DETERMINATION OF INFLUENTIAL FACTORS IN REACTIVE DYE WASH-OFF PROCESS USING PLACKETT-BURMAN EXPERIMENTAL DESIGN

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As water consumption in the final wash-off of reactive dyeing of cotton is significant, this study tries to identify the steps of the process that can be left out in order to save water. Plackett-Burman screening design was used to identify the factors that influence the reactive dye removal in the rinsing process. The experimental design has eleven factors, where each factor is set at two levels, and 20 trial runs were conducted in the study. The analysis of variance, which was used to examine the results, showed that in the case of the mono-chlorotriazinyl dye all the factors, except the third overflow rinse, last hot soaping and last neutralization baths, have statistical significant impact on the hydrolyzed dye removal, while for the di-chlorotriazinyl dye the insignificant factors were the two neutralization baths. The results would lead to further experimentation for thorough investigation of the significant factors and their interaction effects.

Keywords: cotton, exhaust reactive dyeing, wash-off, Plackett-Burman design

INTRODUCTION

The textile industry, the world's oldest branch of consumer goods industry, is severely intertwined with environmental issues, especially in its wet processes, where dyes, auxiliaries, and finishing agents are consumed to convert the raw materials into finished products.

The environmental impact of textile processing depends significantly on the type of fiber, but commonly it includes substantial water use[1] and generation of a high volume of wastewater,[2,3] as the specific water use ranges from 60 to 400 L/kg of textile material, depending on the nature of the wet process.[4]

A constantly growing world population requires an increasing quantity of fresh water, hence decreasing the consumption of water has become a most important subject in the last years. Aware of the depletion of water sources, the textile industry has to develop new technologies that use less water.[5]

Cotton is the most extensively used natural fiber[6] and accounts for almost half of all the fibers used by the world's textile industry. Amongst the numerous wet processes to which cotton is subjected (desizing, scouring, bleaching *etc*.), the dyeing process uses large volumes of water for operations such as dyeing, fixing and washing (rinsing).[7] Textile dyeing (especially exhaust dyeing) is thus such an important consumer of water and generator of contaminated wastewater because the dyeing processes are normally conducted in water-based dyeing baths and they involve the addition of dyes and dyeing auxiliaries.[8,9]

One of the major classes of dyes for cellulose fibers are the reactive dyes, as they have good washing fastness, bright shades and very flexible batch and continuous dyeing methods.[10] As the name implies, the reactive dyes bind to the fiber under alkaline conditions,[11] but hydroxide ions of water also react with the reactive group of the dye, generating hydrolyzed dye and decreasing the efficiency of the fixation process (Fig. 1). All this hydrolyzed dye has to be removed after dyeing by thorough washing to ensure good washing fastness[9] and this process is vital for the final quality of the dyeing. It is estimated that approximately half the cost of usual reactive dyeing may be attributed to the washing stage and the treatment of the subsequent effluent.[12,13]

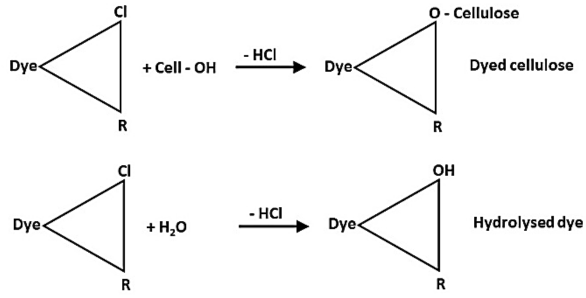

Figure 1: Cellulose and water reactions with reactive dyes

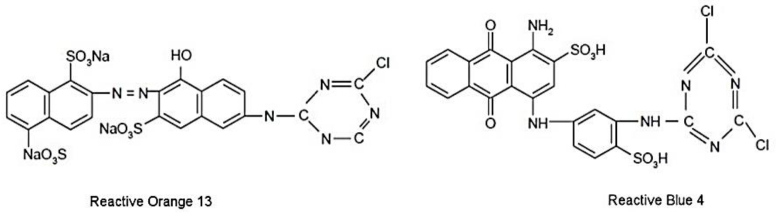

Figure 2: Chemical structures of the studied dyes

The highly reactive dyes, such as the di-chlorotriazinyl dyes, are more prone to hydrolysis and the dye molecules may engage one chlorine atom to react with the fiber, while the other reacts with water forming partially hydrolyzed dye, which is difficult to remove from the dyed cotton. In contrast, the mono-chlorotriazinyl dyes, due to the existence of only one reactive site, are either hydrolyzed or react with cotton, and are easier to remove during the final washing.[14,15]

The consumption of water in the final rinse is significant, as about 75% of total water consumption is related to the rinse.[16]

The present work has been focused on the application of statistical methods for the optimization of the reactive dyeing final rinsing process. In this paper, Plackett-Burman experimental design, a fractional factorial design,[17] has been used to statistically evaluate the importance of each step of the washing-off process in order to reduce water and energy consumption, as well as wastewater pollution in the final washing of reactive dyeing. This design was preferred based on its ability to screen and evaluate the relevant factors that affect a process, indicating how each factor influences the overall response.[18]

EXPERIMENTAL

Materials

We used two reactive dyes: a mono-chlorotriazinyl dye (Reactive Orange 13) and a di-chlorotriazinyl dye (Reactive Blue 4), both supplied by Dintex Dyechem Ltd. The chemical structures of the dyes are illustrated in Figure 2.

The dyes were used without purification. To obtain stock solutions of 10 g/L, each dyestuff was pasted with cold water and dissolved in boiling water, while stirring in a 1 L volumetric flask. The solutions were boiled to ensure complete dissolution and then filtered. The dyeing solutions were prepared by diluting the stock solutions using volumetric pipettes and volumetric flasks.

Scoured and bleached woven 100% cotton (weight 197 g/m^2) was used for all the dyeing processes.

All the chemicals used in this study (NaOH, Na_2CO_3, CH_3COOH) were purchased from Merck with the exception of the soaping agent (Cotoblanc NSR), which was obtained from CHT Bezema.

Dyeing/rinsing procedure

All dyeings were performed at a liquor ratio of 20:1 in an Ahiba lab dyeing machine, according to the recipes shown in

Table 1. The final washing process comprises several rinsing baths, as indicated in Table 2.

Table 1
Dyeing recipes and stepwise conditions

	Mono-chlorotriazinyl dye	Di-chlorotriazinyl dye
Dye concentration, %	3	3
Starting temperature (°C)	40	30
Dyeing before salt addition (min)	25	25
Salt (g/L)	75	40
Time of salt treatment (min)	60	45
Temperature of salt treatment (°C)	80	45
Na_2CO_3 (g/L)	8	8
NaOH (g/L)	2	-
Temperature for fixation (°C)	75	45
Time of fixation (min)	45	45

Table 2
Final washing of reactive dyeing

	Temperature	Chemicals
Overflow rinse	15	-
Warm rinse	50	-
Neutralization	50	3 g/L Acetic acid
Overflow rinse	15	-
Hot soaping	95	2 g/L Cotoblanc NSR
Warm rinse	50	-
Overflow rinse	15	-
Hot soaping	95	2 g/L Cotoblanc NSR
Warm rinse	50	-
Overflow rinse	15	-
Neutralization	40	2 g/L Acetic acid

Calculation of hydrolyzed dye removal

Calibration curves were used in order to find the concentration of the hydrolyzed dye in the global washing wastewater. The calibration curves were obtained by measuring the absorbance of the dye solution of known concentrations. Absorbance was measured with a Spectro UV/Vis Dual Beam Labomed UVS-2800 spectrophotometer at the wavelength of maximum absorption (488 nm for Reactive Orange 13 and 598 nm for Reactive Blue 4).

Experimental design

Experimental design is the branch of statistics that deals with planning the experiment according to the objective of the study, leading the experiment according to the planning, gathering the results, analyzing the data by the analysis of variance technique and, as a final point, drawing the conclusions on the basis of analysis.[19]

The experiments were designed according to the Plackett-Burman design to find the washing process steps that significantly influence the hydrolyzed dye removal. The Plackett-Burman design, a two-level multifactorial design based on the rationale known as balanced incomplete blocks, is an effective method to screen for the significant factors among a large number of variables,[20] which can be used to rapidly search for key factors from a multivariable system, allowing the study of multiple factors in a systematic and logical way,[21] which can provide essential information about each factor from few experiments.[22,23,24] The Plackett-Burman experimental design identifies the process variables by screening *n* variables in $n + 1$ experiments,[25] when the number of runs is a multiple of 4. This design involves that the frequency of each level of a factor should be equal and that in each test the number of high and low factors should be equal.[26]

The statistical software package MINITAB (Release 17.1.0.0, PA, USA) has been used. The design, being an orthogonal design, reflects only the main effect of the variables,[27] assuming that there are no interactions between the studied variables in the range taken into consideration.[28] The Plackett-Burman experimental design can be characterized by a first-order polynomial equation:[29]

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i \quad (1)$$

where Y = the response; β_o = the model intercept; β_i = the coefficients of the model; x_i = the variables.

The Plackett-Burman design comprised 11 assigned variables (A – L) spanning over 20 runs with each variable fixed at two levels (namely, a low level and a high level)[30] and one response variables (Y): the hydrolyzed dye concentration in the wastewater, expressed in g/L and determined from the calibration curves. The levels of each factor were set based on the experience from preliminary experiments.[31]

The variables of the washing process (Table 2), which were selected for the designed experiments, and the low level (– 1) and high level (+ 1) of each factor are listed in RESULTS AND DISCUSSION

Table 4 presents the eleven assigned variables screened in the 20 experimental runs for the mono-chlorotriazinyl dye Reactive Orange 13 (response Y1) and the di-chlorotriazinyl dye Reactive Blue 4 respectively (response Y2).

In order to establish the influence of the studied variables on hydrolyzed dye removal, statistical analyses were performed by means of ANOVA using the Minitab software, which calculates the sum of squares (SS), F-values, p-values, t-values and confidence intervals.

The results for Reactive Orange 13 are shown in Table 5.

Table 3.

RESULTS AND DISCUSSION

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Table 3
Factors tested in the Plackett-Burman design and their levels

Variables	Overflow rinse	Warm rinse	Neutralization	Overflow rinse	Hot soaping	Warm rinse	Overflow rinse	Hot soaping	Warm rinse	Overflow rinse	Neutralization
Coded	A	B	C	D	E	F	G	H	J	K	L
Low level	without	50°C	without	without	-	50°C	without	-	50°C	without	without
High level	with	95°C	with	with	2 g/L Cotoblanc NSR	95°C	with	2 g/L Cotoblanc NSR	95°C	with	with

Table 4
Plackett-Burman experimental design matrix for screening of significant factors and results for the two studied reactive dyes

	A	B	C	D	E	F	G	J	K	L	M	Y1	Y2
1	+	-	+	+	-	-	-	-	+	-	+	221.77	237.12
2	+	+	-	+	+	-	-	-	-	+	-	258.12	261.65
3	-	+	+	-	+	+	-	-	-	-	+	237.53	237.42
4	-	-	+	+	-	+	+	-	-	-	-	204.08	231.75
5	+	-	-	+	+	-	+	+	-	-	-	209.98	237.17
6	+	+	-	-	+	+	-	+	+	-	-	276.33	290.97
7	+	+	+	-	-	+	+	-	+	+	-	291.13	288.32
8	+	+	+	+	-	-	+	+	-	+	+	257.90	260.89

9	-	+	+	+	+	-	-	+	+	-	+	267.27	264.26
10	+	-	+	+	+	+	-	-	+	+	-	270.20	276.63
11	-	+	-	+	+	+	+	-	-	+	+	267.72	272.00
12	+	-	+	-	+	+	+	+	-	-	+	231.04	251.49
13	-	+	-	+	-	+	+	+	+	-	-	273.02	279.44
14	-	-	+	-	+	-	+	+	+	+	-	201.43	243.73
15	-	-	-	+	-	+	-	+	+	+	+	225.29	246.23
16	-	-	-	-	+	-	+	-	+	+	+	194.76	225.74
17	+	-	-	-	-	+	-	+	-	+	+	222.32	234.12
18	+	+	-	-	-	-	+	-	+	-	+	237.67	258.21
19	-	+	+	-	-	-	-	+	-	+	-	204.11	225.36
20	-	-	-	-	-	-	-	-	-	-	-	147.05	185.87

Table 5
Analysis of Variance (ANOVA) for Reactive Orange 13

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	11	23831.2	98.51%	23831.2	2166.47	48.16	0.000
Linear	11	23831.2	98.51%	23831.2	2166.47	48.16	0.000
A	1	3230.9	13.36%	3230.9	3230.88	71.82	0.000
B	1	9807.1	40.54%	9807.1	9807.13	218.01	0.000
C	1	275.3	1.14%	275.3	275.28	6.12	0.038
D	1	2246.8	9.29%	2246.8	2246.78	49.94	0.000
E	1	845.5	3.50%	845.5	845.52	18.80	0.002
F	1	4458.1	18.43%	4458.1	4458.10	99.10	0.000
G	1	75.0	0.31%	75.0	75.04	1.67	0.233
H	1	74.7	0.31%	74.7	74.73	1.66	0.233
J	1	2398.5	9.91%	2398.5	2398.49	53.32	0.000
K	1	38.7	0.16%	38.7	38.70	0.86	0.381
L	1	3230.9	13.36%	3230.9	3230.88	71.82	0.000
Error	8	359.9	1.49%	359.9	44.99		
Total	19	24191.1	100.00%				

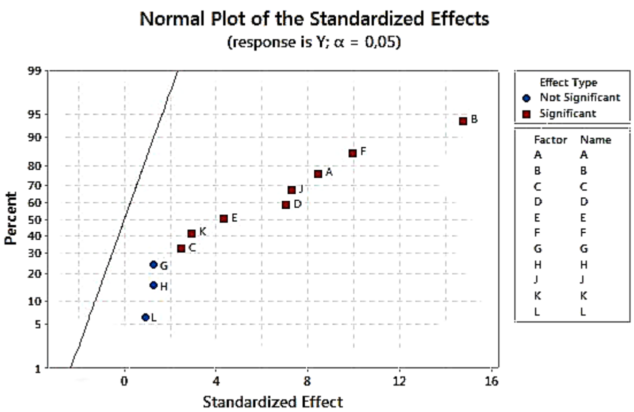

Figure 3: Normal plot of standardized effects of rinsing process factors for Reactive Orange 13 removal

The R^2 value was 98.51%, which indicates that 98.51% of the variability in the response can be described by the model, and it shows an adequate agreement between experimental and predicted values, as a regression model with R^2 closed to 1.0 is considered to have a very high correlation.[32]

The coefficient of determination (adjusted R^2) was 96.47%, signifying a good agreement between the experimental and the predicted values of the response.[25]

The first-order polynomial regression equation for Reactive Orange 13 in uncoded units is:

Y = 234.94 + 12.71 A + 22.14 B + 3.71 C + 10.60 D + 6.50 E + 14.93 F + 1.94 G + 1.93 H + 10.95 J

$+ 4.36\ K + 1.39\ L$ (2)

A large coefficient (either positive or negative) shows that a factor has an important impact on the response, whereas a coefficient close to zero indicates that a factor has little or no effect.

The factors significant at a 95% level (p-value < 0.05) were considered consistent.[33] A normal plot of the standardized effects of process factors, indicating the significance of the individual variables, is shown in Figure 3. In this probability plot, points that do not fall near the line usually indicate significant effects at a 5% significant level. Significant effects are larger and generally further from the fitted line than insignificant effects, which tend to be smaller and centered on zero. As can be seen from this figure, factors G, H and L are not significant and do not influence the response.

The results of the Plackett-Burman experimental design are presented as a standardized Pareto chart consisting of bars with a length proportional to the ratio between the absolute value of the estimated effects and the standard error, shown in order of the size of the effects, with the biggest effects at the top. This Pareto chart of the effects enables the determination of the magnitude and the importance of an effect. The chart displays the absolute value of the effects and draws a reference line on the chart, any effect that ranges past this reference line being statistically significant.

The Pareto plot corroborates the findings in the normal probability plot. From this figure, it can be seen that the temperature of both first and second warm rinsing baths was considered to have the most important effect on the hydrolyzed dye removal. The factors were organized in the order of significance as follows: B (first warm rinsing bath) > F (second warm rinsing bath) > A (first overflow rinse > J (third warm rinsing bath) > D (second overflow rinse) > E (first hot soaping) > K (last overflow rinse) > C (first neutralization) > G (third overflow rinse) > H (second hot soaping) > L (last neutralization).

The main effects plot is a plot of the means at each level of a factor, where a reference line at the grand mean of the response data is drawn. These plots can be used to compare the magnitudes of the main effects (a main effect happens when the mean response changes across the levels of a factor) and to compare the relative strength of the effects across factors.

As shown in Figure 5, all the factors have positive effects on hydrolyzed reactive dye removal, but for five of them (C, G, H, K, L) the effect is negligible. It can be observed that for the mono-chlorotriazinyl dye, the hydrolyzed dye removal process is highly dependent on the hot rinsing baths (especially the first two). An increase in the temperature of these baths leads to a significant improvement of the removal process, while the soaping bath and the neutralization baths have very little influence. Nevertheless, the first rinsing bath (factor A) still plays a significant role in the rinsing process.

The results of the statistical analyses performed by use of ANOVA for the di-chlorotriazinyl dye (Reactive Blue 4) are shown in Table 6.

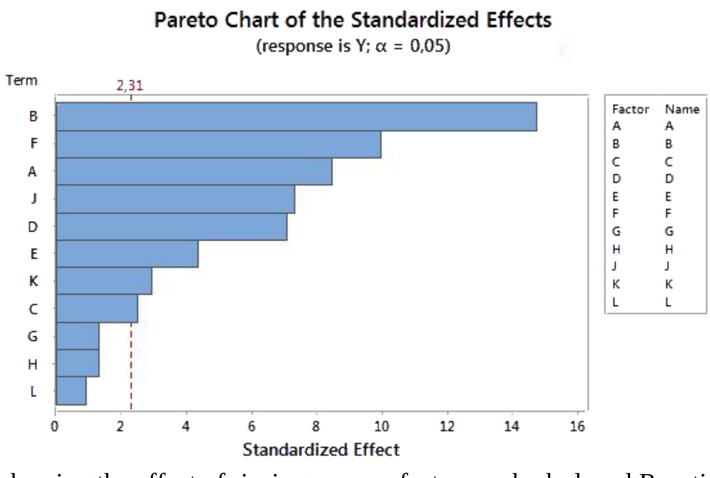

Figure 4: Pareto chart showing the effect of rinsing process factors on hydrolyzed Reactive Orange 13 removal

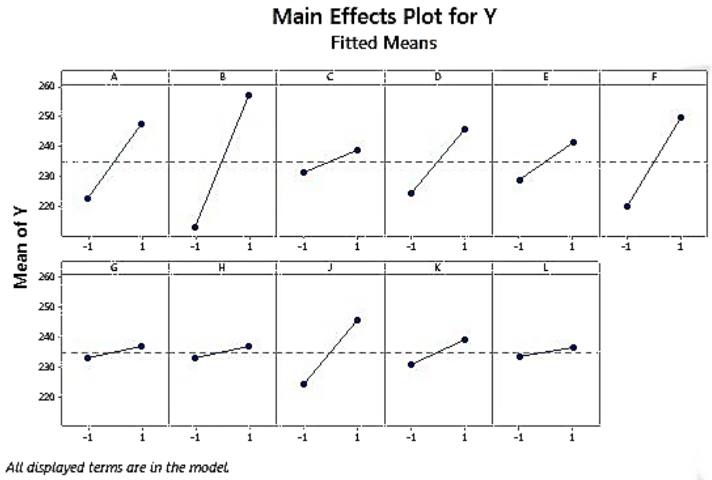

Figure 5: Main effects plot for Reactive Orange 13 removal

Table 6
Analysis of Variance (ANOVA) for Reactive Blue 4

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	11	12038.8	98.95%	12038.8	1094.44	68.58	0.000
Linear	11	12038.8	98.95%	12038.8	1094.44	68.58	0.000
A	1	1707.0	14.03%	1707.0	1707.00	106.97	0.000
B	1	3609.2	29.66%	3609.2	3609.18	226.17	0.000
C	1	32.7	0.27%	32.7	32.69	2.05	0.190
D	1	792.7	6.52%	792.7	792.67	49.67	0.000
E	1	647.0	5.32%	647.0	646.95	40.54	0.000
F	1	2170.9	17.84%	2170.9	2170.90	136.04	0.000
G	1	397.0	3.26%	397.0	397.03	24.88	0.001
H	1	173.8	1.43%	173.8	173.76	10.89	0.011
J	1	2267.0	18.63%	2267.0	2266.96	142.06	0.000
K	1	185.9	1.53%	185.9	185.87	11.65	0.009
L	1	55.8	0.46%	55.8	55.81	3.50	0.098
Error	8	127.7	1.05%	127.7	15.96		
Total	19	12166.5	100.00%				

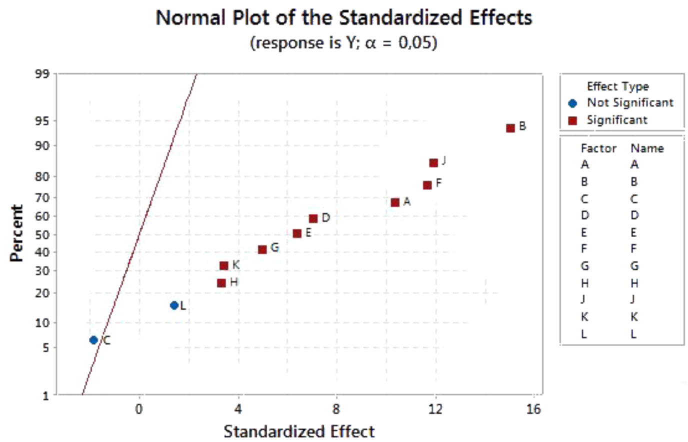

Figure 6: Normal plot of standardized effects of rinsing process factors for Reactive Blue 4 removal

The goodness of fit of the model, checked by the determination coefficient (R^2), indicated that 98.95% of the total variability in the response could be explained by this model and only 1.15% of the total variation was not explained. Consequently, the R^2-value reflected a very good fit between the observed and predicted responses, and implied that the model is reliable for predicting the removal of hydrolyzed Reactive Blue 4. The high value of the adjusted determination coefficient (Adj R^2 = 97.51%) confirmed the significance of the model.

The first-order polynomial regression equation in uncoded units for Reactive Blue 4 is:

$$Y = 250.419 + 9.239 A + 13.434 B + 1.278 C + 6.295 D + 5.688 E + 10.419 F + 4.455 G + 2.948 H + 10.647 J + 3.049 K - 1.671 L \quad (3)$$

From the normal plot of the standardized effects of process factors (Fig. 6), it can be seen that factors C and L are not significant and do not influence the response.

From the standardized Pareto chart, it can be seen that the temperature of the three warm rinsing baths has the most important effect on Reactive Blue 4 hydrolyzed dye removal. The factors were organized in the order of significance as follows: B (first warm rinsing bath) > J (third warm rinsing bath) > F (second warm rinsing bath) > A (first overflow rinse > D (second overflow rinse) > E (first hot soaping) > G (third overflow rinse) > K (last overflow rinse) > H (second hot soaping) > L (last neutralization) > C (first neutralization).

The main effects plot shows the high strength of the effect of B, F and J factors, as in the case the mean response changes significantly across the levels of the factor.

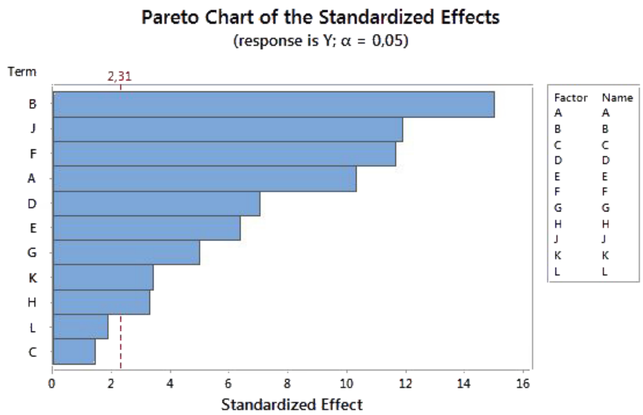

Figure 7: Pareto chart showing the effect of rinsing process factors on hydrolyzed Reactive Blue 4 removal

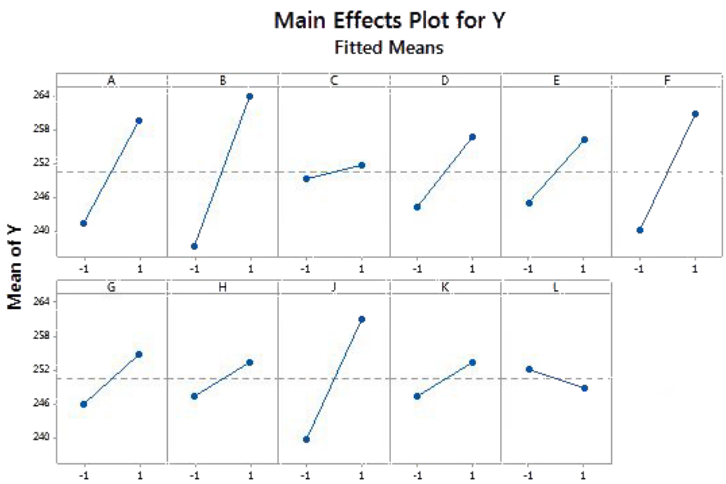

Figure 8: Main effects plot for Reactive Blue 4

As can be seen from Figure 8, all the factors have positive effects on hydrolyzed reactive dye removal, with the exception of the last one, which has a minor negative effect.

CONCLUSION

Plackett-Burman design was employed to screen the parameters of reactive final wash-off of two reactive dyes. This study shows the usefulness of using the Plackett-Burman experimental design as an exploratory optimization method, which helps in screening and assessing the wash-off steps affecting hydrolyzed reactive dye removal.

The analysis of the results demonstrated that, in the case of the mono-chlorotriazinyl dye (Reactive Orange 13), the first two warm rinses and the first overflow rinse were the main effective parameters on hydrolyzed dye removal, while for the di-chlorotriazinyl dye (Reactive Blue 4), the main effective parameters were the three warm rinse steps. The third overflow rinse, the last hot soaping and the last neutralization proved to be insignificant for the removal process of Reactive Orange 13, while both neutralization steps showed limited influence on the removal of Reactive Blue 4.

As a result, it can be concluded that using high temperature rinse, the number of cold washing baths may be reduced, especially for the di-chlorotriazinyl dyes, and the neutralization can be completely left out for the same class of reactive dyes, while only one neutralization bath can be beneficial for the removal of the mono-chlorotriazinyl dyes. In this way, water and time consumption, as well as the use of detergent and alkali, can be significantly reduced. Not only water and chemicals consumption is lower, but also the wastewater generated is less polluted.

The results require further experimentation for thorough investigation of the significant factors and their interaction effects.

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