

# A Study of Reusing Vinyl Sulfone Based Reactive Dye for Dyeing Cotton Fiber

C. W. Kan\* and K. W. F. Fong

*Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*  
(Received May 15, 2017; Revised July 27, 2017; Accepted September 18, 2017)

**Abstract:** Reactive dye is a popular dye for dyeing cotton fiber due to its very good color fastness which is explained by the formation of covalent bond between dye and fiber. In this study, practicality of reuse of reactive dye by compensating for the hydrolyzed part of the dye solution is examined. A monofunctional dye (vinyl sulfone type) was used and it was found that dyeing cotton fiber with reused dyebath is possible. Since bifunctional dye can improve the chance of dye-fiber bond formation, vinyl sulfone based bifunctional reactive dyes were also selected in this study. Three types of bifunctional dyes were used and they basically share the same vinyl sulfone group; other reactive groups are monochlorotriazine, dichlorotriazine and vinyl sulfone. Such dyes were chosen in order to compare their respective efficiencies under the effect of one common reactive group. The aim of this study was to compare the effect of hydrolyzed and unhydrolyzed proportions of mono- and bifunctional reactive dyes on cotton fiber and study the possibility and efficiency of the two different reuse dyebath systems.

**Keywords:** Reactive dye, Monofunctional, Bifunctional, Cotton, Reuse

## Introduction

Cotton fibers are commonly dyed with reactive dyes as they offer bright colors with very good color fastness, as well as washing fastness and are easy and convenient in application. Most of them have excellent color fastness to light [1]. Cotton is a kind of cellulosic fiber, which is a polysaccharide. The hydroxyl groups present in cellulose molecules act as nucleophiles, which reactive dyes react with. The dyes are induced to react with the cellulose in aqueous alkali such that deprotonation of the hydroxyl groups takes place. As a result, Cell-OH is converted into Cell-O<sup>-</sup>. Cell-O<sup>-</sup> is regarded as an active nucleophile in reactive dyeing of cellulose [2]. The reactive dye reacts with fiber molecules by aromatic nucleophilic substitution or by nucleophilic addition to alkenes through the formation of a covalent bond [3]. Reactive group in the reactive dye may or may not be attached to the fiber. If the reactive group of the reactive dye is attached to the reactive site on the fiber (-OH in Cell-OH), dyed fiber can be produced. If the reactive group of the reactive dye is combined with the -OH in water, hydrolyzed dye is the result and this hydrolyzed dye does not attach to the cotton fiber and is wasted.

There are problems associated with dyeing of cotton with reactive dye. Firstly, the affinity of reactive dyes to cellulose is not very high. Although a lot of salt (50-100 g/l) is used to improve dye sorption, the efficiency of fixation on cellulosic fibers is generally low (50 %) [4]. Such low fixation efficiency leads to low utilization of reactive dyes and the effluent produced contains much of reactive dye which is wasted. Also, the high concentration of salt and alkali required in cellulose fiber dyeing add to the effluent problem

[5,6]. Reactive dyes need alkali for fixation. If the reactive group is in an aqueous environment, the dye-water reaction (hydrolysis) competes with dye-fiber reaction (fixation). The hydrolyzed dye no longer reacts with the fiber. As hydrolyzed dye cannot be fixed on fiber, they are left unused in the dyebath and hence wasted [7]. In addition, different affinities of reactive dyes towards textiles lead to either problem of efficiently washing off residual dyes or of insufficient dyeing if the affinity of reactive dyes towards a substrate is too high or too low [7]. The hydrolyzed reactive dye resulting from reactive dyeing has to be washed off thoroughly in order to achieve the desired wet fastness of the dye. Up to 50 % of the total cost of a reactive dyeing process can be attributed to the washing off stages and treatment of the resulting effluent [7].

A considerable amount of research has been devoted to the search for reactive dyes with improved fixation and reusing dyebath in order to better utilize resources [8-10] as well as using different advanced technology [11-17], to minimize the production cost and to reduce effluent generation and hence protecting the environment [4,18-20]. There are findings showing that reuse of dyebath for synthetic fibers is possible [18-20]. Apart from saving in resources, research has also showed that the plant cost is reduced in reuse of dyebath through using suitable machines and dyeing systems [4]. A reuse dyebath is categorized into one-bath application and two-bath application. For one-bath, the dyebath is directly reused by replenishing hydrolyzed dye, adding the amount of dyes which has been exhausted. For the two-bath application, no alkali is added in the first bath. After exhaustion, the goods are transferred to a second bath, the fixation bath, which contains the requisite amount of alkali for fixation. Reusing the first dyebath by replenishing the exhausted dye is feasible as there is no hydrolyzed dye

\*Corresponding author: kan.chi.wai@polyu.edu.hk

present. Previous work shows that reusing monofunctional reactive dye for dyeing cotton is possible. A study on reusing reactive dye by compensating the hydrolyzed dye has been conducted [21]. A monofunctional dye was used and it was found that dyeing cotton fibers with reused dyebath is possible. Since a bifunctional dye improves the chances of dye-fiber bond formation, it is selected in this project to verify the possibility of reusing bifunctional reactive dye for cotton dyeing.

Therefore, the aim of this study is to (i) investigate the effect of reusing dyebath on different reactive groups; (ii) find out the possibility of reusing bifunctional reactive dyes in reuse dyebath; and (iii) compare the efficiency of different reactive groups in reuse dyebath.

## Experimental

### Material

100 % cotton ready-for-dyeing interlock fabric was used. The fabric weight was 268 g/m<sup>2</sup>; the density of course and wale was 10 and 12 per cm, respectively. The yarn count was 32.8 Nm. The fabric was cleaned in 30 m//l acetone RG (Sigma-Aldrich, Germany) for 10 min to remove any grease and dirt. Subsequently, the fabric samples were rinsed with water and hydro-extracted for 5 min. Finally, the fabric samples were dried for 15 min using a tumble dryer. All the cleaned samples were conditioned under standard conditions of 65±2 % relative humidity and at 21±1 °C temperature for at least 24 h prior to all experiments.

### Dyes

A monofunctional dye and three types of bifunctional reactive dyes were selected (Supplied by DyStar, China. Due to commercial issues, the dye names are not disclosed). They have reactive groups of vinyl sulfone (VS), vinyl sulfone/vinyl sulfone (VS-VS), monochlorotriazine/vinyl sulfone (MCT-VS), and dichlorotriazine/vinyl sulfone (DCT-VS). All of them have the same reactive group, i.e. vinyl sulfone (VS). Three other reactive groups were selected for three reactive dyes which are monochlorotriazine (MCT), dichlorotriazine (DCT), and vinyl sulfone (VS). Such dyes were chosen in order to compare the efficiency of different reactive groups in cotton dyeing under the effect of one common reactive site as well as compare the efficiency of monofunctional reactive and bifunctional reactive dyes. The dyes were used as received without further purification.

### Preparation for Calibration Curve

An absorption curve with absorbance versus wavelength (400 nm to 700 nm) for each dye was prepared by using an ultra-violet-visible light (UV-vis) spectrophotometer of Spectronic 20 Gensys. Based on the absorption curve, wavelength at the maximum absorbance ( $\lambda_{\max}$ ) for each dye was recorded. A calibration curve, a plot of absorbance (at

$\lambda_{\max}$ ) versus dye concentration, for each dye which obeys the Beer-Lambert law ( $A=\epsilon bc$ ; where  $A$ : absorbance,  $\epsilon$ : Molar absorptivity,  $b$ : path-length of curvette, and  $c$ : concentration of dyebath) was obtained. It was essential to obtain the calibration curve in order to obtain the corresponding concentration of the dyebath before and after dyeing stage by measuring the absorbance of the dyebath. Hence, the percentage of fixation, the amount of dye exhausted could be calculated so that dyebaths could be recharged.

### Dyeing Procedures

Dyeing was carried out at liquor-to-goods ratio of 50:1 (using shaking water bath) and the dyeing curve is as shown in Figure 1. The amount of chemicals added is shown in Table 1 according to different dyes as recommended by the dye supplier. Three dye concentrations were used which are 0.1 %, 1 %, and 3 % (on-weight of fabric, owf). Generally speaking, the fabric was added initially at 25 °C in the dyebath and kept for 10 min. Then common salt was added and the dyebath was run for another 30 min followed by addition of the dye. In order to have good exhaustion, the dyeing process was carried out for a further 40 min before addition of soda ash alkali for fixation. The fixation of dye was carried out by increasing the temperature from 25 °C to 60 °C. The fixation process was conducted for 45 min. After fixation, the dyed fabric was washed with water, followed by soaping with 1 g/l non-ionic detergent at 95 °C for 10 min to remove unfixed dye. The soaped fabrics were washed with water again. Finally, the washed fabrics were dried and conditioned at 65±2 % relative humidity and 21±1 °C for at least 24 h prior to further experiments.

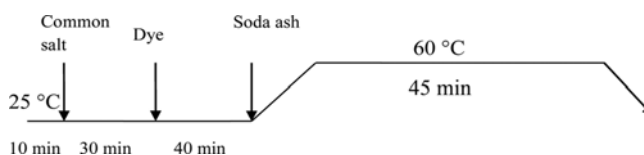


Figure 1. Dyeing curve.

Table 1. Amount of chemicals for dyeing

Dye type	Chemical used	Dye concentration (%)		
		0.1	1	3
VS	Common salt (g/l)	20	40	60
	Soda ash (g/l)	5	5	5
VS-VS	Common salt (g/l)	20	40	60
	Soda ash (g/l)	5	5	5
MCT-VS	Common salt (g/l)	20	40	60
	Soda ash (g/l)	5	5	5
DCT-VS	Common salt (g/l)	60	60	60
	Soda ash (g/l)	5	5	5

Salt: common salt and Alkali: soda ash.

### Design of Dyeing Process

Fabrics were dyed using two different bath applications, one-bath and two-bath application in order to study the reuse of reactive dye in a dyeing process.

#### One-bath Application

For one-bath application, the samples were dyed according to the procedure shown in Figure 1. After dyeing, the residual bath was saved and reused for dyeing the next batch. For one-bath dyeing, the dyebath was directly reused by replenishing hydrolyzed dye through adding the amount of dye required for replenishment of dye exhausted by the first sample.

#### Two-bath Application

For the two-bath application, samples were dyed with a similar procedure as one-bath dyeing method except no alkali was added in the first bath. After exhaustion, the dyed fabrics were transferred to a second bath, the fixation bath, which contained the requisite amount of alkali for fixation. Reusing the first dyebath was feasible as there was no hydrolyzed dye present. The residual dyebath was reused after replenishing the amount of dye that had been exhausted in the first dyeing. Again, a separate bath containing requisite amount of alkali was prepared for dye fixation.

In both one-bath and two-bath dyeing methods, we define "1st dyeing" as the samples first dyed according to the procedure shown in Figure 1 and "2nd dyeing" (reuse dyebath) as the use of the residual bath for second time dyeing according to the procedure shown in Figure 1. This design of the experiment was suitable for comparing the effect of hydrolyzed and unhydrolyzed monofunctional and bifunctional reactive dyes on cotton fiber and the possibility and the efficiency of reuse of the dyebath in the two different systems.

### Percentage of Exhaustion (%E)

The percentage of exhaustion (%E) was calculated from absorbance, based on equation (1):

$$\%E = [(A_1 - A_2)/A_1] \times 100\% \quad (1)$$

where  $A_1$  and  $A_2$  are the absorbance value before and after dyeing, respectively.

The absorbance was measured by a spectrophotometer Spectronic 20 Gensys. Percentage of exhaustion represents the amount of dyes exhausted in the process of dyeing.

### K/S Value and Reflectance Measurement

Color fixation of samples was examined by measuring the reflectance and hence the  $K/S$  values by Macbeth ColorEye 7000A spectrophotometer under illuminant D65 and using a  $10^\circ$  standard observer. The reflectance ( $R\%$ ) was measured after the first and second time dyeing, to compare whether there was any shifting of  $\lambda_{\max}$  before and after dyeing. The color yield of dyed samples was evaluated. For each individual dye, the sum of the  $K/S$  values at all wavelengths represents the total color yield in each dyed sample.  $K/S$  value was calculated from reflectance. Equation (2) is used for calculating the  $K/S$  value for opaque specimens at a specified wavelength:

$$K/S = (1 - R^2)/2R \quad (2)$$

where  $R$  is the reflectance value at the specific wavelength.

### Color Fastness Test

Two color fastness tests were carried out: (i) Color fastness to accelerated laundering, according to AATCC Test Method 61 (Test 2A); and (ii) Color fastness to crocking, as determined by AATCC Test Method 8 (Crockmeter method).

## Results and Discussion

### Percentage of Exhaustion

#### VS Dye

Table 2 summarizes the percentage of exhaustion of different dyes using one-bath and two-bath dyeing procedures. VS dye, which is alkali-controllable, has the lowest percentage of exhaustion, before adding alkali. VS dye is a monofunctional dye while the others are bifunctional dyes. Other reactive groups may give rise to higher percentage of exhaustion.

For one-bath application, alkali was added to the same

**Table 2.** Percentage of exhaustion (%) of different dyes

Dye type	Dyeing procedure	Dye concentration (%)					
		0.1		1		3	
		1st dyeing	2nd dyeing	1st dyeing	2nd dyeing	1st dyeing	2nd dyeing
VS	One-bath	24.12	3.78	16.74	4.41	21.88	6.58
	Two-bath	22.38	23.63	19.75	20.52	18.22	28.85
VS-VS	One-bath	82.65	24.88	69.43	26.03	78.74	26.22
	Two-bath	76.02	14.56	60.52	16.27	56.38	15.76
MCT-VS	One-bath	53.53	32.61	40.29	29.80	59.67	24.58
	Two-bath	35.67	31.53	42.22	26.78	27.90	20.70
DCT-VS	One-bath	65.51	17.81	55.58	23.99	42.97	15.78
	Two-bath	87.04	8.20	91.34	5.29	91.31	6.29

dyebath which contains salt, dye, and fabric and the absorbance was measured for the whole exhaustion and fixation process. For two-bath application, only fabric with adsorbed dye was transferred to a separate dyebath containing alkali. Absorbance of dye in the exhaustion process was measured. Although exhaustion process stops once alkali is added, dye is continuously attached onto the fiber physically during fixation stage in one-bath while there is no such attachment in the two-bath method. Due to physical adsorption in fixation stage in one-bath, the percentage of exhaustion in one-bath is higher than that in two-bath.

In case of reuse of the dyebath (i.e. 2nd dyeing), generally the exhaustion in 1st dyeing and 2nd dyeing is comparable in the two-bath method, whereas there is a significant difference in case of the one-bath method. This may be due to accumulation of chemicals and hydrolyzed dye. Unhydrolyzed dye from the original bath remains in the dyebath in case of the two-bath method. In case of one-bath method there is an accumulation of salt, alkali and unhydrolyzed and refreshed dye at the time of reuse application (2nd dyeing). The decrease in exhaustion in one-bath reuse may be due to such accumulation of chemicals.

Two-bath reuse dyeing (2nd dyeing) achieved a higher exhaustion than the original bath. This may be due to avoidance of hydrolysis from the original dyebath which may have given rise to a higher amount of unhydrolyzed dye in the recharged bath; with the recharging amount of refreshed dye, it allows more VS dye to be exhausted. With the combined effect of larger amount of unhydrolyzed dye (and recharged dye) and the larger amount of salt accumulated in the recharged bath, VS is able to achieve a higher exhaustion in 2nd dyeing.

#### ***VS-VS Dye***

Undoubtedly, as shown in Table 2, VS-VS dye has a higher exhaustion percentage than VS dye because it has an extra identical reactive group compared to VS dye. This extra reactive group contributes to the higher percentage of exhaustion. Monofunctional VS dye achieves a good percentage of exhaustion in two-bath application in 2nd dyeing (Table 2). It is expected that its behavior towards two-bath reuse is same as VS dye. Surprisingly, though it bears the same two functional groups as VS dye, it cannot achieve high exhaustion as in two-bath application in 2nd dyeing. The percentage of exhaustion of original dyebath is good while in 2nd dyeing there was poor exhaustion in both applications. As we have discussed previously, the percentage of exhaustion of monofunctional VS dye in one-bath reuse (2nd dyeing) decreases due to accumulation of chemicals. However, reuse in the two-bath of VS-VS dye should have achieved a higher exhaustion, as VS dye. For that reason, VS-VS dye behaves in a different way from VS dye in exhaustion stage though it has an extra identical reactive group.

#### ***MCT-VS Dye***

MCT-VS dye achieves exhaustion percentage closest to

the original dyebath (1st dyeing) when compared with other dyes (Table 2). For one-bath reuse (2nd dyeing), it may be due to the fact that MCT-VS dye has a strong reduced hydrolysis towards alkali. The MCT group has low reactivity towards alkali and the alkali-induced hydrolysis in the original dyebath can be minimized. It can be shown by high exhaustion in the one-bath reuse (2nd dyeing). Much of the dye does not get exhausted after 1st dyeing and it can be reused for 2nd dyeing.

In addition, MCT is a salt controllable dye, it can achieve high exhaustion in neutral pH, before addition of alkali in fixation stage. It has already been shown to achieve high exhaustion and level dyeing during exhaustion stage. When it is later subjected to alkali, the dye gets fixed onto the fiber. Therefore, in two-bath reuse (2nd dyeing), the difference between exhaustion in one and two-bath methods is negligible. The difference between exhaustion during 1st and 2nd dyeing in two-bath application is the smallest when compared to the other dye types. The main driving force is the avoidance of hydrolysis of dye in the original bath and its ability to control salt.

#### ***DCT-VS Dye***

DCT-VS dye achieves generally the best exhaustion (Table 2). Its two chlorine atoms account for its high reactivity and high exhaustion once alkali is added. One molecule of DCT is able to react with two molecules of cellulose (ratio of DCT:cellulose=1:2) while one molecule of VS can react with only one molecule of cellulose. It is very effective in achieving a high percentage of exhaustion since three molecules of cellulose are dyed by a single molecule of DCT-VS dye.

The percentage of exhaustion from two-bath 1st dyeing is higher than that of one-bath 1st dyeing. Without the effect of alkali, DCT-VS is able to exhaust more of dye in the two-bath 1st dyeing than in one-bath 1st dyeing. However, the reuse dyebath (2nd dyeing) of one-bath application has a higher percentage of exhaustion than that of two-bath, which is opposite to the original bath. Since alkali is added to the same dyebath containing dyes and fabric for one-bath application, the increased exhaustion is due to the ionic character triggered by accumulated soda ash in the reuse dyebath.

The percentage of exhaustion in 2nd dyeing is very low when compared to that of the original (1st dyeing). The results show that after first dyeing, DCT-VS dye becomes ineffective for reuse purpose, regardless of the bath application. This can be ascribed to DCT having high reactivity. After 1st dyeing, DCT-VS dye is already exhausted and it becomes not suitable for 2nd dyeing. Even after recharging the dyebath, low substantivity of DCT-VS dye cannot adsorb onto the substrate.

Exhaustion of dye in monofunctional and other bifunctional systems shows that an extra reactive group always contributes to a higher percentage of exhaustion. VS dye achieves a

higher exhaustion in reuse dyebath because of the combined effect of larger amount of unhydrolyzed dye and the larger amount of salt in the recharged bath. VS-VS dye behaves differently from VS in the exhaustion stage even though it has an extra identical reactive group. MCT-VS dye overall achieved exhaustion closes to each other in both bath applications. DCT-VS gets easily exhausted and it is not suitable for reuse due to its too high reactivity.

### Percentage of Fixation

#### VS Dye

As shown in Table 3, one-bath reuse (2nd dyeing) has a lower percentage of fixation than the original bath (1st dyeing) whereas for two-bath, the results are the opposite. The reason why low percentage of fixation in one-bath reuse will be discussed in the "Color yield" section (Color yield).

#### VS-VS Dye

Bifunctional reactive dye (VS-VS) achieves a higher percentage of fixation than a single reactive group VS dye as shown in Table 3. Such a result was expected since an extra reactive group could improve fixation of dye onto fabric.

#### MCT-VS Dye

MCT-VS dye has a high percentage of fixation (Table 3). It is notable that reuse dyebath (2nd dyeing) has a higher

fixation than the original bath. In addition, fabric dyed from two-bath achieved a higher percentage of fixation than one-bath. Such satisfactory result can be ascribed to the nature and property of reactive groups of MCT and VS. They have a resistance towards hydrolysis, which will be explained in the "Color yield" section.

#### DCT-VS Dye

The percentage of fixation of DCT-VS dye in one-bath is higher than in two-bath (Table 3). The fixation in DCT-VS is rather unsatisfactory. The main reason is probably the low substantivity of DCT-VS sulfone after first-dyeing.

Tables 2 and 3 show that there is no direct relationship between amount of exhaustion and fixation. For a dye that can achieve a high exhaustion percentage does percentage of fixation is not necessarily high. Reusing two-bath of VS dye (Table 3) gives a good fixation whereas reusing one-bath cannot. VS-VS dye achieves a higher fixation than VS dye. MCT-VS dye gives the most satisfactory results in terms of fixation when reusing one and two-bath. Dyebath of DCT-VS is not suitable for reuse due to its low percentage of fixation.

### Color Yield

Table 4 summarizes *K/S* sum values of different dyes

**Table 3.** Percentage of fixation (%) of different dyes

Dye type	Dyeing procedure	Dye concentration (%)					
		0.1		1		3	
		1st dyeing	2nd dyeing	1st dyeing	2nd dyeing	1st dyeing	2nd dyeing
VS	One-bath	86.60	39.92	97.70	45.56	84.65	49.47
	Two-bath	48.08	96.35	66.41	85.16	69.19	80.47
VS-VS	One-bath	96.16	89.44	95.19	86.65	95.16	85.78
	Two-bath	92.08	72.12	91.91	70.66	93.13	69.78
MCT-VS	One-bath	77.40	79.53	82.22	93.68	84.54	86.83
	Two-bath	94.44	97.86	90.92	95.06	83.96	96.35
DCT-VS	One-bath	90.60	61.54	93.65	65.73	92.74	66.35
	Two-bath	76.63	62.48	69.21	63.88	73.73	60.89

**Table 4.** Color yield (measured as *K/S* sum) of different dyes

Dye type	Dyeing procedure	Dye concentration (%)					
		0.1		1		3	
		1st dyeing	2nd dyeing	1st dyeing	2nd dyeing	1st dyeing	2nd dyeing
VS	One-bath	0.67	1.11	16.18	4.29	43.33	14.91
	Two-bath	0.55	0.50	3.09	1.57	5.02	2.30
VS-VS	One-bath	15.26	10.23	73.70	18.07	87.02	68.05
	Two-bath	3.17	0.97	9.07	5.53	5.51	3.79
MCT-VS	One-bath	6.77	1.99	39.26	14.68	113.02	50.55
	Two-bath	2.41	1.68	14.04	7.73	22.81	17.00
DCT-VS	One-bath	14.99	5.28	96.71	26.09	308.13	80.16
	Two-bath	2.24	1.03	4.82	5.34	18.27	20.50

under different dyeing conditions.

#### **VS Dye**

It is found that in general, the  $K/S$  value of the one-bath dyeing method is better than the two-bath dyeing method for the same color depth but the difference between color yield of 1st dyeing and 2nd dyeing varies greatly. There are factors which hinder fixing of dye onto the fabric but they do not affect exhaustion of dye. As discussed in the previous section, reuse dyebath (2nd dyeing) has a high amount of salt and chemicals which can promote exhaustion. Although salt promotes exhaustion, salt does not promote fixation with an increased concentration. However, using a higher amount of salt does not promote fixation of dye; the accumulation of salt and chemicals in the reuse dyebath for 2nd dyeing may hinder the dye-fiber bond formation. Such postulation is supported by the resultant percentage of fixation (Table 3). Such assumption is demonstrated in an increased concentration of salt in the bath from 1st and 2nd dyeing of one-bath dyeing method. Table 4 shows that such increment leads to a decrease in  $K/S$  sum values. In addition, concentration of dye exerts no effect on fixation (Table 3). For this reason, we can conclude that accumulation of salt and building up of chemicals hinder the fixation of VS onto fabric.

The two-bath method could achieve high exhaustion in the 2nd dyeing (Table 2) but could not achieve high color yield on the fabric (Table 4). In two-bath dyeing method, the amount of dye fixed onto the fiber depends on the substantivity of dye to cellulose during exhaustion. It was physically adsorbed onto the substrate during exhaustion stage and later chemically reacted with substrate in the fixation stage. While in one-bath dyeing application, alkali was added to the same dyebath containing salt, dyes and fiber. Dye-fiber formation and adsorption of dye occurred at the same time. The amount of dyes fixed onto substrate both chemically and physically is of course, higher than that through solely chemical bonding.

Comparing the exhaustion percentage (Table 2) to  $K/S$  value of VS dye (Table 4), high exhaustion percentage for two-bath dyeing application does not match the  $K/S$  result. Exhausted dyes have not been adsorbed and fixed onto the substrate. This may be due to low affinity of VS towards cellulose. Before addition of alkali in the exhaustion stage, VS dye is just physically attached onto the substrate. There is no chemical reaction in the exhaustion process. Alkali (soda ash) is required to activate the carbon-carbon double bond for fixation. It chemically reacts with cellulose in the presence of alkali. In one-bath dyeing method, though hydrolysis competes with dye-fiber reaction, soda ash, as a weak nucleophile, ensures that a fairly good amount of dye reacts with cellulose.

In contrast to the two-bath method, in the separate alkali bath, there is no dye in the dyebath environment and no such competition occurred. Alkali fixes dyes which are formerly adsorbed onto substrate and this results in low  $K/S$  value. All

in all, VS dye easily gets exhausted and the affinity towards fiber is low. It requires a higher temperature for fixation. At exhaustion stage, a high amount of VS dyes has been exhausted while the temperature at fixation is not high enough for successful fixation. This is demonstrated by the high extent of exhaustion even as  $K/S$  value is low.

#### **VS-VS Dye**

VS-VS dye is a bifunctional reactive dye with homo-functional reactive group which contains one extra and identical reactive group than VS dye. It is expected that having one extra reactive group, it should have a better performance than with single VS reactive group. From Table 4, the results show that it is generally true and the extra VS reactive group improves the affinity of dye when compared with dyeing with single VS reactive group. However, this too is subject to the same problem as VS dye in which alkali is required to activate the carbon-carbon double bond. It refrains VS group from producing a good color yield in two-bath dyeing method.

Without the intervention of hydrolysis and having physical attachment of dye onto substrate during exhaustion stage, Table 4 shows that VS-VS dye is better adsorbed and fixed than VS dye. It is owing to the fact that an extra VS group that VS-VS dye bears.

#### **MCT-VS Dye**

MCT-VS dye for one-bath and two-bath dyeing methods achieves generally a better color yield than VS type reactive dye (Table 4). Reuse of dyebath (2nd dyeing) also achieves better color yield than VS type of reactive dye. Since the MCT reactive group has strong resistance towards hydrolysis under alkaline conditions, there is a build-up of unhydrolyzed dye in the bath in 2nd dyeing. They can accomplish a good fixation in one-bath (2nd dyeing) when we collate other reactive dye types (Table 3). Obviously, because MCT-VS dye carries two reactive groups, it is more effective in producing color than VS dye. A higher molecular weight of MCT-VS than VS gives rise to a higher substantivity towards substrate and it also contributes to a high  $K/S$  value.

MCT chemically reacts with cellulose once alkali is added. Such reaction occurs simultaneously as MCT is highly reactive whereas time is needed for VS to be activated. For that reason, a higher amount of VS dye is hydrolyzed than MCT-VS dye. In other words, more of MCT-VS dye gets fixed onto the substrate. In addition, MCT-VS dye performs better than DCT-VS in one-bath dyeing method in the 2nd dyeing (Table 4). They are able to achieve a high exhaustion in neutral pH and are better adsorbed than DCT during exhaustion stage [14]; a larger amount of colorants can be fixed in later fixation stage.

#### **DCT-VS Dye**

On the whole, MCT-VS dye and DCT-VS dye achieve a better color yield than VS dye in both bath dyeing applications as shown in Table 4. Probably it is due to the fact that MCT and DCT are more reactive than VS.

High reactivity of MCT and DCT can be interpreted in view of energetics. The energy levels of MCT and DCT are lower than of VS. They enjoy a better stability in transition state by having a resonance form whereas VS is less stable in the transition state. The route of cellulose reacting with MCT and DCT is more preferable. On top of that, the stability of the dye-fiber bond also testifies the high reactivity. The linkages based on MCT and DCT are the consequences of substitution reaction while that in VS are resulted from additional reaction. The ester bonds which are formed from triazine types of MCT and DCT are highly stable, more stable than the ether bonds that are formed from VS types. In terms of energetics, forming an ester bond is more energetically favorable than forming an ether bond as it gives a more stable product.

Though DCT is more reactive than MCT, it is less effective in reproducing color shade than MCT in one-bath 2nd dyeing. MCT being stronger in resisting alkali-induced hydrolysis is one of the reasons. Also, from the results, it is evident that for DCT, the effect of hydrolysis is more prominent than the increase in reactivity. That is, the higher reactivity of DCT could not compensate the negative effect brought by hydrolysis when compared with MCT.

The effect of hydrolysis is significant on efficacy of DCT-VS if we compare the color yield from one-bath and two-bath dyeing. Without hydrolysis, DCT-VS dye can result in a closer  $K/S$  value in the two-bath dyeing method, which means DCT-VS is very sensitive to alkali. In one-bath dyeing method, there is no avoidance of hydrolysis and it cannot not achieve the desired color depth. Again, it shows that DCT-VS has no ability to reduce the hydrolysis.

Another noteworthy point is that two-bath 2nd dyeing with DCT-VS dye (Table 4) results in a closer color depth than MCT-VS and VS-VS. This can be ascribed to an extra chlorine atom that DCT bears and its higher reactivity. In the absence of any interference of hydrolysis, such high reactivity allows most of the fixation process to take place [22], so that it achieves nearly the same color yield.

Besides, according to [16], DCT as a monofunctional system does not give satisfactory results in reuse (2nd dyeing). They found that this may be due to high reactivity of DCT dyes leading to a lower hydrolysis. Our experimental results coincide with findings reported in the literature [23]. The  $K/S$  value is low in the case of reuse bath (2nd dyeing) for both bath methods (Table 4). Since DCT-VS reacts with cellulose at low temperature, when one of the halogen atoms is displaced by a dye-fiber reaction or dye-water hydrolysis, reactivity is greatly reduced by the presence of the new hydroxyl substituent. Then, DCT-VS dyes are not suitable for reuse purpose since they lose their reactivity towards cellulose.

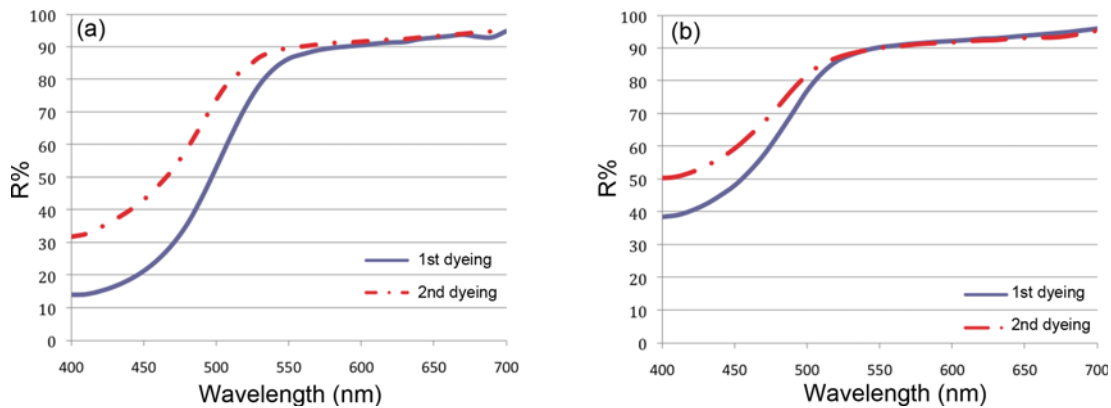
An interesting point is that when we refer to Table 4, for the two-bath reuse (2nd dyeing) with DCT-VS, they accomplished a color yield close to the original bath. But the

differences in exhaustion percentages are very extreme (Table 2). In one-bath dyeing method for 2nd dyeing, DCT-VS generally achieves a higher  $K/S$  value (Table 4) than two-bath for the same color depth. This might be due to low substantivity of DCT-VS to cellulose; the dye is merely adsorbed and needs to be fixed by alkali in later stage. In the one-bath dyeing method, alkali and dye are in the same bath and the high reactivity of DCT-VS leads to the dye-fiber reaction taking place relatively faster than dye-water reaction. As a result, more of dye can react with cellulose to give a covalent bond. Apart from dye-fiber reaction, physical dye adsorption also adds to the higher  $K/S$  value. In contrast, low  $K/S$  value in two bath dyeing method is because the dye is just merely attached onto fiber; solely due to force of substantivity during exhaustion stage.

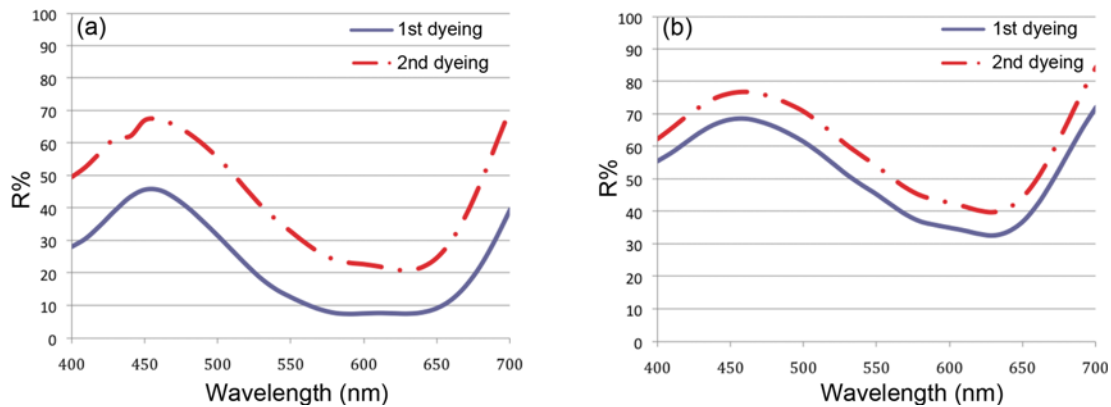
There are some limitations when we discuss the results. We have assumed that there are no synergetic or inhibiting effects from the combination of reactive groups, our discussion is based on individual properties. Also,  $K/S$  value is affected by dye type, dye color and substantivity of dye towards substrate. For example, DCT-VS dye is a black-color dye. Since  $K/S$  is a ratio of absorption coefficient and scattering, black color absorbs most of the radiation effectively while it reflects little of light. Its absorption coefficient is comparatively larger than others. Therefore, we cannot simply compare the concentration of colorant in different dye types in the substrate and we cannot know the amount of dye fixed onto the substrate chemically. However, we can overcome such weakness by comparing the percentage of fixation. The effect of physical adsorption can be ignored. With the accumulation of salt and chemicals in the reuse dyebath in 2nd dyeing, the interaction between dye and substrate in recharged bath becomes complex. There are many other factors which hinder color reproduction and we have only looked into how the hydrolysis factor affects the possibility of reusing dyebath.

### Reflectance

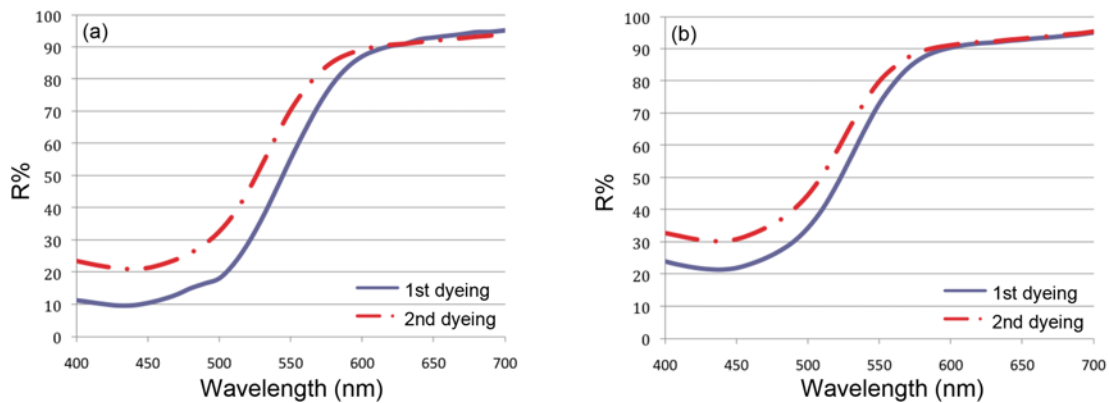
The reflectance curves of fabrics dyed with one-bath and two-bath dyeing methods were recorded. Reflectance curves (shown in Figures 2 to 5) of 1 % of different dyes are used as examples for discussion. The percentage of reflectance was measured after the 1st and 2nd dyeing and the curves are compared to see whether there is any shifting of  $\lambda_{\max}$ . Reflectance curve can act as a "fingerprint" of the dyed samples. Therefore, samples dyed from the same dye should follow a similar pattern while other curves do not match with them. There are some findings regarding the reflectance curves. Firstly, for all reflectance curves, there is no peak shifting of  $\lambda_{\max}$ . This is because the same dye was used throughout the 1st dyeing and 2nd dyeing. From the reflectance curves, we also know that the dye we used is only composed of a single component. That is, there is only pure single dye component, no mixing with other dyes and



**Figure 2.** Reflectance curve of 1 % VS; (a) one-bath method and (b) two-bath method.



**Figure 3.** Reflectance curve of 1 % VS-VS; (a) one-bath method and (b) two-bath method.



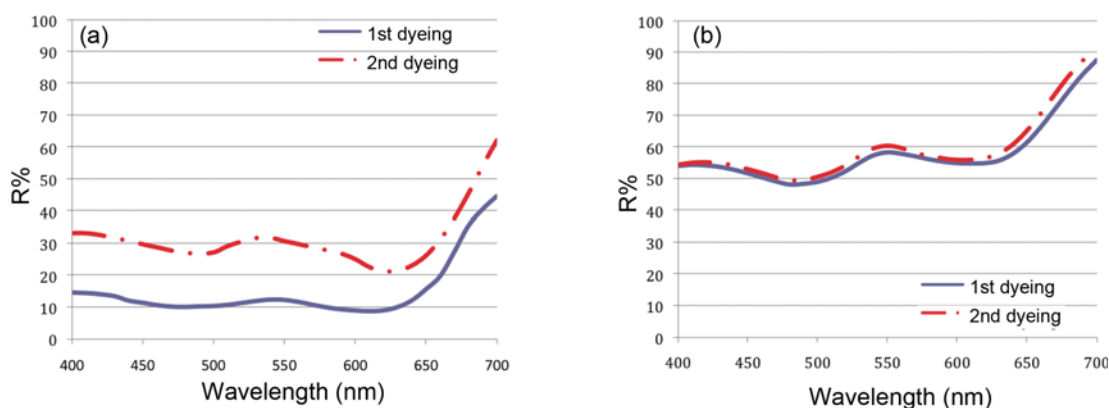
**Figure 4.** Reflectance curve of 1 % MCT-VS; (a) one-bath method and (b) two-bath method.

no other species in the dye that absorb light. If there is more than one component in the dye, more than one  $\lambda_{\text{max}}$  may appear. In addition, they also show that the effect of two-bath dyeing does not change the color of the dye.

The reflectance curve of 1st dyeing is always lower than that of the 2nd dyeing. Since reflectance  $R$  is a measure of how much light is reflected from the fabric, lighter colors reflect more light than darker colors. Therefore, the lighter

color shade of a dyed sample gives a higher reflectance value. The result is consistent with the color yield result ( $K/S$  sum). The higher the reflectance, the lower the color yield. There is a smaller difference in reflectance in two-bath application than in one-bath. Such result is consistent with  $K/S$  values. The difference between 1st dyeing and 2nd dyeing when using the two-bath dyeing method is negligible when compared to one-bath dyeing method.





**Figure 5.** Reflectance curve of 1 % DCT-VS; (a) one-bath method and (b) two-bath method.

### Washing Fastness

Table 5 shows that color fastness to washing is good for all dye types. Their assessment ratings of washing fastness to color change are usually 4-5 or above.

Table 6 shows that color fastness to staining is good for all dye types. In assessing the color staining, only cotton in the

multi-fiber fabrics are stained and the rating is 4-5. It was probably due to the substrate we used in the experiment was also cotton. VS and VS-VS dye show a relatively less satisfactory washing color fastness to staining results. This may be due to its weak covalent bond with cellulose compared to other dye types [24].

**Table 5.** Color change of different dyes (5 is the best rating; 1 is the worst rating)

Dye type	Dyeing procedure	Dye concentration (%)					
		0.1		1		3	
		1st dyeing	2nd dyeing	1st dyeing	2nd dyeing	1st dyeing	2nd dyeing
VS	One-bath	5	5	5	5	4-5	5
	Two-bath	5	5	5	5	5	5
VS-VS	One-bath	5	5	5	5	4-5	5
	Two-bath	5	5	5	5	5	5
MCT-VS	One-bath	5	5	5	5	4-5	4-5
	Two-bath	5	5	5	5	4-5	5
DCT-VS	One-bath	5	5	5	5	4-5	5
	Two-bath	5	5	5	5	5	5

**Table 6.** Color staining of different dyes (5 is the best rating; 1 is the worst rating)

Dye type	Dyeing procedure	Dye concentration (%)					
		0.1		1		3	
		1st dyeing	2nd dyeing	1st dyeing	2nd dyeing	1st dyeing	2nd dyeing
VS	One-bath	5/5/5/5/5*	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/4-5/5/5/5	5/4-5/5/5/5
	Two-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5
VS-VS	One-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/4-5/5/5/5	5/5/5/5/5
	Two-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5
MCT-VS	One-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5
	Two-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5
DCT-VS	One-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5
	Two-bath	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5	5/5/5/5/5

\*The rating refers to the staining in multifiber fabric in the sequence Cellulose acetate/Cotton/Acrylic/Polyamide/Polyester/Wool.

**Table 7.** Color change of different dyes (5 is the best rating; 1 is the worst rating)

Dye type	Dyeing procedure	Dye concentration (%)											
		0.1				1				3			
		1st dyeing		2nd dyeing		1st dyeing		2nd dyeing		1st dyeing		2nd dyeing	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
VS	One-bath	5	5	5	5	5	5	5	5	4-5	4-5	5	5
	Two-bath	5	5	5	5	5	5	5	5	5	5	5	5
VS-VS	One-bath	5	5	5	5	4-5	4-5	5	5	4-5	4	5	5
	Two-bath	5	5	5	5	5	5	5	5	5	5	5	5
MCT-VS	One-bath	5	5	5	5	5	4-5	5	5	4-5	4	5	5
	Two-bath	5	5	5	5	5	5	5	5	5	5	5	5
DCT-VS	One-bath	5	5	5	5	5	5	5	5	4-5	4-5	5	5
	Two-bath	5	5	5	5	5	5	5	5	5	5	5	5

### Croaking Fastness

The color fastness of dry croaking is good in general (Table 7). Most of the dye types have a rating of 5. VS-VS dye is relatively weaker in maintaining a good croaking fastness but it is still 4-5. Compared to results of washing fastness, VS-VS dye gives a less satisfactory result in terms of fastness. This may be due to its weak covalent bond with cellulose compared to other dye types. It is easier for a sample with darker color shade to have a lower color fastness because of higher amount of colorants it has, resulting in a higher chance for it to lose color.

The croaking fastness of wet croaking is good in general. Most of the dye types have a rating of 5. VS-VS dye is relatively weaker in maintaining a good croaking fastness but it still manages to attain a rating of 4 or 4-5. Compared to results of washing fastness, VS-VS dye gives a less satisfactory result in terms of fastness. This might be due to the same reason as described above, i.e. a weak covalent bond with cellulose [24].

### Conclusion

Monofunctional and other bifunctional systems show that an extra reactive group always contributes to a higher percentage of exhaustion. VS dye achieved a higher exhaustion in reuse dyebath. VS-VS dyes behaved differently from VS in the exhaustion stage even though it has an extra identical reactive group. MCT-VS dye overall achieved the closest exhaustion in both bath applications. DCT gets easily exhausted and it is not suitable for reuse due to high reactivity.

From the results of  $K/S$  values, it was found that increasing color depth always increases total color yield.  $K/S$  value of substrate from one-bath dyeing application is always higher than that from the two-bath dyeing application as the driving forces during fixation stage come from physical adsorption and chemical reaction. Moreover, in two-bath dyeing method, there is attribution from physical adsorption. Physical

adsorption also plays an important role in fixation stage. It was also found that the sum of  $K/S$  values from two-bath 1st dyeing and 2nd dyeing was similar.

Reusing dyebath by two-bath dyeing application can reproduce a close color yield due to no interference of hydrolysis. Although in two-bath reuse, the reuse dyebath can reproduce a very close color yield, the difference in original color yield is significant. Reusing DCT-VS dye was not found effective.

With the accumulation of salt and chemicals in the reuse dyebath, the interaction between dye and substrate in recharged bath became complex. There were many other factors which hinder color reproduction and hydrolysis factor was possibly the affecting issue in reusing of the dyebath.

Reflectance curve of each individual dye has its own unique curve pattern, which acts as the "fingerprint". There was no peak shifting of  $\lambda_{max}$  for all the reflectance curves. The dye used was only composed of a single component and the effect of two-bath did not change the color of the dye. The reflectance curve of first dyeing was always lower than that of the second. Such result is consistent with the color yield results.

Color fastness results generally show that all of them could achieve a good washing fastness to color change and staining; dry and wet croaking fastness was good. Most of the dye types have a rating of 5. VS-VS gave a less satisfactory color fastness than others. This might be due to its weak covalent bond with cellulose than other dye types.

The reuse of bifunctional reactive dyebath is possible. Dye containing MCT and VS reactive group was found to be the most efficient. MCT-VS dye gave the most satisfactory results in reusing dyebath due to its ability to reduce hydrolysis to alkali. Apart from achieving a good exhaustion, fixation and color reproduction, it also showed a good fastness towards washing and croaking. However, more investigations and experiments are needed to produce the exact color depth as the original dyeing.

### Acknowledgement

This work is part of final year project submitted by F. K. W. Fong in partial fulfilment of the requirements for BA (Hons) degree in the Institute of Textiles and Clothing, The Hong Kong Polytechnic University. Authors would like to thank the financial support from The Hong Kong Polytechnic University for this work.

### References

1. J. Shore, "Cellulosics Dyeing", pp.190-213, Society of Dyers and Colourists, Bradford, 1995.
2. H. Zollinger, "Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments", 3rd ed., p.226, Wiley-VCH, Weinheim, 2003.
3. A. D. Broadbent, "Basic Principles of Textile Coloration", pp.332-357, Society of Dyers and Colourists, Bradford, 2001.
4. Y. Yang and A. Haryslak, *Text. Chem. Color.*, **29**, 38 (1997).
5. C. W. Kan, C. K. Y. Lo, and W. S. Man, *Color. Technol.*, **132**, 4 (2016).
6. D. M. Lewis, *Color. Technol.*, **130**, 382 (2014).
7. R. M. Chrisitie, "Colour Chemistry", pp.135-147, Royal Society of Chemistry, London, 2001.
8. Y. S. Jung and D. G. Bae, *Fiber. Polym.*, **15**, 138 (2014).
9. F. X. Zhang, C. Chen, G. X. Zhang, L. Zhong, Y. S. Zhang, and S. Tan, *Color. Technol.*, **131**, 259 (2015).
10. M. S. Javadi, J. Mokhtari, M. Nouri, and F. Mazaheri, *Fiber. Polym.*, **14**, 920 (2013).
11. M. P. Gashti, A. Elahi, and M. P. Gashti, *Compos. Pt. B-Eng.*, **48**, 158 (2013).
12. M. P. Gashti, A. Pournaserani, H. Ehsani, and M. P. Gashti, *Vacuum*, **91**, 7 (2013).
13. M. Parvinzadeh, *Tenside Surf. Deter.*, **46**, 335 (2009).
14. Z. Nooralian, M. P. Gashti, and I. Ebrahimi, *RSC Adv.*, **6**, 23288 (2016).
15. M. P. Gashti, R. Rashidian, A. Almasian, and A. B. Zohouri, *Pigm. Res. Technol.*, **42**, 175 (2013).
16. M. P. Gashti and S. Eslami, *Funct. Mater. Lett.*, **8**, 1550073 (2015).
17. M. P. Gashti, F. Alimohammadi, and A. Shamei, *Surf. Coating Technol.*, **206**, 3208 (2012).
18. F. L. Cook and W. C. Tincher, *Text. Chem. Color.*, **12**, 15 (1980).
19. F. L. Cook, *Text. World*, **133**, 40 (1983).
20. S. Yi, Y. Deng, and S. Sun, *Fiber. Polym.*, **15**, 2131 (2014).
21. E. R. Trotman, "Dyeing and Chemical Technology of Textile Fibre", 6th ed., pp.447-462, Charles Griffin & Company Ltd., High Wycombe, 1984.
22. A. Johnson, "The Theory of Coloration of Textiles", 2nd ed., pp.196-209, Society of Dyers and Colourists, Bradford, 1989.
23. L. E. Chiweshe, V. Rai, and A. Scheyer, *Text. Res. J.*, **70**, 59 (2000).
24. J. Benz, *J. Soc. Dyer. Colour.*, **77**, 734 (1961).