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The contribution of different vinyl sulphone-reactive dyes to an effluent

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Abstract

Three types of vinyl sulphone dyes were measured in the effluent in this study. The selected dyes were Remazol Yellow RR (mono-functional), Remazol Blue RR (homo bi-functional) and Remazol Red RR (hetero bi-functional). The extinction coefficients of these dyes were measured by creating absorbance versus concentration curves. The absorbance values were obtained by testing standard solutions of each dye in a UV–visible spectrophotometer. The dyeing process was carried out at 4 different dye concentrations (0.025 g/40 ml, 0.05 g/40 ml, 0.10 g/40 ml and 0.15 g/40 ml) on a 5-g fabric sample for each of the dyes. The post-dye liquors and post-wash liquors were tested in an UV–visible spectrophotometer, and their concentrations were calculated using the Beer–Lambert law. The contribution of these dyes to the effluent was calculated and compared, and their adsorption isotherms (Langmuir and Freundlich isotherm) were analysed. The homo bi-functional dye (Blue RR) performed well in the dye bath, but it contributed significantly to the effluent during the washing stages. The mono-functional dye (Yellow RR) was able to adsorb, but it did not perform well due to its greater heterogeneity. The hetero bi-functional Red RR dye was found to be the most environmentally friendly in comparison with the other vinyl sulphone dyes.

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Keywords: Effluent; Contribution; Adsorption isotherm; Mono-functional; Bi-functional

1. Introduction

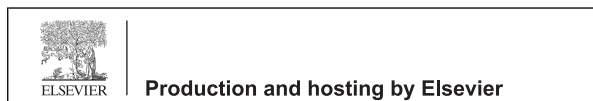
Removing the colour from effluent is currently an expensive process. In the case of vat or sulphur dyes, the unfixed dyestuffs can be separated by flocculation; however, with reactive dyes, sometimes up to 30%

of the dyestuffs can remain unbound from the fibre and require difficult processes to remove [1]. Vinyl sulphone-reactive dyes are very popular and are the class of dyes that are involved in a nucleophilic addition reaction with cellulose fibres [2]. Reactive dyes show different substantivities and reactivities due to their different reactive groups. Vinyl sulphone (VS) reactive dyes have a higher reactivity than monochlorotriazine (MCT) dyes [3]. Currently, bi-functional dyes, which combine more than one reactive group in the same molecule, are used substantially in dye houses. If the reactive groups are the same, the dye is called homo bi-functional; if the groups are different, the dye is called hetero bi-functional [4]. These dyes are known for their excellent efficiency and have strong exhaustion and

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fixation properties [1]. An advantage of MCT–VS dyes over those containing an MCT group is the higher degree of fixation of the former [5]. Greater colour strength was found for the VS dye over the MCT–VS dye [6]. Two different reactive groups offer a wider temperature range for application (MCT 80 °C and VS 50 °C) [7].

Hydrolysis is one of the main reasons behind reactive dye degradation, and it occurs because of the dye reactivity, which increases with pH and temperature [8]. The hydrolyzed dye and the regular dye behave in almost the same fashion during the dyeing process, but only the un-hydrolyzed dyes will react with the fibre, while the hydrolyzed version contributes to the effluent [9]. As vinyl sulphone-reactive dyes, which have different functional groups, are very popular, it is important to find ways to ensure that most of the dye remains in the bath, while the amount in the effluent is reduced.

Adsorption isotherm analysis can provide a great deal of useful information about the dye molecules' behaviour with the fibre surface [10]. The literature shows some curves obtained by plotting the dye adsorbed by a fibre against the remaining dye in the solution at a constant temperature [11]. Reactive dyeing on cellulose generally can be described by the Langmuir and Freundlich isotherm models [12].

Adsorption isotherm analyses were performed by several researchers on removing reactive dyes from solutions, such as the effluent [13–16]. However, there are very few studies showing the adsorption isotherm of the reactive dye on cellulose fibres during the dyeing process [17]. The objective of this paper was to determine the adsorption behaviour of different types of vinyl sulphone dyes and to calculate their contribution to the effluent as well as to find the reasons behind the contribution differences.

2. Method

2.1. Fabric and dyes

Single jersey scoured and bleached cotton fabric supplied by Impress-Newtex Composite Textile Limited, Bangladesh, was used in this research. The fabric was prepared from 26 Ne combed yarn with a 2.62-mm stitch length and 160 GSM (gram per square metre). Three types of vinyl sulphone dyes were considered for this research [18] as follows: Remazol Yellow RR, mono-functional vinyl sulphone dye (VS); Remazol Blue RR, homo bi-functional vinyl sulphone dye (VS–VS); and Remazol Red RR, hetero bi-functional dye containing one vinyl sulphone and one monochlorotriazine group (MCT–VS). The dyes were

Table 1
Calculated dye extinction coefficients.

Dye	Extinction coefficient (L g ⁻¹ cm ⁻¹)
Yellow RR	9.7
Blue RR	4.9
Red RR	15.8

purchased from Impress-Newtex Composite Textile Limited, Bangladesh from DyStar, Germany.

2.2. Dye extinction coefficient

The absorbance values of the known standard concentrations (0.005 g/L, 0.01 g/L, 0.02 g/L, 0.03 g/L, 0.05 g/L) of the dyestuffs were tested separately in a UV–visible spectrophotometer (UV1800). The absorbance values at λ_{max} (wavelength at maximum absorbance) were 420 nm for Yellow RR, 587 nm for Blue RR and 517 nm for Red RR. From the Beer–Lambert law, the equation can be written as follows:

$$\varepsilon \times l = \frac{A}{c}$$

where A = absorbance, ε = dye extinction coefficient (L g⁻¹ cm⁻¹), l = path length (cm) of solution the light passes through and c = solution concentration (g/L) [19]. The absorbance values were recorded and a graph was drawn by plotting the concentration on the x -axis and the absorbance on the y -axis [20]. According to the above equation, the slope of the curve is ε and the value of l is constant at 1 cm. The slopes or the dye extinction coefficients were then calculated by using the least squares method [21] (Table 1).

2.3. Dyeing and after-treatment

Three different self-shades (red, yellow and blue) were created on fabric (5 g) at four different concentrations (0.025 g/40 ml, 0.05 g/40 ml, 0.10 g/40 ml and 0.15 g/40 ml). Dyeing was carried out for 60 min at 60 °C, while other chemical amounts were maintained according to Table 2.

Dyeing was performed in a Mathis Labomat dyeing machine using 12 sealed, stainless steel dye pots. Individual samples and the required amount of water were added to the dye pot, and the machine was run until the temperature of the bath reached 60 °C. Then, salt was added and the machine was run for another 2 min to create the ideal environment for absorption. Next, the dyestuff was added and the machine

Table 2
Chemicals used in dyeing.

Chemicals	Dye concentrations			
	0.025 g/40 ml	0.05 g/40 ml	0.10 g/40 ml	0.15 g/40 ml
NaCl	30 g/L	50 g/L	50 g/L	60 g/L
Na ₂ CO ₃	5 g/L	5 g/L	5 g/L	5 g/L
NaOH	0 g/L	0.3 g/L	0.3 g/L	0.45 g/L

was run for another 2 min, after which the alkali was added to initiate the reaction between the dye and the fibre. The after-treatment was performed in the following order: hot wash (60 °C) → cold wash (28 °C) → squeezing → drying. During washing, each fabric was soaked in 300 ml of water in a beaker, stirred gently for 5 min and then squeezed. Dyed, washed samples were then dried in a dryer for 30 min at 60 °C. The post-wash liquors from each stage, as well as the post-dye liquors, were saved in the pots for the UV–visible spectroscopy test.

2.4. Analysis of post-dye and post-wash liquors

All of the preserved liquors were tested one by one on a UV1800. From the Beer–Lambert law:

$$c = \frac{A}{\varepsilon \times l}$$

where the dye concentration, c , of the liquors was obtained by inserting the values of ε , l and A into the equation. The amount of dye, d (g), in the post-dye and post-wash liquors was calculated from the following equation:

$$d = c \times V$$

where V is the volume of the liquor (ml). After calculating the amount of dye in the liquors, the percentage of the dye from the initial amount that contributed to the effluent ($X\%$) was calculated by using the formula:

$$X\% = \frac{d}{D_i} \times 10$$

where d is the weight of the dye (g) in the post-dye liquor, post-hot-wash or post-cold-wash liquor and D_i = initial dye weight in the dye bath (g). The total contribution of each of the dyes for a particular dye concentration was calculated by taking the sum of the $X\%$ at all stages.

To confirm the results, they were compared to an industrial scale experiment with the same dyes. For those analyses, 0.05 g/40 ml and 0.15 g/40 ml concentrations were considered for the self-shades of the same three

dyes, but a larger volume of fabric (200 kg) and liquor (1600 l) was used instead.

2.5. Adsorption Isotherm analysis

If C_f = dye adsorbed on the adsorbent (mg/g) and C_s = dye concentration of liquor (mg/L), the linear form of the Langmuir model [22] can be written as follows:

$$\frac{1}{C_f} = \frac{1/(C_{max} + 1)}{bC_{max}C_s}$$

where b = adsorption energy and C_{max} = maximum number of adsorption sites. The linear form of the Freundlich model [23] can be written as follows:

$$\ln(C_f) = \ln(k) + (1/n) \ln(C_s)$$

where n = heterogeneity level and k = capacity of adsorption. The graphs of $1/C_f$ against $1/C_s$ (Langmuir model) and $\ln(C_f)$ against $\ln(C_s)$ (Freundlich model) were drawn. The best fit slope ($1/bC_{max}$ and $1/n$) and the intercept [$1/C_{max}$ and $\ln(k)$] of these models were determined by using the least squares method. The coefficient of determination [21], R^2 , was calculated by the following formula:

$$R^2 = \left[\frac{m \sum (x_i y_i) - \sum x_i \sum y_i}{\sqrt{\left\{ m \sum x_i^2 - (\sum x_i)^2 \right\} \left\{ m \sum y_i^2 - (\sum y_i)^2 \right\}}} \right]^2$$

where m is the number data pairs and x and y are the x - and y -coordinates. The R^2 is the ratio of the explained variation to the total variation according to $0 < R^2 \leq 1$, which denotes the strength of the linear association between x and y and represents the percent of data that is closest to the best fit line. For example, if $R^2 = 0.90$, this means that 90% of the total variation in y can be explained by the linear relationship between x and y , while the other 10% remains unexplained.

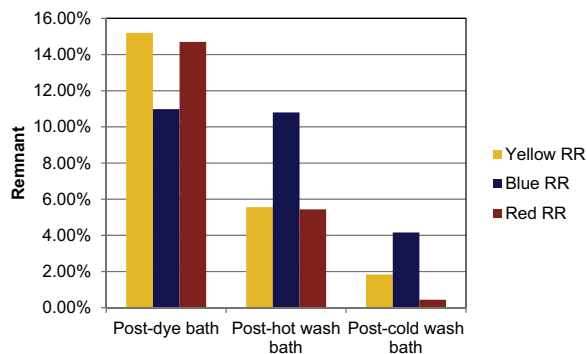


Fig. 1. Dye contribution to the effluent at 0.025 g/40 ml.

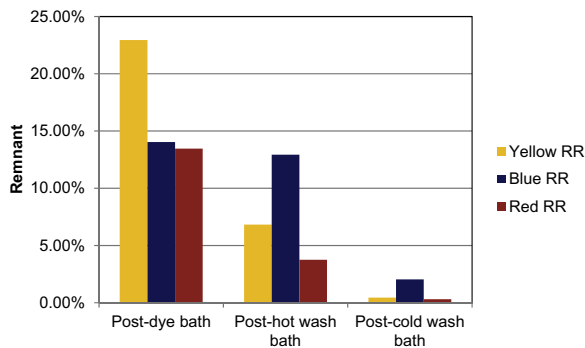


Fig. 4. Dye contribution to the effluent at 0.15 g/40 ml.

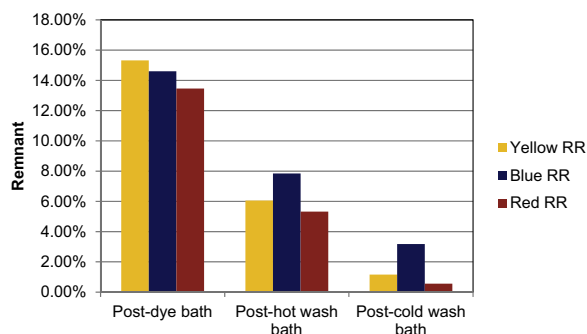


Fig. 2. Dye contribution to the effluent at 0.05 g/40 ml.

3. Results and discussion

3.1. Dye contributions to the effluent

From the analyses in Figs. 1–4, it can be stated that the mono-functional dye (VS) Yellow RR had a greater contribution to the effluent from the post-dye bath than the other types of vinyl sulphone dyes. Moreover, the contribution increased with increasing dye concentration. In the washing stages, its contribution was between the MCT–VS and VS–VS dye during the hot wash, and

almost the same results were found in the case of the cold wash. However, the contribution from the post-wash liquors generally decreased with increasing concentration. The homo bi-functional vinyl sulphone-reactive dye (VS–VS) Blue RR contributed less to the effluent from the post-dye bath. However, it contributed much more than the other vinyl sulphone dyes, especially during the washing stage, which indicates a greater tendency to hydrolyze. The hetero bi-functional vinyl sulphone dye (MCT–VS) Red RR had a moderate contribution to the effluent from the dye bath. Most importantly, its contribution decreased with increasing dye concentration. The dye was very difficult to remove by a cold wash, and its contribution also decreased with increasing dye concentration in the hot washing stage.

In total, from Fig. 5, it was found that the MCT–VS dye had the least contribution to the effluent. However, the VS–VS dye and the VS dye competed with each other in contributing to the effluent. Overall, the VS–VS dye contributed less than the VS dye at higher concentrations, and the VS dye contributed less than the VS–VS dye at lower concentrations.

Table 3 shows the comparison of the selected dyes in industrial-scale dyeing and the effluent effect. The results

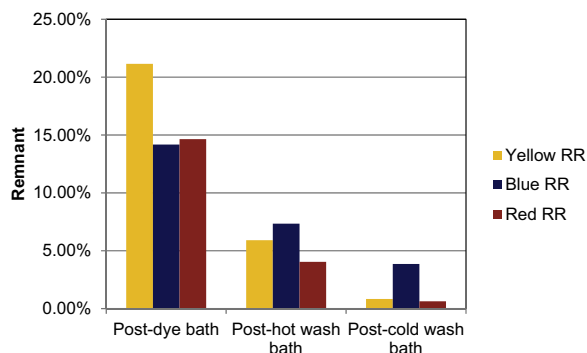


Fig. 3. Dye contribution to the effluent at 0.10 g/40 ml.

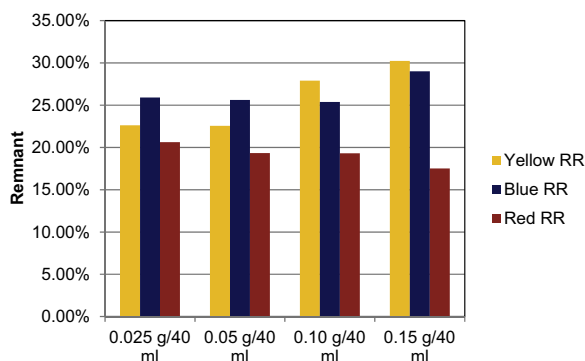


Fig. 5. Overall dye contribution to the effluent.

Table 3
Results from industrial-scale dyeing.

Dyes	Dye concentrations	Fabric weight (kg)	Total liquor (l)	Dye contribution to effluent			
				Post-dye bath (%)	Post-hot wash (%)	Post-cold wash (%)	Total in effluent (%)
Yellow RR	0.05 g/40 ml	200	1600	15.99	6.76	1.53	24.28
	0.15 g/40 ml	200	1600	23.63	7.50	1.15	32.28
Blue RR	0.05 g/40 ml	200	1600	15.33	8.41	3.64	27.38
	0.15 g/40 ml	200	1600	14.84	13.56	2.56	30.96
Red RR	0.05 g/40 ml	200	1600	13.88	5.96	0.89	20.73
	0.15 g/40 ml	200	1600	14.09	4.25	0.83	19.17

are similar, albeit slightly higher, to those found in this study.

3.2. Adsorption isotherm analysis

Figs. 6 and 7 represent the Langmuir adsorption and Freundlich isotherms, respectively, of these three dyes, with the constant values listed in Table 4. The determination coefficient, R^2 , is a relative measure of the regressive line and the model's usefulness. The model has greater fidelity as R^2 approaches 1 [21].

For the Langmuir model, C_{max} is the maximum number of adsorption sites that dye molecules can occupy on the fibre. C_{max} should have a finite value, b , which is the relationship between constant adsorption speed and constant adsorbate desorption speed or adsorption energy. A higher b value means tighter bonding of dyestuffs [22,23]. In Table 4, though the dyes have an R^2 close to 1 for the Langmuir model, but a negative C_{max} for Red RR and infinite C_{max} for Yellow RR, both scenarios are practically impossible.

Therefore, the Langmuir model inadequately describes the adsorption. However, the Freundlich

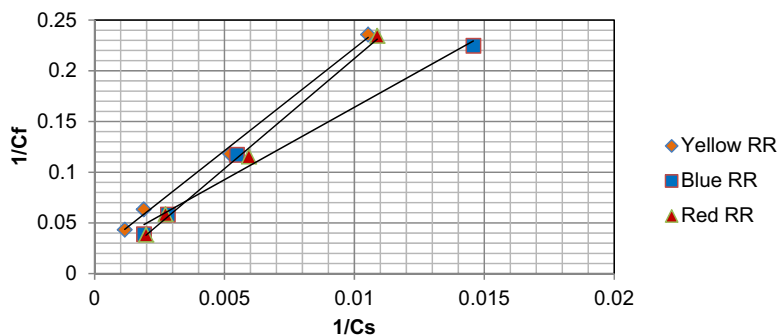


Fig. 6. Langmuir adsorption isotherm model.

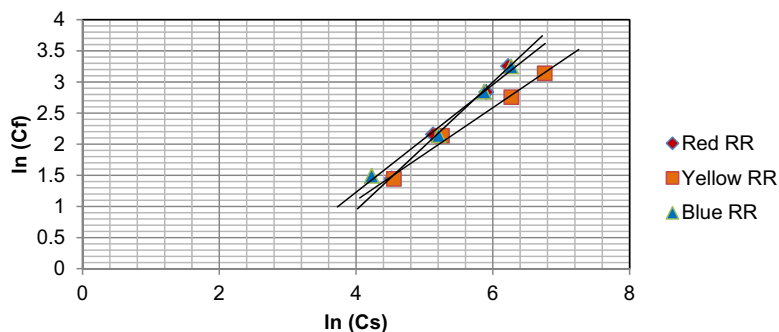


Fig. 7. Freundlich adsorption isotherm model.

Table 4
Analytical illustration of Langmuir isotherm with coefficients.

Dyes	Langmuir constants			Freundlich constants		
	C_{max} (mg/g)	b (L/mg)	R^2	k	n	R^2
Yellow RR	Infinity	0	1	0.159	1.344	0.990
Blue RR	47.62	0.00148	0.979	0.108	1.159	0.986
Red RR	–200	–0.00023	0.995	0.042	0.973	0.995

model also had a determination coefficient close to 1 and gave two constant values, k and n , for each of the dyes, where k is the relative measurement of the adsorption capacity (larger k means greater adsorption capacity) [23]. The slope $1/n$, ranging between 0 and 1, is a measure of the adsorption intensity or surface heterogeneity: as the surface becomes more heterogeneous, its value reaches zero, and a slope greater than 1 indicates cooperative adsorption [10]. As shown in Table 4, the adsorption capacity, k , and the invariable n were greater for Yellow RR. This indicates the heterogeneity in the adsorbent surface. However, Red RR showed cooperative adsorption and a low heterogeneity level.

The Langmuir model refers to homogeneous adsorption, while the Freundlich isotherm is widely used in heterogeneous systems [10]. The Freundlich isotherm is normally used in circumstances where the dye adsorption to the fibre is not limited by a specific number of adsorption sites and the fibre does not become saturated with dye [24]. These vinyl sulphone dyes were well-suited to the Freundlich isotherm model. Therefore, it can be noted that to reduce the dyes' contribution to the effluent, it is necessary to saturate the fibre with the dyes as much as possible. For that reason, the dye homogeneity in the dye bath should be improved. If the dyestuffs had a homogenous distribution along the fibre, more of the dye would be occupied by the adsorbent and would contribute less to the effluent.

4. Conclusions

The VS–VS dye (Blue RR) contribution to the effluent was greater in the washing step, but its contribution from the dye bath was not. This indicates the dye's high substantivity towards the fibre, as well as a tendency to hydrolyze from the higher reactivity. This problem can be resolved by reducing the pH or temperature, which are the main parameters in controlling the dye's reactivity. The VS dye (Yellow RR) was not strong enough in terms of exhaustion and fixation, so its contribution to the

effluent was also high. The adsorption isotherm showed that although the VS dye had the capacity, it did not perform well due to its heterogeneity. Therefore, increasing the homogeneity is necessary for better uptake. The MCT–VS dye (Red RR) had satisfactory performances in all aspects. Thus, it can be affirmed that a hetero bi-functional vinyl sulphone dye, such as MCT–VS, can be more environmentally friendly than other similar dyes.

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