



Study of Desalination and Changing the Counter Ion of Mono-Chlorotriazinyl Reactive Dye on Dyeing Nylon 6.6

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ABSTRACT

A nionic reactive dyes used to dye nylon suffer from failures due to the poor efficiency caused by low degree of exhaustion and fixation. From the previous work, the dyeing efficiency of Procion Rubine XL+ on modified nylon was particularly weak and hence offers the widest scope for an in depth investigation in to variables that affect the dyeing process. In this paper, a number of attempts were made to improve the fixation efficiency of Procion Rubine XL+ on modified nylon. The process variables were studied: (a) the effect of desalination, as well as (b) the effect of changing the counter ion from sodium to trimethyl ammonium. Consequently, reducing the electrolyte concentration and changing the counter ion resulted in reduced fixed color yield which means in all cases fixation yields generally inferior to those obtained from the commercial sample of Procion Rubine XL+. Prog. Color Colorants Coat. 4(2011), 7-14. © Institute for Color Science and Technology.

1. Introduction

The presence of terminal amino end groups in nylon fibres imparts substantivity towards various classes of anionic dyes, specifically acid dyes, direct dyes and reactive dyes. Acid dyes are the most popular for dyeing nylon, with 1:2 pre-metallised acid dyes being used when highest wet fastness is required [1]. However, even these dyes suffer color loss during laundering and cause staining of adjacent fabrics. Whilst an after-treatment to the dyed nylon can result in somewhat improved wet-fastness, repeated washing can still result in loss of color and there remains much room for improvement. Reactive dyes resemble acid dyes in their basic structure but additionally possess fibre reactive groups, their name

being derived from their ability to react chemically with the fibre.

In 1954, Rattee and Stephen [2-5] showed that dyes containing a dichlorotriazinyl reactive group could react with cellulosic fibres, in the presence of alkali, to form covalent bonds. Since that time research in the chemistry and application of reactive dyes has overwhelmingly focused on cellulosic [6, 7] and nylon fibres [8-13]. Compared with the vast numbers of reactive dyes for cellulosic fibres [14] very few commercial reactive dyes are available for application to nylon [15-17], and those that employ the same fibre-reactive groups as for cellulosic fibres [18-22].

In previous studies [10-12], as a first step towards the design of novel cationic reactive dyes for nylon [12], an

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attempt was made to identify the structural features associated with good reactive dyeing performance on nylon. The effects of changes in molecular size, number and type of reactive group, as well as the degree of sulphonation were evaluated [10-11].

In this study, a number of attempts were made to optimise the fixation efficiency of an anionic reactive dye, Procion Rubine XL+, on modified nylon. This dye was selected for further study since under non-optimised conditions fixation efficiency was particularly poor [10], and therefore offered wider scope for significant and readily observable improvements. The following process variables were studied.

- Effect of desalination.
- Effect of changing the counter ion from sodium to trimethyl ammonium.

2. Experimental

2.1. Materials

A scoured, modified nylon 6.6 "Tactel Colorsafe" fabric was supplied by Du Pont (UK) and Procion Rubine XL+, a tris(monochlorotriazinyl) nonasulphonate was obtained from DyStar.

2.2. Dyeing

Dyeing with Procion Rubine XL+ were carried out after desalination, to determine the effect of electrolyte concentration reduced. The dyeing methods used in these studies are illustrated in Figure 1. The final series of dyeing was carried out using modified Procion Rubine XL+, at either pH 4 or 7 to determine the effect of using a volatile amine salt of the dye in place of sodium salt. For this study, two dyeing methods were used. In the first method, stainless steel dye pots were utilised (Figure 1); and in the second one an open beaker (100ml) was used to carry out dyeing (Figure 2).

2.3. Color Strength (K/S) on fabric

Reflectance measurements on the dry dyed fabrics were

carried out using a Datacolor Spectraflash 600 spectrophotometer under a D65. The average of three reflectance measurements taken at different positions on the dyed fabric was used.

2.4. Determination of Dyebath Exhaustion

The extent of dye exhaustion was determined spectrophotometrically. The absorbance of each dyebath solution before and after dyeing process was measured using 1cm path length quartz cells housed in a Philips PU 8720 UV/visible scanning spectrophotometer, at the λ_{max} of each dye.

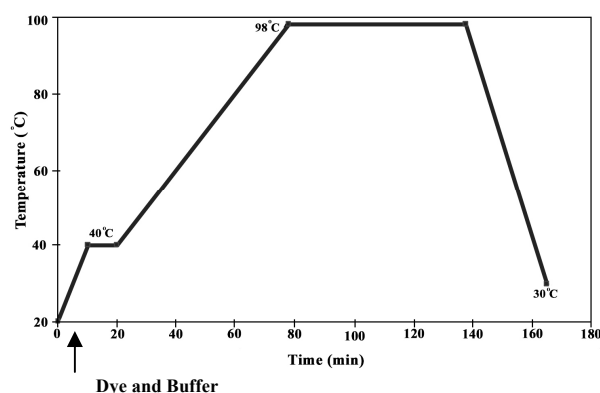


Figure.1: Dyeing profile used.

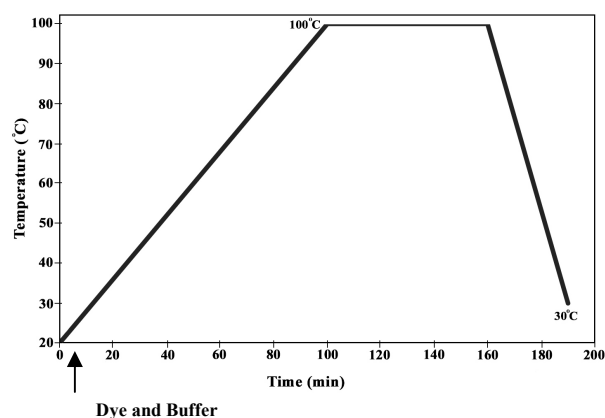


Figure.2: Dyeing profile used in beakers.

Table 1: Commercial dye used for dyeing.

Dye	No of solubilising sulphonate group	Reactive group type	No of reactive groups
Procion Rubine XL+	9	MCT	3

The percentage dyebath exhaustion (%E) was calculated using equation 1, where A_0 and A_1 are the absorbance of the dyebath before and after dyeing, respectively.

$$\%E = \frac{(A_0 - A_1)}{A_0} \times 100 \quad (1)$$

2.5. Wash off and Determination of Degree of Dye Fixation

Only a proportion of the total dye present on the substrate reacts to form covalent linkages, whilst the remaining dye is attached by ionic bonds and by Vander Waals forces. Therefore, in order to determine the degree of dye fixation, the following procedure was used.

A sample (1g) of dyed fabric was immersed in 150 cm³ of 20% aqueous pyridine solution, the temperature was raised rapidly to boiling temperature and the extraction of loose dye was continued under reflux until no further dye was removed from the fibre. This took approximately 3 hours. The extracted dyed fabric was thoroughly rinsed in tap water and allowed to dry in the open air. Initially, the extent of dye fixation was determined spectro-photometrically. The percentage of exhaustion dye which was fixed, %F, was determined by a method used by several earlier workers [18-20] using Equation 2 where $(K/S)_1$ and $(K/S)_2$ represent the color strength of the dyeing before and after stripping

The fixation determination by this method assumes that the concentration of fixed dye is directly proportional to (K/S) ; this is not always so, especially at

heavier depths of shade. The overall fixation percentage, %T, was evaluated from Equation 3.

$$\%F = \frac{\left(\frac{K}{S}\right)_2}{\left(\frac{K}{S}\right)_1} \times 100 \quad (2)$$

$$\%T = \frac{\%F \times \%E}{100} \quad (3)$$

3. Results and discussion

3.1. Effect of Desalination

The effect of removing electrolyte from the dyebath was investigated. Desalination was achieved by reverse osmosis using Visking tubing. Specific amount of dye was dissolved in minimum amount of distilled water, and then poured into the Visking tubing, which had previously been softened by immersion in distilled water for a few minutes. The tube was then sealed and put in a beaker of distilled water, stirred with a magnetic stirrer, and the distilled water replaced every 15 minutes until no chloride ion was detected by AgNO₃. The Mol.In (MI) of the desalinated and commercial dye solution was determined by titration against titanium^{III} chloride [10, [12, 23-24]. Results are shown in Table 2.

Figure 1 shows the dyeing method for desalinated Procion Rubine XL+ on 5g pieces of fabric, and the results are presented in Table 3. Table 3 shows the color strength and the extent of total fixation and exhaustion of desalination Procion Rubine XL+.

Table 2: Mol.In of commercial and desalinated Procion Rubine XL+.

Dye	MI
Procion Rubine XL+	3347
Desalinated liquid Procion Rubine XL+	140032

Table 3: $(K/S)_1$, $(K/S)_2$, %E and %T of desalinated and commercial Procion Rubine XL+.

Dye		0.05	0.1	0.2	0.5	0.8	1	1.5	2
Procion Rubine XL+	$(K/S)_1$	0.85	1.67	2.39	5	6.5	7.6	8.9	9.7
	$(K/S)_2$	0.62	0.9	1.6	3.2	4.26	4.75	5.4	5.7
	%E	100	100	73.5	60	50	48	36	28
	%T	72.9	54	50	39	32	30	22	16.4
Desalinated Procion Rubine XL+	$(K/S)_1$	0.91	1.28	2.15	3.66	4.51	5.2	6.4	7.57
	$(K/S)_2$	0.78	0.97	1.64	2.99	3.8	4.4	5.17	5.53
	%E	100	73	64	42	32	30	25	22
	%T	86	55	49	34	27	25	20	16

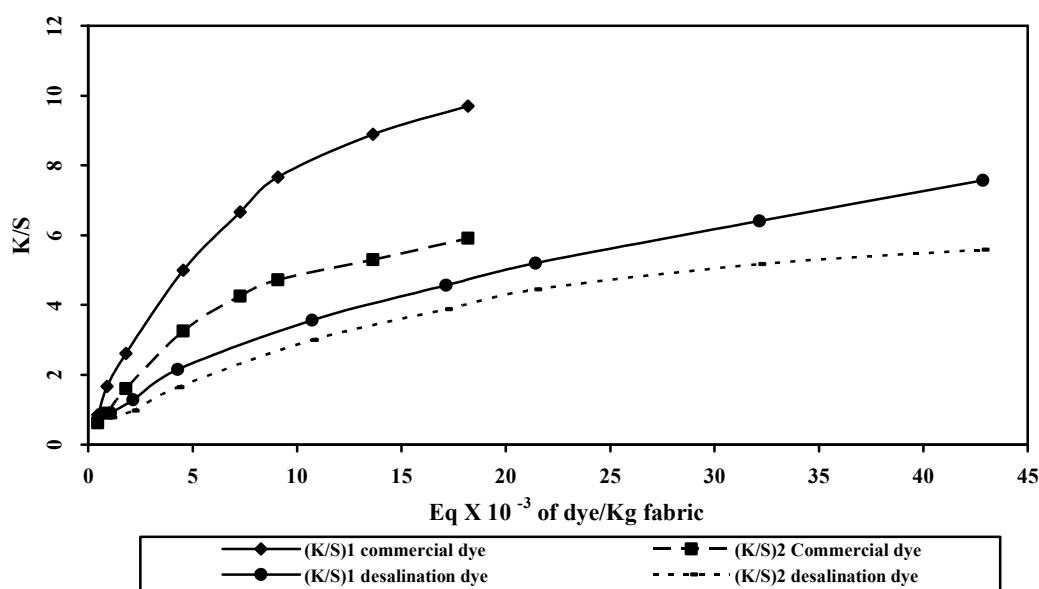


Figure 3: Effect of desalination on (K/S)₁ and (K/S)₂ of Procion Rubine XL+.

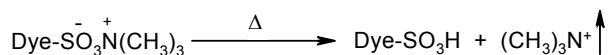


Figure 4: Dissociation of trimethylamine salt.

Table 4: Mol.In of modified liquid Procion Rubine XL+ dyes.

Dye	MI
Modified liquid Procion Rubine XL+ (pH7)	143646
Modified liquid Procion Rubine XL+ (pH4)	143600

Initial and final exhaustion values, together with fixation percentage of commercial and desalinated dye are shown in Figure 3, where the dye concentration on the x-axis is expressed in milli-equivalents of dye per kilogram of fabric.

Dyeing results, as shown in Figure 3 and Table 3 indicate that the initial and final exhaustion, (K/S)₁ and (K/S)₂, of the desalinated dye decreases relative to the commercial sample, suggesting that, in the absence of electrolyte substantivity of the dye for nylon decreases. This observation may suggest that an optimum concentration of electrolyte is needed to get the maximum dye uptake by fabric.

However, it is difficult to explain these results in the light of the reduced yields observed in the presence of

added electrolyte. Additionally, the determining the amount of effective agent in dilute aqueous desalinated solution of dye by titration against titanium^{III} chloride failed to give a clear end point.

Consequently, reducing the electrolyte concentration further resulted in reduced fixed color yield.

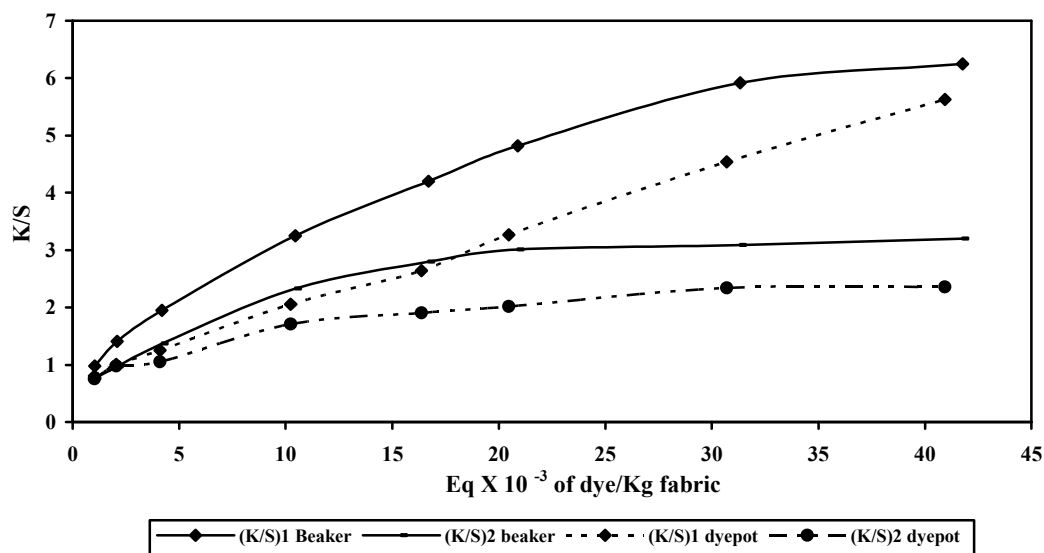
3.1. Effect of replacing sodium by a trimethylammonium salt

Procion Rubine XL+, which is a tri-functional reactive dye, has nine sulphonate groups and is marketed as the sodium salt. The sodium cation, Na⁺, of Procion Rubine XL+ was replaced by trimethyl ammonium ⁺HN(CH₃)₃. It was expected that, during the dyeing process, the trimethylamine salt would dissociate and that trimethylamine would volatilise due to its low boiling point, thus liberating the free sulphonic acid and leading to a gradual reduction of the dyebath pH Figure 4.

Procion Rubine XL+ (2.5g, 0.73mmol) was dissolved in distilled water (20ml) and an excess amount of trimethylamine (12g) was added. The pH was set at pH: 7 and pH: 4 by adding HCl. After desalination, using Visking tubing, (8 x 800ml distilled water over 2 hours), the contents of the tube were poured into a measuring flask and the volume was increased to 100ml. The Mol.In of this solution was determined by titration against titanium^{III} chloride, Table 4.

Table 5: $(K/S)_1$, $(K/S)_2$, %E and %T of commercial (sodium salt) and trimethylammonium salt of Procion Rubine XL+.

Dye		0.05	0.1	0.2	0.5	0.8	1	1.5	2
Procion Rubine XL+	$(K/S)_1$	0.85	1.67	2.39	5	6.5	7.6	8.9	9.7
	$(K/S)_2$	0.62	0.9	1.6	3.2	4.26	4.75	5.4	5.7
	%E	100	100	73.5	60	50	48	36	28
	%T	72.9	54	50	39	32	30	22	16.4
Modified Procion Rubine XL+(pH 7) dyed in beaker	$(K/S)_1$	0.98	1.41	1.9	3.25	4.2	4.85	5.92	6.3
	$(K/S)_2$	0.76	0.97	1.37	2.33	2.8	3.01	3.19	3.35
	%E	39.8	28.1	18.1	15.1	13.9	9.8	8	6.08
	%T	30.8	19.3	13	11	9.2	6.08	4.3	3.23
Modified Procion Rubine XL+(pH 7) dyed in dyepots	$(K/S)_1$	0.8	1.01	1.25	2.06	2.64	3.27	4.54	5.63
	$(K/S)_2$	0.75	0.98	1.05	1.71	1.9	2.01	2.34	2.36
	%E	39.7	25.2	17	10	8.4	7.8	6	5.7
	%T	37	19.4	14.3	8.3	6	4.8	3.1	2.4
Modified Procion Rubine XL+(pH 4) dyed in beaker	$(K/S)_1$	0.69	1.23	1.59	2.11	2.69	3.02	3.87	4.84
	$(K/S)_2$	0.64	1	1.23	1.75	2.2	2.42	2.94	3.24
	%E	59.3	45.7	35	18	15	14	12	10.7
	%T	55	37.15	27	14.9	12.2	11	9	7.2
Modified Procion Rubine XL+(pH 4) dyed in dyepots	$(K/S)_1$	0.61	0.7	1	1.3	1.55	1.73	2.26	2.75
	$(K/S)_2$	0.53	0.6	0.88	1.05	1.26	1.47	1.7	1.82
	%E	52	29	22	11	8.8	8	7.4	6
	%T	45	25	19.3	8.8	7.15	6.8	5.5	3.9


Figure 5: Effect of dyeing method on exhaustion and fixation of trimethylammonium salt of Procion Rubine XL+ at pH 7.

Two different methods were applied for both pH: 4 and pH: 7 solutions: one in 200cm³ stainless steel dyepots according to Figure 1, and the other in an 100ml open beaker (Figure 2) to allow liberated trimethylamine to evaporate. The liquor ratio was 20:1 and dyeing was carried out in the absence of electrolyte or levelling agent.

Table 5, lists the color strength, dye fixation and exhaustion values of both samples of the trimethylammonium salt and commercial Procion Rubine XL+ and Figures 5-7 show the results graphically. Figures 5-7 show that dyeing in a beaker seems to yield better build up and fixation than dyeing in dyepots.

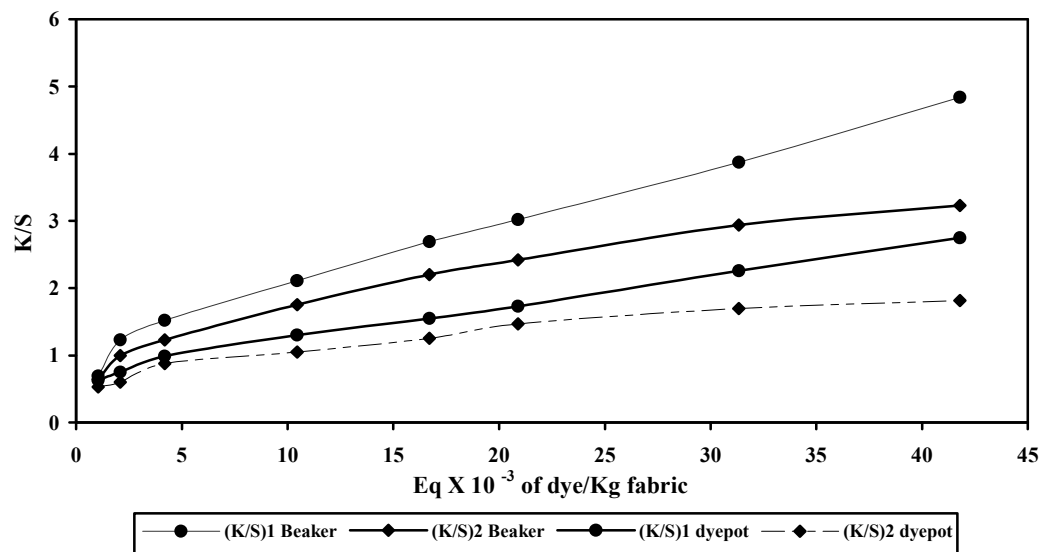


Figure 6: Effect of dyeing methods on exhaustion and fixation of trimethylammonium salt of Procion Rubine XL+ at pH 4.

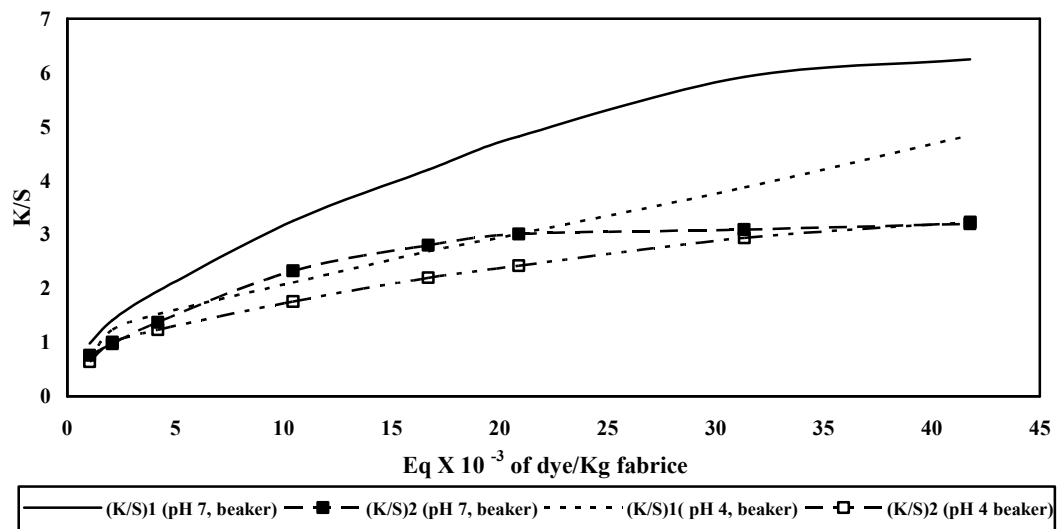


Figure 7: Evaluation of trimethylammonium salt of Procion Rubine XL+ at pH 4 & 7.

This is attributed to the fact that trimethylamine is free to evaporate from beakers but not from sealed dyepots. However, in all cases fixation yields were modest (55% fixation in open beaker at pH 7) and generally inferior to those obtained from the commercial sample of Procion Rubine XL+ according to Figure 8.

FTIR spectra of polymeric precursor, powder precursor were shown in Figures 2(a) and 2(b).

As seen in Figures 2(a) and 2(b), in the spectrum of

the polymeric resin precursor broad absorption bands around 3400 cm^{-1} and 1732 cm^{-1} are attributed to the stretching vibration of the hydrogen-bonded O-H groups and uncoordinated carbonyl group, respectively. Those at $2930\text{--}2990\text{ cm}^{-1}$ are the aliphatic C-H stretch.

An absorption band at 1074 cm^{-1} is the C-O stretch related to the formation of ester from $-\text{CH}_2\text{-OH}$ group in ethylene glycol and the carboxyl group of the citric acid [21, 22].

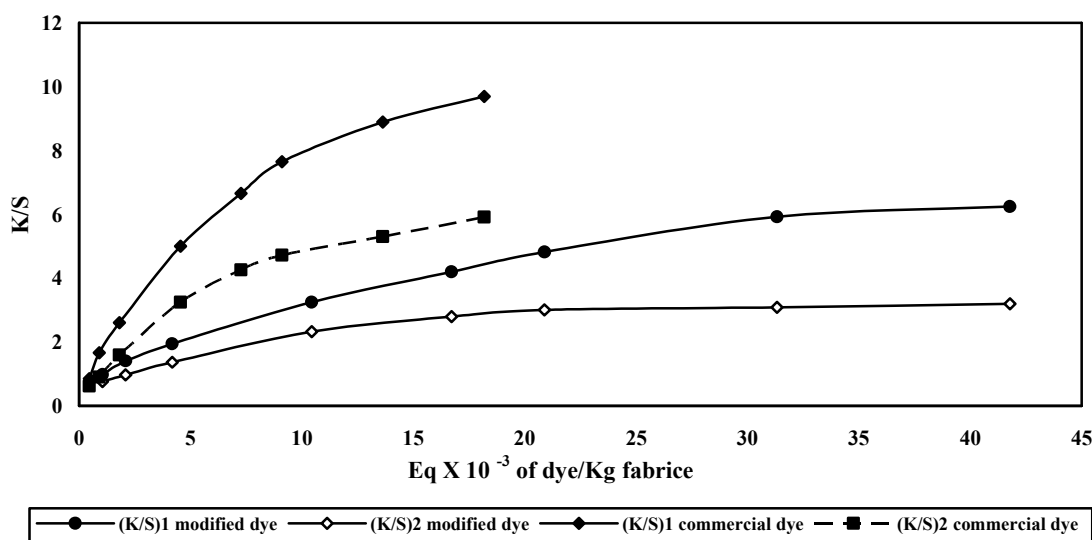


Figure 8: Evaluation of modified Procion Rubine XL+ with Procion Rubine XL+.

The bands at $\sim 1380\text{cm}^{-1}$ and $\sim 1600\text{cm}^{-1}$ are the asymmetric and symmetric C=O stretching modes, respectively, which confirm coordination of the carboxylate groups by metal ions to form a chelated complex and successive esterification reaction between CA (free and complexed) and EG [23].

In the FT-IR spectra of the powder precursor (Figure 2(b)) the absence of some organic bands could be ascribed to the decomposition of most organic ligands in the gel after primary calcination [22].

The FT-IR spectra of calcined powder are reported in Figure 3. As seen in these spectra all the previously mentioned absorption bands have disappeared and only strong absorption bands around 500cm^{-1} and 600cm^{-1} due to the metal-oxygen bonds are observed [24].

4. Conclusions

The removal of electrolyte from Procion Rubine XL+ has

no beneficial effect on color yield. This observation may suggest that an optimum concentration of electrolyte is needed to get the maximum color yield via competing with the anionic dye for the protonated amino end groups present in the fibre. The results from the evaluation of the effect of changing the counter ion from sodium to trimethyl ammonium in dyeing process (beaker and sealed dyepots) show that dyeing trimethylammonium salt of *Procion Rubine XL+* in open beaker gives marginally better fixation levels than in sealed dyepots. This was attributed to the fact that trimethylamine is free to evaporate from beakers, thus liberating the free sulphonic acid and leading to a gradual reduction of the dyebath pH, whereas trimethylamine was not free to evaporate from sealed dyepots. However, fixation yields were inferior to those obtained from the commercial sample of dye which may reflect much poorer control of the dyeing process in a beaker.

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