

# Study of Fluorescent Dyeing Process and Influence of Mixture Dyes on High-visibility

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## ABSTRACT

In this paper, we present the results of an investigation and analysis of an experimental study of fluorescent disperse dyes used for dyeing polyester fabrics to high-visibility colors. This paper describes the results of spectrophotometric color measurements for yellow luminous, red luminous and orange luminous fluorescent dyes and their matching with the requirements of the EN 471 standard. The results of this study showed that the adsorption isotherms of polyester dyeing with fluorescent disperse luminous dyes follow the Nernst equation; the Nernst constants were determined and interpreted. The adsorption kinetics of fluorescent disperse dyes on polyester is studied by using the pseudo-first-order model, the pseudo-second-order equation and the intraparticle diffusion equation. The results show that pseudo-second-order models fit well the experimental data with higher average regression coefficients ( $R^2 > 0.98$ ). They also show that high-visibility is influenced by the dye concentration, and that the dye mixtures can affect the high-visibility.

## INTRODUCTION

The application of fluorescent dyes involves various fields. Recently, the application of fluorescent dyes in biochemical investigations and medical diagnoses [1,2] has known a great development. Fluorescent dyes have also been used in the construction of lasers, photoelectric cells, and solar batteries. For example, fluorescein class dyes are commercially available and used as coloring additives in food, cosmetics, and drugs [3,4].

For safety uses in other fields, American Tire has patents pending relating to the production of bicycle tyres that are available in a yellow fluorescent that can be seen at night by headlights from a distance of about feet [5]. Also, the fluorescent dyes were used in the coloration of plastics, in solvent-based inks for the printing of packaging, in waxes and polishes, in the detection of flaws in metals, glass, ceramics, and plastics [5].

But fluorescent dyes have long been used mainly for the dyeing of flat materials, especially textiles. The use of fluorescent dyes causes a significant increase in color brightness, which makes the dyed materials more easily perceptible, or more accurately visible. Indeed, fluorescent dyes are considered to be those dyes which absorb and emit radiation in the visible spectral range light and causes fluorescence. These dyes are defined as a group of organic dyestuffs which, when applied to a textile material, give rise to fluorescence under UV radiation and in daylight.

In the textile field, the main use of fluorescent dyes is in the coloration of synthetic fibers, especially polyester [6], polyamide and acrylics in conjunction with elastane fibers, for fashion, leisure, sportswear uses and especially for safety.

In industry, many textile materials are dyed with mixtures of dyes to achieve the exact reproducibility of the required color. The use of two or three fluorescent dyes with non-identical properties can affect the sorption of the dye and the high visibility.

In this paper, we studied the adsorption mechanism of the fluorescent disperse dyes on polyester fabrics from an aqueous solution and analyzed the experimental data to determine the adsorption isotherms equation and kinetic models. Finally, the influence of mixture dyes on the high visibility and fluorescence of the polyester fabrics was determined and analyzed.

## MATERIALS AND METHODS

Experiments were carried out on interlock-knitted fabrics made of 100% polyester. The commercial dyes used in this study are shown in *Table I*.

TABLE I. Dyes characteristics and measured wavelengths when the absorbance attains maxima.

N°	Commercial Name	Category	$\lambda_{\max}$ (nm)
1	Yellow Luminous	Disperse dye	430
2	Red Luminous	Disperse dye	564
3	Orange Luminous	Disperse dye	484

Prior to dyeing, all polyester fabrics were prepared at 60°C for 30 min in a solution containing 1g /L detergent and 0.5 g/L sodium carbonate. Then, the fabric was rinsed at 40°C for 10 minutes. Finally, the sample was dried 120°C for 1 minute using a Mathis KTF-S continuous dryer.

The dyeing procedures were carried out according to the manufacturer’s instructions outlined in Figure 1, with the amounts of dispersing agent and acetic acid as shown in Table II. The dyeing processes were achieved in a laboratory apparatus (AHIBA Nuance speed, DataColor), with a liquor-to-fiber ratio of 10:1.

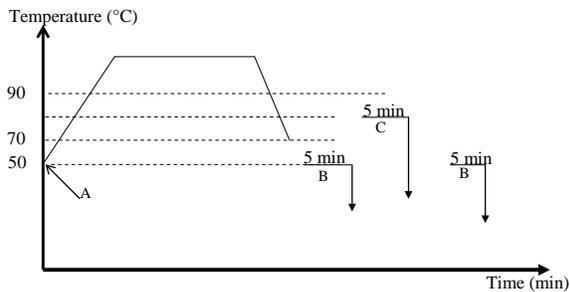


FIGURE 1. Dyeing procedure.

TABLE II. Amount of Materials used for dyeing.

Step	Materials	Concentration
A	Dispersing agent	0.5 g/L
	Disperse dye	y%
	Acetic acid	5 g/L
B	Water to rinse the fabric	10:1
C	sodium carbonate	2 g/L
	Sodium dithionite	2 g/L
	Dispersing agent	0.5 g/L

To study high-visibility colors, we used the basic parameter in accordance with the standard NF EN471; the color is characterized by the chromaticity co-ordinates x and y which determine the chroma saturation and hue, and the luminance factor (determining luminosity)  $\beta = Y/Y_0$ , where  $Y_0 = 100$  is the three-chromatic co-ordinate for a perfect reflecting diffuser, and Y the co-ordinate for the color tested.

Textile materials are fluorescent when the chromaticity co-ordinates x and y are included within the boundaries of the area determined by the standard NF EN471, and the luminance factor was equal to or greater than the value given by the standard NF EN471. These parameters were determined on the dyed sample by using the DATACOLOR Spectrocolorimeter. The luminous factor and the chromaticity co-ordinates x and y were determined by the standard NF EN471 of the dyes used in this study and presented in Table III.

In this part of the study, nine dye mixtures were prepared in various concentration ratios as shown in Table IV. The dyed sample was tested by using the DATACOLOR spectrocolorimeter to determine the chromaticity co-ordinates x and y and to calculate the luminance factor  $\beta = Y/Y_0$ .

TABLE III. Luminous factor and the chromaticity co-ordinates x and y as determined by the standard NF EN471 of the dyes used in study.

Dye	X	Y	Minimum value of luminous factor $\beta_m = Y/Y_0$
Luminous Yellow	0.387	0.610	0.7
	0.356	0.494	
	0.398	0.452	
	0.460	0.540	
Luminous Red	0.655	0.345	0.25
	0.570	0.340	
	0.595	0.315	
	0.690	0.310	
Luminous Orange	0.610	0.390	0.4
	0.535	0.375	
	0.570	0.340	
	0.655	0.345	

TABLE IV. Composition of the mixtures dye solutions prepared to study the high-visibility.

Sample designation	Composition of the dyes mixtures (g/L)		
	Luminous Yellow	Luminous Red	Luminous Orange
RY	0.1	0.4	0
YR	0.4	0.1	0
RO	0	0.4	0.1
OR	0	0.1	0.4
YO	0.4	0	0.1
OY	0.1	0	0.4
Y(RO)	0.3	0.1	0.1
R(YO)	0.1	0.3	0.1
O(YR)	0.1	0.1	0.3

## CHARACTERIZATION OF THE DYEING SYSTEM

### Adsorption Equilibrium Study

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of the adsorbent, as a function of the equilibrium concentration at constant temperature, were studied. In order to evaluate the time necessary for reaching the equilibrium for each fluorescent disperse dye and dyeing temperature, a series of preliminary experiments were carried out at two temperatures of 120°C and 130°C. The initial dyebath concentrations of the studied dye varied from 0.1 g/L to 0.5 g/L. After dyeing each solution, the equilibrium concentration ( $C_f$ ) was determined by means of the calibration curve and measurement of the absorbance using the BIOCHROM spectrophotometer. Then, by subtracting the equilibrium concentration from the initial concentration, the adsorbed dyestuff concentration was calculated. This value was converted into mg of dye per g of polyester fiber. The obtained isotherms are plotted in *Figure 2*.

The results presented in *Figure 2* show that the distribution of the substance to be adsorbed between the polyester fabrics and dispersed phases is expressed by proportionality constant. There is a constant ratio between the adsorbed and aqueous concentrations of

the dye, and the slope of the isotherm is equal to K. So, the adsorption isotherms of polyester dyeing with the fluorescent disperse luminous dyes follow the Nernst equation. The Nernst model is given in the following equation:

$$C_f = K_{ad} C_b \quad (1)$$

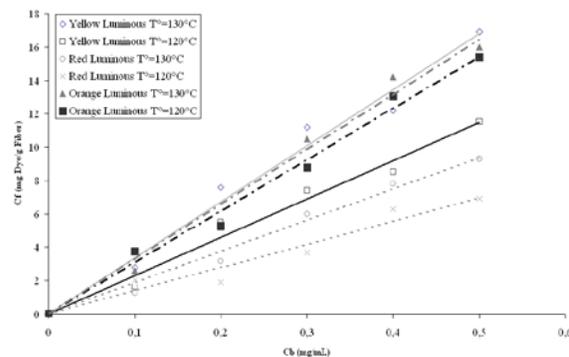


FIGURE 2. Experimental data and predicted Nernst isotherms of three fluorescent disperse dyes at two temperatures.

The Nernst adsorption constants of each dye at 120°C and 130°C calculated from the isotherms with the correlation coefficients are presented in *Table V*.

Table V shows the results of the Nernst isotherm, indicating the reasonably good correlation between the experimental data and Nernst model for the yellow, red and orange fluorescent disperse dyes at both temperatures of 120 °C and 130 °C, as reflected by correlation coefficients ( $R^2$ ) (nearer to 1). For all dyes (yellow, red and orange), the Nernst adsorption constant ( $K_{ad}$ ) increased as the temperature was increased, suggesting that the adsorption of fluorescent luminous disperse dyes used in this study onto polyester fabrics was controlled by an exothermic process.

TABLE V. Parameter values from fitting the adsorption equilibrium data with isotherm Nernst model.

Dye	Temperature	$K_{ad}$ (mL/g)	$R^2$
Yellow	130°C	33.648	0.9803
	120°C	23.005	0.9789
Red	130°C	18.776	0.9858
	120°C	13.933	0.9458
Orange	130°C	32.964	0.9806
	120°C	30.893	0.9884

### Kinetics Study

In order to study the mechanism of the adsorption of the fluorescent dye on polyester fabric, kinetic models were used to test experimental data. These kinetic models included the pseudo-first order equation [7,8], the pseudo-second order equation [8,9] and the Intra-particle diffusion model [10,11].

### Pseudo-First Order Model

The pseudo-first order equation of Lagergren [7,8] is generally expressed as follows:

$$\frac{dq_t}{dt} = K_1 (q_\infty - q_t) \quad (2)$$

Where:

$q_\infty$  and  $q_t$  are, respectively, the sorption capacity at equilibrium and at time  $t$  ( $\text{mg g}^{-1}$ ), and  $K_1$  is the rate constant of the pseudo-first order sorption ( $\text{min}^{-1}$ ).

Integrating equation (2) with respect to boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ . the integrated form of the equation becomes:

$$\ln (q_\infty - q_t) = \ln (q_\infty) - K_1 t \quad (3)$$

So, the first order rate constant  $K_1$  can be obtained from the slope of plot between  $\ln (q_\infty - q_t)$  versus time  $t$ , and  $q_\infty$  can be obtained from intercept (see Figure 3).

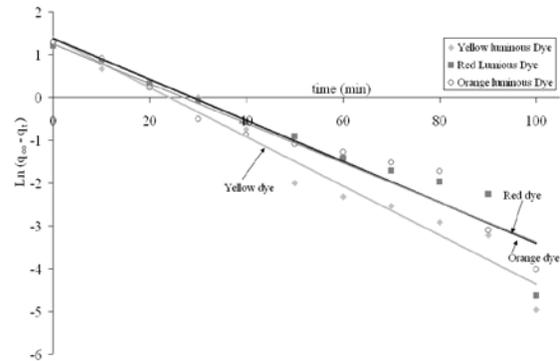


FIGURE 3. Pseudo-first-order kinetics of fluorescent dyes tested ( $C_0 = 400 \text{ mg/L}$ ).

### Pseudo-Second Order Model

The pseudo-second order model [8,9] is represented by:

$$\frac{dq_t}{dt} = K_2 (q_\infty - q_t)^2 \quad (4)$$

Separating the variables gives:

$$\frac{dq_t}{(q_\infty - q_t)^2} = K_2 dt \quad (5)$$

By integrating the Eq. (5) with respect to boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the form of the equation becomes the one that has a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_\infty^2} + \frac{t}{q_\infty} \quad (6)$$

The plot of  $\frac{t}{q}$  versus  $t$  of equation (10) should give a linear relationship, from which  $q_\infty$  and  $K_2$  can be determined from the slope and intercept of the plot (Figure 4).

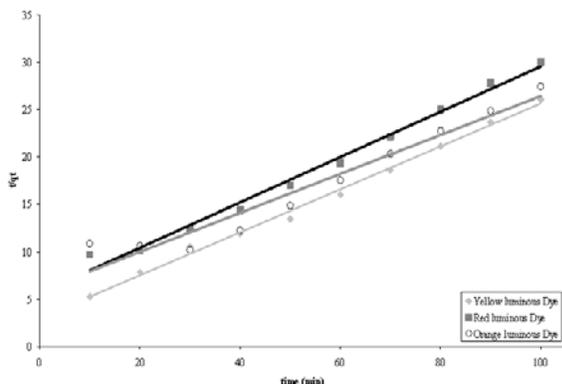


FIGURE 4. Pseudo-second-order kinetics of fluorescent dyes tested ( $C_0 = 400 \text{ mg/L}$ )

### Intra-Particle Diffusion Model

To describe the mass transfer of intra-particle diffusion, Weber-Morris found that in many adsorption cases, the solute uptake varies almost proportionally with  $t^{1/2}$  rather than with the contact time  $t$  [10,11]:

$$q_t = K_{\text{int}} t^{1/2} \quad (7)$$

where:

$K_{\text{int}}$  ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) is the intra-particle diffusion rate constant of the plot between  $q_t$  versus time  $t^{1/2}$  (Figure 5).

In all cases of models, the amount of dye adsorbed per gram of cotton ( $\text{mg/g}$  cotton) at any time ( $q_t$ ) was calculated as follows:

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (8)$$

where:

$C_0$  is the initial dye concentration ( $\text{mg/L}$ ) and  $C_t$  is the dye concentration after dyeing time  $t$  ( $\text{mg/L}$ ),  $V$  is the volume of dye solution ( $\text{L}$ ) and  $W$  is the weight of the polyester fabric ( $\text{g}$ ) used.

As has been shown in *Table VI(a)* and *Table VI(b)*, the correlation coefficients for the pseudo-second-order kinetic model ( $R^2 > 0.98$  for all dyes tested) were higher than those for the pseudo-first-order kinetic model. These results imply that the adsorption system studied (fluorescent disperse luminous dye / polyester fabrics) obeys to the pseudo-second-order kinetic model.

TABLE VI(a). Kinetic parameters for Fluorescent disperse dyes adsorption on polyester fabrics (first-order model).

Dyes	$q_{\infty, \text{exp}}$ ( $\text{mg/g PES}$ )	Pseudo-first-order model		
		$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{\infty, \text{th}}$ ( $\text{mg/g PES}$ )
Lum. Y. Dye	3.840	0.0574	0.9665	3.969
Lum. R. Dye	3.340	0.0478	0.9162	3.934
Lum. O. Dye	3.658	0.0463	0.9404	3.493

TABLE VI(b). Kinetic parameters for Fluorescent disperse dyes adsorption on polyester fabrics (second-order model).

Dyes	$q_{\infty, \text{exp}}$ ( $\text{mg/g PES}$ )	Pseudo-second-order model		
		$K_2$ ( $\text{g PES/ mg min}$ )	$R^2$	$q_{\infty, \text{th}}$ ( $\text{mg/g PES}$ )
Lum. Y. Dye	3.840	0.0171	0.9953	4.411
Lum. R. Dye	3.340	0.0101	0.9892	4.178
Lum. O. Dye	3.658	0.0128	0.9824	4.351

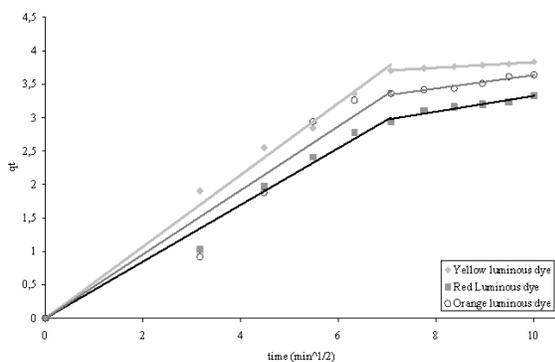


FIGURE 5. Intra-particle diffusion model of fluorescent dyes tested ( $C_0 = 400 \text{ mg/L}$ ).

As shown from the experimental data presented in *Figure 5*, the plots present multi-linearity, indicating that two steps were taking place. Similar behavior has also been reported in the literature [12, 13].

As shown in *Figure 5*, an initial linear portion (from 0 to  $\approx 50 \text{ min}$ ) followed by a second one (after 50 min). The initial linear portion is the gradual adsorption stage, where the intra-particle diffusion is rate-controlled ( $K_{int1} > 0.4242 \text{ min}^{-1}$  for dyes tested). The second portion is the final equilibrium stage where the intra-particle diffusion slows down ( $K_{int2} = 0.0413 \text{ min}^{-1}$  for the yellow dye). Also, the results presented in *Table VII* indicate that the intra-particle diffusion model fits the experimental data very well in both periods ( $R^2 > 0.9392$ ).

TABLE VII. Kinetic parameters for Fluorescent disperse dyes adsorption on polyester fabrics.

Dyes	Intraparticle diffusion rates			
	$K_{int1} (\text{min}^{-1})$	$R^2$	$K_{int2} (\text{min}^{-1})$	$R^2$
Yellow	0.5364	0.9905	0.0413	0.9887
Red	0.4242	0.9811	0.1181	0.9453
Orange	0.4786	0.9392	0.0995	0.9611

## High-Visibility

### 1. Influence of dye concentration

The results of the color analyses of the dyeing obtained with the use of different concentrations of the fluorescent dyes tested are presented in *Figures 6, 7 and 8*.

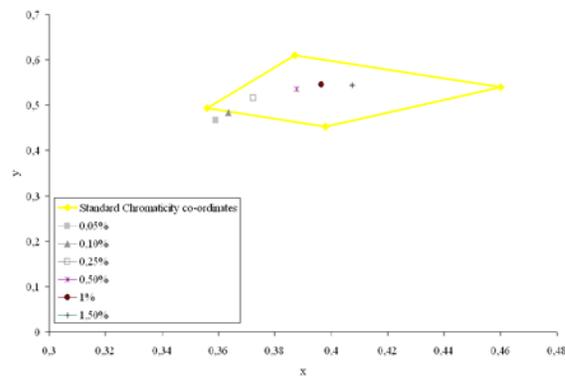


FIGURE 6. The x-y chromaticity co-ordinates of the Yellow dye relative to the area boundaries in accordance with the EN-471:1994 standard.

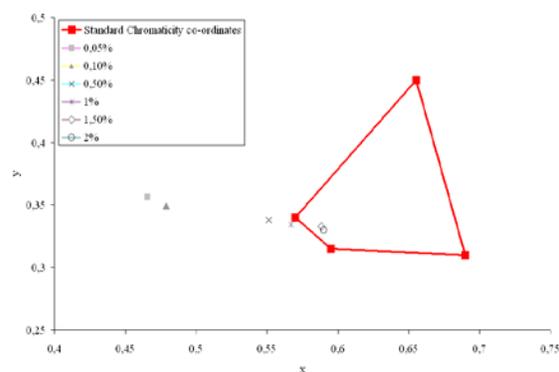


FIGURE 7. The x-y chromaticity co-ordinates of the Red dye relative to the area boundaries in accordance with the EN-471:1994 standard.

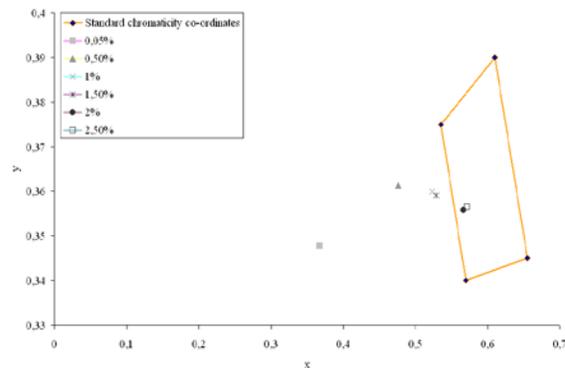


FIGURE 8. The x-y chromaticity co-ordinates of the Orange dye relative to the area boundaries in accordance with the EN-471:1994 standard.

The chromaticity co-ordinates of dyeings obtained through the use of the Disperse Luminous Yellow, Disperse Luminous Red, and Disperse Luminous Orange dyes changed with concentration. For example, the chromaticity co-ordinates obtained with the use of the yellow dye with a concentration higher than 0.10% also fall within the required area. However, the color parameters of dyeings carried out with the use of the red and the orange dye were positioned outside the area required by the standard for a concentration higher than 1% and 1.5%, respectively. Generally, the x-y co-ordinates of dyeings obtained with the use of the Red and Orange fluorescent dyes tested, unlike the yellow dye, were practically at the boundary of the colors required by

the standard. This means that a minimal change in concentration may have caused undesirable changes in the dyeing and a failure to meet the standard NF EN471 requirements for color.

## 2. Influence of mixture dyes

To observe the effect of mixture dyes on the high-visibility of the obtained color, nine different compositions of the three dyes tested were prepared as shown in *Table IV*. After dyeing, the dyed sample was tested using DATACOLOR Spectrocolorimeter to determine the luminous factor. The results of this study are presented in *Table VIII*:

TABLE VIII. Influence of mixture dyes on luminous factor and high-visibility color.

Sample designation	Luminous factor measured $\beta$	High-visibility color
RY	0.4063	Yes
YR	0.6091	No
RO	0.3897	Yes
OR	0.4550	Yes
YO	0.6964	No
OY	0.5100	Yes
Y(RO)	0.5642	No
R(YO)	0.4507	Yes
O(YR)	0.4913	Yes

*Table VIII* lists the results obtained from the calculation of the luminous factor. For a dyeing which meets the requirements of the above mentioned standard, the luminance factor  $\beta$  should be equal to or greater than the value given by the standard NF EN471.

By analyzing the results obtained and presented in *Table VIII*, the color of the dyeing accessed by using the yellow dye, characterized by a significantly important value of  $\beta_m$ , at concentration of 0.4% in binary mixtures or 0.3% in tertiary mixtures lose the high-visibility. On the contrary, all the other dyeings resulting from the use of the Disperse Luminous Yellow, Red, and Orange had a high-visibility color.

## CONCLUSION

For the three dye/polyester fabric system, the kinetics of adsorption of fluorescent disperse Yellow Luminous, fluorescent disperse Red Luminous, and fluorescent disperse Orange Luminous were fitted well by the pseudo-second-order model ( $R^2 > 0.98$  for all dyes tested) and adsorption was dominated by a two-step intra-particle diffusion process (a gradual adsorption stage and a final equilibrium stage). The adsorption isotherms of polyester dyeing with fluorescent disperse luminous dyes followed the

Nernst equation as reflected by the correlation coefficients ( $R^2$ ) (nearer to 1). For all dyes (yellow, red and orange), the Nernst adsorption constant ( $K_{ad}$ ) increased with increasing temperature.

Throughout the study, we demonstrated that a minimal change in concentration and a mixture of dyes may cause undesirable changes in dyeing and a failure to meet the standard NF EN471 requirements for color.

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