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Optimization of Dyeing Wool Fibers Procedure with *Isatis tinctoria* by Response Surface Methodology

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The response surface method (RMS) was used to optimize the color strength (K/S) of the wool fibers dyed with Isatis tinctoria. *The eight independent variable terms, in which two of them are categorical and the other six numerical, were selected at two levels (low and high). The ANOVA test results of the linear model showed that the model terms, including reducing agent amount, dyeing temperature, dyeing time, and dyestuff percentage, have a significant effect on K/S. The actual values agreed with the predicted values and the suggested equation model was satisfactory and accurate.*

KEYWORDS Isatis tinctoria, *wool fiber, optimization, response surface method*

INTRODUCTION

Natural dyes are being reintroduced to the textile dyeing industry due to growing attention on harmful effects of synthetics dyes, such as water pollution, sustainability of raw materials, and environmental aspects. Compared to the synthetic dyes, natural dyes are preferred because of its environment-friendly nature, lower toxicity, antibacterial properties, biodegradability, and harmonizing natural shades.

The chemical structures of major natural dyes are similar to anthraquinone (madder), alpha naphthoquinones (henna), flavones (weld),

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indigoids (indigo and woad), and carotenoids (annatto and saffron; Samanta and Agarwal 2009). Indigo is the most important and oldest natural blue dyestuff (C.I. Natural Blue 1) (Ensley et al. 1983). Indigo dyestuffs have been obtained from various plant sources such as *Indigofera*, *Polygonum tinctorium*, and *Isatis tinctoria* (Woad). Indigo does not exist in the leaves of indigo-producing plants by itself. Instead, there are its precursors: indican in *Indigofera* species and *Polygonum tinctorium* and isatans in woad (Balfour-Paul 2000).

Indigo is produced after extracting the precursors from the leaves of woad plant (isatans) (Clark et al. 1993; Epstein et al. 1967; Maugard et al. 2001). These compounds are extracted by steeping the leaves in warm water (Stoker et al. 1998). With woad, adding alkali to the steeping water releases free indoxyl, which produces indigo after a vigorous aeration (Epstein et al. 1967; Garcia-Macias and John 2004). To produce indigo from the precursors, the carbohydrate moiety is hydrolyzed from the indoxyl group and two of the resulting indoxyl molecules combine oxidatively to produce indigo, which precipitates from the solution. Indigotin is an asymmetrical dye molecule that has good light fastness properties that are independent of substituent groups. These factors, combined with the physical state of the dye, may explain its superior light fastness compared to other natural dyes (Doherty et al. 2008).

Natural dyes have variable chemical compositions due to the conditions and the place of growing, harvesting period, extraction methods and conditions, application method, and technological process followed (Samanta and Agarwal 2009). In this study, the dyeing conditions of wool fiber were optimized by response surface method (RSM). The eight independent variables, in which two of them are categorical factors and the other six numerical, were selected at two levels (low and high). The independent numerical factors are: preparation time of woad dyestuff, reducing agent percentage, dyeing temperature, dyeing procedure time, liquor ratio, and dye percentage. The independent categorical factors are the alkali type (ammonia, sodium hydroxide, sodium carbonate) and oxidation method (Air, H_2O, H_2O_2). The dependant factor (responses) is the K/S of dyed samples. D-optimal, which is a widely used form of RSM, was employed for optimizing the dyeing conditions.

MATERIAL AND EXPERIMENTAL

Reagents and Supplies

Wool yarn with linear density of 200 Tex was scoured with 1% non-ionic detergent at 50°C for 20 min, then dried at the oven for 20 min at 60°C. Analytical grade of ammonia (NH_3), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), hydrogen peroxide (H_2O_2), and sodium dithionite

($Na_2S_2O_4$) were purchased from Merck. The woad leaves (*I. tinctoria)*, as a natural dye, was supplied from Yazd Province, Iran.

Dyestuff Extraction

The dyestuff extraction was done as follows: The well-milled woad leaves were preserved in water solution in a dark place according to the proposed time of experimental design, and then this solution was used for preparation of each dyeing baths.

Dyeing and Oxidation Procedures

Wool fibers were dyed with *I. tinctoria* as follows: Sodium dithionite (5% up to 20% owf), alkalis, and dye solution, which were prepared as mentioned before, were mixed at the appropriate liquor ratio. A yellow-green solution was obtained by the reduction of *I. tinctoria* constituents to their leuco-forms (Figure 1). The temperature of dyeing bath was raised to the proposed temperature according to the experimental design. The wool fibers were then added to the dye bath at the appropriated temperature and left according to the proposed time. Then it was removed from the dye bath and the absorbed dye was oxidized from the soluble form into the insoluble state (indigoid). Three methods were used for the oxidation step, which are: aeration in an ambient air for 15 min, oxidation at flowing tap water for 15 min, and oxidation with hydrogen peroxide (5% v/v solution) for 15 min at an ambient temperature. Then the samples were rinsed thoroughly with distilled water and dried at room temperature.

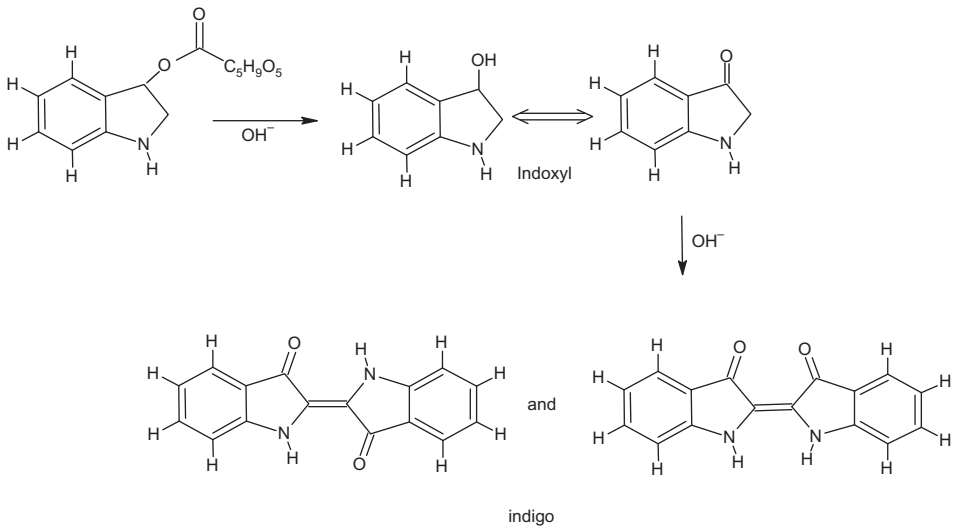

FIGURE 1 Formation of indigo from precursor.

Color Measurement

The reflectance spectrum of the samples was measured using a Color-Eye spectrophotometer from GretagMacbeth in the visible region. To evaluate the color of the samples, the CIE color-coordinates namely, L*, a*, b*, and C* were measured under illuminant D_{65} and 10° standard observer. K/S values of the dyed samples were calculated using Kubelka-Munk equation as follows:

$$K/S = (1 - R)^2/2R, \tag{1}$$

where R is the observed reflectance at the wavelength of maximum adsorption ($\lambda_{max} = 650$ nm), K is the absorption coefficient, and S is the light scattering coefficient.

D-optimal Design of Experiments

D-optimal design provides maximum accuracy in estimating regression coefficients (Dean and Voss 1999). In this study, the dyeing conditions of wool fibers with *I. tinctoria* were optimized by RSM using the trial version of Design Expert 8.0.1.0 from Stat-Ease Inc. (Minneapolis, MN, USA). The independent variables were coded with low and high levels in D-optimal design as shown in Table 1, while K/S was the response (dependent variable). The D-optimal designed experiments were augmented with five replications to evaluate the pure error and were carried out in a randomized order. The D-optimal design of the software suggested 70 experiments to be done.

Mathematical Modeling and Optimizing

An equation including a response Y (dependent factor), which depends on the input factors (independent) such as $\zeta_1, \zeta_2 \ldots \zeta_n$, was taken.

TABLE 1 Experimental range and coded levels of numerical independent dyeing variable factors

		Real values of the coded levels	
Process variables	Code	−1	1
Preparation time (h)	X_1	6	24
Reducing agent (%, owf)	X_2	5	20
Dyeing temperature (°C)	X_3	30	60
Dyeing procedure time (min)	X_4	20	60
Liquor ratio	X_5	30	50
Dye percentage (%, owf)	X_6	30	60

In general, the relationship can be described as:

$$Y = f(\zeta_1, \zeta_2 \ldots \zeta_k) + e, \tag{2}$$

where f is the true response function and its format is unknown and perhaps complicated, and usually e is treated as a statistical error, often assuming it to have a normal value. The input factors in Equation 2 are called the natural variables, because they are expressed as natural measurements. So, they are transformed to the dimensionless codes such as: $x_1, x_2 \ldots x_k$. In terms of coded variable, Equation 2 can be written as:

$$Y = f(x_1, x_2 \ldots x_k) + e. \tag{3}$$

Because of the unknown form of the true function, it should be approximated. The responses can be simply related to chosen factors by linear or quadratic models. In this study, a linear model is given as (Carlson 1991):

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j, \tag{4}$$

where β_0 is the constant coefficient and β_i is the interaction coefficient for each factor.

Regression coefficient (R^2) was determined for checking the fitting quality of the model equation, which is a measure of variability in the observed response values and is between 0 and 1 ($0 \leq R^2 \leq 1$). If R^2 approaches to unity, the empirical model fits to the actual data well. Smaller values of R^2 are an indicator for the less relevance of the dependent variables in the model used in explaining the variation behavior (Zivorad 2005). Statistical significance of the model was judged by F-value (Fisher variation ratio), probability value (Prob > F), and adequate precision. The probability value less than 0.05 was taken as the level of significance.

RESULTS AND DISCUSSIONS

Model Fitting and ANOVA Results

The model adequacy check is an important part of the data analysis procedure, as the approximating model would give poor or misleading results if it were an inadequate fit. The data were fitted to various models and their resulting ANOVA results are shown in Table 2. According to the probability and F-values, the dyeing procedure of wool fibers with *I. tinctoria* can be decided, which was most suitably described with the linear model. The probability value is less than 0.0001, which is much lower than 0.05, and the high F-value (6.65) shows that this model is significant. In addition,

TABLE 2 ANOVA results of the fitting of the experimental data to various models

Response	Source model	Sum of squares	*df*	Mean square	*F*-value	Prob > *F*
Color strength (*K*/*S*)	Mean vs total	1775.109	1	1775.109		
	Linear vs mean	278.64	10	27.864	6.645418	< 0.0001
	2FI vs linear	195.1698	43	4.538832	1.390811	0.2404
	Quadratic vs 2FI	21.1347	6	3.52245	1.133335	0.4096
	Cubic vs quadratic	18.73173	5	3.746347	1.516905	0.3293
	Residual	12.34865	5	2.46973		
	Total	2301.133	70	32.87333		

TABLE 3 ANOVA results of the linear model of *Isatis tinctoria* dyeing of wool fibers

Response	Source	Sum of square	*df*	Mean square	*F*-value	*p*-value
Color strength (*K*/*S*)	Model	278.64	10.00	27.86	6.65	< 0.0001
	1. Preparation time	9.23	1.00	9.23	2.20	0.1433
	2. Reducing agent	20.85	1.00	20.85	4.97	0.0296
	3. Dyeing temperature	141.27	1.00	141.27	33.69	< 0.0001
	4. Dyeing procedure time	43.99	1.00	43.99	10.49	0.0020
	5. Liquor ratio	1.30	1.00	1.30	0.31	0.5800
	6. Dye percentage	49.20	1.00	49.20	11.73	0.0011
	7. Alkali type	0.57	2.00	0.28	0.07	0.9344
	8. Oxidation type	0.75	2.00	0.37	0.09	0.9150
	Residual	247.38	59.00	4.19		
	Lack of fit	235.04	54.00	4.35	1.76	0.2755
	Pure error	12.35	5.00	2.47		
	Cor total	526.02	69.00			

the lack-of-fit test probability (0.4064) is higher than 0.1, which means the lack-of-fit test is not significant.

ANOVA results of the applied linear model to navigate the design space of wool fibers dyed with *I. tinctoria* are presented in Table 3. The probability value of the independent variable is an indicator to determine the significant or the insignificant factors. So, probability value less than 0.05 suggest that the effect of this independent variable on response is significant. According to the ANOVA results of the first-order model, it can be inferred that the reducing agent amount, dyeing temperature, dyeing procedure time, and dye percentage are the significant independent factors impacting on the *K*/*S* of dyed wool fiber with woad in this study, because they have probability values less than 0.05 and their *F*-values are high. The independent variables such as preparation time, liquor ratio, alkali type, and oxidation are insignificant because their probability value is high and their *F*-value is low. So, changing these independent variables in woad dyeing of wool fibers at the proposed range could not leave significant effects on the *K*/*S*.

TABLE 4 The constant regression coefficient of linear model for *Isatis tinctoria* dyeing of wool fibers

	Ammonia			Sodium hydroxide			Sodium carbonate		
Coefficient	Air	H_2O	H_2O_2	Air	H_2O	H_2O_2	Air	H_2O	H_2O_2
β_0	−3.848	−3.731	−3.986	−3.705	−3.588	−3.844	−3.625	−3.509	−3.764

Equation 5 shows the response values of K/S in terms of actual factors:

$$\frac{K}{S} = -\beta_0 - 0.044248X_1 + 0.083292X_2 + 0.10294X_3 + 0.042865X_4 - 0.042865X_5 + 0.061346X_6, \quad (5)$$

where $X_i = X_{1\text{–}6}$ are preparation time, reducing agent, dyeing temperature, dyeing procedure time, liquor ratio, and dye percentage, respectively, and β_0 is the constant regression coefficient of three categorical variables at three levels, the value of which are presented in Table 4.

The applied approximating model was examined by the residual plots. The normal probability and studentized residual plots are shown in Figure 2. Residuals are the difference between actual and predicted values for each point and show how well the model satisfies the assumptions of the ANOVA. Studentized residuals in Figure 2 are the residuals divided by the estimated standard deviation of that residual. It measures the number of standard deviations separating the actual and predicted values. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line.

The actual K/S values obtained from the experimental data and the predicted ones from the model are presented in Figure 3. The results of analysis showed the actual values are agreeing with the predicted values and suggested the equation model was satisfactory and accurate.

Response Surface Plots

Figures 4–6 show the response surface plots that are obtained from the mathematical linear model. Effects of dyeing temperature and dyeing procedure time on K/S are illustrated in Figure 4, which shows they have significant effects on K/S. Increase in dyeing temperature and dyeing procedure time increases the K/S of the dyed wool fibers (Nagia and El-Mohamedy 2007; Shin et al. 2009). This increase can be attributed to the better dye exhaustion at higher temperature (Ali et al. 2007, 2009). Diffused dye molecules enter more easily into the wool fibers and more dye molecules would absorb on the wool fiber at higher temperature. The longer dyeing procedure time

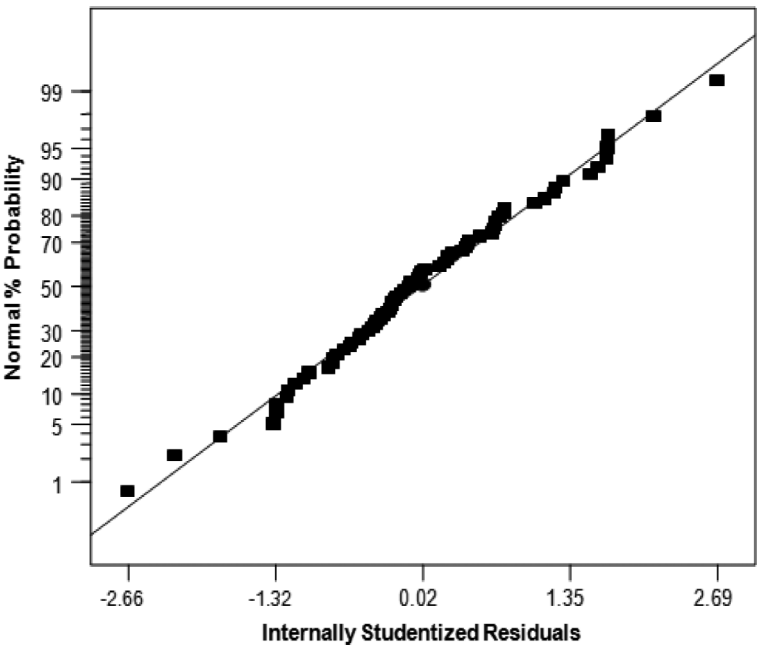

FIGURE 2 The studentized residuals versus normal % probability plot of *Isatis tinctoria* dyeing of wool fibers.

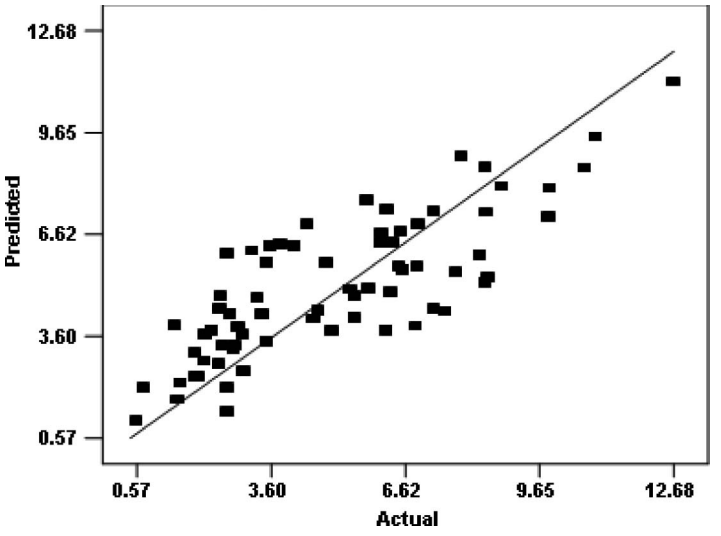

FIGURE 3 Predicted color strength (K/S) values versus actual values that were obtained from experimental results.

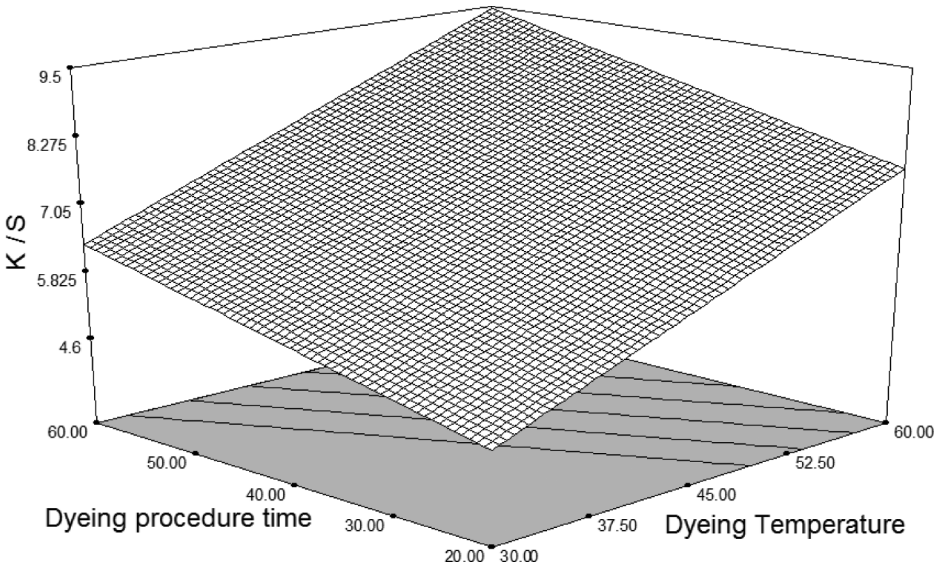

FIGURE 4 Response surface plot showing interactive effects of dyeing procedure time and dyeing temperature on color strength.
Note: Variables and their values are: preparation time, 6 h; reducing agent, 20; dye percentage, 60; liquor ratio, 50; alkali type, NaOH; oxidation type, H_2O.

causes wool fibers to reach higher exhaustion equilibrium during 60 min of dyeing because of higher diffusion of the dye molecules (Alam 2007; Ali et al. 2007), while more than 60 min of dyeing can shift this equilibrium to the lower value (Ali et al. 2009).

Figure 5 displays the effects of dye percentage and preparation time on K/S of dyed wool fibers. Increasing the dye percentage from 30% to 60% increases K/S, while the preparation time has a reverse effect. Increase in the preparation time for dye extraction lowers the K/S significantly. This happens because of the breaking up of the dye ingredients during this time, which reduces the uptake of the dye molecules (Ali et al. 2009; Nagia and El-Mohamedy 2007). More dye is transferred into the wool fibers with increasing dye concentration, which leads to higher K/S (Shin et al. 2009).

Figure 6 presents the effects of reducing agents and liquor ratio on K/S of dyed wool fibers. Low liquor ratio of dyeing solution can lead to increase in dye concentration and agglomeration of dye molecules that reduces dye exhaustion (Ali et al. 2009). The size of dye particles in solution usually depends on temperature, concentration of electrolyte, and concentration of dyes. The size of dye particles always increases with an increase in dye concentration (Alam 2007). The applied liquor ratio from 30 to 50 suggests the concentration in this range can prevent agglomeration of dye components. So, the applied liquor ratio range does not have a significant effect on the exhaustion equilibrium.

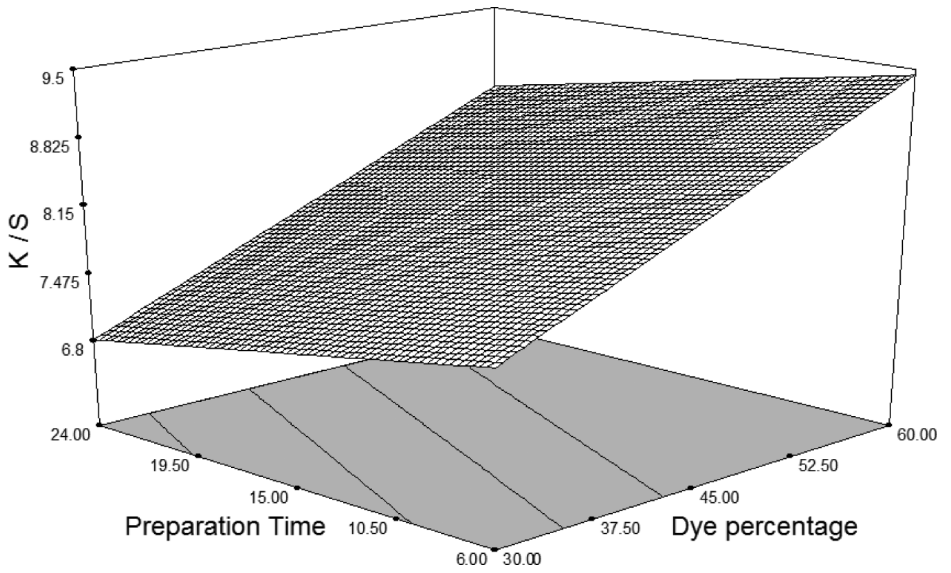

FIGURE 5 Response surface plot showing interactive effects of preparation time and dye percentage on color strength.
Note: Variables and their values are: dyeing temperature, 60°C; liquor ratio, 50; reducing agent, 20; alkali type, NaOH; oxidation type, H_2O.

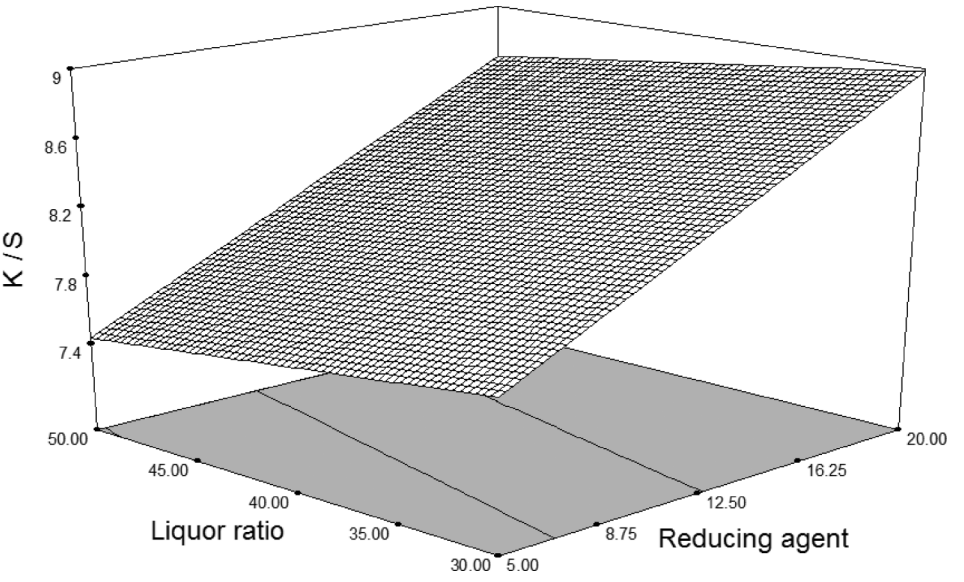

FIGURE 6 Response surface plot showing interactive effects of reducing agent and liquor ratio on color strength.
Note: Variables and their values are: preparation time, 24 h; dyeing temperature, 60°C; dyeing procedure time, 60 min; dye percentage, 60; alkali type, NaOH; oxidation type, H_2O.

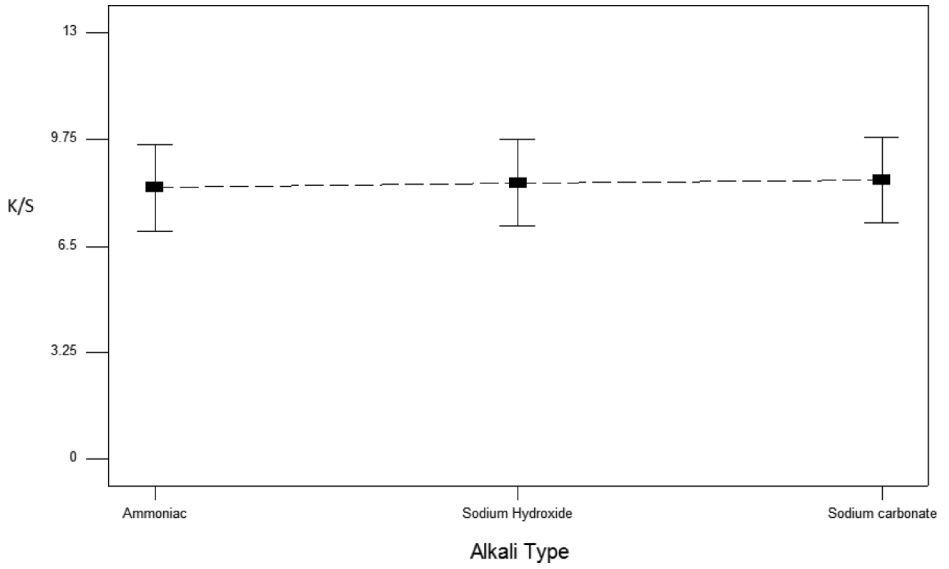

FIGURE 7 Effects of alkali type on the color strength of dyed wool fibers.
Note: Variables and their values are: preparation time, 24 h; reducing agent, 20; dyeing temperature, 60°C; dyeing procedure time, 60; liquor ratio, 50; dye percentage, 60; oxidation type, H_2O_2.

Effects of alkali and oxidation types on the K/S of dyed wool fibers are presented in Figures 7 and 8. It can be seen that changing the type of alkalis does not have significant effect on the K/S, which seems that only a mild alkali condition can be enough for transformation type in Figure 1. In addition, the same trend was followed for oxidation type, which means only a mild oxidation condition can be enough for transformation and coupling molecules of dye components.

Optimization of Dyeing Condition

The optimum condition for the *I. tinctoria* dyeing of wool fibers (Figure 9) was predicted using the optimization function of the Design Expert software. Figure 9 shows the optimum condition variables for achieving the highest amount of K/S. The value of preparation time was selected as of lowest time according to the ANOVA results and the other variable terms were selected in the proposed value range.

The predicted amount of K/S of woad dyed wool fibers is 9.66, whereas the experimental value obtained for K/S is 9.34 at the proposed condition. Comparison of experimental and predicted values (Table 5) revealed good correspondence between them, implying that empirical model derived from RSM can be used to adequately describe the relationship between the factors and response in woad dyeing of wool fibers.

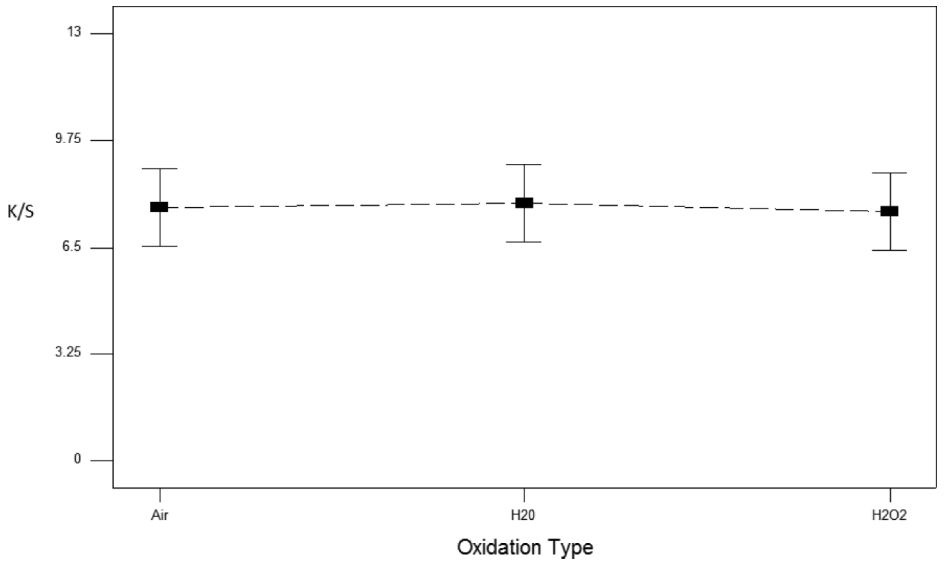

FIGURE 8 Effects of oxidation type on the color strength of dyed wool fibers.
Note: Variables and their values are: preparation time, 24; reducing agent, 20; dyeing temperature, 60°C; dyeing procedure time, 60; liquor ratio, 50; dye percentage, 45; alkali type, sodium carbonate.

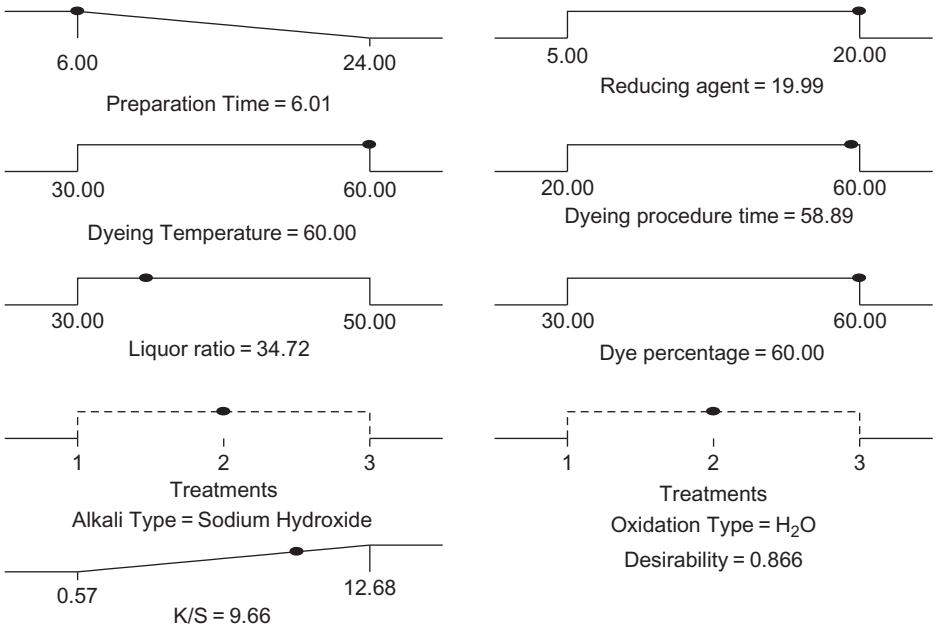

FIGURE 9 Optimized condition for *Isatis tinctoria* dyeing of wool fibers.

TABLE 5 Actual and predicted values of optimization condition for *Isatis tinctoria* dyeing of wool fibers

Optimum condition								Actual value	Predicted value
Preparation time (h)	Reducing agent (%, owf)	Dyeing temperature (°C)	Dyeing procedure time (min)	Liquor ratio	Dye (%, owf)	Alkali type	Oxidation type	*K/S*	*K/S*
6	20	60	58.89	34.72	60	NaOH	H_20	9.34	9.66

CONCLUSIONS

The *I. tinctoria* dyeing of wool fibers was most suitably described with the linear model, which is the first-order model. The probability value of this model is less than 0.0001 and a high *F*-value (6.65) indicates that this model is significant. The ANOVA results of the first-order model indicate that the amount of reducing agent, dyeing temperature, dyeing procedure time, and dye percentage have a significant effect on the *K/S* of woad-dyed wool fibers. The optimum condition for the woad dyeing of wool fibers as means of higher *K/S* was predicted. So, the *K/S* of *I. tinctoria* dyed wool fibers at the optimized condition was predicted by the first-order model, which was 9.66. The *K/S* of *I. tinctoria* dyed wool fibers by the experimental results of woad dyeing at optimum condition was 9.34, which can indicate that the model is accurate to predict the *K/S* of dyed wool fibers with *I. tinctoria*.

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