Influence of hydrophobicity on dye sorption into wool and physical properties of dyed wool fibre

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The effect of wool fibre hydrophobicity on anthraquinonic dye sorption into wool and on physical properties of dyed wool fibres was evaluated in this research. Dyeing experiments were performed on wool fabric samples, untreated and pretreated with a chloroform and methanol mixture. Newly synthesized Blue and Green anthraquinonic dyes and commercially available C. I. Acid Blue 80 dye were used for wool fabric dyeings. Wool samples were dyed in aqueous solutions of dyes as well as in dye and surfactant solutions at 60 °C and 90 °C temperatures. The data of dyeing experiments have shown that dye sorption into wool fibre mostly depends on the dye structure. The physical properties of dyed wool fibres varied depending on removal of hydrophobic outer layer of wool fibre as well as surfactants used in dyeing solutions.

Key words: wool fibre, dye, hydrophobicity, dyeing, physical properties

INTRODUCTION

Problems in diffusion may be reduced by use of small dye molecules, swelling agents for wool as the best model substrate for other protein fibres [1], and use of solvent-assisted processes [2]. The dyeing temperature also affects the amount of dye which penetrates into the wool fibre [3]. Some biopolymers are dyed at low temperatures in order to decrease the possibility of damaging; however, the sorption of dye at low

temperatures is usually insufficient. Therefore, to accelerate low temperature dyeing and to obtain even penetration of the dye into the wool various additives, usually surfactants, are used in dyeing solutions.

The hydrophobic nature of the outer layer of the wool fiber often becomes an obstacle for the quality in the staining, dyeing or other processes dependent on the diffusion of chemicals into the fibers [4]. The authors [5] suggested that the surface of wool fibers should be coated with long-chain fatty acids linked to the surface by ester linkages. A dramatic reduction in fiber hydrophobicity can be demonstrated by

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the treatment of fibers with organic solvents, alcoholic alkali solutions, anhydrous potassium tertiary butoxide in a non-swelling solvent, butanol. The release of bounded lipids after treatment of fibers with potassium tertiary butoxide supports the current hypothesis that these lipids are located on the exposed surface. The authors also concluded that the removal of bound lipids might facilitate the access of the surfactant to the wool fiber.

The topicality of the investigations on the influence of surfactants, particularly nonionics, in the dyeing of protein fibre is increasing in terms of the improvement of dye diffusion and its distribution equality in the fibre, or the diminution of fibre destruction running in this process [6]. Nonionic surfactants were initially believed to have a low affinity for wool. The recent studies [7] show that the nature of the fibre surface significantly influences the adsorption of the nonionic surfactant. The presence of the surfactant on the modified fibre surface enhances the wettability of the fibre. It is suggested that the removal of the lipid layer may facilitate access of the surfactant molecules to the fibre surface and the subsequent action of the surfactant may expose more hydrophilic regions of the underlying protein [7, 8]. Nonionic alkylphenolethoxylate type surfactants are known as adducts forming complexes with wool fibre by means of hydrophobic interactions between hydrophobic sites [9].

Many types of dyes can be used in the wool dyeing process, for example, acid, reactive dyes and others [10]. Dyes which consist of a core anthraquinone structure usually are nonionic aromatic compounds, poorly soluble in water, but soluble in organic solvents [5]. Commercial anthraquinone dyes contain auxiliary materials, particularly dispersants. Auxiliaries used in the dyeing solution can form dye / surfactant complexes. However, the formed complexes could cause a decrease in dye uptake. Therefore, it is very important to make a careful selection of dyes and surfactants to combine good exhaustion with satisfactory dyeing uniformity. Dye sorption isotherms showed that dye distribution in the fibre and the dyeing solution depends on the temperature, the pH of the dyeing solution, and the concentration of electrolyte in the dyeing solution [2, 11]. Nowadays the levelness of dyeing is frequently evaluated through the use of CIELAB colour coordinates [12–14].

Chemical treatment, bleaching and dyeing are known to be the factors that produce hair cuticle and cortex damage and impair their properties [6, 15]. The mechanical properties of α-keratin fibres, such as hair fibers and wools, are primarily related to the two components of the elongated cortical cells, the highly ordered intermediate filaments (microfibrils) which contain the α-helices, and the matrix in which the intermediate filaments are embedded [16].

The aim of this work was to evaluate the effect of wool fibre hydrophobicity on anthraquinonic dye sorption into wool and physical properties of dyed wool fibres.

EXPERIMENTAL

The fabric of pure merino wool complying with the regulations of ISO 150/F–1985 (E) was used for the dyeing experiments. Wool fabric samples were prepared for the dyeing experiments by extraction in a Soxlet apparatus (10 cycles) with a methanol ant chloroform mixture.

Wool fabric samples were dyed in the aqueous solutions of newly synthesized anthraquinonic Blue (1), Green (2) and C. I. Acid Blue 80 (3) dyes. The synthesis of Blue and Green dyes was carried out by Professor V. Mickevičius group at the Department of Organic Chemistry, Kaunas University of Technology. Molecular weights of the dyes, respectively, were: Blue (I) 349, Green (II) 379 and C. I. Acid Blue 80 (III) (Aldrich) 634. Acid dye C. I. Acid Blue 80 was recrystallized using dimethylformamide and acetone.

(I)

(II)

(III)
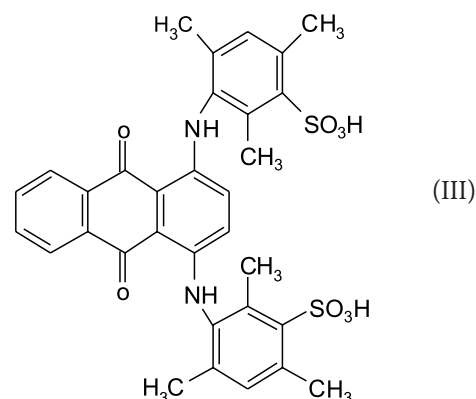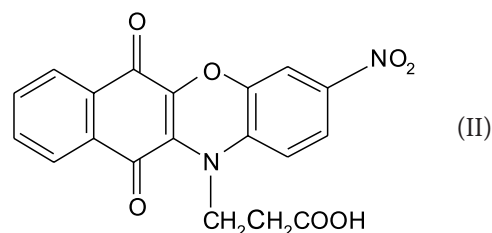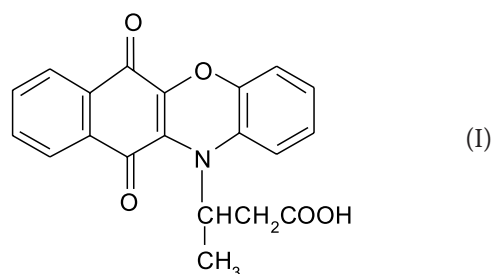
Some surfactants were used in the dyeing solutions such as anionic sodium dodecyl sulfate (SDS) (Merck-Schuchardt); nonionics: nonylphenoletoxylate (NPE) (Lanasan LT, Clariant), hydrophilic-lipophilic balance (HLB) – 12.8, alkoxylated (7.5) alcohol (Berol 175) (Akzo Nobel), HLB – 12.5, alkoxylated (32) alcohol (Berol 199) (Akzo Nobel), HLB – 12.3, alkoxylated (20) alcohol (Berol 828) (Akzo Nobel), HLB – 10.2, polyoxyethylene octyl phenyl ether (Triton X-100) (Fluka), HLB – 13.5.

The samples of unextracted and extracted wool fabric were dyed under such dyeing conditions: for 0.12 g/l of Blue, Green or C. I. Acid Blue 80 dye, surfactant molar ratio in aqueous solution was 1 : 1, pH 4.2, dyeing temperatures 60 and 90 °C. Wool samples were dyed in a glass tube with constant stirring. Dyeings were carried out for 100 minutes in the dyeing solutions with or without surfactants. At the end of dyeing the samples were rinsed thoroughly with distilled water and dried in the open air. Dye concentration in the dye-bath was measured at the start (0 min) of the dyeing and after 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 min. The dyed samples were rinsed thoroughly with distilled water and dried in the air. The percentage of dye-bath exhaustion E was calculated using Eq. 1:

$$E = \left(\frac{c_0 - c_d}{c_0} \right) \times 100, \tag{1}$$

where c_o and c_d are the concentrations, respectively, of initial dye-bath (0 min) and after different dyeing times (from 5 min to 100 min). The calibration curves created for each dyeing solution were used for the calculation of the dye concentrations. Absorbances A_o of the initial dye-bath and A_d after different dyeing times mentioned earlier were measured at 400–600 nm (λ_{max}). The optical density of dyeing solutions was measured using a Shimadzu UV-260 spectrophotometer which had five quartz cells (10.0 mm in light pass length). The average of the dye-bath exhaustion was calculated from three independent dyeing experiments and the standard deviation of the measurements did not exceed 0.007.

The dye concentration c^{pl} mol/g in the wool fibre was calculated using Eq. 2 [11]:

$$c^{pl} = \frac{c_0 \cdot E_{ave}}{100}, \tag{2}$$

where c_0 is the initial dye concentration, E_{ave} is the average of the percentage of dye-bath exhaustion.

The breaking force and extension at the break of wool yarns were evaluated using a dynamometer ZWICK Z005. The initial distance between the upper and lower clamps was 50 mm. The device automatically stops at the moment of burst and shows the strength that the wool yarn can withstand. The arithmetic average of the breaking force and extension at the break was calculated from 30 individual measurements.

Colour intensities of the dyed wool sample were determined by light diffuse reflectance measurements which were performed using a spectrophotometer Spektroflash SF 450 PLUS (Datacolor), and colour yield values were calculated according to the Kubelka-Munk function (K/S) by Eq. 3 [11]:

$$K/S = \frac{(1 - R)^2}{2R}, \tag{3}$$

where K is absorbance, S is scattering, and R is reflectance. The arithmetic average of the colour intensity was calculated from 3 measurements in one dyed wool fabric sample. To compensate for the colour of the undyed wool fabric the intensity was subtracted from the reflectance of the sample before the calculation of K/S.

RESULTS AND DISCUSSION

The data presented in Fig. 1 show that the color intensities of wool fabric samples dyed 100 min in aqueous anthraquinonic Green dye or Green dye/surfactant mixture solutions were higher, approximately 6 times, comparing with those dyed in Blue dye solutions, respectively. This might be explained by the difference in the molecular structure of Green and Blue dyes. Green dye has got a functional nitro group, whereas Blue dye has not. The nonionic surfactants which differ in HLB value were used in the dyeing solutions in order to evaluate the effect of surfactants on the color intensity of the dyed wool fabric. The data presented in Fig. 1 show that
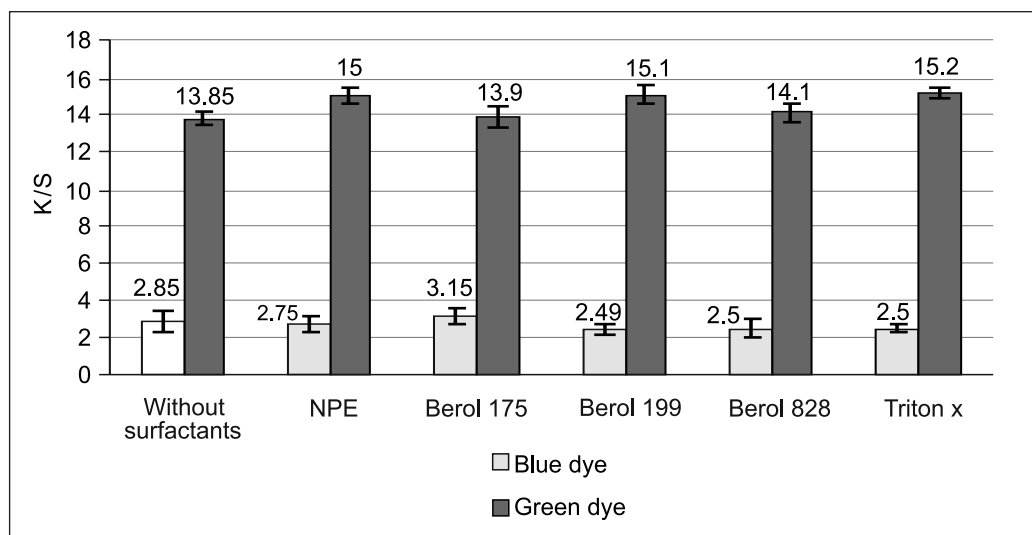

Fig. 1. The colour intensity of the wool fabric dyed with Blue or Green dye, when different types of surfactants were used in dyeing solutions

nonionic surfactants have a negligible effect on the dye sorption into wool fabric. The color intensity of the wool fabric increased only in that case when ethoxylated alcohol Berol 175 was used in an aqueous Blue dye solution. However, when the nonionic surfactants were used in Green dye solutions, the increase of colour intensity was determined for all wool samples. The *K/S* value of the wool fabric sample dyed in the Green dye and nonionic Triton x solution was 1.35 units higher comparing with that dyed in the Green dye solution without any surfactant. Due to the nonionic surfactants Berol 199 or NPE addition to the Green dye aqueous solution, the color intensity value of wool fabric samples increased in 1.25 and 1.15 relative units, respectively. Assuming the results presented in Fig. 1, it can be postulated that the value of nonionic surfactants HLB had no significant effect on the color intensity of the dyed wool fabrics. These experimental data are in correlation with the literature data [7] that nonionic surfactants adsorb on the wool fiber surface, but the intensity of sorption depends on the pretreatment of wool fibers.

Due to higher intensities of colour (*K/S* values) and, possibly, of Green dye penetration into the wool fibre comparing with that of Blue dye, for further dyeing studies Green dye and commercial C. I. Acid Blue 80 dye were chosen. In our previous research work [17] it was shown that the sorption of C. I. Acid Blue 80 dye could be enhanced by using nonionic surfactants in the dye solution. In this research we pursue to evaluate and to compare the influence of the molecular weight and structure of dye on its sorption to the wool fibre. Nonionic Berol 175 and anionic SDS were chosen as additives in dyeing solutions. In order to evaluate the influence of hydrophobicity of the wool fiber surface, experiments were made with unextracted and extracted wool fabric samples.

The data presented in Fig. 2 show the kinetic curves of C. I. Acid Blue 80 dye sorption into the unextracted wool when the temperature of the dyeing solution was 60 °C. When the unextracted wool fabric was dyed with C. I. Acid Blue 80 dye and nonionic Berol 175 additive in the dyeing solution, the equilibrium dye concentration was 0.07 mol/g. When the unextracted wool samples were dyed in the solutions of dye or the dye and SDS surfactant, the values of equilibrium dye concentration were 0.04 mol/g in both cases. It is evident from Fig. 2 that when wool samples were dyed in the aqueous C. I. Acid Blue 80 dyeing solution or the dye and anionic SDS mixture, the equilibrium dye concentration isotherms overlapped. The only difference between them was observed that the dye particles from the dyeing solution with SDS additive penetrated to the wool fiber from the beginning of the dyeing process. When the wool fabric was dyed with the aqueous C. I. Acid Blue dye solution, the sorption began after five minutes from the beginning of dyeing. These data could be explained by the diminishing action of SDS on the barrier of the initial dye diffusion into the wool fiber.

The data presented in Fig. 3 show C. I. Acid Blue 80 dye sorption behaviour into the extracted wool when dyeing was performed in aqueous dye solutions with or without any nonionic surfactant. The temperature of the dyeings was 60 °C. According to the results, removal of the hydrophobic layer reveals differences between the sorption isotherms of the aqueous C. I. Acid Blue dye solution and anionic SDS in the dyeing solution. Dye sorption was not observed in the wool fiber the first 50 minutes when dyeing was carried out using the aqueous Acid Blue dye solution with SDS additive in it. These results might be explained by the influence of the anionic surfactant. Comparing the equilibrium dye concentration in the wool fiber when it was dyed after pretreatment with the methanol and chloroform solutions mixture (Fig. 2) or without pretreatment (Fig. 3) at 60 °C temperature, it can be assumed that the removal of the hydrophobic layer did not change the value of the equilibrium dye concentration. When
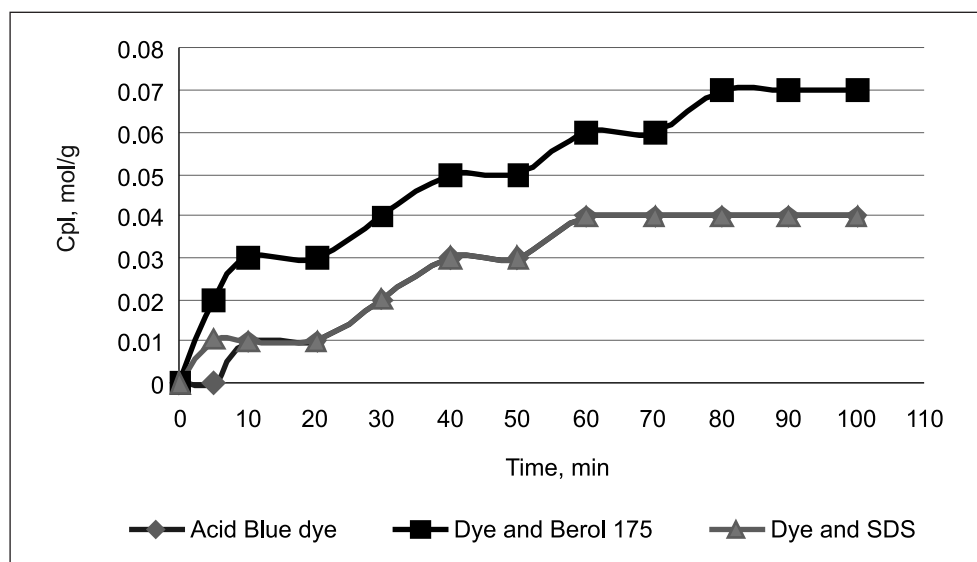

Fig. 2. Acid Blue 80 kinetic dyeing of the unextracted wool fabric at 60 °C temperature
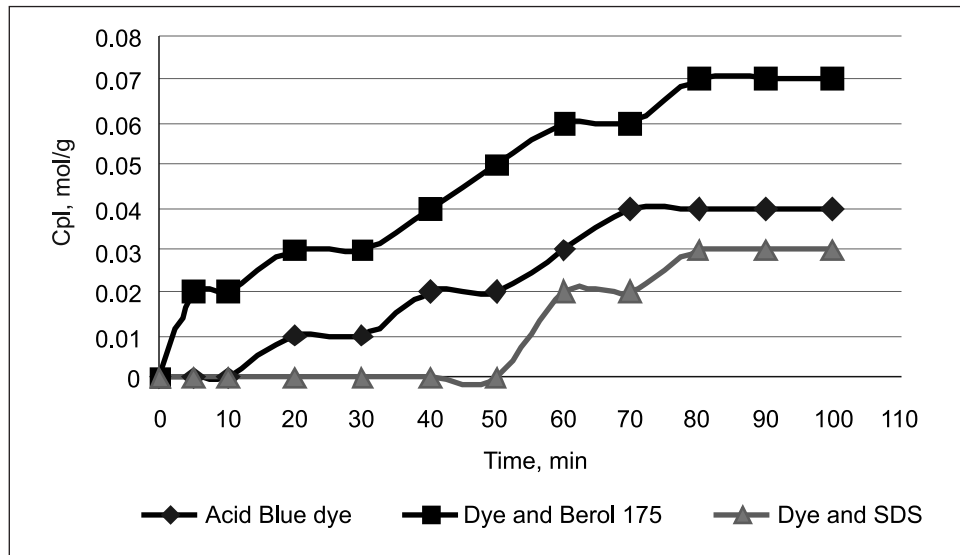
Fig. 3. Acid Blue 80 kinetic dyeing of the extracted wool fabric at 60 °C temperature

the wool fiber was dyed with the C. I. Acid Blue dye solution with nonionic Berol 175 in it, the equilibrium dye concentration was 0.07 mol/g; and when it was dyed in the aqueous dye solution without additives, it was 0.04 mol/g. Only when SDS was used in the dyeing solution, the equilibrium dye concentration decreased to 0.03 mol/g when extracted wool fabric samples were dyed.

Analogous experiments were done using antraquinone Green dye for the dyeing of wool fabric samples. The data presented in Fig. 4 and 5 show the sorption isotherms of dye into the unextracted and extracted wool fabric, dyed with Green dye at 60 °C temperature. The kinetic curves show (Fig. 4) that the highest equilibrium dye concentration in the wool fibre was when it was dyed in the aqueous dye solution. Due to the presence of nonionic or anionic surfactants

in the dye solution, the concentration of the penetrated dye into the fibre decreased and the equilibrium concentration was reached in half an hour of dyeing at 60 °C temperature. Removing of the hydrophobic layer revealed differences between sorption isotherms of the Green dye mixture with the nonionic Berol 175 dyeing solution and the dye mixture with the anionic SDS dyeing solution. When the wool fabric was dyed with the Green dye and Berol 175 solution, a higher amount of the dye penetrated into the wool fibre comparing with dye migration to the wool fibre from the dye and anionic surfactants solution. The data presented in Fig. 5 show that 0.04 mol/g of Green dye was sorbed in the wool fibre at the first 5 minutes. When the dyeing was carried out using C. I. Acid Blue dye and Berol 175 (Fig. 3), the dye concentration was twice as low at the first 5 minutes of
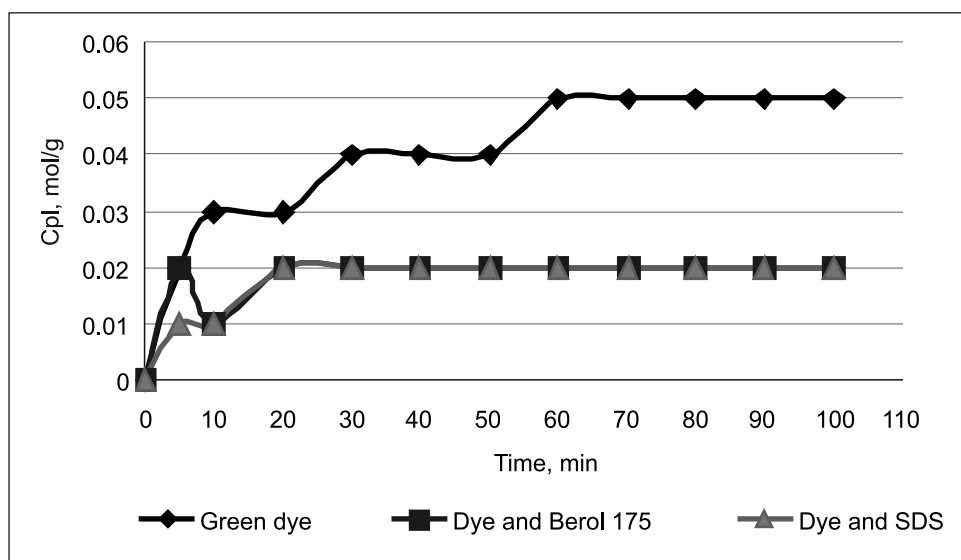

Fig. 4. Green dye kinetic dyeing of the unextracted wool fabric at 60 °C temperature
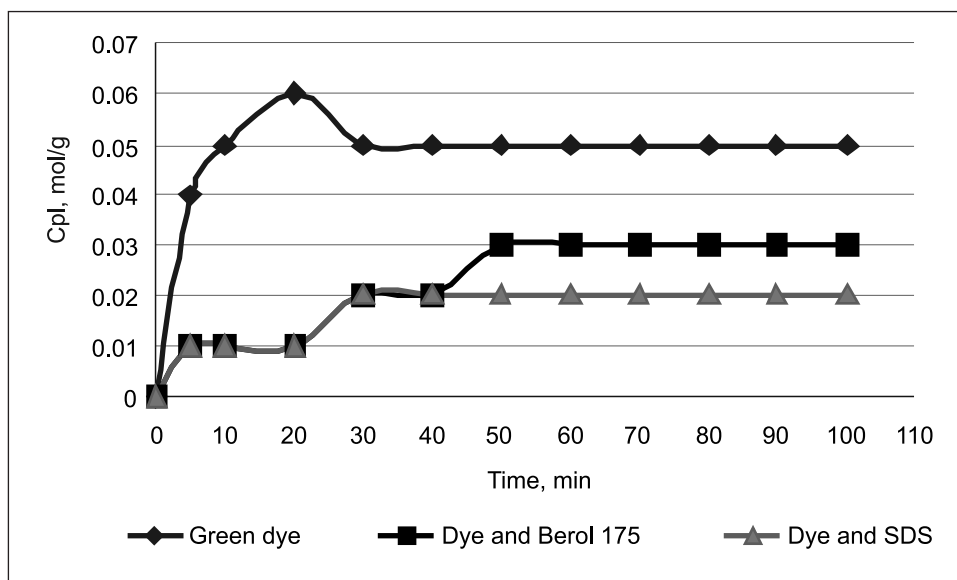
Fig. 5. Green dye kinetic dyeing of the extracted wool fabric at 60 °C temperature

the dyeing process. These results could be explained by the higher ability of Green dye with a smaller molecule to penetrate into the wool fiber when the hydrophobic barrier was released. The results of the dyeing process kinetics with the aqueous Green dye solution of extracted wool fabric samples show that smaller dye molecules can penetrate into the fibre, but the same amount of the dye can form the sites with the active fibre centres regardless of fibre preparation for dyeing (Fig. 4 and Fig. 5). Comparing the data of the dyes Green and C. I. Acid Blue 80 equilibrium sorption, it is possible to summarize that a higher amount of C. I. Acid Blue 80 dye penetrates into the wool fibre.

The data of the breaking force of a single wool yarn from unextracted and dyed wool fabric samples are presented in Table 1. The loss of strength was determined for wool

yarns which were removed for physical experiments from the unextracted wool fabric and dyed in aqueous solutions of C. I. Acid Blue 80 or Green dye with nonionic Berol 175 when dyeing was proceeded at 60 °C temperature. This deterioration of strength might be explained by the influence of the nonionic surfactant on the outer hydrophobic layer of the wool fiber. When the extracted wool fabric was dyed with smaller molecular mass Green dye, the protective effect of nonionic Berol 175 can be observed (Table 2). The increase of the dyeing temperature to 90 °C did not reveal the protective effect of surfactants, with the exception of the unextracted wool fabric dyed with SDS or Berol 175 additive in the dyeing solution, and the extracted wool fabric dyed with the aqueous Green dye and dye with SDS additive in it.

Table 1. Data of the breaking force (N) of a single wool yarn from the unextracted and dyed wool fabric

Additive in dye solution	Dyeing temperature			
	60 °C		90 °C	
	Dye			
	Green	Acid Blue	Green	Acid Blue
Without additive	2.70 ± 0.41	2.85 ± 0.32	2.52 ± 0.32	2.75 ± 0.31
SDS	2.71 ± 0.33	2.58 ± 0.32	2.80 ± 0.34	2.68 ± 0.27
Berol 175	2.52 ± 0.25	2.43 ± 0.27	2.91 ± 0.39	2.61 ± 0.26

Table 2. Data of the breaking force (N) of a single wool yarn from the extracted and dyed wool fabric

Additive in dye solution	Dyeing temperature			
	60 °C		90 °C	
	Dye			
	Green	Acid Blue	Green	Acid Blue
Without additive	2.55 ± 0.3	2.89 ± 0.28	2.90 ± 0.33	2.72 ± 0.37
SDS	2.55 ± 0.26	2.44 ± 0.31	2.70 ± 0.33	2.41 ± 0.22
Berol 175	2.70 ± 0.32	2.65 ± 0.31	2.70 ± 0.4	2.50 ± 0.31

CONCLUSIONS

Wool fibre dyeing with two newly synthesized dyes shows that Green dye, which differs from Blue dye in -NO$_2$ functional group, penetrates into the wool fiber intensively, independent of the composition of the dyeing solution.

The dyeing experiments at 60 °C temperature show that the removal of the hydrophobic layer from the wool fiber surface does not enhance the equilibrium of dye sorption into wool samples. Either intensity of the dye penetration into the wool fibre depends on the molecular weight and structure of the dye.

The removal of the hydrophobic wool surface and dyeing at 60 °C or 90 °C temperatures in solutions of different compositions have a negative effect on the strength of wool yarns.

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HIDROFOBIŠKUMO ĮTAKA DAŽIKLIŲ SORBCIJAI VILNOS PLUOŠTE IR DAŽINIŲ FIZIKINĖMS SAVYBĖMS

Santrauka

Atlikti vilnos pluošto hidrofobiškumo įtakos antrachinoninių dažiklių sorbcijai vilnoje ir dažytos vilnos pluošto fizikinėms savybėms tyrimai. Buvo dažomi vilnonio audinio bandiniai, prieš dažymą ekstrahuoti chloroformo ir metanolio mišiniu, ir to pačio audinio bandiniai, tik prieš dažymą neapdoroti tirpikliais. Vilnonio audinio bandiniai buvo dažomi naujai susintetintais antrachinoniniais mėlynuoju ir žaliuoju dažikliais, taip pat C. I. rūgštiniu mėlynuoju 80 dažikliu. Vilnonio audinio bandiniai buvo dažomi vandeniniuose dažiklių, dažiklių ir paviršinio aktyvumo medžiagų vandeniniuose 60 °C bei 90 °C temperatūros tirpaluose. Dažymo eksperimentų duomenys rodo, kad dažiklių sorbcija vilnos pluošte priklauso nuo dažiklio struktūros. Dažytos vilnos pluošto fizikinės savybės kito priklausomai nuo vilnos pluošto paviršiaus hidrofobiškumo ir paviršinio aktyvumo medžiagų, naudotų dažymo tirpale.