INVESTIGATION INTO AN ECO-FRIENDLY REACTIVE DYEING PROCESS OF COTTON FABRICS USING AN ETHANOL-WATER MIXTURE THROUGH DESIGN OF EXPERIMENT

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Textile industry professionals are unanimous that there is a great need to develop environmentally sustainable methods of cotton dyeing. Among various problems related to conventional dyeing, some of the main problems consist in the large volumes of discharge effluent with a high concentration of salt and their impact on the environment. This investigation explores the use of ethanol as a solvent in the reactive dyeing of cotton fabric, to reduce the concentration of salt and the volume of water used. The dyeing process employed a 90:10 (v/v) ethanol-water mixture. Time and temperature were varied periodically to improve the degree of exhaustion, and the effects of time, temperature and salt content were studied and compared with conventional reactive dyeing. It was observed that the colour strength of solvent-assisted reactive dyeing is comparable to the conventional process. The dyed sample under the optimum condition had good wash fastness, both in terms of shade change and staining, and its dry crocking fastnesses were found similar or acceptable in comparison with the water-dyed sample. However, all the samples of the solvent-assisted reactive dyeing process have better wet crocking fastnesses compared to the conventional reactive dyeing process. The process parameters of eco-friendly reactive dyeing have been optimised using the composite desirability function. The optimal process parameters for the solvent-assisted reactive dyeing process were found to be 60 minutes of dyeing at 80 °C with 20 g/L of salt.

Keywords: ethanol, eco-friendly dyeing, wash fastness, design of experiments, reactive dyes

INTRODUCTION

Cotton has been the most important fibre resource since the beginning of time, due to its exceptional properties, such as softness, breathability, dye uptake, hydrophilicity and biodegradability. Despite these outstanding properties, cotton requires an immense amount of water for dyeing.[1]

Cotton can be dyed with various types of synthetic dyes, including direct dyes, vat dyes, sulphur dyes, insoluble azo dyes and reactive dyes, among which the reactive dyes have become the most preferred ones due to their brilliant colours, excellent wet-fastness and low price. Among all the other dyes, reactive dyes show the best colour fastness on cotton due to their covalent bonding with the fibre polymer in the presence of alkali.[1]

The textile dyeing industry has consistently been a major contributor to global environmental pollution,[2] owing to the heavy discharges during the dyeing processes. This includes a huge variety of fibres, inorganic salts, alkalis, surfactants, finishing products, and organic matter such as dyes. Predominantly, reactive dyeing of cotton fabric generates effluents with high oxygen demand, colour, and salt load.[3,4] The discharge of alkaline wastewater with high concentrations of electrolytes and hydrolyzed dyes makes reactive dyeing an unsustainable process.[5] There are two approaches to dealing with the effluent problem: by using alternative dyeing techniques/technology or by effluent treatment after dyeing. The latter requires additional capital investment and high treatment and maintenance costs. Therefore, the first approach is always preferable.[6]

The recent trends in the textile industry are aimed to improve the environmental performance of the processes by reducing the consumption of energy, water and chemicals. The traditional dyeing procedure requires a huge amount of water, chemicals, dyestuff, acid, alkali and auxiliaries. These processes can have harmful effects on the environment; especially the dye process effluent can cause major complications in marine and coral life. Furthermore, the use of salt in reactive dyeing can lead to the increased salinity of water.[1,7]

Various reactive dyeing techniques have been investigated, which have substituted dyeing additives and water with alternate solvents.[1,6–8]

Conventional reactive dyeing requires a large amount of water for the dyeing of fabric, which is a threat to the increasing scarcity of water. Over time, the replacement of water with green solvents is gaining popularity. Green solvents are defined as solvents that have minimal environmental influence arising from their use in chemical production.[9] As a green solvent, ethanol has the advantages of wide availability,[10] non-toxicity,[11,12] low boiling point,[11,13] low surface tension,[14] low price[15] and biodegradability.[11] Studies have revealed that ethanol-water mixtures are environmentally favourable compared to pure ethanol.[9] Furthermore, ethanol can be recycled using the azeotropic distillation method, which is considered a mature procedure for producing absolute ethanol from ethanol-water mixtures.[16]

The present study is aimed to explore the possibility of replacing water with an ethanol-water mixture and reducing the amount of salt in the dyeing process. The eco-friendly reactive dyeing process at three different dyeing times (40, 60 and 80 minutes), dyeing temperatures (40, 60 and 80 °C) and concentrations of salt (0, 20, 40 g/L) were investigated using DOE (design of experiments) to achieve the best dyeing performance. The ethanol-water dyeing method was compared with that of the conventional aqueous dyeing method by examining colour strength (K/S), colour fastness to laundering (colour change and staining) and colour fastness to dry and wet crocking. The process parameters of solvent-assisted dyeing have been optimised using multi-response optimisation through the desirability function.

EXPERIMENTAL

Materials

Bleached and mercerized cotton fabric with a GSM (grams per meter square) of 87 was used in this study. The ends and picks per inch of the fabric were measured to be 76 and 70, respectively.

Dyes and auxiliaries

The fabric was dyed with Reactive dye (Drimaren Red CL-4BN) kindly donated by Archroma Limited (Pakistan). Sodium sulfate (Na_2SO_4) salt was used to assist the conventional dyeing method. Soda ash was used to adjust the pH of the reactive dye bath for cellulosic fabric. In the presence of these chemicals, the dye reacts with the cellulosic substrate, making a permanent connection that holds the dye to the fibre. Pure ethanol was used as a solvent along with water to assist the eco-friendly dyeing method.

Dyeing methods

All dyeings were carried out in sealed stainless steel dye pots housed on an Ahiba Nuance ECO laboratory dyeing machine at a liquor-to-goods ratio of 20:1.

Conventional dyeing

Following the manufacturer's guidelines, the cotton fabric was introduced into a dye bath containing 2% o.w.f (weight of the fabric) dye and treated for 10 minutes at 60 °C, followed by the addition of 40 g/L sodium sulfate into the dye liquor. After another 30 minutes, 15 g/L sodium carbonate was added and allowed to fixate for an hour (60 minutes). The sample was rinsed firstly with warm water and then with cold water and air-dried after washing.

Eco-friendly dyeing (solvent-assisted dyeing)

For eco-friendly dyeing, the fabric was dipped in 15 g/L sodium carbonate for 30 minutes, then dyed in a bath containing a 9:1 ethanol-water mixture, with and without salt, at three different time intervals (40, 60 and 80 minutes) and temperatures (40, 60 and 80 °C). The parameters and their respective levels are exhibited in Table 1.

Determination of fastness properties

The colour fastness of the dyed fabrics was tested according to ISO standard methods, including fastness to washing (ISO 105 C06/C1S) and rubbing (ISO 105 X12).

Colour measurement

The colourimetric data of the dyed fabrics were measured using a Datacolour Spectroflash 600 spectrophotometer, with a 10º standard observer and D65 illuminant, and were the average of four measurements. The colour strength (K/S) was evaluated using the Kubelka–Munk equation (1):

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1-R_\lambda)^2}{2R_\lambda} \quad (1)$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance expressed as a fractional value at a wavelength of maximum absorption λ.

Experiment design

Design of Experiments (DOE) is a powerful research and analysis tool that can be used when more than one input factor is supposed to influence an output. It allows for multiple input factors to be manipulated, determining their effect on the desired output (response). 3^3 full factorial design has been selected to examine the effect of three potential factors, namely: (A) dyeing time, (B) dyeing temperature, (C) amount of salt, on the eco-friendly reactive dyeing process employed with the ethanol-water mixture using the design of experiment (DOE) technique. The factors and their respective levels are outlined in Table 1.

The eco-friendly reactive dyeing process was explored at three different dyeing times (40, 60 and 80 minutes), dyeing temperatures (40, 60 and 80 °C) and concentrations of salt (0, 20, 40 g/L). The depth of shade was maintained at 2% o.w.f. The dyeing process employed a 90: 10 (v/v) ethanol-water mixture. Time and temperature were varied periodically to improve the degree of exhaustion, and the effects of time, temperature and salt content were studied and compared with the conventional reactive dyeing process. The experiments were performed in random order as per the design matrix shown in Table 2.

To examine the effect of eco-friendly reactive dyeing, five responses, namely, colour yield (K/S), colour fastness to laundering (colour change and staining) and colour fastness to dry and wet crocking were measured. Each response variable has been tested as per the standard test procedure described above. The results of the conventional reactive dyeing process and eco-friendly reactive dyeing using an ethanol-water mixture were presented in Table 3. The analysis of variance (ANOVA) was conducted using Minitab 17 software to scrutinize the significant factors and interactions of the selected responses. The summary of ANOVA, significant factors and interactions of leading responses were tabulated in Table 4. The process parameters of eco-friendly reactive dyeing have been optimised using the composite desirability function.

Table 1
3^3 Full factorial design matrix of the eco-friendly reactive dyeing process

Factor	Name	Level		
		-1	0	+1
A	Dyeing time (minutes)	40	60	80
B	Dyeing temperature (°C)	40	60	80
C	Amount of salt (g/L)	0	20	40

Table 2
Randomized complete experimental run order

Run No.	Time (minutes)	Temperature (°C)	Amount of salt (g/L)
1	80	80	40
2	80	80	20
3	80	80	0
4	80	60	40
5	80	60	20
6	80	60	0
7	80	40	40
8	80	40	20
9	80	40	0
10	60	80	40
11	60	80	20
12	60	80	0
13	60	60	40
14	60	60	20
15	60	60	0
16	60	40	40
17	60	40	20
18	60	40	0

19	40	80	40
20	40	80	20
21	40	80	0
22	40	60	40
23	40	60	20
24	40	60	0
25	40	40	40
26	40	40	20
27	40	40	0

Table 3
Experimental results of eco-friendly reactive dyeing using ethanol-water mixture

Run order	K/S	Wash fastness		Crocking fastness	
		Shade change	Staining	Dry	Wet
Conventional	12.56	4-5	3-4	3-4	2-3
1	11.27	4	3-4	4-5	3
2	10.92	4	3	4-5	3
3	7.69	3-4	3-4	4	3-4
4	5.72	3	3-4	4-5	3-4
5	10.31	3	3	4	2-3
6	9.55	3-4	2-3	4-5	3
7	3.78	4-5	3-4	4	3
8	3.63	3-4	4	4-5	2
9	3.95	3-4	4	4-5	4
10	7.83	4	3-4	4-5	3
11	11.04	4	3-4	4-5	3-4
12	2.89	3-4	4	4-5	4-5
13	8.64	3-4	3	4-5	3-4
14	8.77	4	3	4-5	3-4
15	5.17	3-4	3-4	4-5	3-4
16	8.79	3	3-4	4-5	4
17	6.15	3	3-4	4-5	4
18	5.70	3	4	4-5	4
19	8.91	4	3-4	4-5	3
20	4.77	4-5	4	4-5	3
21	7.61	3-4	4	4-5	3
22	10.59	3-4	4	4-5	3
23	10.59	3-4	3-4	4-5	3
24	6.53	3-4	4	4-5	3
25	5.90	1-2	3	4-5	3
26	6.15	2	3-4	4-5	3-4
27	6.75	1-2	3	5	4

RESULTS AND DISCUSSION

Analysis of variance

The analysis of variance (ANOVA) is the statistical tool for testing the number of variables that affect a response of the experimental design to identify significant factors and interactions leading towards quantitative concrete conclusions. The summary of ANOVA of all five responses has been presented in Table 3. With a 95% confidence interval, the model p-value less than 0.05 implies the significance of the respective response. From the analysis of variance, it is ascertained that all responses have a significant impact on the eco-friendly reactive dyeing process. The significant factors and interactions of the individual responses are outlined in Table 4 and discussed below.

Investigation of colour strength (K/S)

The colour strength values of the eco-friendly reactive dyeing process using an ethanol-water mixture were assessed for all the experimental runs. The K/S value for conventional dyeing was found to be 12.56. To obtain the maximum colour strength from the solvent-assisted dyeing process, the effect of three different levels of dyeing time, dyeing temperature and amount of salt were investigated by ANOVA. The summary of ANOVA presented in Table 4 revealed that the K/S value of the reactive dyed fabrics using an ethanol-water mixture is substantially dependent on dyeing temperature, amount of salt and the interaction of dyeing time and temperature. The main effects and interaction plot for colour strength are presented in Figures 1 and 2.

It is evident from the main effect plot of K/S that reactive dyeing using an ethanol-water mixture with a dyeing temperature of 60 °C and 20 g/L salt concentration leads to higher colour strength value. However, the interaction of dyeing time and temperature was found to be significant through the analysis of variance. Consequently, it is requisite to make inferences of colour strength through the interaction plot of K/S rather than the main effect plot.

Table 4
Summary of ANOVA results of 3^3 full factorial design

Source	DF[a]	Adj SS[b]	Adj MS[c]	$F_{Statistics}$[d]	p-value[e]	Remarks
Colour strength (K/S)						
Model	18	165.715	9.206	2.028	< 0.001	Significant
Error	8	36.27	4.539			Insignificant
[f]R^2= 0.9729; [g]R^2adj = 0.9523						
Significant factors: Temperature, Amount of salt						
Significant Interactions: Time*Temperature						
Wash fastness (change of shade)						
Model	18	12.0741	0.6707	3.29	< 0.001	Significant
Error	8	1.6296	0.2037			Insignificant
[f]R^2= 0.9523; [g]R^2adj = 0.9235						
Significant factors: Temperature, Amount of salt						
Significant Interactions: Time*Temperature, Temperature*Amount of salt						
Wash fastness (staining)						
Model	18	13.3519	0.5133	5.99	< 0.001	Significant
Error	8	0.6852	0.0856			Insignificant
[f]R^2= 0.9813; [g]R^2adj = 0.9713						
Significant factors: Time, Temperature						
Significant Interactions: Time*Temperature						
Dry crocking						
Model	18	2.389	0.1327	1.37	< 0.001	Significant
Error	8	0.7778	0.0972			Insignificant
[f]R^2= 0.9029; [g]R^2adj = 0.895						
Significant factors: Time						
Significant Interactions: Temperature* Amount of salt						
Wet Crocking						
Model	18	4.500	0.2500	1.47	< 0.001	Significant
Error	8	1.809	0.17361			Insignificant
[f]R^2= 0.9132; [g]R^2adj = 0.892						
Significant factors: Time, Temperature, Amount of salt						
Significant Interactions: NIL						

Notes: [a]Degree of freedom; [b]Adjusted sum of squares; [c]Adjusted mean squares; [d]The test statistic used in the analysis of variance; [e]A measure of the probability that an observed difference could have occurred just by random chance; [f]Coefficient of determination/goodness of fit; [g]Adjusted coefficient of determination

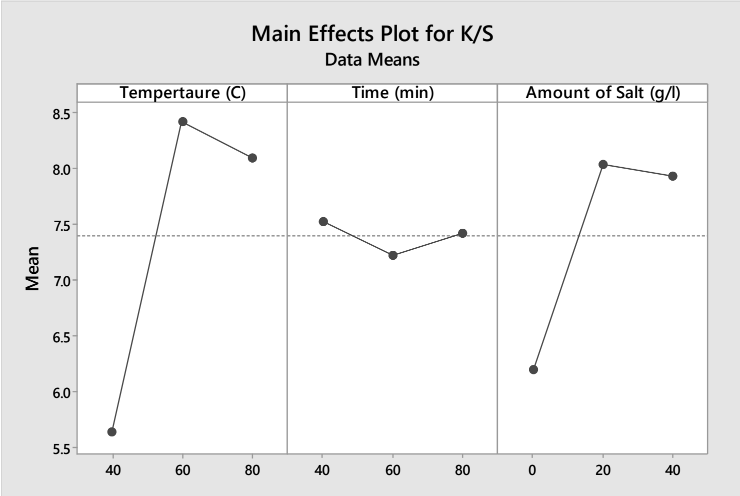

Figure 1: Main effects plot for K/S of solvent-assisted reactive dyeing

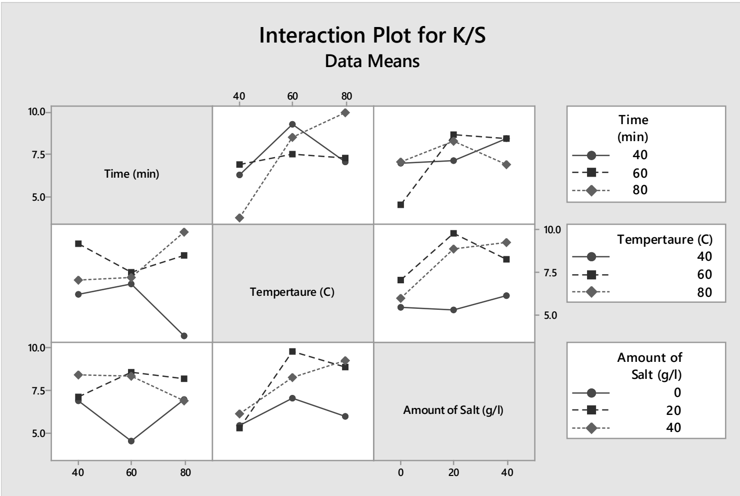

Figure 2: Interaction plot for K/S of solvent-assisted reactive dyeing

By examining the dyeing time and temperature interaction plot of K/S, it is revealed that maximum colour strength was observed at 80 °C with 80 minutes of dyeing with a value of 10.92. This is because the fixation temperature has a great influence on the dyeing properties of the cotton fabric. A higher temperature and duration can swell the fibres and support the adsorption, diffusion and penetration of the dyes. Although, comparable results of colour strength were obtained with 60 minutes of dyeing at 80 °C. It was observed that at lower temperatures and times, the dyeing was uneven and also showed poor results in terms of colour strength and fixation rate. The colour strength of solvent-assisted reactive dyeing is comparable to the conventional reactive dyeing process.

The K/S values of solvent-assisted reactive dyeing with salt concentrations 0, 20 and 40 g/L at a dyeing time-temperature profile of 80 °C for 80 minutes were recorded to be 7.69, 10.92 and 11.27, respectively. Hence, it is not only the dyeing time and temperature that would affect the colour strength and fixation rate, but the salt concentration also played an imperative role in the solvent-assisted dyeing process. Salt increases the affinity of reactive dye to cellulosic fibre. The presence of 20 g/L of salt makes the dye liquor more ionic, which, together with the application of heat to the dye liquor, increases the energy of the reactive dye molecules in the dye bath, leading to increased absorption of the dye.

Investigation of colour fastness to washing

The colour fastness to washing of solvent-assisted reactive dyeing was tested by assessing shade change and staining on adjacent fabric resulting from desorption and or abrasion action by ISO 105 C06/C1S. Fastness ratings were assigned by using a grey scale for colour change and a grey scale for colour staining. It is confirmed from the ANOVA results presented in Table 4 that two of the main factors, namely, dyeing temperature and amount of salt, as well as the interactions of time-temperature and temperature-amount of salt, are significant for the change of shade in the eco-friendly colouration process. Meanwhile, the interaction of time-temperature is dominating for colour staining of solvent-assisted reactive dyeing. The main factor and interaction plots for the change of shade are presented in Figures 3 and 4.

The main factor plot presented in Figure 3 reveals that samples dyed with a salt concentration of 20 g/L at a dyeing temperature of 60 °C have fair to good colour retention with GS for colour change of 3-4. As time*temperature and temperature*amount of salt are in interaction with each other, the investigation through the interaction plot presented in Figure 4 should be conceded. It is ascertained from the interaction plot that a dyeing time of 80 minutes would give good results of shade change GS for colour change 4, irrespective of the dyeing temperature of 60 or 80 °C. It is evident from the interaction plot of temperature*amount of salt that 20 g/L salt concentration at 60 °C is desirable for attaining good results of colour retention in solvent-assisted reactive dyeing as in reactive dyeing, the function of salt is to promote dyeing as an accelerant. Figure 2 shows that with the increase of the salt concentration, the colour strength gradually increased, but after the amount of sodium sulphate reached 40 g/L, the exhaustion and fixation levels decreased significantly. As for Reactive Red CL-4BN, the best salt concentration was 20 g/L sodium sulfate.

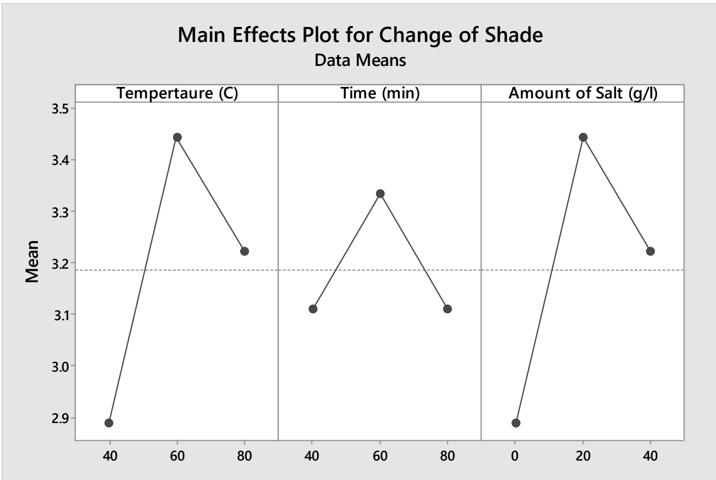

Figure 3: Main effects plot for shade change in solvent-assisted reactive dyeing

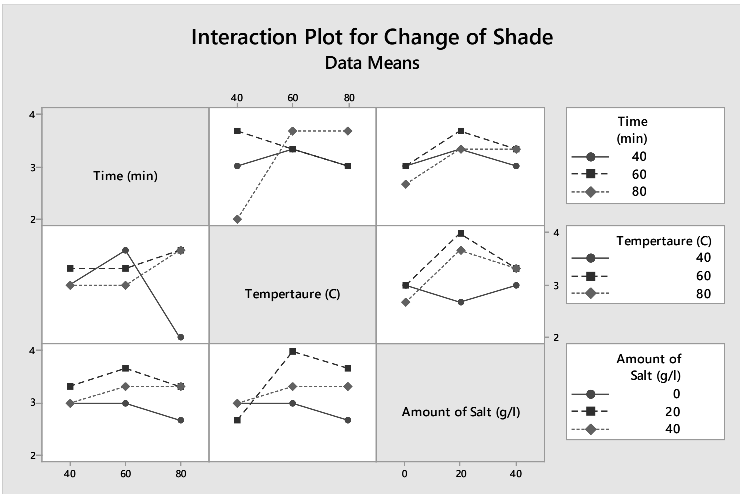

Figure 4: Interaction plot for shade change in solvent-assisted reactive dyeing

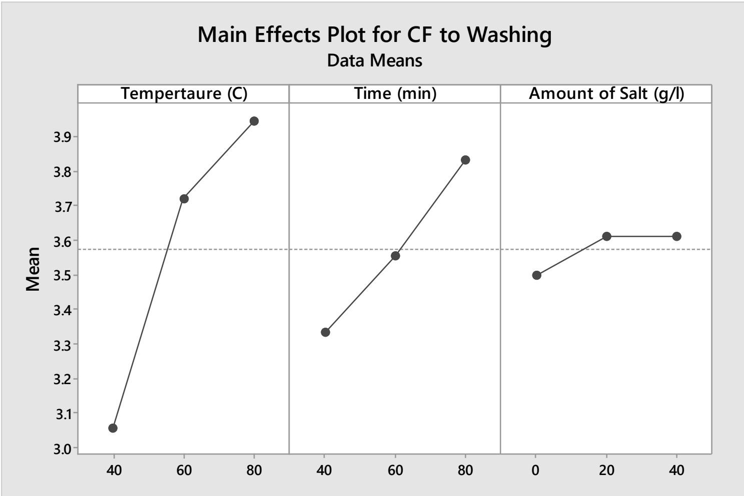

Figure 5: Main effects plot for colour staining in solvent-assisted reactive dyeing

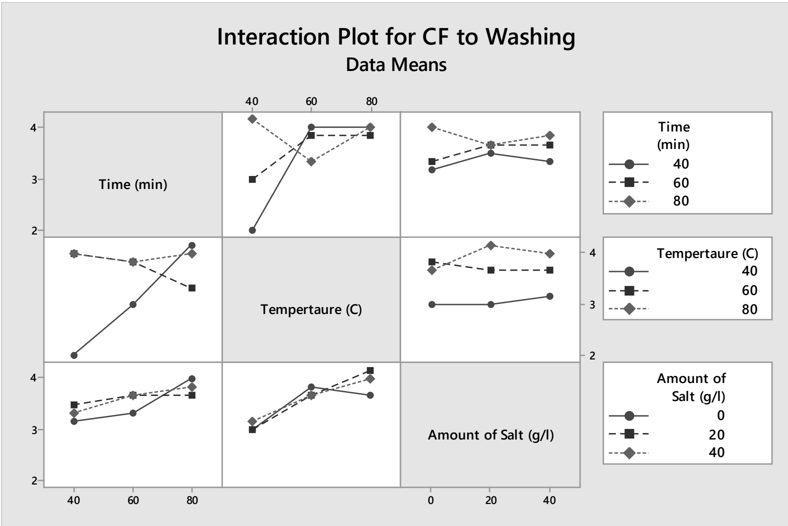

Figure 6: Interaction plot for colour staining in solvent-assisted reactive dyeing

For staining, the grey scale ratings illustrate that dyed samples transfer colour to multi-fibre made from wool, acrylic, polyester, polyamide, cotton, and diacetate in the washing fastness test. Nevertheless, staining is minimum at higher dyeing temperature and time with a GS rating of 4. Also, as inferred from Figures 5 and 6, staining was neither affected by the dyeing time of 60 or 80 minutes nor by the salt concentration of 20 or 40 g/L at 80 °C. Therefore, the dyeing time of 60 °C with 20 g/L of salt is recommended for attaining the benefit of cost and energy savings. Furthermore, the results of both shade change and staining of solvent-assisted dyeing are comparable with those of the conventional reactive dyeing process.

Investigation of colour fastness to crocking

Crocking refers to the rubbing off of colour from fabric when subjected to abrasion; tests were performed that involved wet and dry crocking. The ratings for the crocking fastness of solvent-assisted dyeing were found good to excellent, with GS 4-5 for dry conditions, and fair to good, GS 3-4 for wet conditions, irrespective of the dyeing time, temperature and amount of salt. However, the ANOVA data presented in Table 4 indicate that dry crocking is dependent on the dyeing time and the interaction of dyeing temperature and the amount of salt. The main factor plot presented in Figure 7 displays that samples dyed without salt at lower dyeing temperatures with 60 minutes of dyeing have good to excellent dry crocking (GS 4.5). It is ascertained from the interaction plot in Figure 8 that the same results of dry crocking have been obtained with 20 g/L of salt concentration at 60 or 80 °C (GS 4.5) for the solvent-assisted dyeing.

The wet crocking fastness of the conventional reactive dyeing process was found to be poor to fair GS 2-3, whereas it is evident from Figure 9 that all the samples of solvent-assisted reactive dyeing process have better wet crocking results lying in the range of fair to good GS 3-4. However, the critical examination of the main effects plot revealed that a lower dyeing temperature of 40 to 60 °C with 0–20 g/L of salt at 60 minutes of dyeing is recommended for the attainment of good wet crocking fastness.

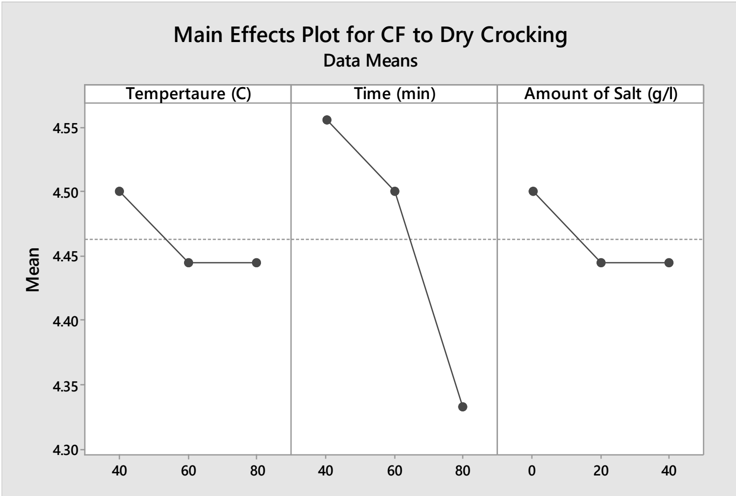

Figure 7: Main effects plot for dry crocking in solvent-assisted reactive dyeing

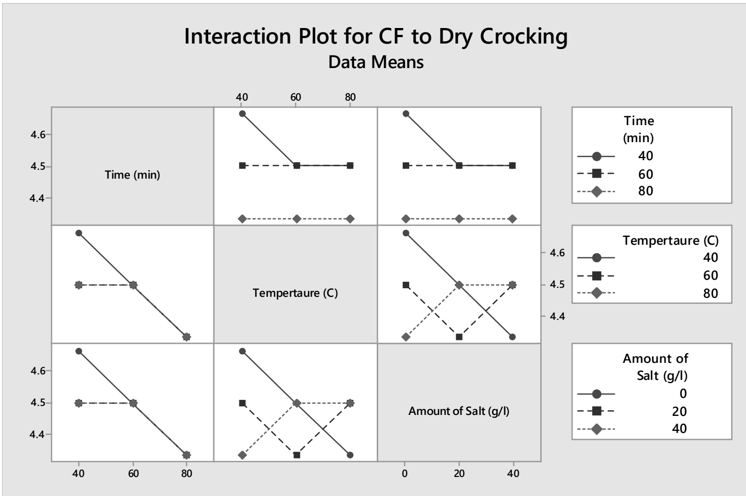

Figure 8: Interaction plot for dry crocking in solvent-assisted reactive dyeing

Table 5
Desired ranges of responses of the solvent-assisted reactive dyeing process

Source	Desired range
Colour strength (k/S), Y_1	Y_1 = Maximize
Change of shade, Y_2	$4 < Y_2 < 5$
Staining, Y_3	$4 < Y_3 < 5$
CF to dry crocking, Y_4	$4 < Y_4 < 5$
CF to wet crocking, Y_5	$3 < Y_5 < 4$

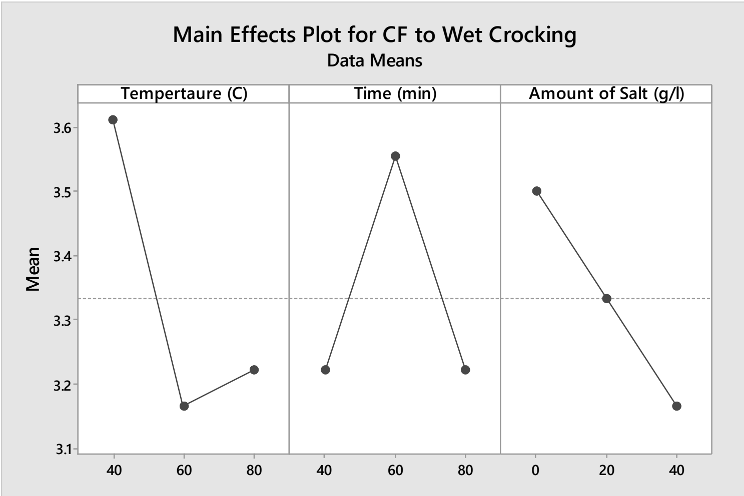

Figure 9: Main effects plot for wet crocking in solvent-assisted reactive dyeing

Table 6
Optimum values of process parameters for solvent-assisted reactive dyeing process

Variable factors	Levels	Individual desirability (di)	Composite desirability (D)
A: Time (min)	60		
B: Temperature T (°C)	80		
C: Amount of salt (g/L)	20		
Responses (Y_i)			0.7208
Y_1: K/S	11.04	0.97255	
Y_2: Change of shade	4	1.000	
Y_3: Staining	4	0.8000	
Y_4: CF to dry crocking	4-5	0.5000	
Y_5: CF to wet crocking	3-4	0.5000	

Optimization of process parameters

To maximize the colour strength and fastness attributes, the process parameters of the solvent-assisted reactive dyeing process have been optimised using composite desirability (D). The desirability function approach is one of the most widely used methods in the industry for the optimization of multiple response processes. It is based on the idea that the quality of a product or process that has multiple quality characteristics, with one of them outside of some "desired" limits, is completely unacceptable. The method finds operating conditions x that provide the "most desirable" response values.

For each response, $Y_i(x)$, a desirability function $d_i(Y_i)$ assigns numbers between 0 and 1 to the possible values of Y_i, with $d_i(Y_i) = 0$ representing a completely undesirable value of Y_i and $d_i(Y_i) = 1$ representing a completely desirable or ideal response value. The individual desirabilities are then combined using the geometric mean, which gives the overall desirability D.

$$D=[d_1(Y_1)d_2(Y_2)\ldots\ldots\ldots d_k(Y_k)]^{1/k} \quad (2)$$

where k denotes the number of responses.

The Minitab 17 software has been used to estimate the composite desirability. The desired ranges of the responses and a summary of the result obtained from the composite desirability function approach are presented in Table 5 and Table 6 (all five responses have assigned equal weightage). The optimal process parameters for the solvent-assisted reactive dyeing process were found to be 60 minutes of dyeing at 80 °C with a 20 g/L concentration of salt. The composite desirability (D) was estimated to be 0.7208, leading to the maximum colour strength and good fastness properties.

CONCLUSION

The optimum reactive dyeing process based on an ethanol-water mixture was defined and found feasible for cotton fabric. The dyeing showed good colour retention and the colourfastness of the dyed samples could meet the general requirements. The optimal process parameters for the solvent-assisted reactive dyeing process were found to be 60 minutes of dyeing at 80 °C with a 20 g/L concentration of salt. The sustainable dyeing of cotton fabrics by reactive dyes, using an ethanol-water mixture, can be used to minimise the consumption of water, leading to an environmentally sustainable method of cotton dyeing.

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