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Green Process for Indigo Dyeing: Effect and Modeling of Physico-chemical Parameters Using Statistical Analysis

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ABSTRACT: Textile Industries use different chemicals in indigo dyeing processes. Interest in eco-friendly processing in the textile industry has recently increased because of a larger awareness of environmental issues. For the case of indigo dyeing process, the reducing agent conventionally used is the - environmentally unfavourable – sodium dithionite, which will be replaced in this study with an ecological reducing agent called acetol that is also known as hydroxyacetone. In this paper, measurements of the redox potential at various experimental conditions were carried out in a dyeing bath, where acetol is the reducing agent of indigo. Moreover, an unconventional but eco-friendly indigo dyeing process of cotton was investigated. The effects of: reduction duration, dyeing duration, reduction temperature, alkalinity and the amount of indigo on the performances of this dyeing process were studied, and the dyeing results were evaluated by measuring the colour yield parameter (*K/S*) of the dyed samples at 660 nm. Finally, a factorial design was employed for the experimental plan; mathematical model equation and statistical analysis were derived by computer simulation applying the least squares method using Minitab 15.

Key words: Eco-friendly, Reducing process, Indigo dyeing, Acetol, Statistical analysis

INTRODUCTION

Indigo is one of the oldest dyes used by mankind. Today, it is considered as one of the world's most important industrial chemicals, with the current annual world consumption of indigo and other vat dyes being over 33 million kilogrammes (Roessler *et al.,* 2003). Indigo –as a vat dye- needs to be reduced to its water soluble leuco-form before dyeing (Roessler *et al.,* 2004). So far, most of the industrial reduction has been performed chemically by a continuous process using sodium dithionite as a reducing agent (Schlüter, 1990). This process has two major limitations: the choice of the reducing agent and the method of application. Indeed, using sodium dithionite is the cause of certain engineering problems, such as instability, storage, corrosivity, etc, (Camacho *et al.,*1997) and ecological problems because of the production of large amounts of sodium sulphate and sulphite (Božič *et al.,* 2008; Kulandainathan *et al.,*2007), known to increase the cost of wastewater treatment (Roessler *et al.,*2003). On the other hand, dyeing with indigo in a continuous process presents a well known limit: the inability to satisfy all consumers' expectations and to follow the evolution in fashion tendencies, which are easier to accomplish by an exhausting process. These problems were the main motivation to conduct this work. Firstly, it is required in the case of indigo to develop a new process and achieve a better dyeing quality than the one obtained in a conventional process. Secondly, the environmentally unfavourable sodium dithionite has to be substituted by an ecologically more attractive alternative. Investigations focused on the replacement of sodium dithionite by an organic reducing agent: the acetol (Baumgarte, 1987; Marte, 1989) of which the oxidation products are biodegradable. It has been used in conventional dyeing processes (Baugmarte, 1987), where the reducing system is biocompatible. In addition to that, acetol -also known as hydroxyacetone- offers the facility of storage in alkaline solution, and has non toxic by-products with minimal effects on the environment.

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MATERIALS & METHODS

Indigo (BEZEMA AG, Switzerland), sodium dithionite (Fluka, Germany), acetol (Fluka, Germany) and sodium hydroxide (CDM chemicals developing and manufacturing, Germany) were used for the reduction without purification. Commercially bleached but unfinished cotton fabric with the following specifications was used: plain weave; ends per inch, 33.02; picks per inch, 38.1; warp count, 10.5 Nm Open End; weft count, 15 Nm Open End; weight, 204 g/m^2. A solution of 2 g/L of indigo, 12 g/L of sodium hydroxide, 4 g/L of acetol, was brought to the appropriate temperature of 50°C for 120 minutes. Reaction was carried out in the AHIBA and measurements of the redox potential were taken at the end of the process with a combined redox electrode (Biolock Scientific 90417, Portugal).Equations of Reducing indigo and oxidation of acetol are presented in Fig. 1 and 2.The dyeing process is described in Fig. 3. The dyeing was performed by an exhaustion process. In fact, the reaction medium obtained after the reduction procedure was used to dye the cotton fabric and was set at a temperature of 25°C with a liquor ratio of 1:50 (fabric weight (g): dyeing bath volume (mL)) .The fabrics were introduced into the bath and the dyeing lasted 40 min in the autoclave machine. Afterwards, fabrics were oxidized for 20 min. The dyed samples were subject to a hand washing with hot water for 5 minutes at 70°C. The samples were then cold-rinsed, and finally dried at room temperature.

The dyeing quality was evaluated using a colour yield parameter (K/S) measured by a Spectroflash SF 300 spectrophotometer with DataMaster 2.3 software (Datacolor International, USA). The colour yield *(K/S)* value was measured at 660 nm according to the following equation (Kubelka & Munck, 1931):

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

Where R is the decimal fraction of the reflectance of dyed fabric, R_0 is the decimal fraction of the reflectance of undyed fabric, K is the absorption coefficient and S is the scattering coefficient. Regression and variance analysis (ANOVA) were used to test the effect of each experimental parameter selected from the obtained results. Minitab (Version 15, State College, PA, USA) was used for the statistical analysis of data. Comparison of means was conducted using ANOVA with Post Hoc Tukey's test with a p-value < 0.05 (Margarita Enid Carmona *et al.,* 2005).

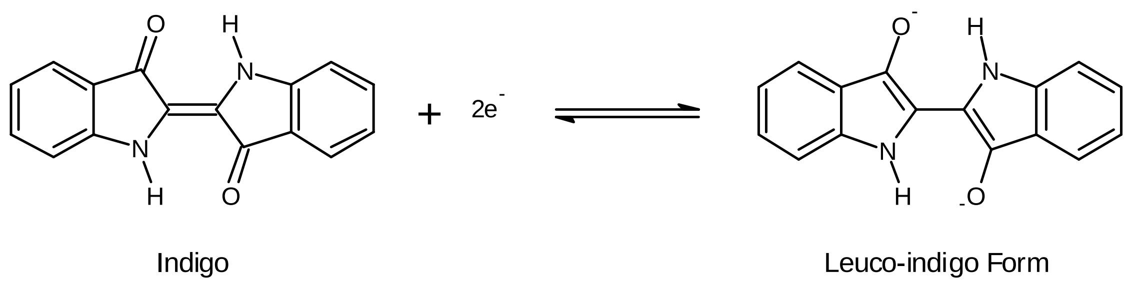
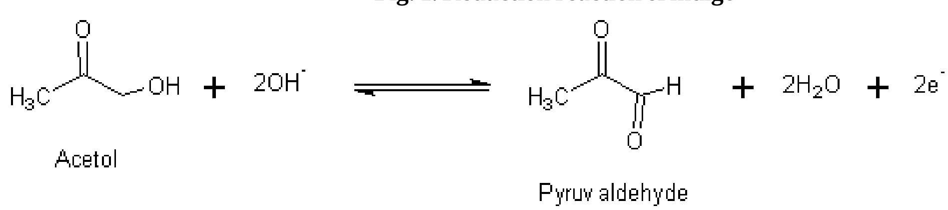


Fig. 1. Reduction reaction of indigo



According to the experimental conditions, Pyruvaldehyde can be also oxidized as follow:

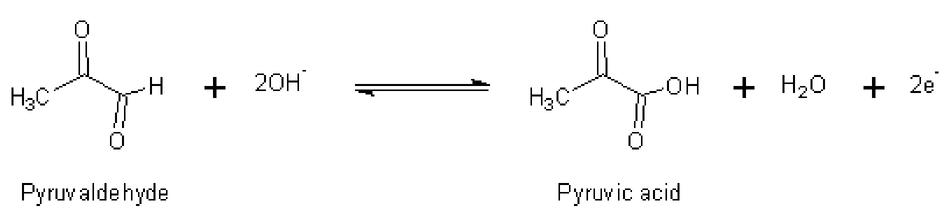


Fig. 2. Oxidation of acetol

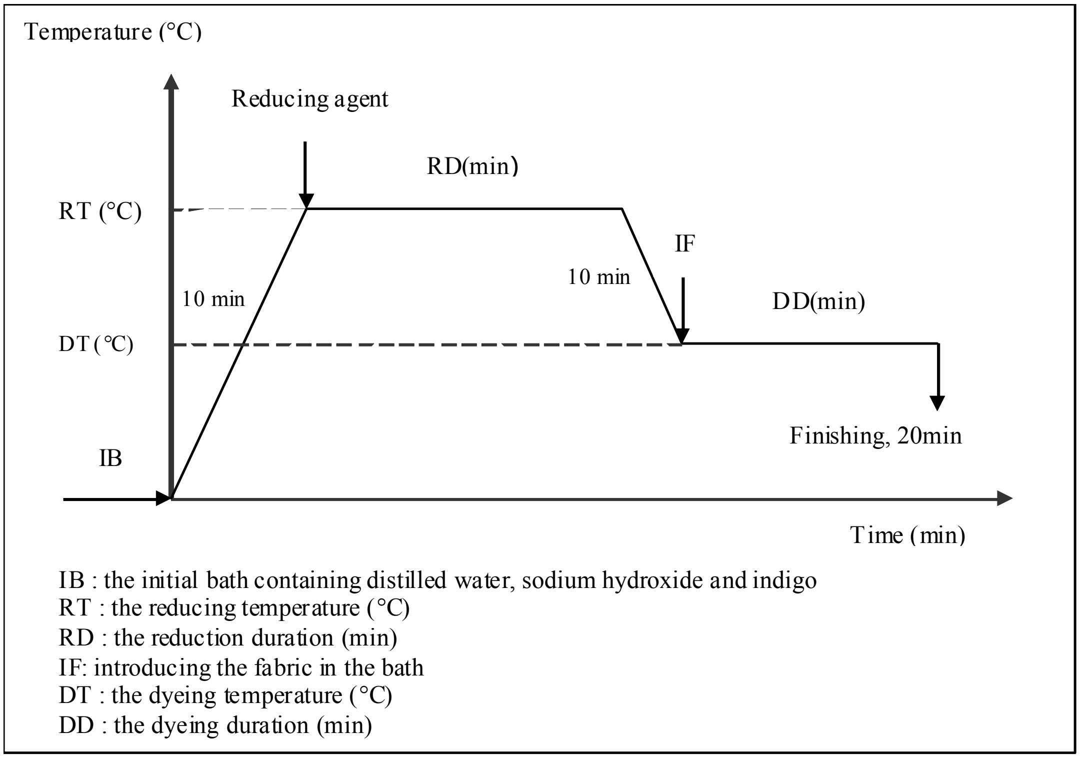


Fig. 3. The exhaust dyeing process investigated

RESULTS & DISCUSSION

The reducing power generated in a dyeing bath was evaluated using measurements of the redox potentials. It is important to mention that redox potentials, determined experimentally are influenced by the concentration of the dye and the reducing agent (Idiapo, 1989). In this study, each experimental point shown in all figures is the mean of three experimental values.The temperature of reduction varied between 40 and 70°C, and the evolution of the redox potential of the dyeing bath was studied according to the variation of the amount of acetol in the medium. Based on Fig. 4, it can be seen that all curves representing the evolution of the redox potential *versus* temperature have the same shape whatever the temperature of reduction was. These curves illustrate that the redox potential remains quasi-stable irrespective of the amount of acetol. The reducing power improved with the increase of temperature and the best result was obtained at 70°C.

The amount of sodium hydroxide varied between 1 and 30 g/L in the medium, and the evolution of the redox potential generated in the dyeing bath was studied. From the results shown in Fig. 5, the variation of the amount of sodium hydroxide in the medium was investigated, and the required amount of alkali was deduced. It could be seen that the obtained curve consists of two parts: the first one represents a fast decrease in the redox potential when the amount of alkali in the medium increases. The second part illustrate that the redox potential generated in the dyeing bath remains quasi-stable. This stability indicates that the best reduction of indigo by acetol is observed starting from a concentration of alkali of about 12 g/L.

The amount of indigo ranged from 1 to 10 g/L in the medium, and the evolution of the redox potential generated in the dyeing bath was studied. From the results shown in Fig. 6, the variation of the amount of indigo in the medium was investigated and the adequate amount of indigo giving the best reduction process was deduced. It is observed in Fig. 6 that the curve is composed of two parts: the first part represents a fast decrease of the redox potential when the amount of indigo in the medium increases. The second part shows that the redox potential in the dyeing bath remains quasi-stable. This stability of the redox potential measured in the bath indicates that, for this range of indigo amount, the best reduction process for indigo is obtained.

The reduction process lasted from 20 to 250 minutes. The effect of this variation on the evolution

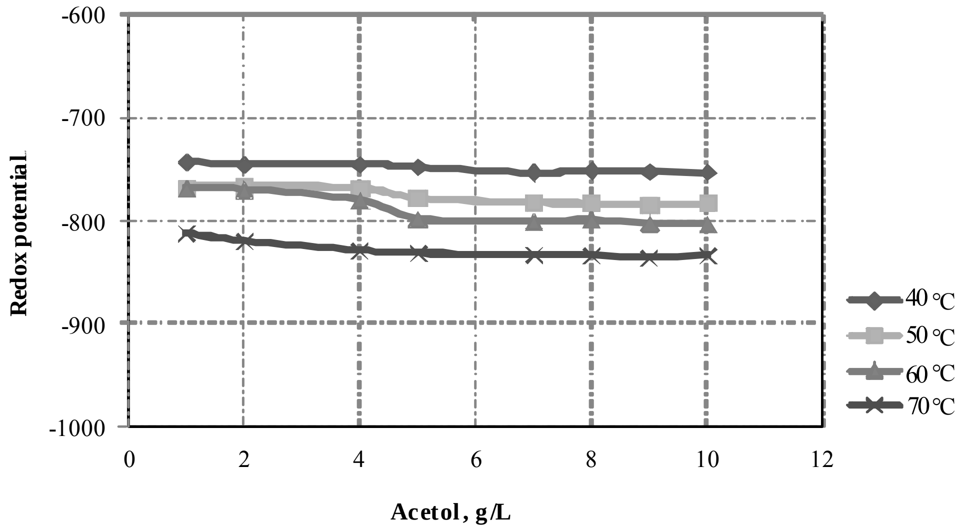


Fig. 4. Effect of the reduction temperature on the evolution of redox potential according to the variation of the amount of acetol in a dyeing bath

of the colour yield (*K/S*) was studied. The experimental results are shown in Fig. 7. Three cases were investigated: the first curve corresponds to the reduction of indigo by sodium dithionite in the presence of 4 g/L of sodium hydroxide in the medium. The second curve corresponds to the reduction of indigo by acetol in the presence of the same amount of alkali. The third one corresponds to the reduction of indigo by acetol in the presence of 12 g/L of sodium hydroxide in the medium. Furthermore, the effect of indigo reduction duration with sodium dithionite and acetol was compared. The duration of indigo reduction required for acetol at two different alkalinities was also studied. It can be seen from Fig. 7 that 20 minutes are sufficient for sodium dithionite to reach the maximum yield of reduction in the presence of 4 g/L of sodium hydroxide in the medium. For the same alkalinity, the reduction of indigo by acetol required 180 minutes to reach its maximum reduction yield. When alkalinity increased to 12 g/L, the reduction duration slightly decreased. However, the maximum yield of reduction in the presence of 12 g/L of sodium hydroxide was higher than the one obtained in the presence of 4 g/L. In all cases, both maximum reduction yields for the acetol were lower than the one obtained for sodium dithionite.

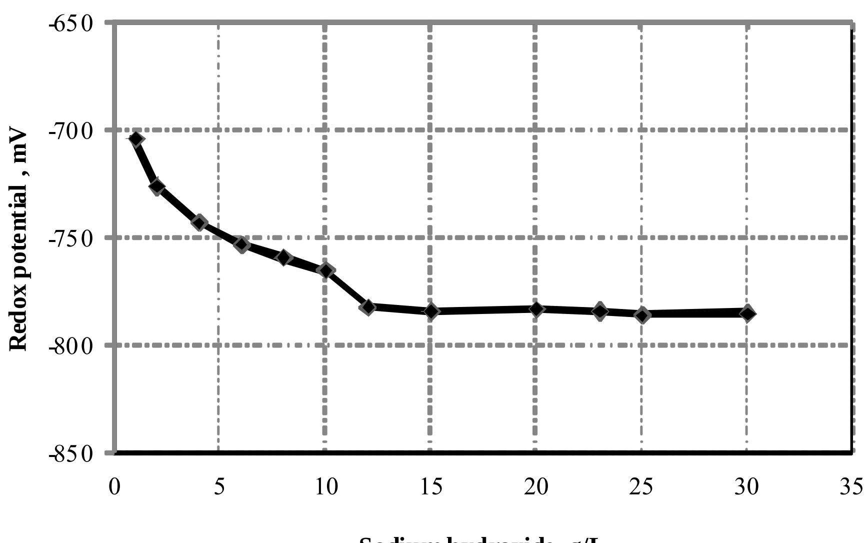


Fig. 5. Effect of the sodium hydroxide amount on the evolution of redox potential in a dyeing bath

Reduction of indigo by acetol was carried out in the presence of 12 g/L of sodium hydroxide for 180 minutes. The effect of dyeing duration on the evolution of the colour yield (*K/S*) was studied for a time range of 5 to 150 minutes. The results are reported in Fig. 8. Here, it can be observed that the curve representing the evolution of the colour yield is mainly composed of two parts: In the first part, a rapid increase of the colour yield (*K/S*) is seen for dyeing durations less than 90 minutes. This can be explained by the increase of the reduction yield and the concentration of leuco-indigo in this time range. In the second part starting at 90 minutes, the colour yield (*K/S*) remained constant. It seems that cotton fibres have reached the absorption saturation of the leuco-indigo. It could be deduced that a dyeing duration of about 90 minutes is sufficient to obtain the best quality of dyeing under these operating conditions.

The effect of temperature on the performance of the reduction reaction of indigo at different concentrations of acetol was studied for a temperature range of 40 to 70°C. The performance of this reaction was evaluated by measuring the colour yield of the dyed samples. The experimental results are reported in Fig. 9. It can be seen from this graph that all curves

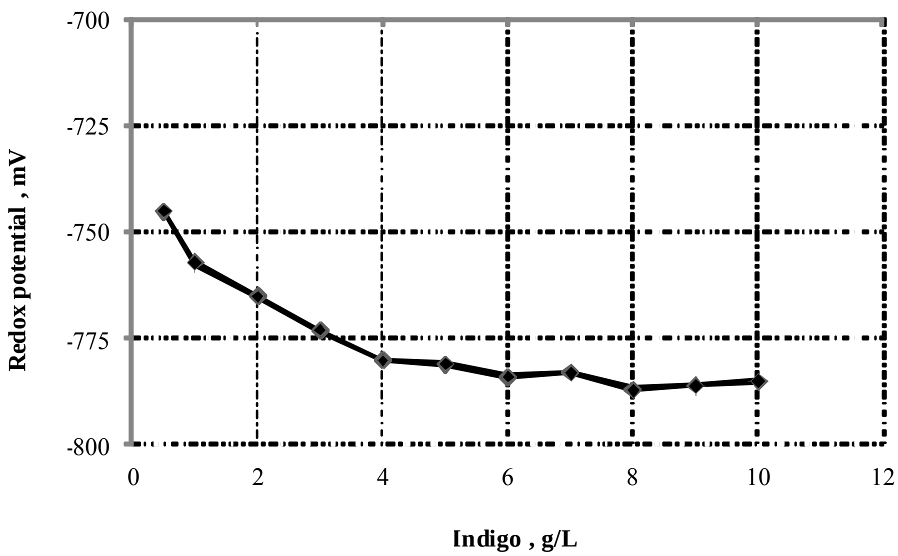


Fig. 6. Effect of the indigo amount on the evolution of redox potential in a dyeing bath

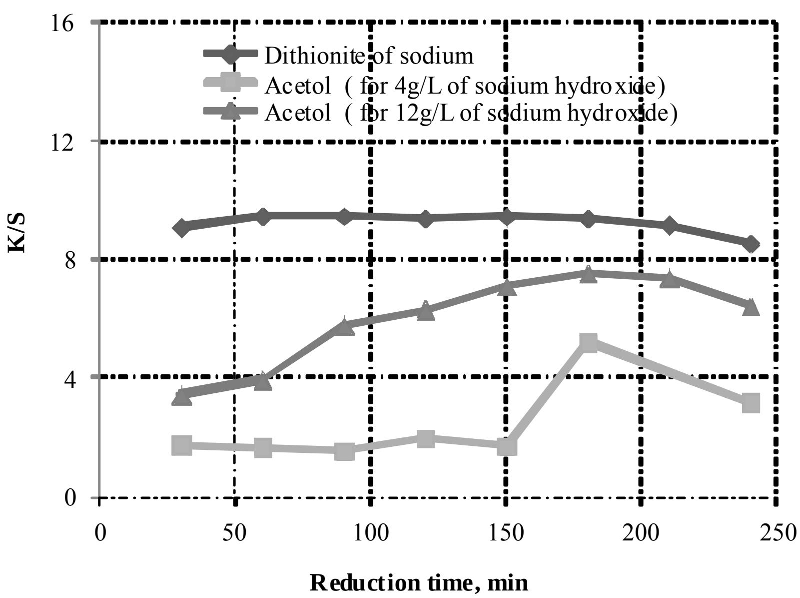


Fig. 7. Effect of the reduction duration on the evolution of the colour yield parameter K/S

representing the evolution of the colour yield with temperature show a similar pattern irrespective of the temperature of reduction. These curves are composed of two different parts. One part shows an increase for a concentration of acetol from 5 to 7 g/L, where a maximum value of 10 for the colour yield is obtained at a concentration of 7 g/L of the reducing agent. This can be explained by the increase of the indigo reduction yield in this concentration range. The second part of the curve begins at 7 g/L of acetol. It shows a slow decrease of the colour yield, probably due to an over-reduction of indigo. It could also be noted that when the temperature increases the colour yield value also increases, hence, it is recommended to perform reduction at higher temperatures.

The amount of sodium hydroxide varied between 1 and 30 g/L in the medium, and the evolution of the colour yield for dyed cotton was studied. The experimental results are shown in Fig. 10. From these results, the variation of the amount of sodium hydroxide in the medium was analyzed, and the required amount of alkali to achieve the best dyeing quality was determined.

The obtained curve is composed of two parts: the first part shows that the colour yield increases when the amount of alkali increases. In the second part, the colour yield remains stable near a value of 10. This stability indicates that, for the amount of sodium hydroxide used, the quality of dyeing was optimal. As a result, a concentration of 12 g/L of alkali is sufficient

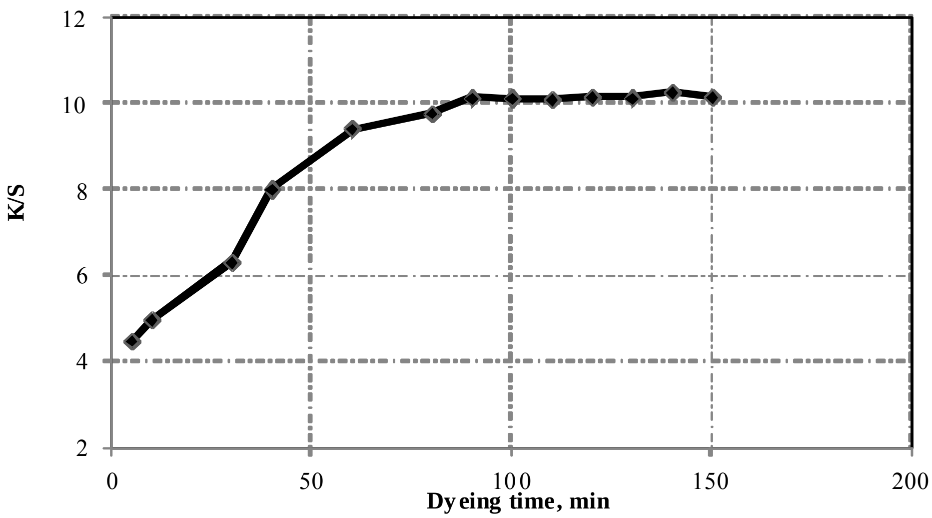


Fig. 8. Effect of the dyeing duration on the evolution of the colour yield parameter K/S

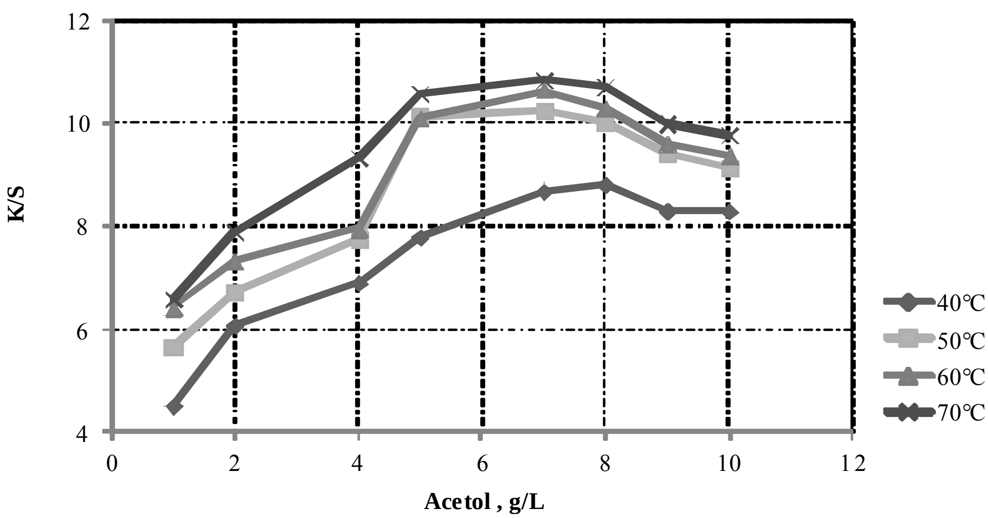


Fig. 9. Effect of the reduction temperature on the evolution of the colour yield parameter K/S at different concentration of acetol

to obtain the optimal dyeing quality resulting from the reduction of indigo by acetol.

The effect of the amount of indigo on the dyeing quality of cotton was studied. This quality was estimated by measuring the colour yield. The experimental results are shown in Fig. 11. For a concentration of indigo going from 1 to 5 g/L, it can be observed that there is a rapid increase of the colour yield which attains a maximum value of 13 for an amount of indigo equal to 5 ,above which, the colour yield starts to decrease. Indeed, cotton absorbs the dye up to 5 g/L at which it reaches saturation and the colour yield parameter attains its maximum; this can be explained by the increase of the concentration of leuco-indigo in the bath, and so, the increase of the dye absorption by cotton. When the concentration of indigo in the bath exceeds 5 g/L, the colour yield decreases: this can be explained by the increase of the viscosity of the dyeing bath which becomes less diluted. Therefore, the amount of water in the bath becomes insufficient to carry the dye to the cotton fibres, and hence, the dye absorption will be negatively affected. Moreover, after saturation, a plating phenomenon of indigo on the surface of cotton appears which would affect the dyeing quality and leads to the decrease of the colour yield.

The results were analyzed using the software Minitab 15 (Viertl, 1996; Shacham, 1995) and the regression model, the main effects, and interactions between factors were determined. The effect of a factor is defined as the variation of the response produced by a change in the level of this same factor (Montgomery, 1997). This is frequently called a “main effect” as it refers to the primary factors of interest in the experiment (Montgomery, 1997).

The regression coefficients, the associated standard errors, and the effects are shown in Table 3 and Table 5. In this study, the general behaviour of some phenomena can be simulated by a mathematical equation: this equation represents the regression model. There are many types of equations that can give a good correlation between parameters, but the choice of which one should be used is dependent of the R^2-value of each model.

There are four types of equations that can be used in order to model the results of this study:

- Type 1: A linear equation:

$$R_i = K + a_1.X_1 + a_2.X_2 + a_3.X_3$$

- Type 2: A linear equation with interactions:

$$R_i = K + a_1.X_1 + a_2.X_2 + a_3.X_3 + b_1.X_1.X_2 + b_2.X_1.X_3 + b_3.X_2.X_3$$

- Type 3: A quadratic equation:

$$R_i = K + a_1.X_1 + a_2.X_2 + a_3.X_3 + c_1.X_1^2 + c_2.X_2^2 + c_3.X_3^2$$

- Type 4: A quadratic equation with interactions

$$Ri = K + a_1.X_1 + a_2.X_2 + a_3.X_3 + c_1.X_1^2 + c_2.X_2^2 + c_3.X_3^2 + b_1.X_1.X_2 + b_2.X_1.X_3 + b_3.X_2.X_3$$

The analysis of the regression equations stated above is performed in order to determine the appropriate equation to use. The evaluation was based on the p-value obtained for each parameter treated in each model.

In order to analyse statistical results, one recalls the following definitions:

• R^2: is the squared multiple correlation coefficient. It is also called the coefficient of determination. R^2 is the ratio of the regression sum of squares to the Total sum of squares. It is the proportion of the variability in the response that is fitted by the model. R^2 is also

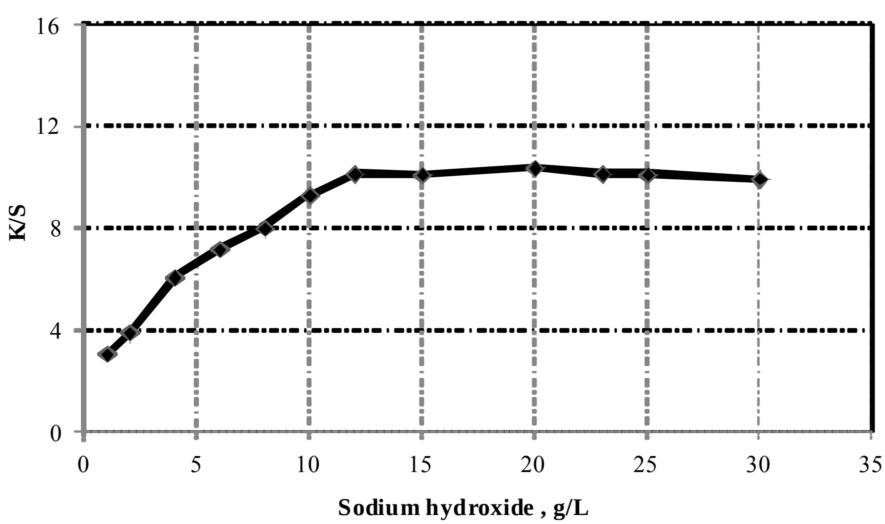


Fig. 10. Effect of the sodium hydroxide amount on the evolution of the colour yield parameter K/S

known as the proportion of the variance explained by the model.
- A model with perfect predictability would have $R^2=1$ (100%).
- A model with no predictive capability would have $R^2=0$.

As additional variables are added to the regression equation, R^2 increases even when the new variables have no real predictive capability.

• p-value: the p-value tells us whether a variable has statistically significant predictive capability in the presence of the other variables, that is, whether it adds something to the equation. In some circumstances, a non-significant p-value might be used to determine whether to remove a variable from a model without significantly reducing the model's predictive capability. However, the p-value should not be used to eliminate more than one variable at a time. A variable that does not have a predictive capability in the presence of the other predictors may have a predictive capability when some of those predictors are removed from the model. In addition to the regression model, other statistical results could be achieved. It would be interesting to investigate the interaction between factors treated and their main effects on the redox potential and the dyeing parameter. The analysed factorial design is illustrated in Table 1.

The multiple parameters studied in this work were tricky to analyze. For this reason, it was necessary to use the previous parts of the study (see section 3.1 and 3.2) in order to select the most important parameters to run the model. The chosen parameters were: temperature, sodium hydroxide concentration, and acetol concentration. In this section, they will be called factors or variables (see Table 2). The analysed results were the redox potential and the colour yield parameter, which will be called responses.

In this study, different regression models were run. The most appropriate one was taken and analyzed for each response.

The most appropriate regression model obtained for the redox potential (RP) is the following:

$$RP = -767.24 - 77.67*[T] - 44.39*[CS] - 54.28*[CA] + 84.83*[T]^2 + 12.17*[CS]^2 + 52.70*[CA]^2 \quad \text{With } R^2 = 89\%$$

Where:

RP Redox potential (mV)
[T] Temperature (°C)
[CS] Sodium hydroxide concentration (g/L)
[CA] Acetol concentration (g/L)

According to Table 1, an analysis of the regression model reveals a particular behaviour for the redox potential. In fact, a significant linear effect for T, CS and CA ($p= 0.00 <0.01$), a significant squared effect for CA*CA and T*T ($p= 0.00 <0.01$), and an insignificant squared effect for CS*CS ($p=0.462 >> 0.01$), were observed. Hence, it can be deduced that temperature, acetol and sodium hydroxide concentrations have a remarkable impact on the experimental redox potential. According to the results described in Table 4, the analysis of variance (ANOVA) proves that for the redox potential, the regression model is highly significant ($p=0.00 <0.01$). Moreover, and for this response, there is a significant squared effect ($p=0.00 <0.01$) and a significant linear effect ($p= 0.00 <0.01$).

The most appropriate regression model obtained for the colour yield (*K/S*) is the following:

$$K/S = 8.2306 + 0.4839*[T] + 1.8461*[CS] + 2.3819*[CA] - 2.0559*[CA]^2 - 0.4848*[T]*[CA] - 0.4867*[CA]*[CS] \quad \text{with } R^2 = 94\%$$

Where:

K/S Colour yield parameter
[T] Temperature (°C)
[CS] Sodium hydroxide concentration (g/L)
[CA] Acetol concentration (g/L)

Based on the results illustrated in Table 5, an analysis of the regression model reveals a particular behaviour for the colour yield parameter. Indeed, it can be noticed that there is a significant linear effect for CS and CA ($p= 0.00 <0.01$), and an insignificant linear effect for T ($p=0.021> 0.01$). For CA*CA, a significant squared effect ($p= 0.00 <0.01$) was obtained. However, an insignificant interaction effect ($p=0.05 > 0.01$) was observed for CS*CA and T*CA. According to Table 6, the analysis of variance (ANOVA) proves that, for the colour yield parameter, the regression model is highly significant ($p= 0.00 <0.01$).

Moreover, the following results were obtained for this response:
- Insignificant interaction effect ($p= 0.027 > 0.01$).
- Significant squared effect ($p= 0.00 <0.01$).
- Significant linear effect ($p= 0.00 <0.01$).

The analysis of the main effect diagrams point out the effect of each factor on the response. In fact, the main effect diagram shows the behaviour of the response through the different variations of factors. As shown in Fig. 12 and 13, the behaviour varies from one response to another. But, it is clear that sodium hydroxide concentration has the highest effect on the resulting reducing power and the dyeing quality. Concerning the temperature, it can be noticed that it has a great effect on both responses until 50°C, and above this value, its effect starts to decrease. The analysis of the interactions between the experimental factors studied is shown in Fig. 14 and 15. As seen, the behaviour changes from one response to another, but the interaction between different factors is obvious for the colour yield parameter.

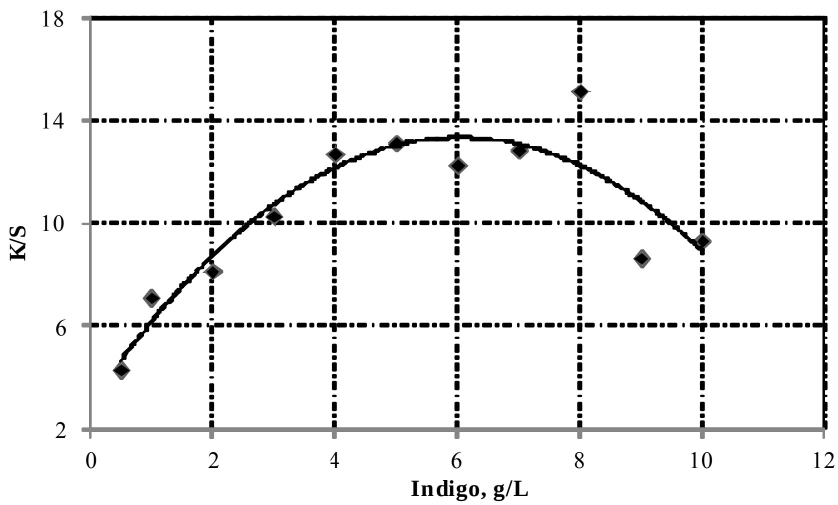


Fig. 11. Effect of the indigo amount on the evolution of the colour yield parameter K/S

Table 1. Coded actual levels of studied variables and results obtained for a factorial design

Run	Coded level of variables			Actual level of variables			Responses	
	X1	X2	X3	T(°C)	CS(g/L)	CA(g/L)	RP (mV)	K/S
1	-1	-1	-1	35	4	2	-478	1.20
2	-1	-1	0	35	4	5	-528	3.60
3	-1	-1	1	35	4	10	-540	7.00
4	-1	0	-1	35	8	2	-508	3.30
5	-1	0	0	35	8	5	-546	6.50
6	-1	0	1	35	8	10	-569	9.30
7	-1	1	-1	35	12	2	-589	4.00
8	-1	1	0	35	12	5	-616	8.20
9	-1	1	1	35	12	10	-629	10.50
10	0	-1	-1	50	4	2	-538	1.80
11	0	-1	0	50	4	5	-743	6.08
12	0	-1	1	50	4	10	-749	7.20
13	0	0	-1	50	8	2	-599	3.80
14	0	0	0	50	8	5	-781	8.01
15	0	0	1	50	8	10	-783	8.20
16	0	1	-1	50	12	2	-662	6.72
17	0	1	0	50	12	5	-741	10.13
18	0	1	1	50	12	10	-754	9.14
19	1	-1	-1	70	4	2	-600	2.20
20	1	-1	0	70	4	5	-652	6.50
21	1	-1	1	70	4	10	-654	7.40
22	1	0	-1	70	8	2	-648	2.80
23	1	0	0	70	8	5	-765	7.70
24	1	0	1	70	8	10	-792	8.50
25	1	1	-1	70	12	2	-700	7.90
26	1	1	0	70	12	5	-761	10.58
27	1	1	1	70	12	10	-829	9.77

Table 2. Variables studied and their levels for a factorial design

Variable	Symbol	Coded variable level		
		Low	Center	High
		-1	0	1
Temperature (°C)	T	35	50	70
Hydroxide of sodium concentration (g/L)	CS	4	8	12
Acetol concentration (g/L)	CA	2	5	10

Table 3. Parameters of model for the redox potential RP

Terms	RP		
	Coef	T	P
Constant	-767.24	-36.192	0.000
T	-77.67	-8.293	0.000
CS	-44.39	-4.74	0.000
CA	-54.39	-5.796	0.000
T*T	84.83	5.105	0.000
CS*CS	12.17	0.750	0.462
CA*CA	52.70	3.014	0.007

Table 4. Analysis of Variance for the redox potential *RP*

Source		Regression	Linear	Square	Residual Error	Total
RP	DF	6	3	3	20	26
	Seq SS	236770	180388	56382	31578	268347
	F	24.99	41.61	11.90		
	P	0.000	0.000	0.000		

Table 5. Parameters of model for the colour yield K/S

Terms	K/S		
	Coef	T	P
Constant	8.2306	27.854	0.000
T	0.4839	2.508	0.021
CS	1.8461	9.536	0.000
CA	2.3819	12.346	0.000
CA*CA	-2.0559	-5.718	0.000
T*CA	-0.4848	-2.083	0.050
CS*CA	-0.4867	-2.085	0.050

Table 6. Analysis of Variance for the colour yield *K/S*

Source		Regression	Linear	Square	Interaction	Residual Error	Total
K/S	DF	6	3	1	2	20	26
	Seq SS	189.517	161.884	21.833	5.800	13.356	202.874
	F	47.30	83.10	32.69	4.34		
	P	0.000	0.000	0.000	0.027		

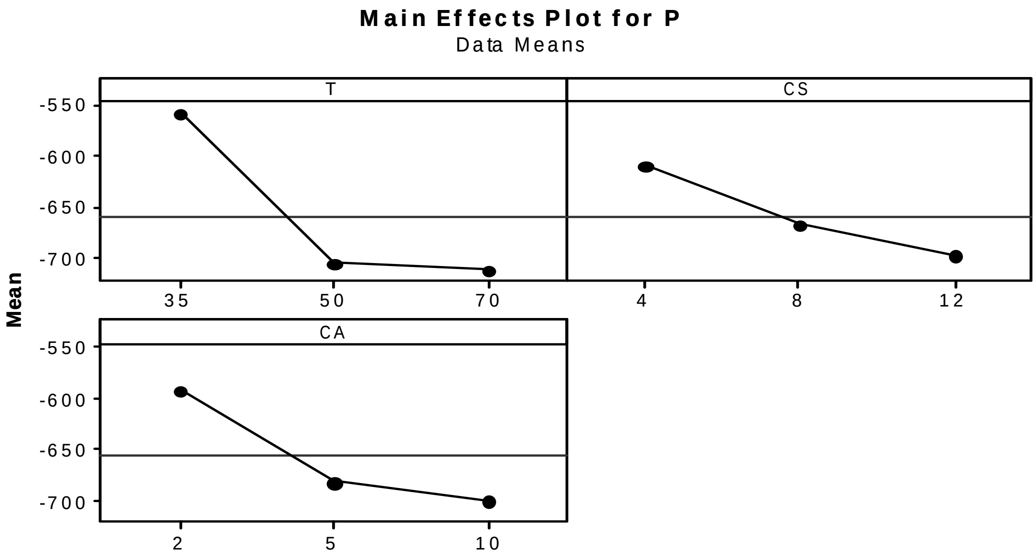


Fig. 12. Main effects plot for the redox potential P

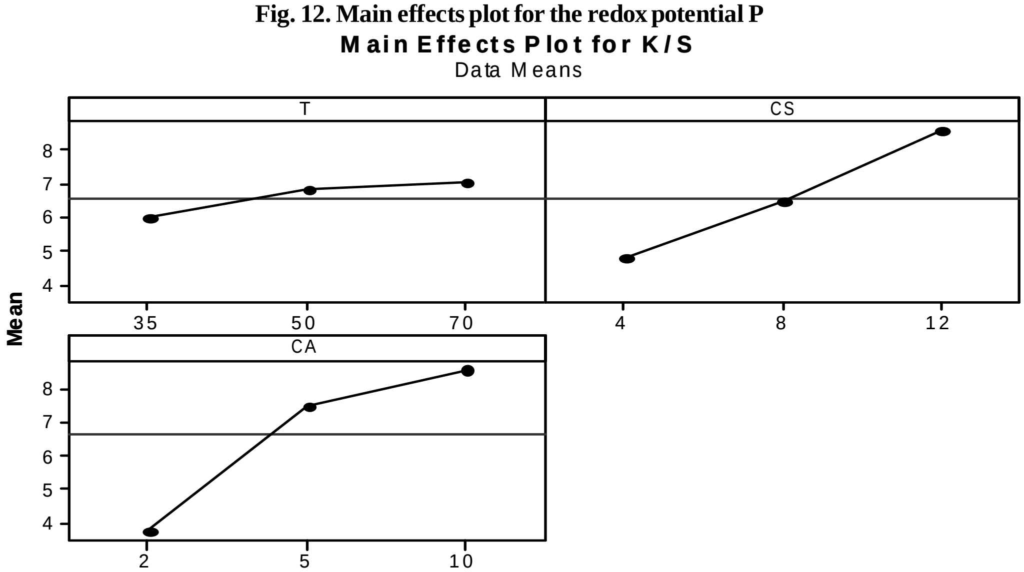


Fig. 13. Main effects plot for the colour yield parameter K/S

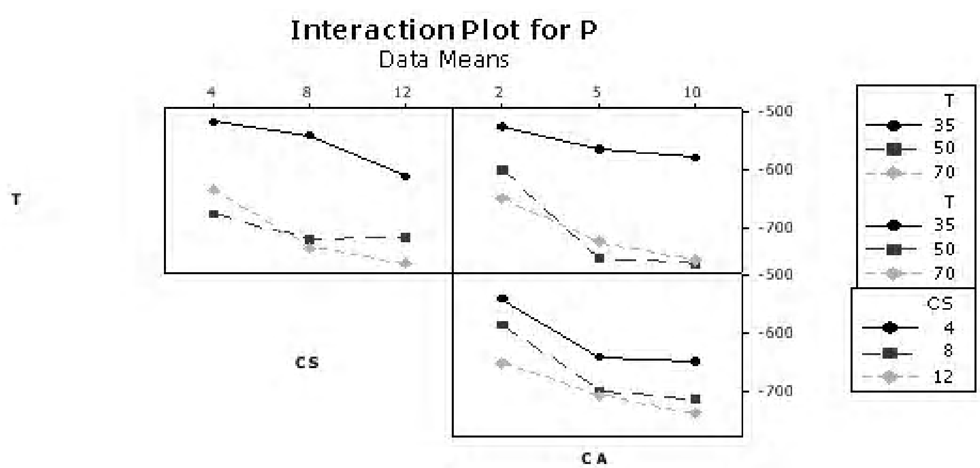


Fig. 14. Interaction plot for the redox potential P

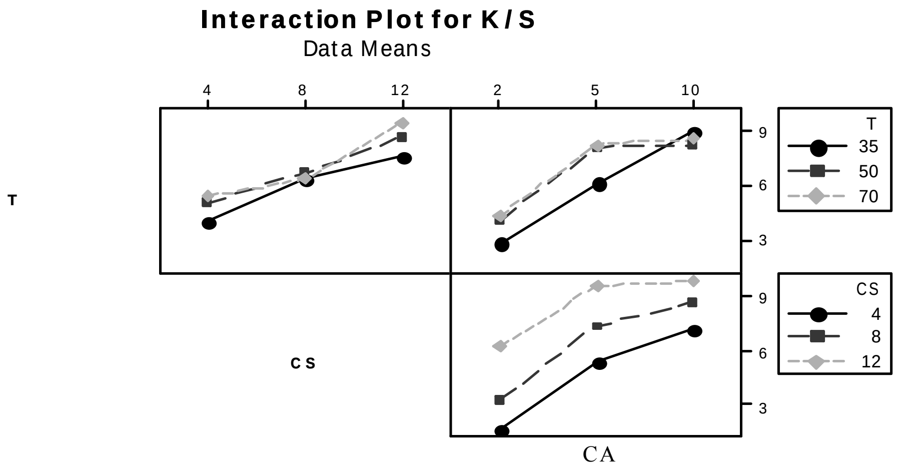


Fig. 15. Interaction plot for the colour yield parameter K/S

CONCLUSION

In the dyeing bath, while varying experimental conditions, it was observed that the reducing power of acetol largely depends on temperature and alkali. The acetol has the best reducing activity at high temperature and alkalinity, more specifically at a temperature higher than 50°C and a sodium hydroxide concentration of 12 g/L. Thus, the dyeing bath was adjusted according to these results in order to determine the optimal physico-chemical parameters of the dyeing process.

As a result, it can be noted that for the reduction of indigo by acetol, a concentration of 12 g/L of sodium hydroxide, 5 g/L of acetol, 5 g/L of indigo, a reduction time of 180 minutes, a dyeing time of 90 minutes, and a reduction temperature of 50°C, are the optimal conditions to obtain the best dyeing quality of cotton fibres with indigo reduced by acetol. Finally, factorial design was analysed, and regression models were performed for the experimental values of redox potential and colour yield parameter. The analysis depended on three factors: temperature, sodium hydroxide and acetol concentrations. Moreover, the interactions between different factors as well as their main effects on both responses studied were determined.

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