uncoded data)	Coef. (coded data)	SE Coef	T	P
Constant	-4.486	-4.5	1.97	-2.274	0.042
col(%)	1.498	1.5	0.35	4.309	0.001
T(°C)	0.222	0.2	0.06	3.654	0.003
t(min)	0.434	0.4	0.13	3.466	0.005
Cs(g/*l*)	305.682	305.7	145.72	2.098	0.058
col^2(%)	-0.1688	-0.2	0.03	-5.331	0.000
T^2(°C)	-0.0026	-0.00	0.00	-3.979	0.002
t^2(min)	-0.016	-0.00	0.00	-4.390	0.001
Cs^2(g/*l*)	-32519.214	-32519.2	7536.62	-4.315	0.001
col(%)×*T*(°C)	0.0007	0.00	0.00	0.184	0.857
col(%)×*t*(min)	0.011	0.0	0.01	1.002	0.336
col(%)×*Cs*(g/*l*)	6.294	6.3	17.18	0.366	0.720
T(°C)×*t*(min)	-0.002	-0.0	0.00	-1.553	0.146
T(°C)×*Cs*(g/*l*)	-0. 126	-0.1	2.02	-0.063	0.951
t(min)×*Cs*(g/*l*)	0. 366	0.4	5.60	0.065	0.949

Table 4. Variance analysis for the color strength parameter (*K/S*)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	11.6851	11.68507	0.83465	4.41	0.007
Linear	4	3.0374	5.09237	1.27309	6.73	0.004
Square	4	7.9904	8.09596	2.02399	10.70	0.001
Interaction	6	0.6572	0.65723	0.10954	0.58	0.740
Residual error	12	2.2690	2.26896	0.18908		
Total	26	13,9540				

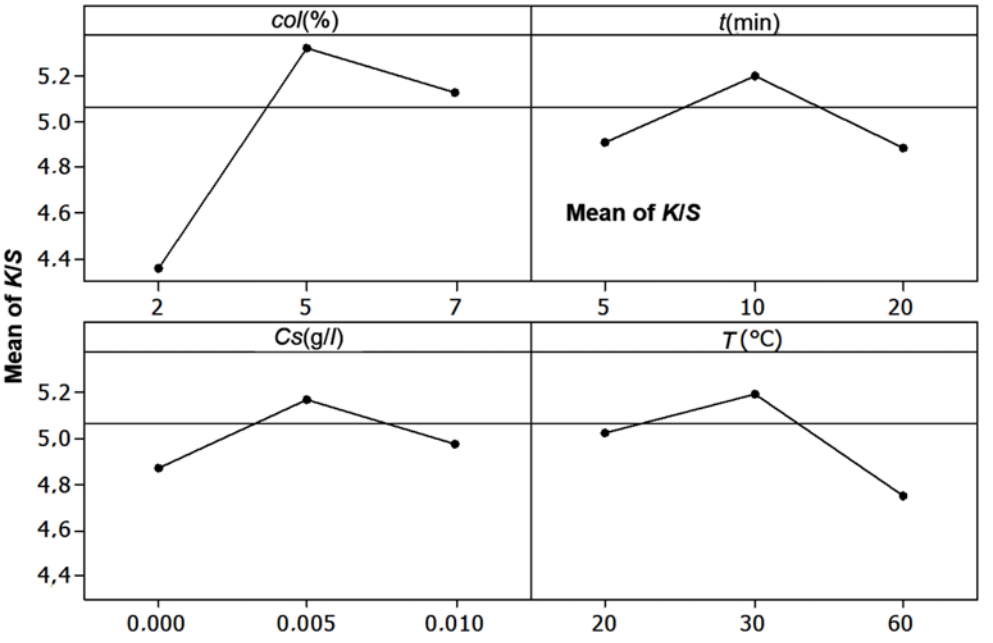

Figure 3. Analysis of main effects plot of the color strength (*K/S*).

according to which the variance in a particular variable is divided into components attributable to different sources of variation [30]. From a statistical point of view, a result is significant when a probability (p value) is less than a predefined threshold value indicating the degree of significance. The ANOVA (Table 4) revealed that the regression model for color strength (equation (2)) was significant ($p=0.007<0.05$)

Analysis of the Main Effects Plot

The main effects plot depicts the influence of each experimental parameter on the *K/S* response separately from the other parameters. As shown in Figure 3, the amount of indigo carmine had the greatest effect on color strength. Concerning temperature, the response parameter had the greatest effect at 30 °C; above this value, this effect decreased gradually. Moreover, the color strength was highest at a sodium carbonate concentration of 0.005 g/*l*. Finally, the dyeing time had the greatest effect on color strength at a duration of 10 min.

Interactions Plot

An interaction plot was used to visualize possible interactions between the studied parameters and to compare the relative strengths of the effects across factors. In an interaction plot, parallel lines indicate the absence of interactions, whereas greater deviation from the parallel indicates a higher degree of interaction. An analysis of the interaction diagram is presented in Figure 4. This diagram showed obvious interaction between factors for the color strength parameter, justifying the choice of an experimental design that allowed for the determination of optimal conditions while taking into account the interactions between the factors and their levels.

Surface Plot

The surface plot displays a three-dimensional relationship in two dimensions with the factors on the *X* and *Y* axes and the response variable on the *Z* axis, represented by a planar surface. This graphic may be used to depict zones that may optimize color strength by combining two input parameters.

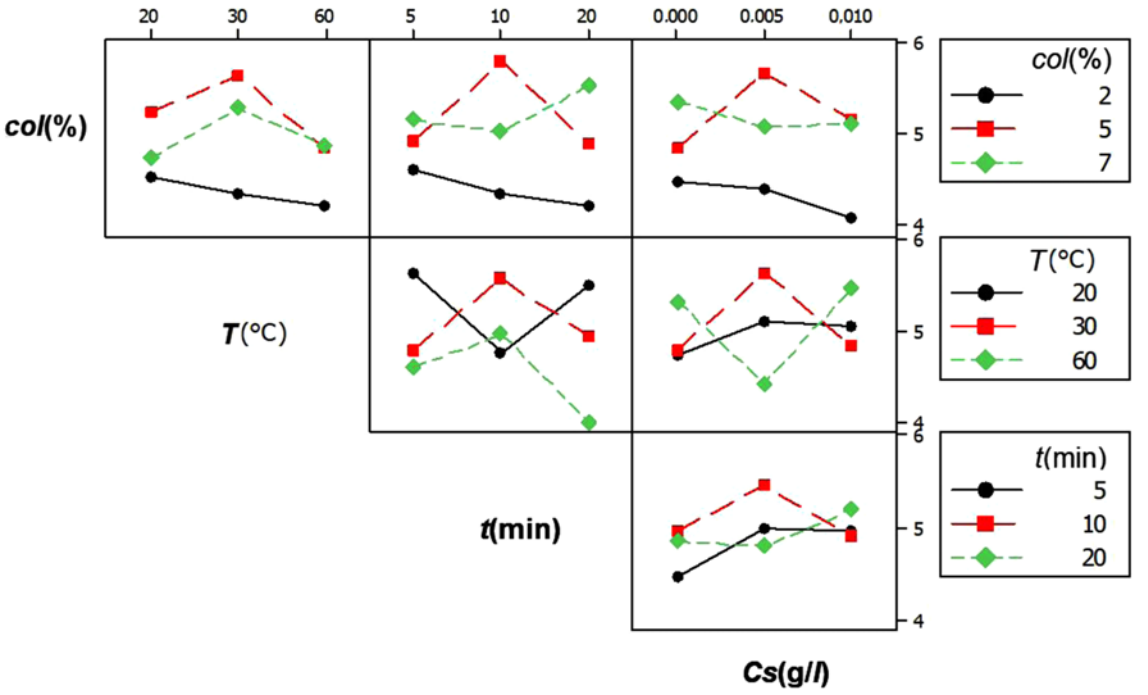

Figure 4. Analysis of interaction plot of the color strength (*K/S*).

Figure 5 shows the color strength (*K/S*) of modified cotton dyed with indigo carmine as a function of each of two factors, while the third factor was kept at a constant center level. According to Figure 5, the highest color strength values were obtained at an indigo carmine concentration of 6 % and a dyeing duration of 20 min (Figure 5b) and at a temperature of 30 °C and a dyeing duration of 20 min (Figure 5c).

Response Optimization

The optimum conditions of the indigo carmine dyeing process after surface modification were predicted for a maximized response using a response optimizer tool in Minitab 14 software. The response optimization process described in Figure 6 showed that the optimum operating conditions included an indigo carmine concentration of 5 %, a dyeing temperature of 40 °C, a dyeing time of 12.5 min, and a sodium carbonate concentration of 0.005 g/*l*. In the present study, the Minitab software estimated a theoretical optimal color strength of approximately 6.94.

Model Validation

In order to confirm the validity of the optimized conditions given by the Minitab software, experiments were performed to compare the experimental results with the predicted response values using the regression equation. The results of these experiments indicated an optimal color strength of 6.91 (the average of three experimental values). Based on the comparison of this value with the theoretical value of 6.94, it was deduced that the optimal experimental conditions proposed by this model were suitable.

Effect of Salt Concentration on Dyeing Quality

The addition of electrolytes to the dye bath is often performed to improve the affinity of cellulosic fabric to anionic dyes. The treated cotton samples were dyed with indigo carmine under optimal conditions in a dye bath containing different concentrations of sodium chloride ranging from 0 to g/*l*. The influence of electrolytes on color strength is reported in Figure 7. As shown in this figure, increasing the salt concentration in the dye bath resulted in substantial improvements in dyeing quality. In fact, a salt concentration of 15 g/*l* increased the color strength to 9.13. This increase could be explained by the fact that the addition of salts promotes exhaustion of the dye bath; as the solubility of a dye decreases, its affinity to the fiber increases. When a concentration of 15 g/*l* was exceeded, a gradual decrease in the color strength was observed. Indeed, for high salt concentrations, there is a risk of dye precipitation and a resulting decrease in dye concentration.

Evaluation of Fastness Properties

Untreated cotton, cationized cotton, and cationized cotton dyed with indigo carmine in the presence of electrolytes were investigated in terms of fastnesses to washing, light, and rubbing. The results are summarized in Table 5. This table shows that washing fastness improved from 1 (very weak solidity) to 3/4 following the modification of the cotton fibers. This result can be explained by the fact that the anionic dye and the modified cotton fibers were able to form strong ionic bonds after cationization. The rubbing fastness

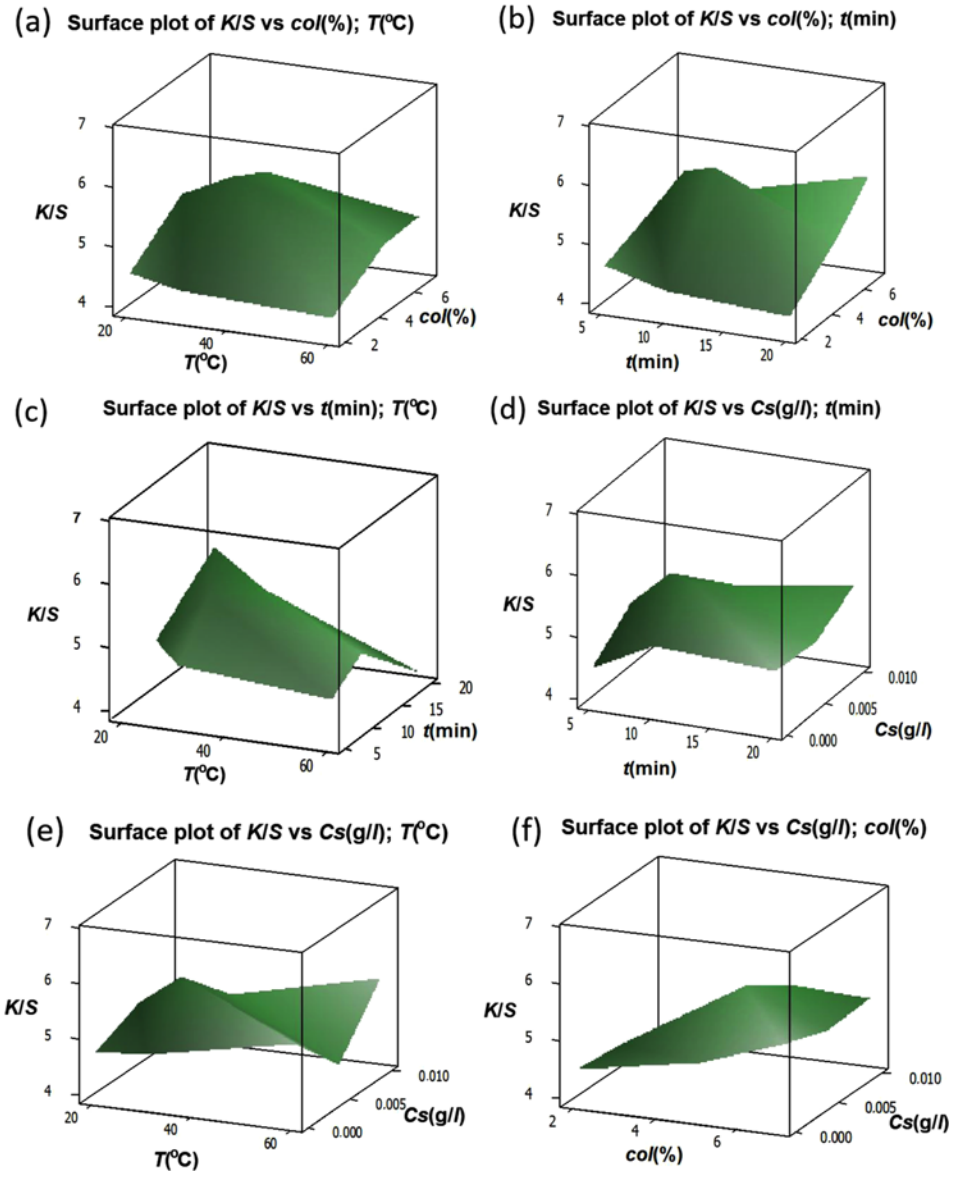

Figure 5. Response surface representations of the color strength obtained with combined effects of (a) concentration of indigo carmine and temperature, (b) concentration of indigo carmine and duration, (c) temperature and duration, (d) duration and concentration of alkali, (e) temperature and concentration of alkali, and (f) concentration of indigo carmine and concentration of alkali.

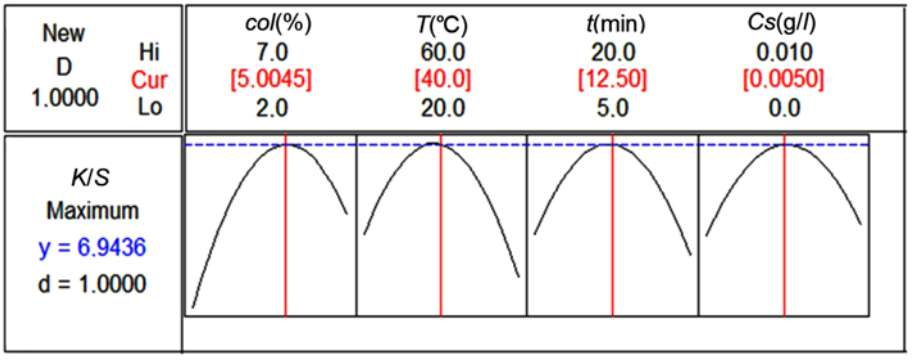

Figure 6. Response optimization of the dyeing process.

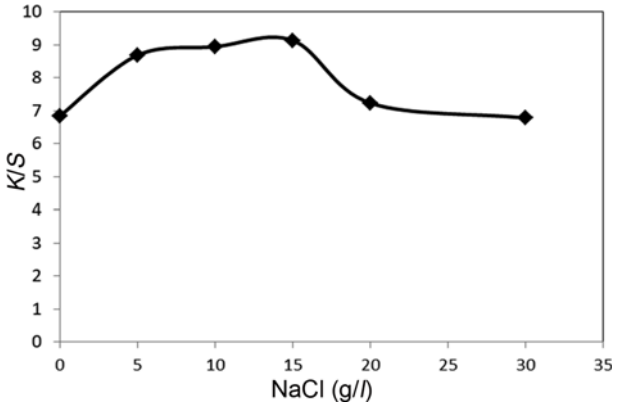

Figure 7. Effect of NaCl concentration on the evolution of the color strength (*K/S*).

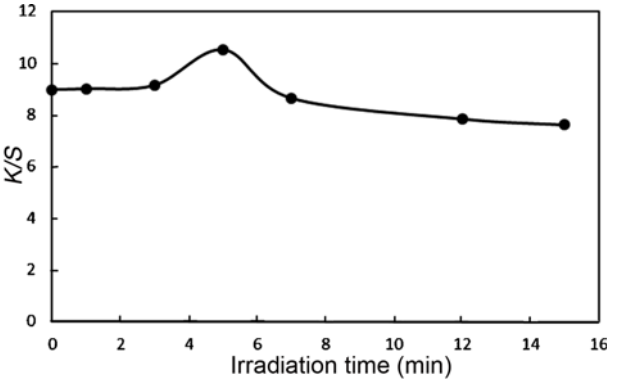

Figure 8. Effect of microwave irradiation time on the evolution of the color strength (*K/S*).

ratings of the various processes were generally good. Further, the washing fastness ratings were slightly reduced following the addition of a significant amount of salt.

Effect of Microwave Pretreatment on Dyeing Quality

Effect of the Pretreatment Time on the Color Strength

To promote the dyeing performance of cationized cotton fabric dyed with indigo carmine, the surface of the cotton fabric was modified through microwave treatment. The duration of the microwave treatment of the cotton fabric varied from 1 to 15 min. Figure 8 shows the evolution of color strength as a function of microwave radiation time. According to this figure, irradiation times of 1 and 3 min did not ameliorate color strength, while an irradiation time of 5 min increased color strength to 10.5. This increase may have been due to structural rearrangements of the molecular chains resulting from microwave radiation, leading to better absorption of the dye [31-34]. Exceeding a duration of 5 min, color strength decreased considerably; this can be explained by the fact that long durations of radiation can weaken cellulosic fibers.

Effect of Pretreatment on Dyeing Fastness

Table 6 shows the effect of pretreatment microwave irradiation time on the fastness properties of the dyed samples. This table shows that when the pretreatment duration did not exceed 7 min, the microwave treatment had no significant effect on washing or light fastness. Beyond this duration, the overall fastness to washing and light decreased slightly. Concerning fastness to rubbing, the dyed cotton samples had good fastness levels to both wet and dry rubbing.

Based on these results concerning the effects of microwave irradiation time on color strength and dyeing fastness, it can be concluded that an irradiation time of 5 min produced the

Table 6. Evaluation of fastness properties of untreated and treated cotton with microwave

Sample	Wash ISO 105-B01	Rubbing ISO 105-X12		Light ISO 105-B01
		Dry	Wet	
Unradiated cotton	3/4	4/5	3/4	3
Radiated 1 min cotton	3/4	4/5	3	4
Radiated 3 min cotton	3/4	4/5	3/4	4
Radiated 5 min cotton	3/4	4/5	3	3
Radiated 7 min cotton	3/4	4/5	3	4
Radiated 12 min cotton	3	4/5	3	2
Radiated 15 min cotton	2/3	4/5	3/4	2

Table 5. Evaluation of fastness properties for different process

Process	Wash ISO 105-B01	Light ISO 105-B01	Rubbing ISO 105-X12	
			Dry	Wet
Dyeing process of unmodified cotton	1	1	3/4	3
Optimized dyeing process of cationized cotton	3/4	3	4/5	3/4
Optimized dyeing process of cationized cotton with the use of 5 g/*l* of salt	3/4	3	4/5	3/4
Optimized dyeing process of cationized cotton with the use of 10 g/*l* of salt	3/4	3	4/5	3/4
Optimized dyeing process of cationized cotton with the use of 15 g/*l* of salt	3/4	3	4/5	3/4
Optimized dyeing process of cationized cotton with the use of 20 g/*l* of salt	3/4	2/3	4/5	3/4
Optimized dyeing process of cationized cotton with the use of 30 g/*l* of salt	3/4	2/3	4	3

best color strength of 10.5 and good fastness properties.

Mechanical Properties of Samples

Treating cotton fabric with microwave irradiation may impact the mechanical properties of the fibers. The effects of treating cotton samples with microwave radiation on their mechanical properties were studied in both directions (warp and weft) of the fabric. The tensile strength and elongation at break of the untreated and microwave-treated samples are shown in Figures 9 and 10, respectively. Based on these figures, it can be concluded that for a treatment duration less than 12 min, both the breaking strength and elongation at break of the cotton remained almost constant in the weft direction; however, longer exposure to microwave radiation caused these mechanical properties to decrease.

In the warp direction, increasing the duration of microwave irradiation treatment had no effect on breaking strength, while elongation at break increased up until a duration of 12 minutes. This result may have been due to the existence of bound water molecules in cotton fibers, which promote adjustments in cotton fiber structure and result in the absorption of microwave energy, thereby eliminating the residual stress of the cotton fibers [30]. Exceeding this duration, elongation at break decreased.

Conclusion

The aim of this study was to develop an ecological process of dyeing cotton fibers via the elimination of the harmful reduction step from the indigo dyeing process through the substitution of insoluble indigo with soluble indigo carmine. In order to improve the dyeing quality resulting from this process, cotton fabric was treated with a cationic agent prior

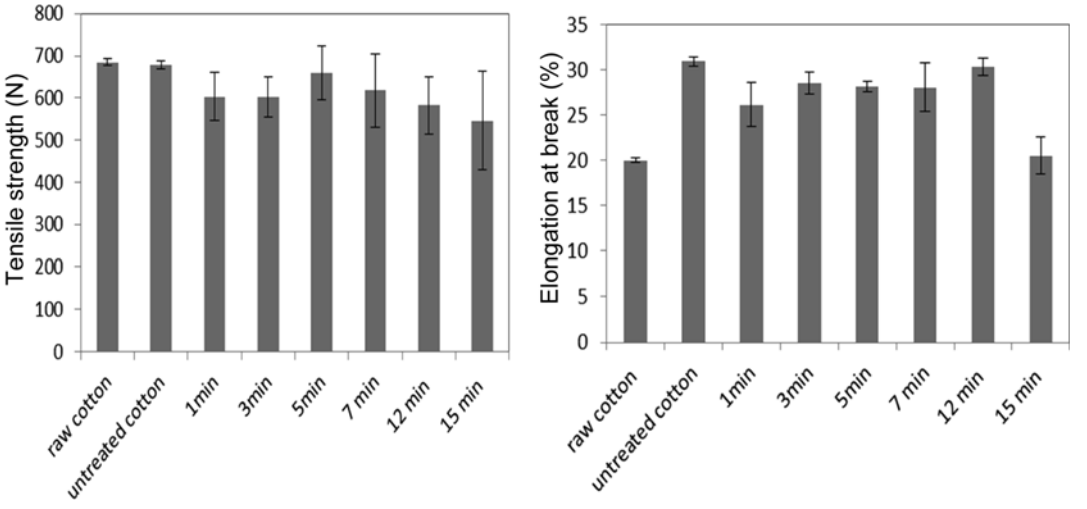

Figure 9. Tensile strength and elongation at break in the weft direction of the samples before and after microwave irradiation.

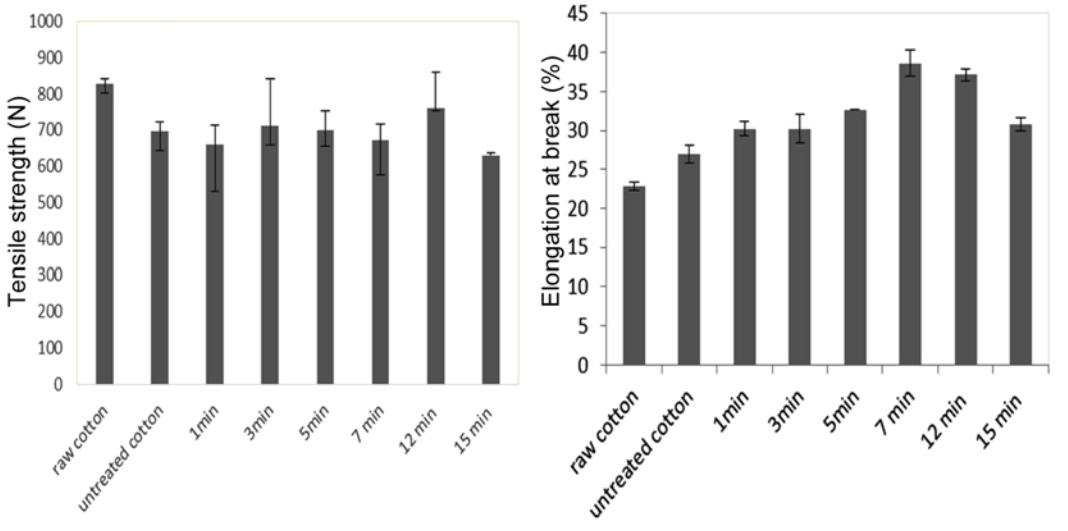

Figure 10. Tensile strength and elongation at break in the warp direction of the samples before and after microwave irradiation.

to dyeing. A model of the experimental surface plan revealed that the optimal experimental conditions included an indigo carmine concentration of 5 %, 0.005 g/*l* of sodium carbonate, a dyeing temperature of 30 °C, and a dyeing time of approximately 13 min. Moreover, the results showed that adding a salt concentration of 15 g/*l* to the dye bath raised the color strength to 9.13. Finally, the effects of treating cotton with microwave energy before dyeing were evaluated by measuring the color strength, fastness properties, and mechanical properties of the material. The results proved that 5 min of exposure to microwave radiation is sufficient to enhance the dyeing quality of modified cotton dyed with indigo carmine without altering the mechanical properties of the cotton fibers. Thus, by the means of this new process, dyeing cotton with indigo carmine may be viable and may achieve higher dyeing quality and fastness properties compared to the process of dyeing untreated cotton with indigo carmine.

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