Properties of pre-modified linen fabric dyed with reactive dyes

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Abstract. Reactive dyes are one of the most popular dyes for cotton goods and other cellulosic fibres. The main investigations for application of reactive dyes for cellulosic fibres are devoted to cotton textiles. In this paper the research results of investigation of colour properties, colour and rubbing fastness, mechanical properties of pre-modified with alkali and enzyme linen fabric dyed with colour triad of Cibacron reactive dyes are presented.

The investigation results show that the main factor influencing the colour properties of linen fabric dyed with examined reactive dyes is used dye. The modifiers use increases the rubbing fastness of dyed linen textile. The modifiers influence on colour and colour properties before and after light test is selective for used dye, but not significant.

1. Introduction

Cellulosic fibres can be dyed with more types of dyes than other ones – mostly they are water-soluble dyes applied by one batch process [1]. Reactive dyes having been developed in the 1950s, in market from 1956 are very popular for dyeing and printing of cellulosic textiles [2]. Reactive dyes are today the most popular and most developed dyes for natural fibers due to its high level of washing fastness, and versatility of application [3, 4, 5, 6]. They are the only textile colorants designed to form covalent bond, with the substrate during the application process [1, 7, 8]. The functional groups presented in the structure of reactive dye molecule have distinct influence on dyeing behaviour [9].

Conventional immersion application processes employed for reactive dyes customarily involve the use of significant amounts of added inorganic electrolyte to promote dye uptake; indeed, traditional dyeing theory dictates that either NaCl or Na2SO4 must be added to a reactive dye dye bath in order to achieve adequate dyeing [8]. The major attempts on reduction or elimination of salt content in dye bath can be summarized under three categories; reduction of liquor ratio during the dyeing process, modification of dyes, such as usage of polyfunctional dyes [10] like Cibacron LS, Novacron LS, Teegafix HE reactive dyes and modification of cotton, using chemicals, compounds, enzymes, nanoparticles, ultrasonic waves, plasma, gamma, ozone treatments [11]. With the increasingly view on health, “Green” and environmentally friendly clothing obtain the popularity [12]. The textile industry is now facing many constraints. The creation of huge water and air pollutions and cost enhancement due to high energy consumption are two major constraints. The waste minimisation by process control can reduce the problem to a large extent, and the toxic chemicals can be replaced by eco-friendly enzymes and biopolymers [13].

The main investigation for application of reactive dyes for cellulosic fibres is devoted to cotton textiles [1, 3, 6, 13].
With the trend of appearance natural, comfortable yet elegant fabrics, linen and linen-blended fabrics accept acquired authority and added in acceptability attributable to the fabric qualities of comfort, hygiene, and elegance recently. Linen reduces $\gamma$-radiation nearly by bisected and protects the human organism towards sun radiation. It is an array of nice actual for advantageous applications due to its transfer and permeability to air. Heat conductivity of linen is five times as high as that of wool and 19 times as that of silk, additionally, the tensile strength of linen thread is twice as high as that of cotton and three times that of wool. Dye ability is the main barrier that unable its wider applications in the real life [12].

2. Materials and Methods
The local bleached, plain weave 100% linen fabric with density of 167.7 g/m$^2$ (Ltd, Larelini, Latvia) was used.

Reactive dyes (Huntsman International LLC): Cibacron Yellow F-4G - single monofluorotriazine, azo class dye (final exhaustion 65%, fixation 52%, washing-off properties – very good), Cibacron Red FN-R heterobifuncio monofluorotriazine–sulfatoetilsulphone, azo class dye, (final exhaustion 82%, fixation 72%, washing-off properties – very good) and Cibacron Blue FN-R heterobifuncio monofluorotriazine–sulfatoetilsulphone dye final exhaustion 92%, fixation 77%, washing-off properties – very good) [13] were applied.

2.1. Methods of Production
Before the modification linen fabric was washed in water at 75 ± 2 °C temperature for 15 min, after it treated in distilled water solution of washing agent Felosan NOF (designation VAV) 2 g/L at 98±2 °C temperature for 1 h. The rinsing in warm /cold water followed (designation of sample U).

2.1.1. Mercerization. The mercerization of fabric without tension with NaOH solution (200 g/L; liquid ratio VM 50) at 16±2 °C temperature for 1 min with followed rinse and neutralization with acetic acid solution 10 g/L at 16±2 °C temperature for 1 min and final rinse was done (designation of sample A).

2.1.2. Enzyme pre–treating. The pre-treating of fabric with 4% solution of enzyme Beisol PRO and 1% Felosan NOF (VM 25) at 55 ± 2 °C temperature for 15 ± 1 min with following rinsing in warm /cold water was managed (designation of sample E).

2.1.3. Dyeing Technology. The dyeing (Figure 1) was realized according to the recommendation of the Cibacron Reactive dyes producer.

![Figure 1. CIBACRON F/FN method of dyeing with alkali agent for 100 % cellulose. A –auxiliaries, B – dye, C – salt, D –alkali agent [13].](image)

The pad dyeing was subjected; using solutions of 2% Cibacron dyes (VM 50, NaCl – 60 g/L; Na$_2$ CO$_3$ –20 g/L and Felosan NOF –2 g/L). After dyeing the treating with Felosan NOF 2g/L (VM 50) at 60 – 80 ± 2 °C temperature and rinse with hot/ cold water was realized.
The general principle of backwise or exhaust dyeing with reactive dyes is to encourage as much dye as possible to move into fibre over a period of 30-45 min by adding a high concentration of salt to the neutral dye bath. During this period, the dye is not reacting with the fibre, but most of dye is exhausted onto the fibre before the alkali is added, thus providing the best possible conditions for fixation before the dye–fibre reaction initiated. When the levelling process is completed, alkali is added and fixation continues for further 30-60 min [1]. The dye molecule has a reactive group which forms a chemical bond with the OH-group of the cellulose fibre. The dyeing process is divided in the migration phase and the fixing phase. The migration phase can be changed in time and temperature, depending on the material and machinery available.

The fixing phase is very susceptible to changes of temperature. It begins with the addition of alkali (soda). Deviations of the prescribed temperature (already at deviations of 5 °C) result that the final dye is much lighter: at too high temperatures due to hydrolysis and at too low temperatures due to an insufficient fixing. Mercerized cotton fabrics require 40% less colorant for the same hue than non-mercerized [14].

| Table 1. Designation of samples, modification method and used dye |
|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Sample               | UR AR ER          | UB AB EB          | UY AY EY          |
| Modification         | - Alkali Enzyme   | - Enzyme          | - Enzyme          |
| Used dye             | Reactive red Cibacron | Reactive blue Cibacron | Reactive yellow Cibacron |

2.2. Methods of Testing

2.2.1. Colour properties. The tests were performed with Easy Colour QA device (Pocket Spec. Technologies Inc. USA), using RGB (red, green and blue) light system in CIELAB-76 colour space on both sides of samples as in [15]. Lightness difference (ΔL), common colour difference (ΔE), hue difference (ΔH) and chroma (S) is a measure of intensity or saturation of colour. Calculations were made following ISO 105-JO3:2009 [16].

2.2.2. Colour Fastness. The colour fastness of dyed samples were tested in light camber (Q-SUN, Xenon Test Chamber, mod. Xe-1-B, Q-LAB) for 72 hours at temperature 55 °C, intensity of radiance 1,1 W/m², according ISO 105-B02:2014 [17]. Xenon lamps emit UV, visible light, and infrared in the same way the sun does, and can therefore provide very accurate data [18]. After testing the main colour properties were examined.

2.2.3. Rubbing Fastness. The color fastness to dry and wet rubbing according of LVS EN ISO 105-X12:2016 [19] was assessed with Croc meter 238 A of SDLA (Shirley Development Laboratories Atlas Inc. USA). The highest rubbing fastness represents 5.

2.2.4. Mechanical Testing. The samples (width – 2,5 cm, length – 16 cm;) in warp and weft direction with INSTRON dynamometer (IntronLtd, UK, between clamps 100 mm, test speed 100,0 mm / min), according LVS EN 13934-1:2013 [20] were tested.

3. Results and Discussion

3.1. Colour properties. The examination of obtained experimental results (Table 2) shows that colour properties of dyed textiles depend on the used dye. The lightness (L) and saturation (S) of unmodified samples forms the line UB < UR < UJ. The use of modifier NaOH causes small decrease of L and S for UB and UR. The enzymes treatment is not significant. The results of ΔL, ΔE and ΔH once more affirm the influence of used dyes on colour properties. The colour properties characteristics differ for UY, in comparison with other dyes. This observation can be explained with the Cibacron Yellow F-4G dye chemical structure.
The influence of modifiers is different. For example, the colour difference (∆E) with alkali modification is higher for UJ and UB samples than for UR, but influence of enzyme modification is observed only for UR sample. The saturation (S) of UJ samples is higher and influence of alkali modification is more notable, than for other dyes. The lowest hue difference (∆H) is observed for untreated and alkali treated UR samples, while for enzyme treated samples increase (5-7 times) of ∆H is observed. For UB and UJ samples the influence of modification methods is insignificant.

3.2. Colour fastness.
After colour fastness test to light the same colour properties were examined (Table 2). As expected, in all cases they are different in comparison with initial samples. It is understandable, that after light influence the lightness (L) of samples are growing and saturation (S) diminishing. The comparison of obtained results (∆L, ∆E and ∆H) show common changes – some colour properties are reducing depending of used dye. The modifiers have not significant influence on colour properties after light test, only small nuances are observed, for example, for UR and UB samples a small increase of lightness after enzyme modification is observed, the reduce of saturation is noticed for all samples, but for UB samples decrease of saturation is less than for others. The highest colour difference (∆E) is for UY samples, while influence of modification was insignificant.

Table 2. Colour properties, colour and rubbing fastness properties of dyed samples

|       | UR  | AR  | ER  | UB  | AB  | EB  | UY  | AY  | EY  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Colour properties |     |     |     |     |     |     |     |     |     |
| Lightness, L        | 39.98| 35.60| 41.01| 33.42| 26.35| 32.42| 79.58| 79.37| 79.75|
| Saturation, S       | 57.94| 56.14| 58.41| 36.46| 35.76| 36.79| 72.88| 79.6 | 75.47|
| Lightness difference, ∆L | -43.74| -48.12| -42.71| -50.29| -57.37| -51.3 | -4.13| -4.35| -3.97|
| Colour difference, ∆E | 67.94| 69.43| 72.48| 62.05| 67.31| 63.00| 73.33| 79.78| 75.83|
| Hue difference, ∆H  | 5.24 | 3.53 | 26.54| 20.14| 19.16| 20.07| 30.24| 30.98| 30.64|

|       | Color properties after light fastness test |     |     |     |     |     |     |     |     |
|-------|-------------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Lightness, L        | 45.24| 36.61| 45.90| 33.56| 26.90| 35.48| 81.31| 80.31| 81.60|
| Saturation, S       | 52.82| 53.57| 52.76| 32.82| 32.69| 33.03| 61.43| 70.5 | 65.4 |
| Lightness difference, ∆L | -38.49| -45.80| -36.51| -47.17| -55.51| -46.94| -2.41| -2.11| -0.11|
| Colour difference, ∆E | 60.58| 67.09| 60.49| 57.32| 63.65| 56.80| 61.60| 71.37| 66.40|
| Hue difference, ∆H  | 5.34 | 0.22 | 1.32 | 19.36| 13.34| 14.56| 27.20| 27.21| 26.56|

|       | Rubbing fastness |     |     |     |     |     |     |     |     |
|-------|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Dry   | 3/4 4/5 4/5 4/5 | 3/4 | 4   | 4   | 4   | 4/5 4/5 | 4/5 4/5 | 4/5 4 |
| Wet   | 3/4 4   4   4/5 | 4/5 | 4/5 4/5 | 4/5 4/5 | 4/5 5 4/5 | 4/5 | 4/5 |

3.3 Rubbing fastness.
The fastness properties on dry and wet rubbing alike to colour properties depends on the used dye. The small increase (Table 2) of rubbing fastness is observed for modified samples.
3.4. Mechanical properties.
The obtained experimental results of mechanical properties of researched linen fabric are presented in Table 3. The error of measurement is within 2 - 3%.
In all cases the tensile strength is higher in warp direction in comparison of weft. As expecting, the alkali treatment without tension (samples U, A) causes the some decrease of tensile strength and significant increase of elongation. Such treatment of linen threads or fabrics can be used for creation of new textiles with higher elasticity.
The influence of enzyme modified textiles on mechanical properties and used dye is not significant.

Table 3. Mechanical properties of dyed fabric.

| Sample | Maximum load, N | Extension at maximum load, % |
|--------|-----------------|-------------------------------|
|        | Warp direction  | Weft direction | Warp direction | Weft direction |
| U      | 370.8           | 275.7           | 9.6            | 14.0           |
| A      | 296.3           | 294.7           | 38.9           | 22.9           |
| E      | 360.9           | 274.4           | 10.3           | 13.2           |
| UR     | 356.7           | 305.6           | 11.2           | 15.8           |
| AR     | 353.5           | 258.5           | 37.5           | 21.3           |
| ER     | 353.1           | 273.2           | 10.1           | 14.4           |
| UB     | 371.6           | 277.6           | 10.0           | 14.5           |
| AB     | 386.1           | 252.5           | 41.5           | 20.2           |
| EB     | 357.6           | 272.1           | 10.3           | 10.8           |
| UY     | 391.7           | 277.7           | 9.7            | 15.3           |
| AY     | 341.4           | 266.9           | 38.7           | 19.5           |
| EY     | 367.9           | 273.1           | 9.4            | 11.5           |

4. Conclusion
- The main factor influencing the colour properties of linen fabric dyed with examined reactive dyes is used dye
- The modifiers influence on colour and colour properties after light test is selective for used dye, but not significant
- The modifiers use increase the rubbing fastness of dyed linen textile
- The use of alkali treatment of linen textile without tension causes the significant increase of elongation characteristics of fabric.

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