

Colour Yield in Two Phase Wet Fixation Dyeing of Cotton Cloth with Reactive Dyes as a Function of Time, Temperature and Alkali Concentration

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ABSTRACT

Reactive dyestuffs are used more than other suitable dyes in dyeing and printing of cotton fabrics with relatively good washing fastness. Time, temperature and alkali concentration constitute the most important parameters affecting the fixation process, in other words, the colour yield. Reactive dyes are fixed on cotton through a covalent link formed between the reactive group of the dyestuff and hydroxyl groups of cellulose. It is the aim of this research to present a model for colour yield as a function of these three parameters. For this purpose, two phase wet fixation dyeing trials were carried out for 9 reactive dyestuffs belonging to vinyl sulphone, monochlorotriazine, dichlorotriazine and trichloropyrimidine groups. The samples were padded with dyestuff solution, dried and fixed in fixation baths with conditions according to a matrix of time, temperature and alkali concentration values. After measuring the reflectance values of these samples, their K/S and F_K values were calculated. These values with their related parameters were used to obtain models through regression analysis. From the first set of obtained models for the nine dyestuffs, only one met the necessary conditions. Modification was carried out for the other eight and at the end five other models could be accepted as a representation of the colour yield of the dyes as a function of time, temperature and alkali concentration.

Key Words:

reactive dyestuff;
cotton cloth;
two phase dyeing;
wet fixation;
colour yield.

INTRODUCTION

Reactive dyestuff is used far more than any other kind for dyeing and printing cotton cloth where relatively good washing fastness is required. When compared with other dyes suitable for dyeing and printing of cotton fabrics, reactive dyes can usu-

ally be fixed on cellulose by a higher number of methods. Pad batch, cold dwell, pad steam and wet fixation are examples of possible fixation methods in two phase dyeing and printing of cotton cloth with many reactive dyes. In one phase

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dyeing and printing, fixation can be carried out with steam or dry heat. The dry heat method requires more urea to compensate the absence of moisture. Reactive dye molecule consists of the following parts [1]:

- Reactive group
- Bridge link
- Leaving group
- Chromogen
- Water solubilizing group
- Chromophore

Monochlorotriazine, dichlorotriazine, trichloropyrimidine and vinyl sulphone constitute the important reactive groups of monofunctional reactive dyes. The fixation of these dyes on cotton occurs through a reaction between the reactive group of dyestuff and hydroxyl groups of cellulose leading to a chemical or covalent link. Reactive groups affect the dyeing behaviour of the related dyestuff.

Alkali concentration, temperature and time constitute the most important factors in any of the above mentioned fixation methods. It is well known that the fixation of reactive dyes on cellulose in acidic or even neutral conditions is almost impossible and an alkaline media for this purpose is very vital. Consulting the literature concerning the required conditions for fixation of reactive dyes on cellulose reveals that a decrease or an increase of the amount of one factor can be compensated by an increase or a decrease in the amount of the other two factors, respectively. In other words, colour yield is somehow a function of alkali concentration, temperature and time.

The main objective of this research is to present a model for the colour yield of reactive dyes fixed on cellulose in two phase wet fixation method as a function of time, temperature and alkali concentration. This was attempted by linear regression analysis of K/S as well as F_K function. K/S and F_K have a direct relationship with the colour yield, in other words, the amount of dyestuff absorbed into the substrate. Extensive literature review revealed very little published information about this subject.

It must be noted that such or similar models can be very interesting not only from a theoretical point of view, but also they can prove valuable in the evaluation of the degree of the separate or mutual effect of the effective parameters, process cost minimizing as well as the process controls.

Literature review shows that a major part of the research is concerned with the representation of a

model for the dyeing behaviour of dyestuff has been limited to dyeing kinetics (the way that a dyestuff is absorbed by a substrate) or the amount of dyestuff absorbed at the end of dyeing period. These works can be summarized as follows:

Cegarra and Fuente [2] reached an equation that relates the rate of dye absorption to the amount of dye absorbed by the substrate at any time during the dyeing process. This model can be used in systems such as isoreactive dyeing. In isoreactive dyeing, dye absorption curve versus time is linear. Dyeing of wool with acid dyes, viscose rayon with direct dyes and acrylic with basic dyes are examples where, Cegarra-Puente equation applies.

Popescu and Segal [3] proposed a non-isothermal system in which the rate of dye absorption speed remains constant as temperature varies. Medley and Holstock [4] had already reached the same conclusion.

Shibusawa [5] obtained a polynomial model which agreed well with the behaviour of non-ionic dyestuff. This model relates the ratio of the time related dyestuff concentration on fibres relative to concentration at equilibrium to the activation energy, rate of dye absorption and time.

Similar models by Hill, Vickerstaff, Shelton and Patterson were compared by Cegarra and Puente [6] for dyeing polyester with disperse dyestuff. It was found out that the Hill equation was the nearest to the practical values obtained followed by the Cegarra-Puente's model.

Ryes and Sperb [7] also proposed mathematical models for the absorption behaviour of monofunctional reactive dyestuff in batch, semi-continuous and continuous dyeing.

ANALYSIS OF LINEAR REGRESSION

Analysis of regression, specifically linear regression is one of the most practical statistical methods. This method investigates the relationship between two or more variables. There are two kinds of variables in this method, namely independent (x) and dependent (y). Independent variables are those that can be chosen or controlled; whereas, dependent variable is affected by the value of independent variables. As an example, in reactive dyeing process, the conditions like time, temperature and alkali concentration are the independent variables and the amount of the absorbed dye (colour

yield or strength) is the dependent variable. If there is more than one independent variable involved, the linear regression is called multiple. As already mentioned, the relationship between these two variables, in other words, the model can be of great interest from different points of view.

It must be noted that in order to accept any model based on linear regression, some requirements must be met. Verification of these conditions can be carried out by means of different methods. If even one of the required conditions is not met, the proposed model cannot be accepted and modification is needed. These will be considered later in this paper.

EXPERIMENTAL

Materials

In this research a plain weave, 100% cotton fabric (108 g/m^2) was used for preparing the dyed samples. This fabric was already desized, boiled off and bleached (no optical brightener). The warp and weft were both single yarns with a density of 25 and 21 per centimeter, respectively. Sodium chloride was used to saturate the fixation baths. As an alkali for the fixation of reactive dyes on cellulose, sodium hydroxide (Merck) was employed. The dyed samples were washed in boiling water containing non-ionic detergent (based on alkyl aryl glycol). The reactive dyes chosen for this research are shown in Table 1. This table shows also the colour index, chemical base and the reactive group of the reactive dyes.

Equipment

The following items were used:

- Laboratory pad machine, a Werner Mathis AG type.
 - Polymat laboratory dyeing machine (AHIBA 1000), Datacolour
 - Reflectance spectrophotometer, Texflash, Datacolour
- Black and white standards: Carbon black and BaSO_4

Methods

Dyeing of the samples was carried out by pad-dry-wet fixation method as follows:

The samples ($8 \times 15 \text{ cm}$) were first padded (2 m/min) with a 20 g/L dye solution (pick up = 75%) and then dried at $115 - 5^\circ\text{C}$. Wet fixation of the dried samples was carried out in baths containing soft water saturated with sodium chloride. The conditions of the fixation baths for the dyestuffs were chosen from a matrix as shown in Tables 2-5. In other words any combination of the time, temperature and alkali concentration in the tables was employed. It must be mentioned that the upper limit of the time and alkali concentration was chosen when further increase did not result in higher colour yield. Some of the samples fixed at room temperature or 0°C for less than 30 s resulted in a very unlevel appearance; these samples were not considered in the calculations.

In order to measure the K/S for the dyed samples, the reflectance of the background was deducted from the reflectance of the dyed samples. To simulate the background, white samples (undyed) were treated in fixation baths according to Table 6.

After the wet fixation process, the samples were

Table 1. Specifications of the reactive dyestuff tested.

Commercial name	C.I. Reactive	Chemical base	Reactive group
Remazol blue 3R	Blue 28	Monoazo	Vinyl sulphone
Remazol brilliant red GD	Red 63	Monoazo	Vinyl sulphone
Remazol brilliant green 6B	Green 38	Phthalocyanin	Vinyl sulphone
Procion red P-4NB	Red 3:1	Monoazo	Monochlorotriazine
Cibacron red 6B	Red 218	Azo	Monochlorotriazine
Procion red MX-5B	Red 2	Monoazo	Dichlorotriazine
Procion navy MX-RB	Blue 82	Azo	Dichlorotriazine
Drimaren red X-6BN	Red 243	Azo	Trichloropyrimidine
Drimaren violet X-2RL	Violet 6	Azo	Trichloropyrimidine

Table 2. Conditions of the wet fixation baths for vinyl sulphone dyestuff.

Time (s)	Temperature (°C)	NaOH 38°Be (mL/L)
3	0	10
6	14	20
9	40	40
15	60	60
30	80	
60	100	
150		
360		
900		
1800		
3600		

rinsed and washed as follows (L:R = 50:1):

- 1- Cold rinse, 1 min
- 2- Warm water (50°C), 1 min
- 3- Boiling water, 3 g/L non-ionic detergent, 10 min,
- 4- Warm water (50°C), 1 min
- 5- Cold rinse

After washing, the samples were sandwiched between two clean cloths and ironed to dry out. Finally,

Table 3. Conditions of the wet fixation baths for monochlorotriazine dyestuff.

Time (s)	Temperature (°C)	NaOH 38°Be (mL/L)
3	0	25
9	14	50
15	50	75
60	75	10.0
150	100	
360		
900		
1800		
7200		
14400		
21600		
28800		

Table 4. Conditions of the wet fixation baths for dichlorotriazine dyestuff.

Time (s)	Temperature (°C)	NaOH 38°Be (mL/L)
3	0	2.5
6	17	5
9	40	10
15	60	20
30	80	
60		
150		
360		
900		
1800		
3600		

the reflectance of each sample was measured and K/S and F_k were calculated by considering the dominant wavelength. For background samples an average reflectance (R) was calculated and deducted from the reflectance value of the dyed samples. In order to make the samples completely opaque, each sample was folded twice so that four layers of the fabrics on top of each other were placed in front of the spectrophotometer.

Table 5. Conditions of the wet fixation baths for trichloropyrimidine dyestuff.

Time (s)	Temperature (°C)	NaOH 38°Be (mL/L)
3	0	25
9	14	50
15	50	75
60	75	100
150	100	
360		
900		
1800		
7200		
14400		
21600		
28800		

Table 6. Conditions of the wet fixation baths for background samples (fixation time (s)).

Room temperature (s)	75 (°C)	Boiling	NaOH 38°Be (mL/L)
15	3 (s)	3 (s)	2.5
60	15	15	10
360	60	60	25
900	150	150	50
3600	360	360	75
7200	900		100
14400	1800		
21600	3600		

The calculation of K/S and F_k was carried out by a programme developed in Matlab.

The ratio K/S shows the absorbed light by an opaque substrate relative to the scattered light from it. This ratio is calculated by Kubelka-Munk theory as follows [8]:

$$K/S = (1-R_\infty)^2/2R_\infty$$

Where, R_∞ is the reflectance of sample of infinite thickness to light of a given wavelength, expressed in fractional form. As an estimation of the amount of dyestuff absorbed by the substrate, K/S is very important. This function is related to the amount of dyestuff on the substrate (C) by the following relationship [9]:

$$K/S = AC$$

A is the proportional factor which is constant for each dyestuff. F_k function is in fact an estimation of the area under the absorption curve which considers K/S in different wavelengths of visible light as well as colour matching functions. F_k function is calculated as follows [9]:

$$F_k = \sum_{400}^{700} (K/S)_\lambda (\bar{x}_{10,\lambda} + \bar{y}_{10,\lambda} + \bar{z}_{10,\lambda})$$

RESULTS AND DISCUSSION

Relationships

It is obvious that when the fixation time is zero there is

no fixation and hence colour yield will be zero. With zero alkali concentration, the colour yield is also very low and it is assumed that it equals zero. The experiments carried out for the fixations at 0°C showed that there could be some degree of fixation and it was unrealistic to assume zero colour yield at 0°C. In order to make this assumption possible, it was necessary to choose the Fahrenheit scale; in other words at 0-212°C, the colour yield was assumed to be zero. The three above assumptions i.e., zero fixation or colour yield with each of the three time, alkali concentration and temperature being zero enables one to consider a general multiple form for the colour yield model as follows:

$$F_k = k_1 \text{ time}^{\beta_1} \text{ conc.}^{\beta_2} \text{ temp.}^{\beta_3}$$

$$K/S = k_2 \text{ time}^{\beta_1'} \text{ conc.}^{\beta_2'} \text{ temp.}^{\beta_3'}$$

In order to change the above form to a linear one, both Napierian and 10 base logarithm were examined. Due to better fitting, 10 base logarithm was chosen to obtain a linear form. Hence, it can be said that:

$$\text{Log}F_k = \text{log}k_1 + \beta_1 \text{log time} + \beta_2 \text{log conc.} + \beta_3 \text{log temp.}$$

$$\text{Log}K/S = \text{log}k_2 + \beta_1' \text{log time} + \beta_2' \text{log conc.} + \beta_3' \text{log temp.}$$

In order to determine the values of the parameter of the regression model, MiniTab with state→regression was employed. The logarithms of time, temperature and alkali concentration as independent variables and logarithm of F_k and K/S as dependent variables constitute the entries for this computing operation. The related results are as follows:

- The regression model parameters (the coefficients of the model).
- The coefficient of variation of the above mentioned parameters and their probability of being zero.
- Coefficient of determination.
- Analysis of variance table.

For the case of C.I. Reactive red 63 as an example, the computer outputs of the results for K/S are given in Table 7. According to these results, the value of R-Sq for the model is 96.8% and the P values for all coefficients are zero. This means that the regression equation is given by:

$$\text{Log}(K/S) = -5.80 + 0.352 \text{log time} + 0.510 \text{log conc.} + 2.26 \text{log temp.}$$

Table 7. The computer outputs of the results for K/S of C.I. Reactive red 63.

The regression equation is $\log(K/S) = -5.80 + 0.532 \log \text{time} + 0.510 \log \text{conc.} + 2.26 \log \text{temp.}$					
165 cases are used, and 55 cases contain missing values					
Predictor	Coeff.	Stan.dev.	t-ratio	P	
Constant	- 5.80049	0.08965	- 64.70	0.000	
Log time	0.35208	0.010502	33.47	0.000	
Log conc.	0.51036	0.03095	16.49	0.000	
Log temp.	2.26120	0.03567	63.38	0.000	
S = 0.1151 R-sq = 96.8% R-sq(adj) = 96.7%					
Analysis of variance					
Source	DF	SS	MS	F	P
Regression	3	64.621	21.540	1625.37	0.0000
Error	161	2.134	0.013		
Total	164	66.755			
Source	DF	Seq SS			
Log time	1	10.040			
Log conc.	1	1.339			
Log temp.	1	53.243			

Also the result of the analysis of variance shows that the above model is highly significant. Computer outputs of the results for K/S and F_k for all other dyes are available in reference [10]. Consequently, the models shown in Tables 8 and 9 are obtained for K/S and

F_k , respectively.

In order to determine the validity of each model, the following conditions must be met [11].

- The residuals must be independent random variables

- The residuals must have a normal distribution

- The residuals must have a constant variance

The following four conditions can be used as a means of verification of the above mentioned three conditions.

- Linear form for the normal plot of the residuals.

- I chart of residuals should lie between upper and lower control limits without any pattern.

- Histogram of residuals should have a normal or Gaussian form.

- Residuals vs. fits should show no specific pattern.

It must be noted that any regression analysis is valid if, these four conditions are met. In order to plot these charts, stat→regression→residual plot in MiniTab has been employed.

Figures 1-9 show the normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the models considered for nine dyestuffs employed in this research, respectively. Considering the above-mentioned four conditions for the acceptance of the models, it can be said that only the model for C.I. Reactive red 63 can be accepted. The other models should be modified. There are different methods for this modification. For example, adding different powers of the independent or dependent variables; root, power, multiply and inverse conversion as well as Box and Cox methods can be mentioned for the purpose of

Table 8. The regression model for F_k .

Reactive group	C.I. Reactive	Model	R ²
Vinyl sulphone	Blue 28	$\log F_k = -3.39 + 0.492 \times \log \text{time} + 0.446 \times \log \text{conc.} + 1.721 \times \log \text{temp.}$	95.8
	Red 63	$\log F_k = -4.96 + 0.36 \times \log \text{time} + 0.521 \times \log \text{conc.} + 2.26 \times \log \text{temp.}$	96.7
	Green 38	$\log F_k = -2.87 + 0.309 \times \log \text{time} + 0.229 \times \log \text{conc.} + 1.74 \times \log \text{temp.}$	97.2
Monochlorotriazine	Red 218	$\log F_k = -4.62 + 0.287 \times \log \text{time} + 0.171 \times \log \text{conc.} + 2.22 \times \log \text{temp.}$	93.4
	Red 3:1	$\log F_k = -4.84 + 0.375 \times \log \text{time} + 0.259 \times \log \text{conc.} + 2.35 \times \log \text{temp.}$	95.2
Dichlorotriazine	Red 2	$\log F_k = 0.867 + 0.0915 \times \log \text{Time} + 0.260 \times \log \text{conc.} + 0.231 \times \log \text{temp.}$	58.2
	Blue 82	$\log F_k = 0.688 + 0.101 \times \log \text{time} + 0.310 \times \log \text{conc.} + 0.308 \times \log \text{temp.}$	50.6
Trichloropyrimidine	Red 243	$\log F_k = -1.05 + 0.115 \times \log \text{time} + 0.0963 \times \log \text{conc.} + 0.910 \times \log \text{temp.}$	85.6
	Violet 6	$\log F_k = -1.81 + 0.197 \times \log \text{time} + 0.0996 \times \log \text{conc.} + 0.18 \times \log \text{temp.}$	84.9

Table 9. The regression model for K/S.

Reactive group	C.I. Reactive	Model	R ²
Vinyl sulphone	Blue 28	Log K/S= -4.33 + 0.491 × log time + 0.429 × log conc. + 1.71 × log temp.	95.8
	Red 63	Log K/S= -5.80 + 0.352 × log time + 0.510 × log conc. + 2.26 × log temp.	96.8
	Green 38	Log K/S= -3.55+ 0.312 × log time + 0.240 × log conc. + 1.55 × log temp.	96.6
Monochlorotriazine	Red 218	Log K/S= -5.26+ 0.272 × log time + 0.173 × log conc. + 2.14 × log temp.	92.2
	Red 3:1	Log K/S= -5.49+ 0.361 × log time + 0.238 × log conc. + 2.30 × log temp.	95.0
Dichlorotriazine	Red 2	Log K/S= -0.156+ 0.103 × log time + 0.312 × log conc. + 0.327 × log temp.	50.0
	Blue 82	Log K/S= -0.149+ 0.0915 × log time + 0.255 × log conc. + 0.235 × log temp.	56.9
Trichloropyrimidine	Red 243	Log K/S= -1.91+ 0.114 × log time + 0.0993 × log conc. + 0.908 × log temp.	85.4
	Violet 6	Log K/S= -2.79+ 0.204 × log time + 0.102 × log conc. + 1.21 × log temp.	85.1

modification [12]. More complex methods like generalized linear models can also be employed.

In order to modify the models, all of the above mentioned modification methods were tried; but no considerable change that could lead to accepting the

models was obtained. An approach that proved to be successful was the elimination of the data related to the fixation times of less than 60 s as well as room temperature and below. This modification was carried out for the following dyestuff:

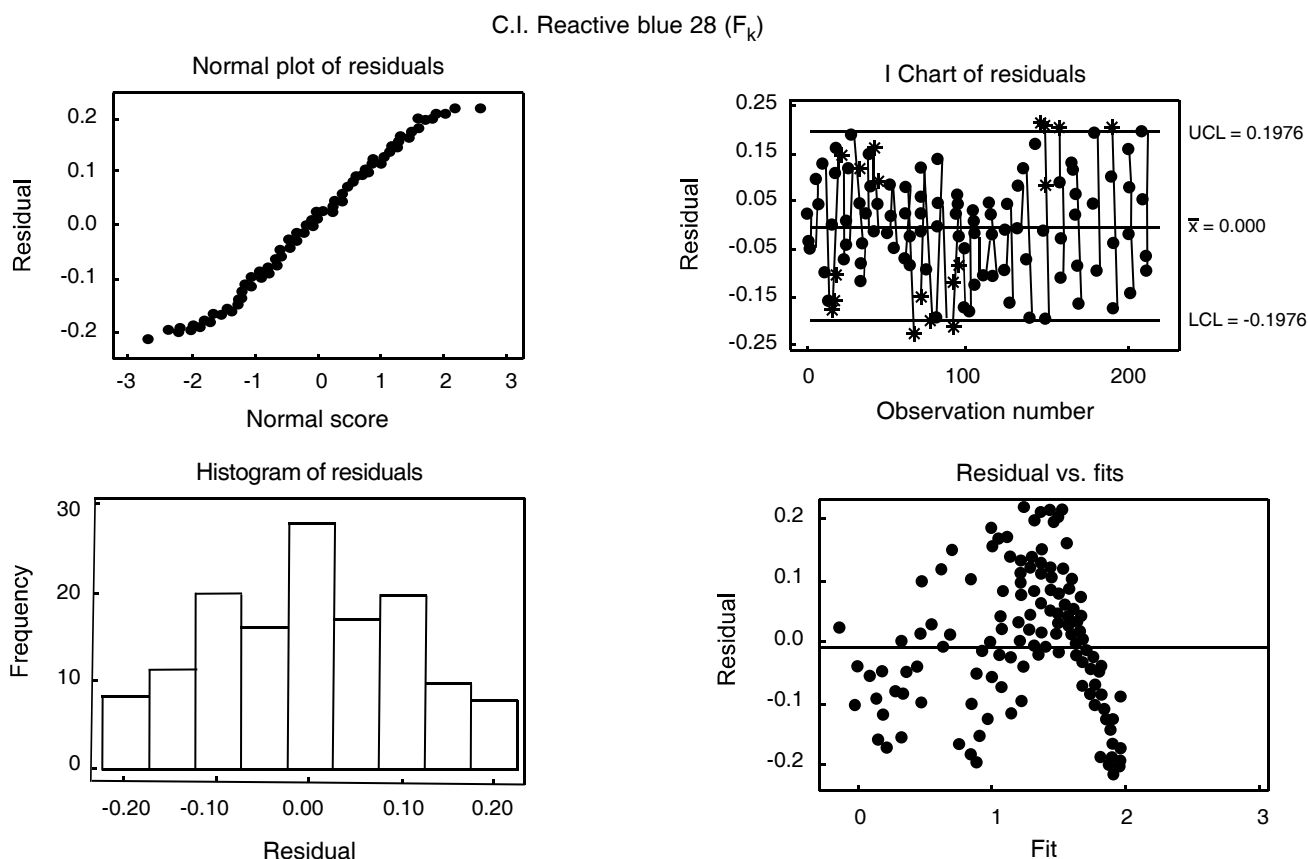


Figure 1. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive blue 28.

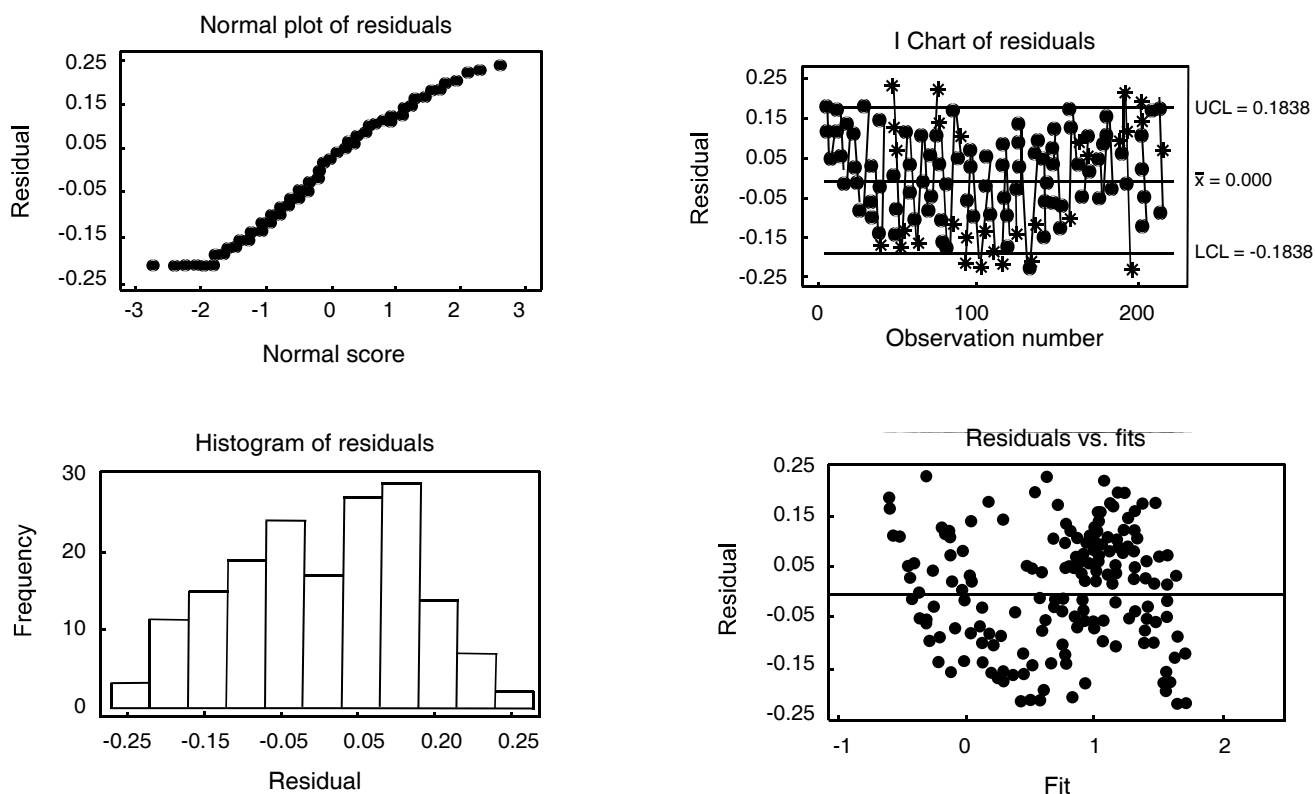
C.I. Reactive red 63 (F_k)

Figure 2. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 63.

- C.I. Reactive green 38
- C.I. Reactive red 218
- C.I. Reactive red 3:1
- C.I. Reactive red 243
- C.I. Reactive violet 6

The modification was continued by adding some parameters as shown in Tables 10 and 11. Figures 10-14 show the normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the dyestuff after modification. These Figures show

Table 10. Modified models for F_k models.

Reactive group	C.I. Reactive	Model	R^2
Vinyl sulphone	Green 38	$\text{Log} F_k = -3.50 + 0.362 \log \text{ time} + 0.326 \log \text{ conc} + 1.67 \log \text{ temp}$	95.7
Monochlorotriazine	Red 218	$\text{Log} F_k = 3.95 + 0.458 \log \text{ time} - 1.68 \log \text{ conc.} - 6.07 \log \text{ temp.} - 0.0176 \log \text{ time}^2 + 0.552 \log \text{ conc.}^2 + 2.26 \log \text{ temp.}^2$	98.6
	Red 3:1	$\text{Log} F_k = 1.71 + 0.389 \log \text{ time} + 0.561 \log \text{ conc.} - 5.47 \log \text{ temp.} + 0.0115 \log \text{ time}^2 - 0.082 \log \text{ conc.}^2 + 2.14 \log \text{ temp.}^2$	98.6
Dichlorotriazine	Red 2	$\text{Log} F_k = 0.246 + 0.0999 \log \text{ time} + 1.55 \log \text{ conc.} + 0.309 \log \text{ temp.} - 0.727 \log \text{ conc.}^2$	59.8
	Blue 82	$\text{Log} F_k = 0.661 + 0.0927 \log \text{ time} + 0.836 \log \text{ conc.} + 0.231 \log \text{ temp.} - 0.341 \log \text{ conc.}^2$	61.8

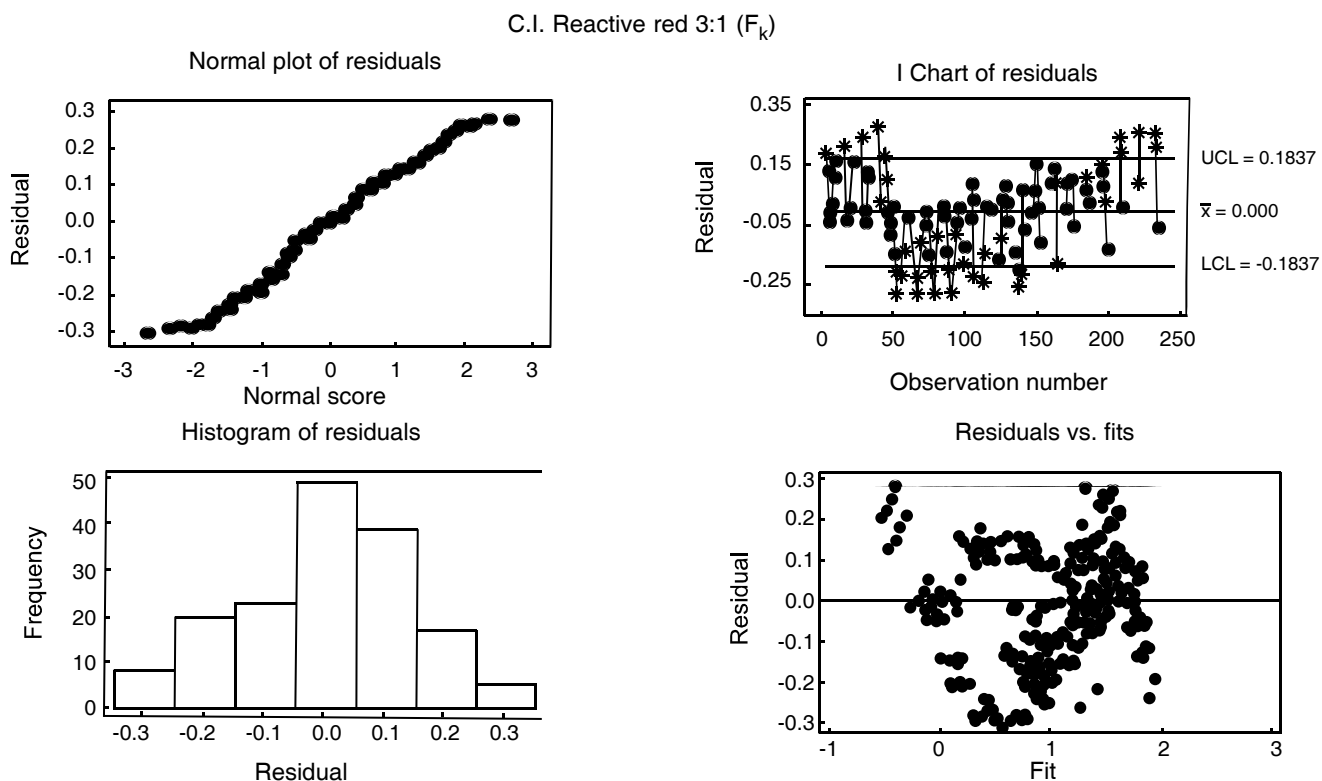


Figure 3. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 3:1.

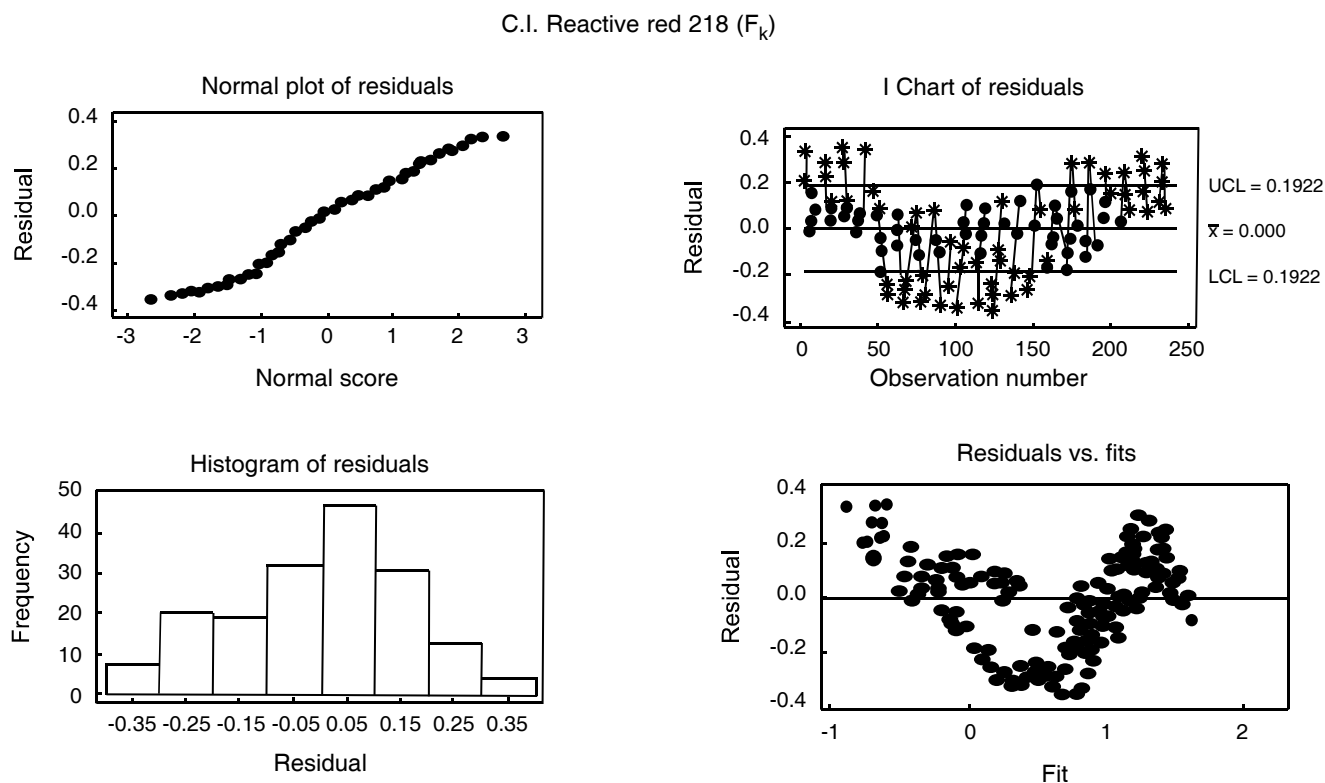


Figure 4. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 218.

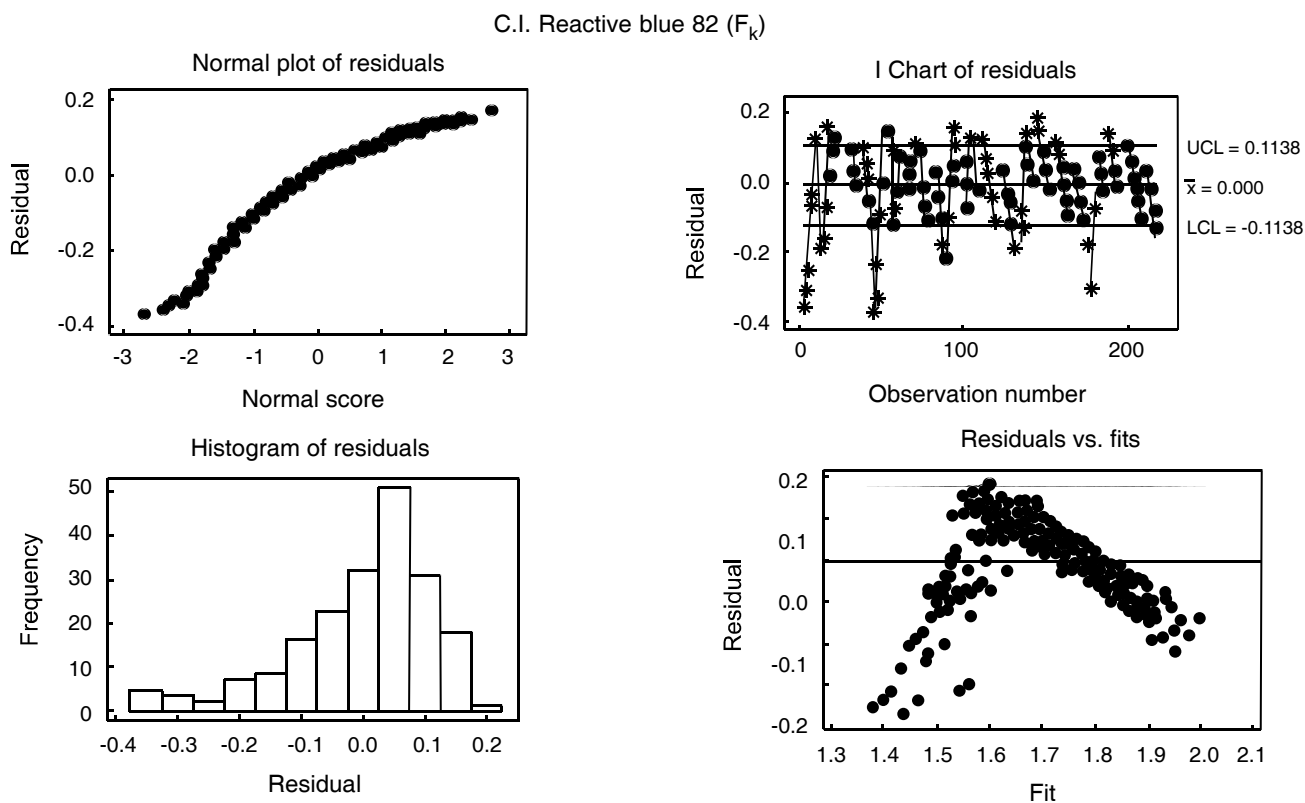


Figure 5. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive blue 82.

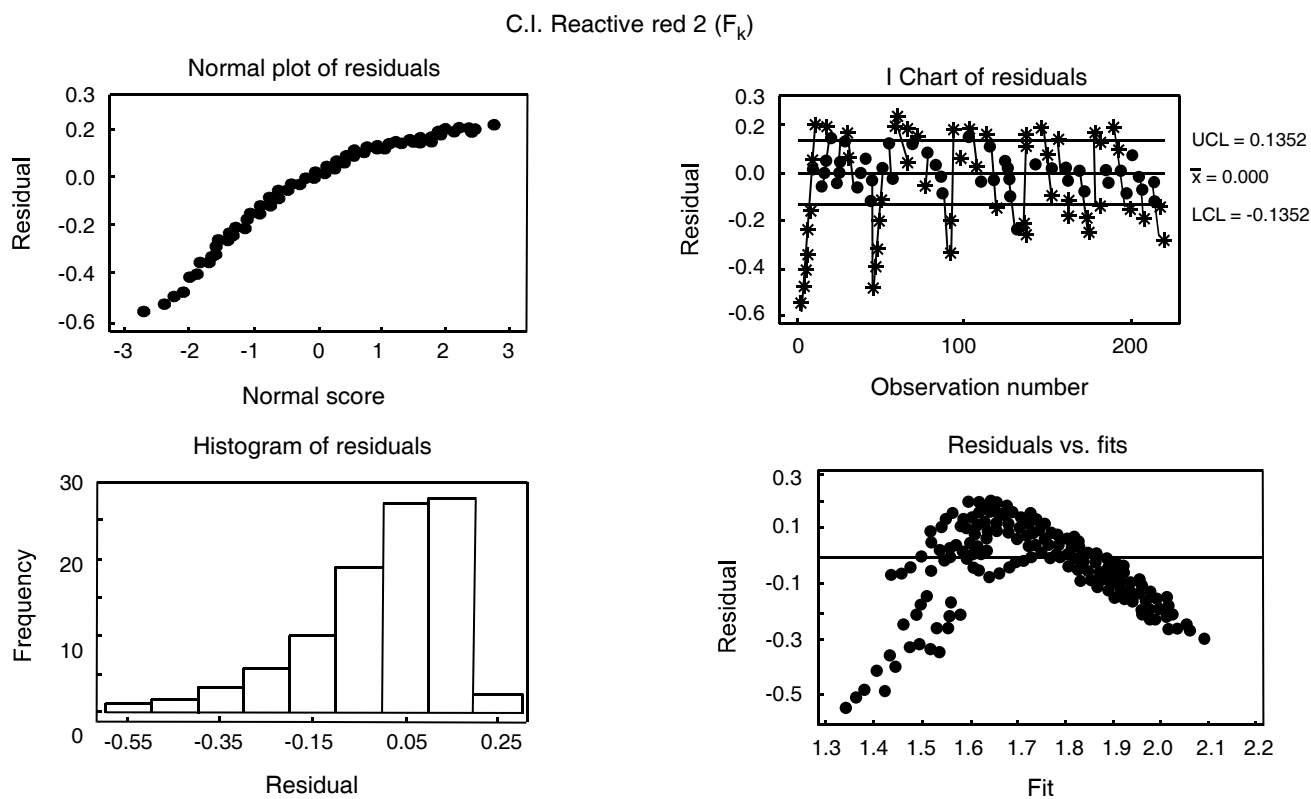


Figure 6. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 2.

C.I. Reactive violet 6 (F_k)

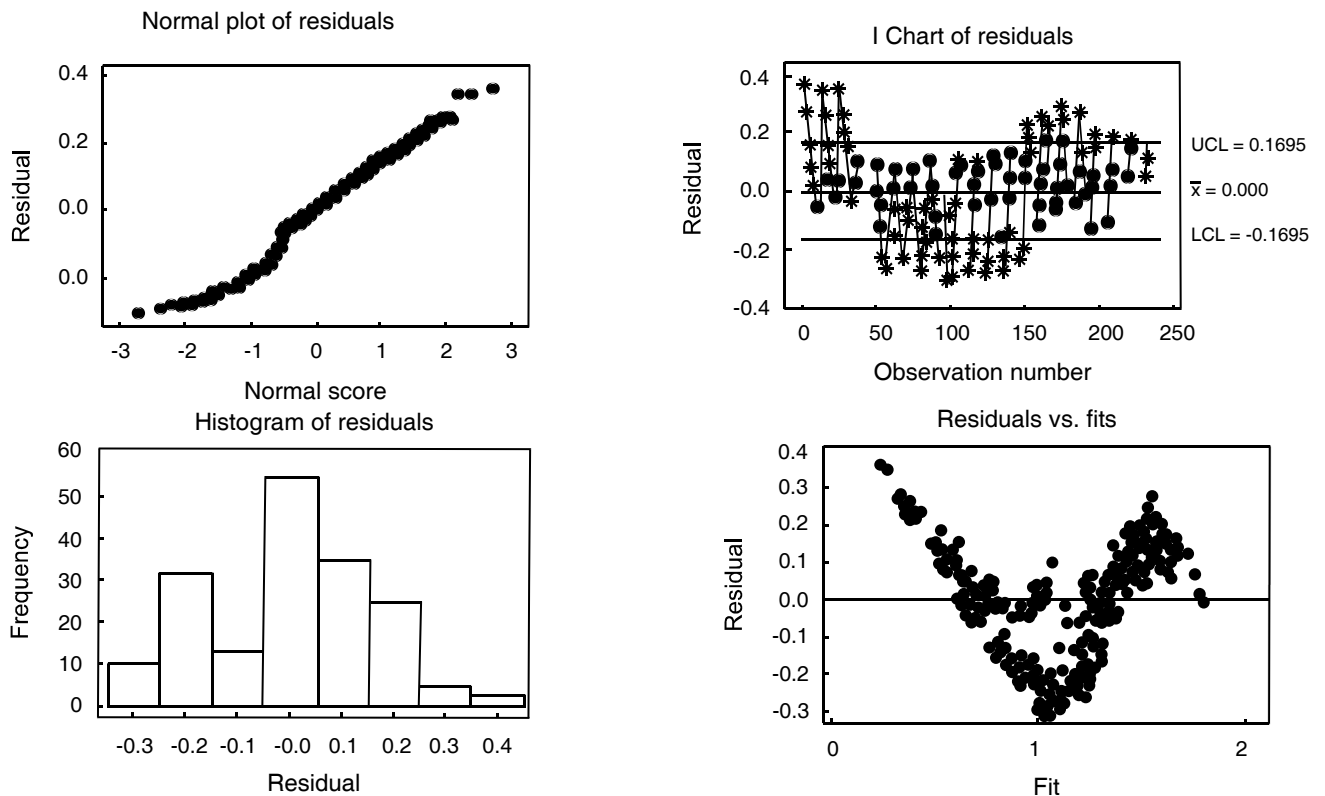


Figure 7. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive violet 6.

C.I. Reactive red 243 (F_k)

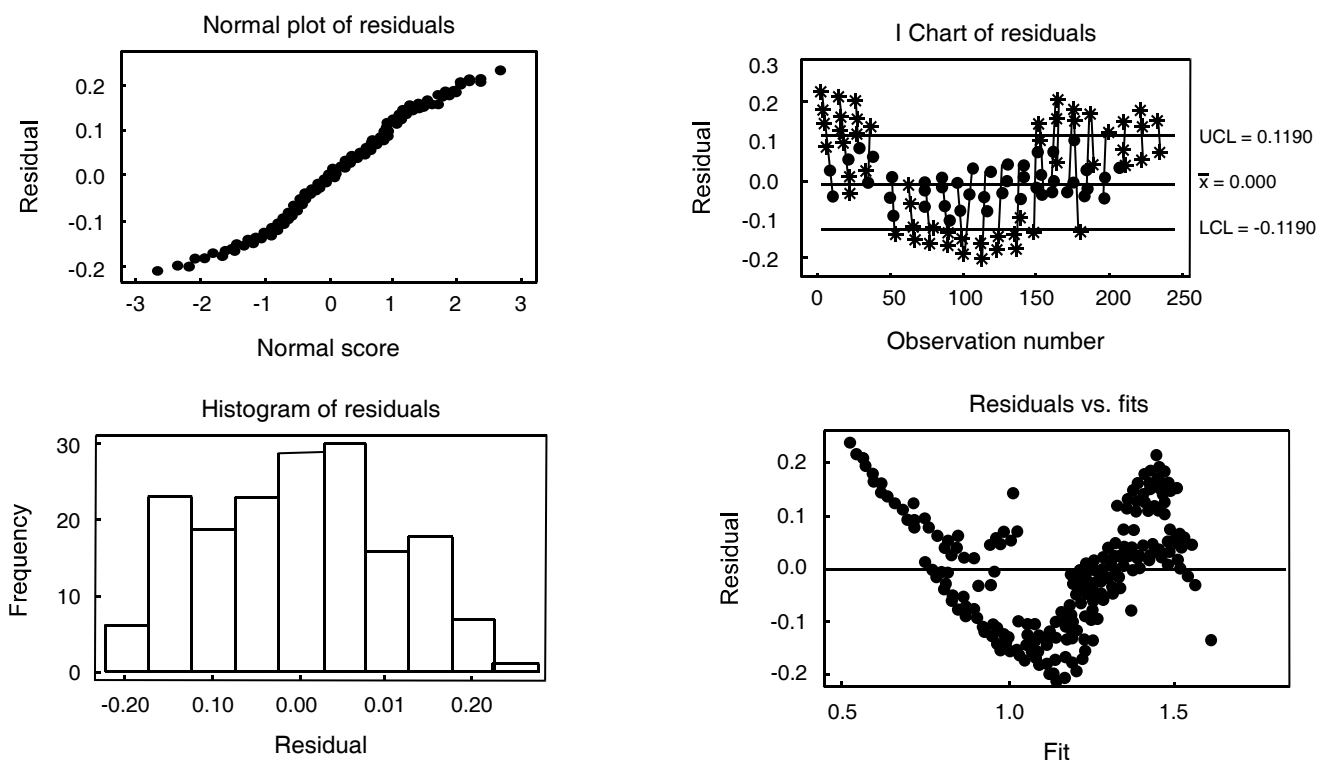


Figure 8. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 243.

C.I. Reactive red 3:1 (F_k)

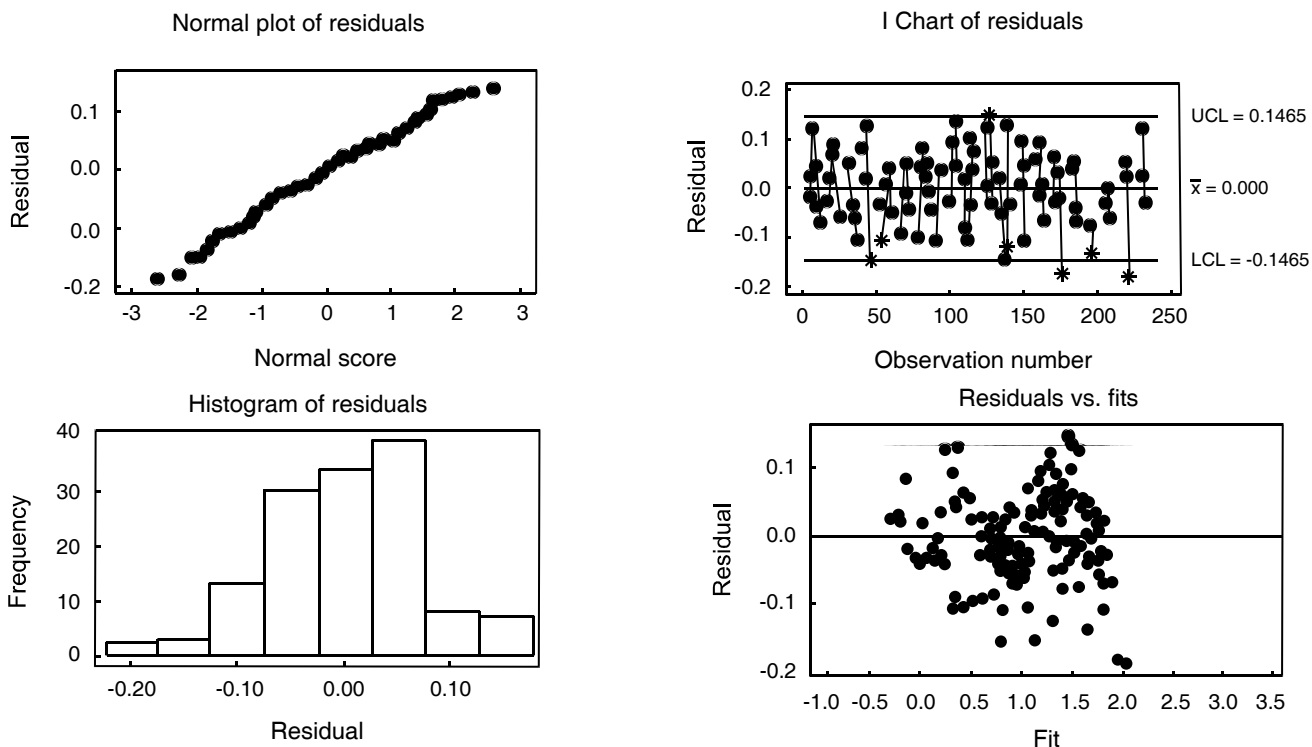


Figure 9. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the relationship considered for C.I. Reactive red 3:1.

C.I. Reactive red 218 (F_k)

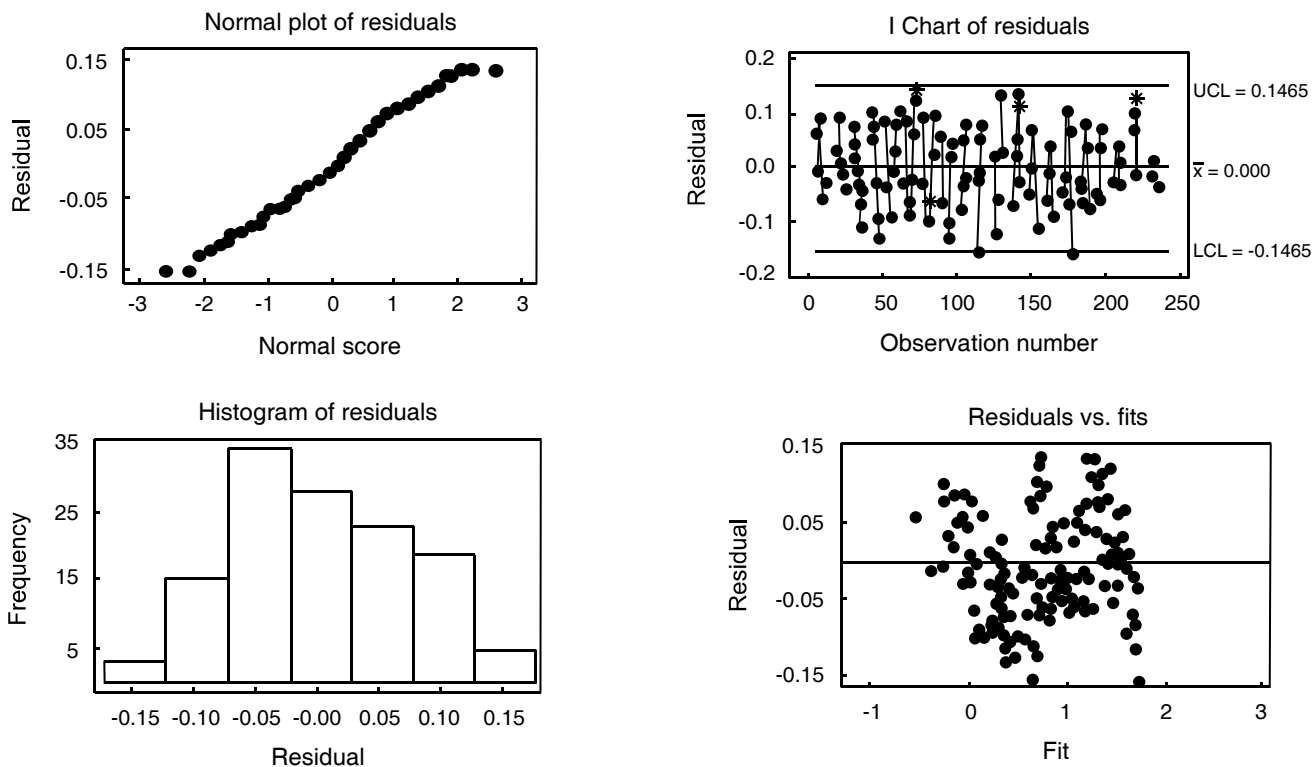


Figure 10. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the modified relationship considered for C.I. Reactive red 218.

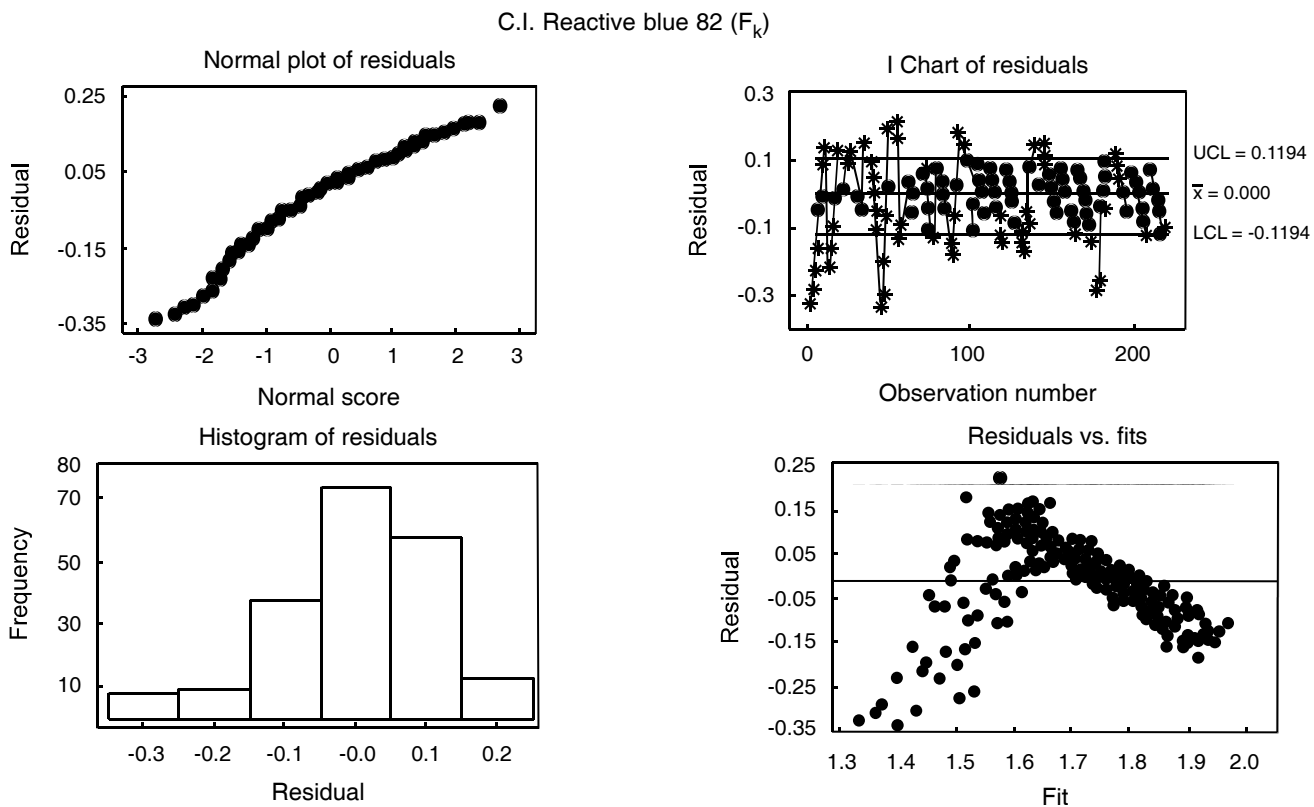


Figure 11. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the modified relationship considered for C.I. Reactive blue 82.

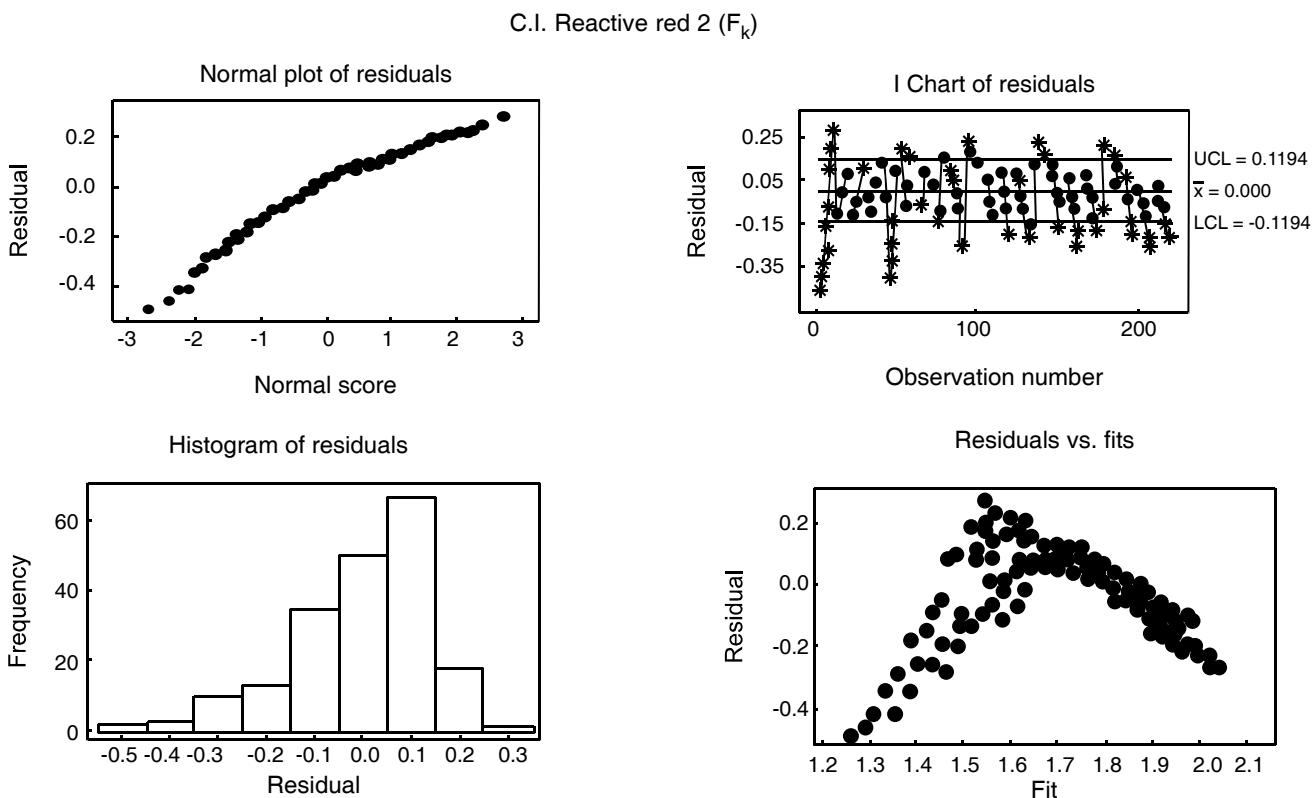


Figure 12. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs. fits for the modified relationship considered for C.I. Reactive red 2.

C.I. Reactive violet 6 (F_k)

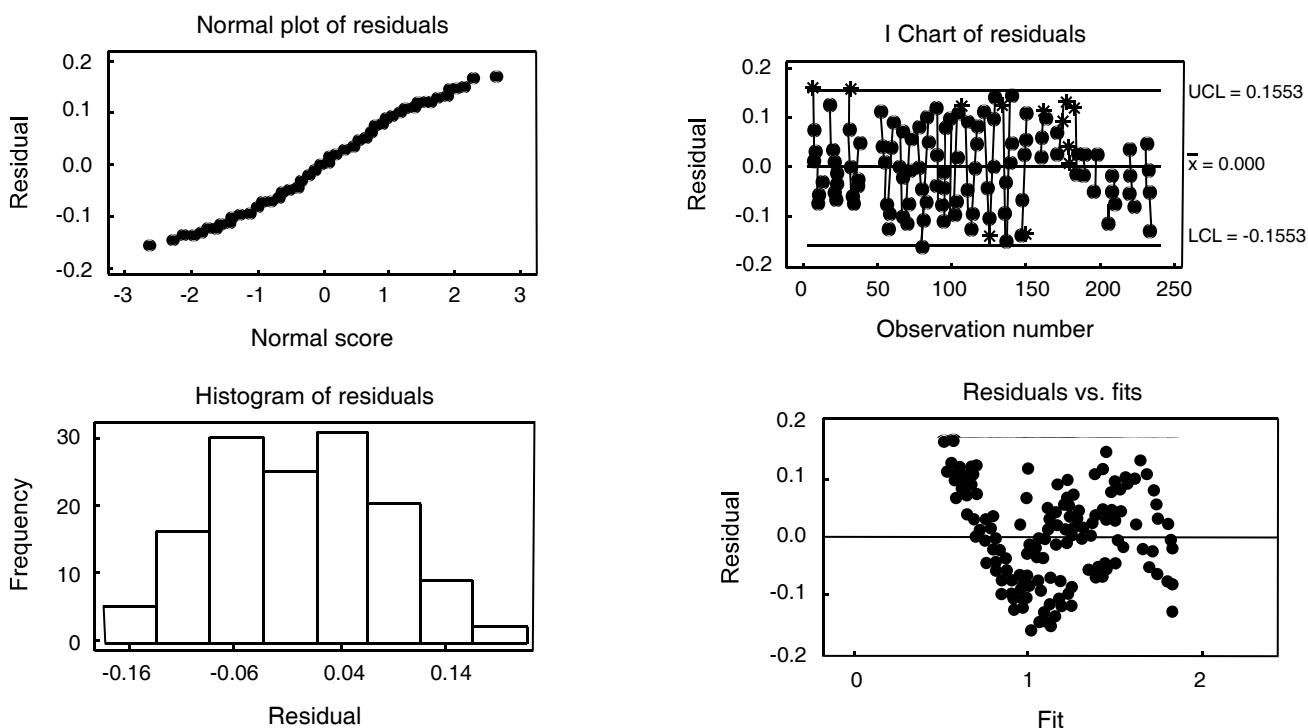


Figure 13. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs fits for the modified relationship considered for C.I. Reactive violet 6.

C.I. Reactive red 243 (F_k)

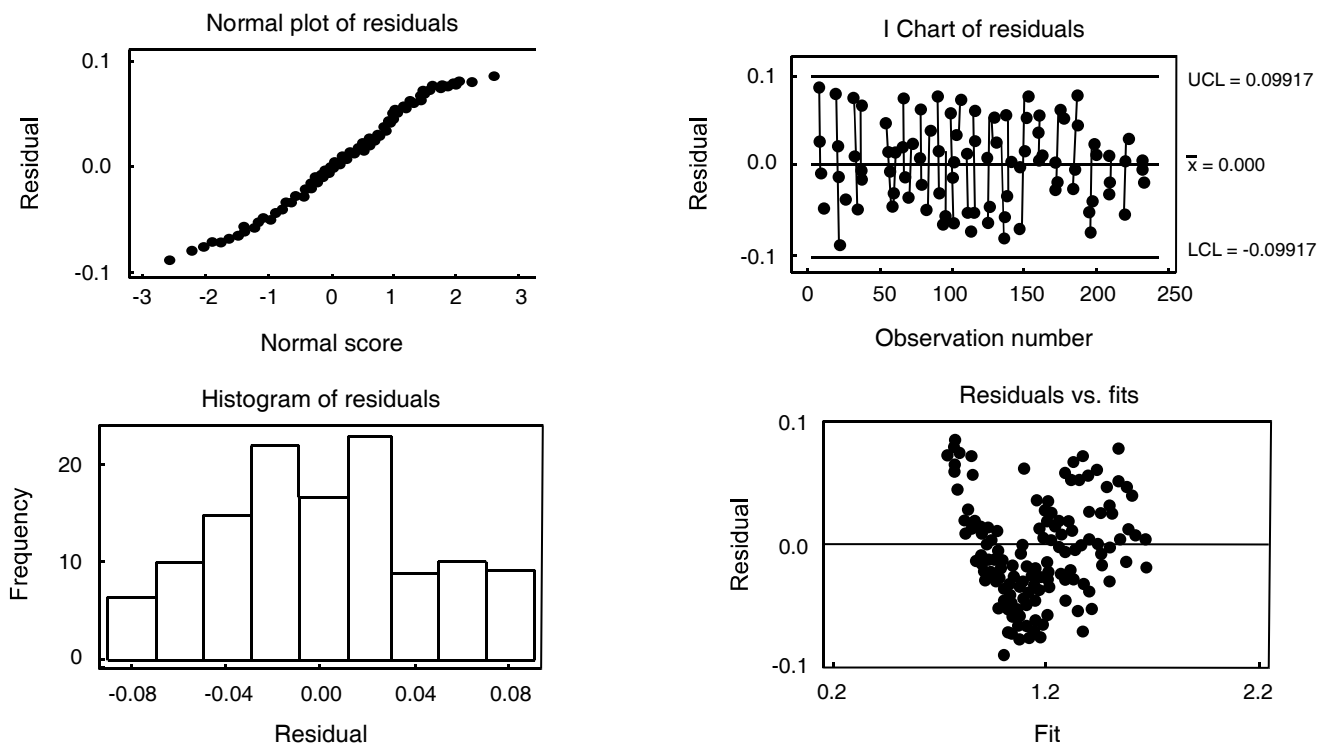


Figure 14. The normal plot of the residuals, I chart of residuals, histogram of residuals and residuals vs fits for the modified relationship considered for C.I. Reactive red 243.

Table 11. Modified models for K/S models.

Reactive group	C.I. Reactive	Model	R ²
Vinyl sulphone	Green 38	Log K/S = - 4.31 + 0.374 log time + 0.354 log conc. + 1.79 log temp.	95.4
Monochlorotriazine	Red 218	Log K/S = 3.17 + 0.467 log time - 1.52 log conc. - 6.15 log temp. - 0.0220 log time ² + 0.504 log conc. ² + 2.27 log time ²	98.4
	Red 3:1	Log K /S = 0.558 + 0.394 log time + 0.849 log conc. - 5.31 log temp. + 0.00864 log time ² - 0.171 log conc. ² + 2.09 log temp. ²	98.5
Dichlorotriazine	Red 2	Log K/S = -0.605 + 0.101 × log time + 1.57 × log conc.+ 0.327 × log temp. -0.737 × log conc. ² -	58.9
	Blue 82	Log K/S = -0.353 + 0.0927 × log time + 0.821 × log Conc.+ 0.235 × logTemp. -0.334 × logConc. ²	60.4
Trichloropyrimidine	Red 243	Log K/S = 2.91 + 0.178 log time - 0.433 log conc. - 4.28 log temp. + 1.29 log temp. ² + 0.309 log conc. * log temp	96.6
	Violet 6	Log K/S = 1.81 + 0.399 log time + 0.462 log conc. - 4.76 log temp. - 0.0249 log time ² - 0.093 log conc. ² + 1.64 log temp. ²	95

that the modification has improved the conditions for the acceptance of the models considerably. The modifications carried out for C.I. Reactive blue 28 did not lead to considerable improvements. As far as C.I. Reactive blue 82 and C.I. Reactive red 2 are concerned; in spite of some improvements the conditions for accepting the models are not yet met.

In order to investigate the relative importance, in other words the degree of effect of the independent variables on the colour yield, stepwise regression com-

putation in Minitab software was carried out for the accepted models. This analysis led to the following order for the three independent variables with increasing importance from top to bottom:

- Concentration
- Time
- Temperature

Comparison of K/S and F_k Relationships

Comparison of the models for F_k and K/S shows that

Table 12. Comparison of the theoretical and practical ratio of F_k to K/S.

Reactive group	C.I. Reactive	Average F _k / K/S (model)	95% Confidence limit for F _k / K/S (model)	Average F _k / K/S (practice)	95% Confidence limit for F _k / K/s (practice)	10 (β ₀ - β ₀)
Vinyl sulphone	Blue 28	*	*	9.302	9.253-9.355	*
	Red 63	7.383	7.362-7.403	7.331	7.304-7.359	6.92
	Green 38	3.160	3.124-3.199	3.175	3.145-3.202	6.46
Monochlorotriazine	Red 218	6.64	6.579-6.689	6.588	6.539-6.629	6.025
	Red 3:1	6.509	6.482-6.536	6.520	6.492-6.557	14.19
Dichlorotriazine	Red 2	*	*	6.353	6.341-6.368	*
	Blue 82	*	*	10.32	10.31-10.34	*
Trichloropyrimidine	Red 243	7.347	7.331-7.362	7.341	7.326-7.355	6.76
	Violet 6	8.048	8.022-8.074	8.075	8.038-8.109	9.33

the coefficients of the logarithms of the independent variables in F_K and K/S are very near to each other. This is true for all the accepted and unaccepted models obtained in this research. From this it can be deduced that the ratio of F_K and K/S for each dyestuff is a constant. The ratio of F_K to K/S can be written as follows: Assuming that:

$$\frac{F_K}{K/S} = \frac{10^{\beta_0} (\text{time}^{\beta_1} \times \text{conc.}^{\beta_2} \times \text{temp.}^{\beta_3})}{10^{\beta_0'} (\text{time}^{\beta_1'} \times \text{conc.}^{\beta_2'} \times \text{temp.}^{\beta_3'})}$$

$$\beta_1 = \beta_1'$$

$$\beta_2 = \beta_2'$$

$$\beta_3 = \beta_3'$$

The ratio could be rewritten as:

This ratio was calculated for each dyestuff theoretical-

$$\frac{F_K}{K/S} = \frac{10^{\beta_0}}{10^{\beta_0'}} = 10^{(\beta_0 - \beta_0')}$$

ly and practically in different conditions of time, temperature and alkali concentration. Table 12 shows the average value and the 95% confidence limit for this ratio for both practical and theoretical conditions as well as $10^{(\beta_0 - \beta_0')}$. As it can be seen, the theoretical and practical values are very near to each other. Table 12 shows also that the ratio of F_K to K/S can be dependent on the shade of dyestuff. Verification of this point needs more research.

CONCLUSION

Nine models representing the colour yield in two phase wet fixation dyeing of cotton cloth with reactive dyes as a function of time, temperature and alkali concentration were obtained by means of linear regression in the first part of the research. Considering the four conditions for the acceptance of the models, only the model for C.I. Reactive red 63 was accepted. The other models were modified. After modification, the models obtained for :

- C.I. Reactive green 38, C.I. Reactive red 218, C.I. Reactive red 3:1, C.I. Reactive red 243, and C.I. Reactive violet 6, met the required conditions for acceptance. As it can be seen the models obtained for the reactive dyes with dichlorotriazine reactive groups

as well as C.I. Reactive blue 28 with vinyl sulphone reactive group did not meet the necessary theoretical conditions completely to be accepted. Further analysis like weighted regression, generalized least square and non-linear regression may lead to an improvement. Considering the reactivity of the reactive groups of the dyes used in this research, it can be concluded that practical data obtained from reactive dyes with low to medium reactivity fit more easily into a model.

Investigation on the relative importance, or the effect of the independent variables on the colour yield led to the conclusion that for all accepted models, the relative importance of the independent variables increases from concentration to time to temperature, respectively.

This research has also led to the conclusion that the ratio of F_K and K/S for all reactive dyes employed in this research is a constant.

Finally it must be pointed out that models like those obtained in this research can be used as a means of minimizing dyeing process cost.

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