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PRACTICAL ASPECTS OF THE EFFECT OF SUITABLE ELECTROLYTES ON COTTON DYEING

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Abstract: *Reactive dyes are the most important class of dyes for cellulose fibers and are most commonly used in industry by the exhaustion method. The low affinity of these dyes requires the addition of large amounts of various salts and auxiliary materials to the dyeing bath. The number of ions formed by the dissociation of the electrolyte determines the ionic strength of the solution and has a stimulating effect on the exhaustion of reactive dyes on cotton cellulose. In this work, the influence of neutral salts (NaCl and Na_2SO_4) and alkaline salt (Na_2CO_3) on the color strength of cotton fabric dyed with bifunctional reactive dyes was investigated. The reactive dye solution with a higher ionic strength of the neutral salt has a higher exhaustion dye and higher color strength. The difference in color strength in the Na_2SO_4 bath compared to the NaCl bath ranged from 1.2 to 36%. The substantivity of the reactive dyes used is 4.5 to 18% higher in the Na_2SO_4 bath. The addition of an alkaline salt to activate the chemical dye/fiber reactions has an additional effect on exaustion dye as a result of further increasing the ionic strength of the solution.*

Key words: *reactive dyes, ionic strength, color strength, substantiality of dyes, promotional effect*

1. INTRODUCTION

Reactive dyes are the most important class of dyes for dyeing cotton and other cellulosic fibers. Different dyeing methods, a wide range of shades and permanent and brilliant dyeing are the advantages that are characteristic of these colors. Today, reactive dyes make up about 60 % of the world's consumption of dyes for cellulose fibers [1]. Despite the enormous popularity of reactive dyes, there are numerous environmental challenges due to the low level of dye utilization. The dyeing bath contains large amounts of electrolytes and supplements that increase the uniformity and durability of the dyeing [2]. Baffoun published a paper in which a comparative study of the effectiveness of two electrolytes on the dyeing of cotton with the reactive dye Sumifix Supra Yellow E-XF was carried out [3]. In a recently published paper, a group of authors used the Taguchi method for evaluation of process parameters on exhaustion and fixation of bifunctional dye C.I. Reactive Red 195 on cotton fabric [4]. The results showed that the concentration of salt has the greatest influence, followed by the concentration of alkali, followed by temperature and dyeing time.

In this work, the influence of inorganic electrolytes on the dyeing of cotton fabric with bifunctional reactive dyes was examined the dyeing, results are related to the ionic strength of the solution.

2. EXPERIMENTAL PART

2. 1. Material and working methods

In the experiment, the 100 % cotton fabric samples were dyed, surface mass 220 g m^{-2} with warp density 43 cm^{-1} and weft 22 cm^{-1}. The fabric is industrially prepared for dyeing. The samples for dyeing had a mass of 5 g. Chemicals used in the work are as follows: Bezaktiv blue S-$FR_{150\%}$, bifunctional reactive dye (MCT/VS, Bezema - Switzerland), Bezaktiv red S-$3B_{150\%}$, bifunctional reactive dye (MCT/VS, Bezema - Switzerland), Bezaktiv yellow S-$3R_{150\%}$, bifunctional reactive dye (MCT/VS, Bezema - Switzerland), NaCl - salt, an agent of increasing dye exhaustion, Na_2SO_4 - salt, an agent for increasing dye exhaustion, Na_2CO_3 - salt, an agent for regulating the pH of the solution.

Dyeing was performed by an Ahiba apparatus (TYP G7B) in glass cuvettes with vertical movement of the material. Dyeing was carried out isothermally at t=60 °C for 60 and 120 minutes. In the bath that contained dye and salt to increase dye exhaustion, the dyeing time was 60 minutes. The samples that were dyed for 120 minutes were first dyed for 60 minutes with the addition of salt to increase the exhaustion of the dye, and then salt was added to regulate the alkaline bath and the dyeing was continued for another 60 minutes. The concentration of the dye was 1.5 and 4 % (based on the mass of the material), and the concentration of NaCl and Na_2SO_4 was 50 and 100 g dm^{-3}. The concentration of Na_2CO_3 was 15 and 20 g dm^{-3} and the volume of the bath is 150 cm^3 (R 1:30). After dyeing and washing with distilled water, the samples that were dyed for 120 min were processed in a soapy solution at 90 °C for 15 minutes, washed again and air dried.

Reflection spectrophotometer Spectraflash SF600X (Datacolor - USA) measured the reflection of the sample at wavelengths 400 - 700 nm and CIELab color coordinates were determined. Based on the reflection value at the wavelength of maximum adsorption for each sample, the color strength (K/S) was calculated according to the Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad \textbf{(1)}$$

Where: *K* – absorption coefficient, *S* – scattering coefficient, *R* – reflection for light D65/10. The maximum absorption wavelengths have the following values: Bezaktiv blue S-$FR_{150\%}$ 630 nm, Bezaktiv red S-$3B_{150\%}$ 550 nm and Bezaktiv yellow S-$3R_{150\%}$ 440nm.

Using a colorimeter CO7500 (WPA England), the absorbance of the solution was measured at the wavelength of maximum absorption, at the beginning and at the end of dyeing (after 120 min). Using equation 2, the percentage of color exhaustion (*E*) is determined [5] :

$$\%E = \left[\frac{(A_o - A_1)}{A_o}\right] \times 100 \quad \textbf{(2)}$$

where:
A_o – absorbance of the solution at the beginning of dyeing,
A_1 – absorbance of the solution at the end of dyeing.

For each dyeing system (with a dyeing time of 120 minutes), dye substantiality (*K*) was determined, which is a measure of the dyes ability to transfer from the solution to the fiber under certain dyeing conditions. Substantiality is determined using equation (3) [6]:

$$K = \frac{[\%E \times L]}{[100 - \%E]} \quad \textbf{(3)}$$

where: $\%E$ – exhaustion dye, L – bath ratio.

The ionic strength *(I)* of the solution was calculated using equation 4 [7]:

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \quad \textbf{(4)}$$

where: c_1, $c_2 \dots c_i$ - concentration of ions present in the solution (mol dm^{-3}), z_1, $z_2 \dots z_i$ - charge of ions present in the solution.

The promotional effect of the neutral salt was determined using equation 5 [8]:

$$\%\,\text{promotional salt effect} = \frac{\%E\text{s} - \%E\text{o}}{\%E\text{s}} \quad \textbf{(5)}$$

where is:

*%E*s – equilibrium dye exhaustion for samples dyed with the addition of salt,

*%E*o – equilibrium dye exhaustion for samples dyed without the addition of salt.

To determine the promotional effect of salt, samples were dyed for 120 minutes with 1.5% dye without and in the presence of salt (NaCl and Na_2SO_4), at 60 ºC. The color fastness to washing (at 60 ºC) of cotton fabric samples was determined according to ISO 105-C06:2010 standard, using AATCC 1993 standard reference detergent. Color fastness to washing was determined on samples dyed for 120 minutes. Table 1 gives the markings of the dyed cotton samples.

Tab. 1. *Designations of samples*

Designations of samples	Concentration of dye (%)	Concentration of NaCl (gdm^{-3})	Concentration of Na_2SO_4 (gdm^{-3})	Concentration of Na_2CO_3 (gdm^{-3})	Dyeing time (min)
B1; R1; Y1	1.5	50	-	-	60
B2; R2; Y2	1.5	-	50	-	60
B3; R3; Y3	1.5	50	-	15	120
B4; R4; Y4	1.5	-	50	15	120
B5; R5; Y5	4	100	-	-	60
B6; R6; Y6	4	-	100	-	60
B7; R7; Y7	4	100	-	20	120
B8; R8; Y8	4	-	100	20	120

B1-B8, samples dyed with Bezaktiv blue S-$FR_{150\%}$; R1-R8, samples dyed with Bezaktiv red S-$B_{150\%}$; Y1-Y8, samples dyed with Bezaktiv yellow S-$3R_{150\%}$

3. RESULTS AND DISCUSSION

3. 1. Substantivity of dyes

Substantivity is the ability of the dye to transfer directly from the solution to the fiber, and it largely depends on the chemical composition and structure of the dye. Substantivity also depends on bath temperature and salt concentration. Dyes of greater substantivity have greater equilibrium exhaustion and vice versa. Dyes to the small molecules, reactive dyes have a low substantivity and the addition of inorganic electrolytes has a great influence on the dyeing from the solution onto the fiber for the following reasons:

1) the color changes from ionic to molecular form, i.e. the solubility of the dye decreases,
2) the negative surface charge of the fiber is reduced, so that the electrostatic repulsive forces between the dye and the fiber are reduced and
3) the chemical potential of the dye in the solution increases.

Table 2 shows the values substantivity of dyes (K) based on dye exhaustion during a dyeing time of 120 min, which corresponds to a real dyeing system. The substantivity of all dyes was higher when dyeing with a higher concentration of dyes and electrolytes and when the bath contains Na_2SO_4. In the range of dyes used, red has the lowest substantivity (K) and blue has the highest. The substantivity of Bezaktiv blue S-$FR_{150\%}$, is 18 and 12% higher when the technological solution contains Na_2SO_4 compared to the system with NaCl for a lighter and darker tone, respectively. When applying Bezaktiv red S-$3B_{150\%}$ increase in substantivity when NaCl is replaced with Na_2SO_4 amounts to 8% (for a light shade) and 13% (for a dark shade). With Bezaktiv yellow S-$3R_{150\%}$ the substantivity is higher by 9% for a lighter shade and 4.5% for a darker shade, for the system with Na_2SO_4 compared to the system with NaCl. The chemical composition and constitution of the molecules of reactive dyes have the greatest influence on the ability of the dye to transfer from the solution to the cotton fiber. The addition of salt, which increases the number of ions in the solution, affects the displacement of the final distribution of reactive dye molecules on the fiber side. The obtained results indicate the important and complex role of the present electrolytes in increasing the exhaustion of reactive dyes on cotton. It is likely that the efficiency of the electrolyte for the transfer of reactive dye molecules to the cotton fiber depends on the number of ions produced by the dissociation of the electrolyte, i.e. from the ionic strength of the solution.

Tab. 2. *Substantivity (K) Bezaktiv blue S-$FR_{150\%}$, Bezaktiv red S- $3B_{150\%}$ and Bezaktiv yellow S-$3R_{150\%}$*

Designations of samples	K	Designations of samples	K	Designations of samples	K
B3	41.4	R3	32.5	Y3	45.0
B4	48.9	R4	35.2	Y4	48.9
B7	95.0	R7	35.2	Y7	48.9
B8	106.4	R8	29.8	Y8	51.1

3.2. Color strength

Color strength (K/S) were calculated using the Kubelka-Munk equation and are shown graphically in Figures 1-3. The color strength of cotton fabrics depen ds on the formulation of the dyeing solution and the dyeing time. Samples dyed with Bezaktiv blue S-FR$_{150\%}$ have higher K/S values when Na_2SO_4 is used as a salt to increase exhaustion compared to samples dyed in a NaCl bath (Figure 1). After 120 minutes of dyeing in a lighter shade, the difference is minimal (2,5%), but after dyeing in a darker shade, the difference is significant and amounts to 33%. These results indicate a greater effect of Na_2SO_4 on the condition of the dye in the solution and the transition to cotton, as well as that this effect becomes more distinct the higher the concentration of the dye in the bath. The addition of alkali (Na_2CO_3), which primarily has the role of regulating the alkalinity of the solution, is also reflected in the increase in the color strength of the dyed samples. On samples of a lighter shade, that increase amounts to 68% (bath with NaCl) and 53% (bath with Na_2SO_4). When dyeing in a darker shade, the effect of added alkali is even greater because the color strength is twice as high after 120 min of dyeing. Color strength of cotton fabric samples dyed with Bezaktiv red S-3B$_{150\%}$ depends on the formulation of the technological solution and the time of dyeing (Figure 2). Samples dyed in a bath with Na_2SO_4 have a higher color strength compared to the system with NaCl, and the difference for the lighter shade is 28%, and for the darker shade 36%. The addition of Na_2CO_3 has a significant influence on the final result of red coloring, which increases the color strength from 15 to 35%. When dyeing with Bezaktiv yellow S-3R$_{150\%}$ in the bath with Na_2SO_4, the color strength is 11 and 14% higher for a light shade, after 60 and 120 minutes of dyeing, respectively, compared to the bath with NaCl (Figure 3). By dyeing in a dark shade, the differences are minimal. When applying this dye, a great influence of the addition of Na_2CO_3 on the dyeing of the cotton fabric is observed, because the exhaustion of the dye increases further and K/S has higher values by about 55% for a lighter shade and a darker shade by about 83% compared to the first 60 minutes of dyeing. The higher color strength of cotton with reactive dyes in the Na_2SO_4 solution is explained by the higher ionic strength of the solution (Table 3), because dissociation produces twice as many Na^+ ions compared to the NaCl solvent. A greater number cations of inorganic electrolyte in the technological solution for dyeing cotton with anionic dyes, to a greater extent reduces the fiber/dye repulsive forces and increases the chemical potential of the dye in the solution, which practically manifests it self as greater dye exhaustion.

Tab. 3. *Electrolyte concentration and ionic strength*

Concentration 50 g dm^{-3}		Concentration 100 g dm^{-3}	
Electrolyte	Ionic strength (I) mol dm^{-3}	Electrolyte	Ionic strength (I) mol dm^{-3}
NaCl	0.85	NaCl	1.71
Na_2SO_4	1.06	Na_2SO_4	2.13

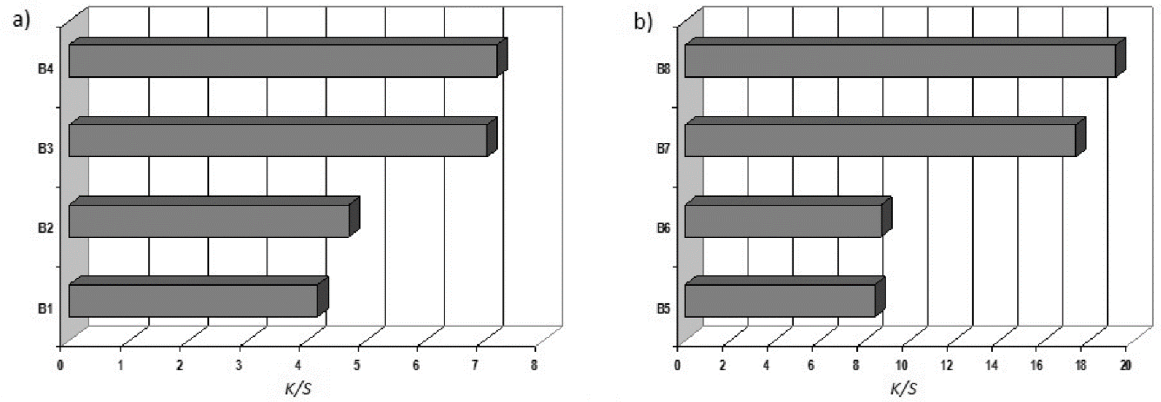

Fig. 1. *Color strength samples dyed with 1.5 % (a) i 4 % (b) Bezaktiv blue S-FR$_{150\%}$*

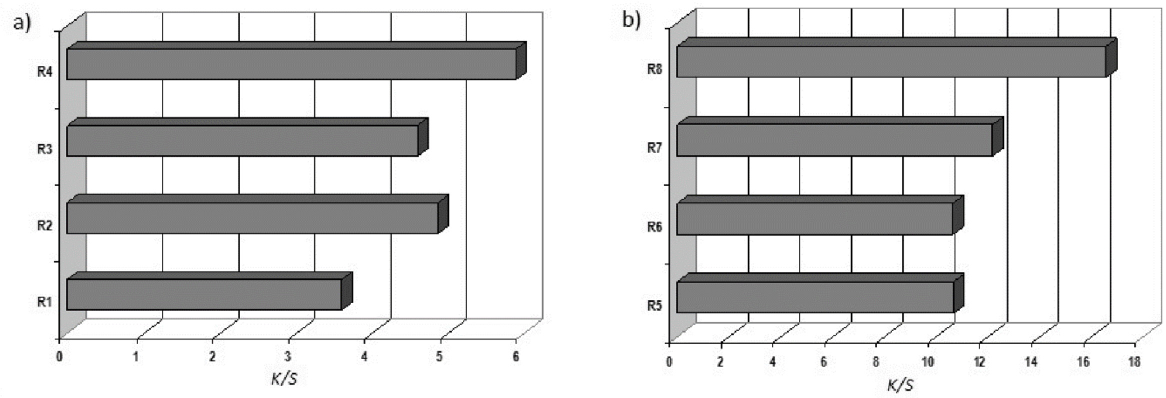

Fig. 2. *Color strength samples dyed with 1.5 % (a) i 4 % (b) Bezaktiv red S-3B$_{150\%}$*

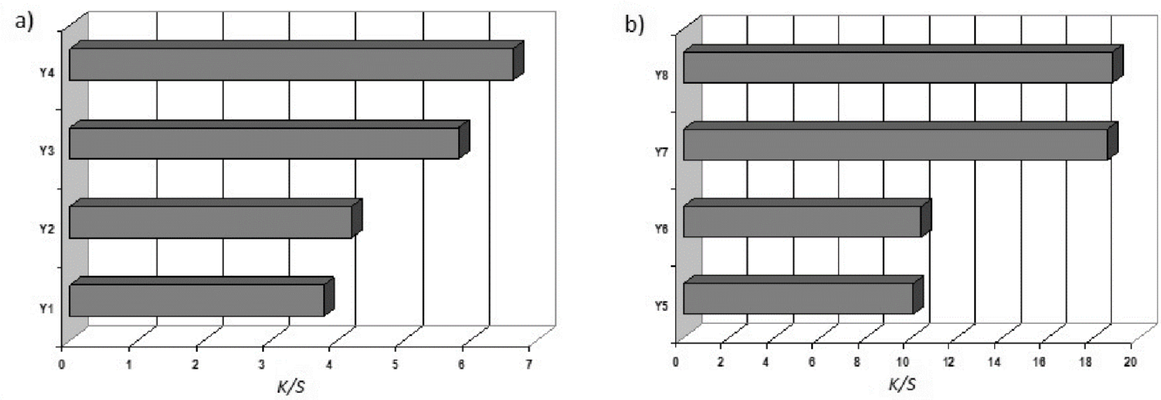

Fig. 3. *Color strength samples dyed with 1.5 % (a) i 4 % (b) Bezaktiv yellow S-3R$_{150\%}$*

3.3. Promotional effect of neutral salt

The promotional effect of neutral salts represents the sensitivity of a dye to the presence of neutral salts in the dyeing bath, i.e. an increase in dye exhaustion in the presence of a neutral salt compared to a salt-free system. From the results shown in table 4, higher values of the promotional effect of Na_2SO_4 can be seen compared to the promotional effect of NaCl. The promotional effect of neutral salts is different for different dyes. The greatest promotional effect is achieved with Bezaktiv yellow S-3R$_{150\%}$, where there is also the smallest difference in promotional effects between the neutral salts used. The lowest promotional effect of neutral salts was achieved with red dye and is twice as small compared to blue to yellow dye in the experiment. This data indicates a very heterogeneous sensitivity of dyes of the same class to the addition of salt, which may have practical implications in trichromatic dyeing in industrial conditions in order to achieve equal coloring.

Tab. 4. *Promotional effect of inorganic salts on the exhaustion of reactive dyes*

Dye	Promotional effect (%)	
	NaCl	Na_2SO_4
Bezaktiv blue S-FR$_{150\%}$	77.4	83.1
Bezaktiv red S-3B$_{150\%}$	29.8	44.3
Bezaktiv yellow S-3R$_{150\%}$	83.1	84.2

3.4. Color fastness to washing

All samples have a high color fastness to washing as a result of established covalent bond of reactive dye groups with the hydroxyl group of cotton cellulose (Table 5).

Tab. 5. *Color fastness to washing*

Samples	Change in color	Samples	Change in color	Samples	Change in color
B3	4-5	R3	4-5	Y3	4-5
B4	4-5	R4	4-5	Y4	4-5
B7	4-5	R7	4-5	Y7	4-5
B8	4-5	R8	4-5	Y8	4-5

4. CONCLUSION

In this work, the influence of neutral salts (NaCl and Na_2SO_4) and alkaline salts (Na_2CO_3) on the color strength of cotton fabric with bifunctional reactive dyes was examined. The samples were dyed for 60 and 120 minutes with the aim of examining the effect of alkaline salt on the secondary exhaustion of the dye, i.e. color strength.

Based on the obtained results, the following conclusions can be drawn:

Substantivity of all colors is higher when Na_2SO_4 is used as a salt to increase exhaustion. The substantivity of Bezaktiv blue S-FR$_{150\%}$ is 18 and 12% higher when the technological solution contains Na_2SO_4 compared to the system with NaCl for a lighter and darker shade, respectively. Substantivity of Bezaktiv red S-3B$_{150\%}$ is higher by 8% for light shade and 13% for dark shade, and for Bezaktiv yellow S-3$R_{150\%}$ by 9% for lighter shade and 4,5% for darker shade, for the system with Na_2SO_4 compared to the system with NaCl.

The color strength of cotton fabrics depends on the formulation of the dyeing solution and the dyeing time. All samples dyed in a bath with Na_2SO_4 at the end of dyeing had a higher color strength compared to samples dyed in a bath with NaCl. The largest difference of 36% was registered on samples dyed with 4% Bezaktiv red S-3$B_{150\%}$, and the smallest difference of 1,2% on samples dyed with 4% Bezaktiv yellow S-3$R_{150\%}$. The higher color strength is the result of the higher ionic strength of the Na_2SO_4 solution due to twice the number of Na^+ ions, which more effectively neutralizes the fiber/dye repulsive forces and facilitates the transfer of dye from the solution to the surface of the fiber.

The promotional effect of neutral salts is different for different dyes. The greatest promotional effect was achieved with Bezaktiv yellow S-3$R_{150\%}$, and twice as little promotional effect with Bezaktiv red S-3$B_{150\%}$. Na_2SO_4 has the greatest promotional effect at all dyes. Heterogeneous sensitivity of dyes of the same class is of practical importance for trichromatic dyeing in industrial conditions in order to achieve equal coloring.

The type of electrolyte is not important for color fastness.

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