Effect of reactive dye mixtures on exhaustion values

Mohamed Hamdaoui1,2,a, Samar Turki2, Zouhaier Romdhani3 & Sabri Halaoua2,3

1Laboratoire d’Etudes des Systèmes Thermiques et Energétiques, University of Monastir, Tunisia
2Département de Génie Textile, Ecole Nationale d'Ingénieurs de Monastir, University of Monastir, Tunisia
3Laboratoire d’Interfaces et Matériaux Avancés (L.I.M.A.), Faculté des Sciences de Monastir, University of Monastir, 5019 Monastir, Tunisia

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The effect of dyes mixtures for the dyeing of textile fabrics on an exhaustion rate has been studied. The exhaustion rate of 3 reactive dyes (Yellow Bezactiv S3R, Red Bezactiv S3B and Blue Bezactiv SGLD), their binary and tertiary mixtures on pre-wetted cotton fabrics has been investigated. The dyeing is carried out at the liquor ratio of 1:40 in a sealed stainless steel dyebath housed on the Ahiba Nuance Speed. The results show that the exhaustion rate of every dye in monochromatic dyeing is different from the exhaustion value of the same dye in presence of another dye. A quantitative measurement technique for identifying each individual dye concentration in the mixtures solution and determining the exhaustion rate is also proposed.

Keywords: Cotton fabric, Dye mixtures, Exhaustion rate, Reactive dyes

1 Introduction

Dyeing processes go through three fundamental stages1. The first one consists of the dissolution or dispersion of the dye to be readily absorbed by the substrate. The second stage consists of the adsorption on the surface of the substrate. Finally, the dyeing process is achieved by the penetration and diffusion of the dye into the substrate. It would be very easy to control these three stages when the dyeing bath contains a single dye. However, practically most of textile materials are dyed with mixtures of dyes to achieve an exact reproducibility of the required colour. After dyeing, one of the main tasks of the colourist is to decide whether a dyeing represents a satisfactory colour match to a given standard or an addition is required to the dyeing as a correction. An absolute colour match between a dyeing and a standard is an exception. As a rule, there is always a slight difference in shade between both samples.

In practice, many problems influence colour reproducibility. Firstly, poor reproducibility may be due to fibre characteristics, textile structure2 (yarn, woven fabric or knitted fabric) and dyeing conditions3. For example, the affinity of cotton for dye depends on the factors exercising an influence on the dyeing process. It varies according to the cotton history, the dye category, the dyeing process (continuous dyeing or exhaust method) and the dyeing conditions (liquor ratio, temperature4, auxiliary4, pH, water quality, etc).

Secondly, poor reproducibility may be due to the errors in weighing out the dyes specified in the recipe or inaccurate volume metering on auxiliary or water. Also, in the case of reactive dyes used in this study, poor reproducibility of required colour may be caused by the dye sorption and affinity which depend on the structure of the dye molecule5 and the reactive system5.

Thirdly, dyeing by using dyes mixtures requires the use of two or three dyes with non-identical properties (affinities and reactivities), which can affect the sorption of the dye when it is used alone in the bath. Porter6 shows the existence of 5 factors that could affect the sorption of a direct dye when it is used in the presence of another dye, viz competition of the two dye anions for the available sorbing surface, decrease in sorption of either dye anions in the mixture, electrical repulsion of a dye from the fibre surface by other sorbed dyes of similar charge, attraction of dyes for each other on the fibre surface, and finally the interaction of dyes with each other in the solution.

For these reasons, to realize the exact reproducibility of the required colour, it is quite important to determine the effect of the dye mixtures
on the colour values. Therefore, in the present study, a quantitative measurement technique has been proposed to identify each individual dye concentration in a single and dye mixtures solution and analyze the experimental data to describe a system containing a single dye, a system containing a mixture of two dyes and a system containing three dyes.

2 Materials and Methods

Experiments were carried out on cotton woven fabrics, having the weaving structure twill of 3, warp count of 36 yarns / cm and filling count of 41 yarns / cm. The weight ratio of the obtained fabric is 261 g/m².

The commercial dyes used in this study were Bezactiv S (Bezema). The UV-visible absorption spectra in water of these dyes were recorded using Biochrom spectrophotometry. The concentration of the dye was 0.1 g/L. The data obtained from the measurements are given in Fig. 1. The maximum wavelengths of the 3 reactive dyes were 446, 542 and 622 nm for Yellow S3R Reactive dye, Red S3B Reactive dye and Blue SGLD Reactive dye respectively.

To remove the warp sizes that were applied to yarns prior to weaving, a desizing treatment was realized. Also, to remove the waxes and oils attached to greige fabrics that interfere with proper dyeing, scouring treatment was given. All tested fabrics were bleached at 90°C for 30 min in a solution containing 4 mL/L hydrogen peroxide (35%), 2 g/L sodium carbonate and 2 g/L stabilizer.

The dyeing was carried out in a laboratory apparatus (Ahiba Nuance, DataColor). Cotton fabric (5 g) was placed in the bath containing 40 g/L of salt in 200 mL water and circulated for 20 min at 60°C. The required amount of dye was added into the liquor and the temperature was kept at 60°C for another 15 min. Once at 60°C, 1/3 of required 5g soda was added and left to circulate for 5 min, after which the rest amount (2/3 of required 5g) was added. Dyeing was continued for 35 min, and the liquor was then drained and refilled to allow neutralization with 1mL/L acetic acid at 50°C for 5 min. The liquor was then drained and refilled with water and soaping off was performed at 90°C with 2 mL/L of dispersant. Finally, the liquor was drained, refilled with water and 1 mL/L softener was applied for 5 min. All samples were then left to air dry in a cabinet dryer.

2.1 Determination of Dye Contents

The most common and popular procedure used in the dyeing and finishing industries for the determination of dye contents in their solutions is the UV-visible absorption Biochrom spectrophotometry. The main principle in the quantitative UV-visible technique is the linear relation between absorbance and concentration which is given by the following Beer-Lambert law:

\[
A = εlC \quad \ldots \ (1)
\]

where \( A \) is the absorbance at a specific wavelength; \( ε \), the extinction coefficient; \( l \), the path length; \( C \), the concentration of dye.

In order to determine the dye concentration in a solution after dyeing, the calibration curves (Fig. 2) were used, which show absorbance as a function of dye concentrations (Yellow Bezactiv S3R, Red Bezactiv S3B, and Blue Bezactiv SGLD dyes) at different wavelengths.

2.2 Theory

For a mixture of three dyes (Yellow S3R, Red S3B and Blue SGLD), the absorbance \( A_s \) of the sample at the wavelengths \( (λ_Y, λ_R \text{ and } λ_B) \) is given in the following equations:

\[
\begin{align*}
A_s(λ_Y) &= A_Y(λ_Y) + A_R(λ_Y) + A_B(λ_Y) \\
A_s(λ_R) &= A_Y(λ_R) + A_R(λ_R) + A_B(λ_R) \\
A_s(λ_B) &= A_Y(λ_B) + A_R(λ_B) + A_B(λ_B)
\end{align*}
\]

\ldots \ (2)
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With:

\[ A_s(\lambda_y), A_s(\lambda_R), A_s(\lambda_B) \] absorbance values of the sample at \( \lambda_y, \lambda_R \) and \( \lambda_B \)

\[ A_y(\lambda_y), A_y(\lambda_R), A_y(\lambda_B) \] absorbance values of the Yellow dye at \( \lambda_y, \lambda_R \) and \( \lambda_B \)

\[ A_R(\lambda_y), A_R(\lambda_R), A_R(\lambda_B) \] absorbance values of the Red dye at \( \lambda_y, \lambda_R \) and \( \lambda_B \)

\[ A_B(\lambda_y), A_B(\lambda_R), A_B(\lambda_B) \] absorbance values of the Blue dye at \( \lambda_y, \lambda_R \) and \( \lambda_B \)

For the component \( i \) of the sample (mixture of three dyes), the Beer-Lambert law [Eq. (1)] at different wavelengths can be written as

\[ A_i(\lambda_j) = k_i(\lambda_j) C_i \quad \ldots (3) \]

This relation [Eq. (3)] permits rewriting the Eq. (2) as

\[
\begin{align*}
A_s(\lambda_y) &= k_y(\lambda_y) C_y + k_R(\lambda_y) C_R + k_B(\lambda_y) C_B \\
A_s(\lambda_R) &= k_y(\lambda_R) C_y + k_R(\lambda_R) C_R + k_B(\lambda_R) C_B \\
A_s(\lambda_B) &= k_y(\lambda_B) C_y + k_R(\lambda_B) C_R + k_B(\lambda_B) C_B \\
\end{align*}
\]

\ldots (4)

Such a set of equations can be written in the following matrix notation:

\[
[A] = [K] [C]
\]

Using this notation, the absorbance \( A_s \) of the mixture sample of Yellow S3R, Red S3B and Blue SGLD dyes used in this study can be written as

\[
\begin{align*}
A_s(\lambda_y) &= k_y(\lambda_y) C_y + k_R(\lambda_y) C_R + k_B(\lambda_y) C_B \\
A_s(\lambda_R) &= k_y(\lambda_R) C_y + k_R(\lambda_R) C_R + k_B(\lambda_R) C_B \\
A_s(\lambda_B) &= k_y(\lambda_B) C_y + k_R(\lambda_B) C_R + k_B(\lambda_B) C_B \\
\end{align*}
\]

\ldots (5)

By using Eq. 6, we can deduce the matrix of concentrations (when \( C_i(1) \neq 0 \)). It is given by the following equation:

\[
[C] = [K]^{-1} [A] \Rightarrow \begin{cases} 
C_i(1) = 0 & \text{if } C_i(1) = 0 \\
C_i(\infty) = 0 & \text{if } C_i(1) = 0 \\
\end{cases}
\]

\ldots (7)

The resolution of the problem amounts to invert the matrix of Beer-Lambert coefficients [K], as shown below:

\[
[K]^{-1} = \begin{pmatrix}
\frac{1}{k_y(\lambda_y)} & -\frac{k_R(\lambda_y)}{k_y(\lambda_R)k_y(\lambda_y)} & -\frac{k_B(\lambda_y)}{k_y(\lambda_R)k_y(\lambda_B)} \\
0 & \frac{1}{k_R(\lambda_R)} & -\frac{k_B(\lambda_R)}{k_R(\lambda_R)k_R(\lambda_B)} \\
0 & 0 & \frac{1}{k_B(\lambda_B)}
\end{pmatrix}
\]

Using Eq. (7), we can determine the concentration matrix identifying each individual dye concentration in the mixtures’ solution. In our case, the invert of the matrix \([K]^{-1}\) of the mixture sample of

![Fig. 2 — Calibration curve of dyes at (a) \( \lambda_y = 446 \text{ nm} \), (b) \( \lambda_R = 542 \text{ nm} \) and (c) \( \lambda_B = 622 \text{ nm} \)]
Yellow S3R, Red S3B and Blue SGLD dyes can be written as:

\[
\begin{bmatrix}
0.07292 & -0.01551 & -0.00402 \\
0 & 0.04943 & -0.02441 \\
0 & 0 & 0.06846
\end{bmatrix}
\]

Hence, after dyeing, the per cent dye exhaustion \((E\%)\) values are determined by calculating the dye concentration before adding fabric into the dyebath \((C_0)\) and after dyeing \((C_f)\) according to Eq. (7), as given below:

\[
E\% = \frac{C_0 - C_f}{C_0} \times 100 \quad \ldots (8)
\]

### 3 Results and Discussion

Firstly, cotton fabrics were dyed in solution of a single dye. The percentage of dye exhaustion \((E\%)\) was calculated using Eq. (8). It is observed that the exhaustion rates of a single reactive dye are different from each other. The exhaustion rate is higher than 85% for the three dyes and range between 86% to 93%. The exhaustion rate of the Blue dye (B) is quite high i.e. 92.75%, whereas the exhaustion of Yellow (Y) and the Red (R) dyes are 87% and 86.10% respectively.

The concentration of dye solution is taken as 0.4 g/L for all the three dyes. However, the concentration of dye solution at the end of dyeing process is found to be 0.0520, 0.0556 and 0.0290 g/L for Y, R and B dyes respectively.

To study the influence of dye mixtures on the exhaustion rate \((E\%)\) values, nine dye mixtures were prepared using various concentration ratios (Table 1). The simultaneous determination of organic dye mixtures by using spectrophotometric methods is a difficult problem in analytical chemistry, due to the complexity of their absorption spectra and the spectral interferences. That’s why in this study, an analytical methodology based on a matrix calculation for possible determination of concentration and exhaustion of an organic dye mixture has been proposed. At the end of the mixture dyeing process, we measured the absorbance of the residual bath (Table 1). This measurement allows us to determine the concentration of each dye in the bath by using Eq. (7). At this point, individual concentrations of Red, Yellow and Blue dyes in the mixture are known, and therefore the exhaustion rate could be calculated from Eq. (8). The calculated results are reported in Table 2.

The three dyes used in the mixture solution of dyeing of the cotton fabric show medium-to-good substantivity which can be detected by the exhaustion rate of the mixture dyes \((E_T\%)\), which is given by

\[
E_T = \frac{([C_B + C_R + C_Y]_{at \, t=0} - [C_B + C_R + C_Y]_{at \, dyeing})}{[C_B + C_R + C_Y]_{at \, t=0}} \times 100 \quad \ldots (9)
\]

As shown in Table 2, the exhaustion rate of the dyeing mixture containing mixtures of two and three dyes is higher than 80% for all samples prepared, and ranges between 80% and 90%. However, the exhaustion rates of each reactive dye in the mixture are different from each other. Also, the exhaustion of each dye in a single dyeing is different from its exhaustion in the dyeing mixture. To determine and analyze this difference, we defined a parameter \(\varepsilon_i\) of the dye \(i\) as

\[
\varepsilon_i = \frac{(E_i)_{in \, single \, dyeing}}{(E_i)_{in \, mixtures \, dyeing}} \quad \ldots (10)
\]

<table>
<thead>
<tr>
<th>Dye mix</th>
<th>Dye mixtures, g/L</th>
<th>Absorbance of dye solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yellow S3R</td>
<td>Red S3B</td>
</tr>
<tr>
<td>RY</td>
<td>0.08</td>
<td>0.32</td>
</tr>
<tr>
<td>YR</td>
<td>0.32</td>
<td>0.08</td>
</tr>
<tr>
<td>RB</td>
<td>0</td>
<td>0.32</td>
</tr>
<tr>
<td>BR</td>
<td>0</td>
<td>0.08</td>
</tr>
<tr>
<td>YB</td>
<td>0.32</td>
<td>0</td>
</tr>
<tr>
<td>BY</td>
<td>0.08</td>
<td>0</td>
</tr>
<tr>
<td>Y(RB)</td>
<td>0.24</td>
<td>0.08</td>
</tr>
<tr>
<td>R(YB)</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>B(YR)</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

where $E_i$ is the exhaustion of the dye $i$. The calculated results of all mixtures samples are reported in Table 3.

Table 3 shows that the exhaustion rate of Blue, Red and Yellow dyes in a single dyeing is, in most cases, higher than in dyeing mixture. For example, the exhaustion rate of blue dye in all mixtures decreases and $E_{\text{blue}}$ ranges between 0.92 and 0.99 except in the case of the binary dyeing mixture in a proportion of 80% Red and 25% blue. The $E_{\text{red}}$ is higher than 1 in the binary mixture with Blue Bezactive dye. However, in all other mixtures, it ranges between 0.86 and 0.99. Except for three mixtures [YB, Y(BR) and R(YB)], the exhaustion rate of yellow dye increases in the dyeing mixture.

Assessing the exhaustion rate values of the three dyes, it can be said that the yellow, blue and red dyes used in this study are not that much compatible to each other but they can be used in dye mixture. The factors that could affect the exhaustion rate of the reactive dye when it is used in the mixture dyeing are as follow:

- Competition of the dyes anions
- Electrical repulsion of a dye from the fibre surface by the other sorbed dyes of a similar charge
- Interaction of reactive dyes with each other in solution
- Attraction of dyes for each other on the fibre surface

4 Conclusion

It is true that the spectrophotometric determination of three dyes can be a difficult problem in view of the complexity of their absorption spectra. However, the matrix method developed in this study can allow to calculate the exhaustion of every dye in a dyeing mixture and to interpret the compatibility of the mixture of these dyes. The experimental results show that the exhaustion rates of each reactive dye in the mixture are different from each other. Also, the exhaustion of each dye in a single dyeing is different from its exhaustion in the dyeing mixture. Consequently, yellow, blue and red dyes used in this study are not that much compatible to each other but they can be used in dye mixture.

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