ADVANTAGES OF DYEING WOOL FIBERS AT 60 °C AFTER PREVIOUS MODIFICATION WITH ALCOHOL

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This research work describes the advantages of dyeing wool fibers at 60 °C after pre-treatment with alcohol. Wool is a natural fiber. This fiber can be dyed with acid, metal-complex and other dyes. Acid dyes should be soluble in water and most commonly used for dyeing wool, silk and nylon. Wool fibers with 100 % chemical composition were used in this study. The wool fiber was pre-treated in alcohol (n-pentanol) at a temperature of 60 °C for 30 minutes. Pre-treated wool fibers were dyed with Supramin Blau acid dye. The time for dyeing samples of wool fibers was 5, 10, 20, 30, 40, 50 and 60 minutes. The process of dyeing wool fibers with acid dye at 60 °C showed a higher degree of exhaustion and adsorption capacity when wool was pre-treated with n-pentanol compared to wool that was not pre-treated with n-pentanol. A constant increase in the degree of dye exhaustion on the pre-treated wool fiber was observed during the increase in initial dye concentration. A longer dyeing time for pre-treated wool results in a higher degree of dye exhaustion. Models *Weber-Morris* and *Elovich* are applicable for describing the adsorption flow because there is very little scatter around the ideal curve, so functional straight lines cover most points very well.

Keywords: wool, alcohol, dyeing, pre-treatment

Introduction

Wool is made up of keratin, a very complex protein, as well as many active side groups. These groups play an important role in the side chain linkages in wool. Using X-ray diffraction, it was discovered that wool has two structures. Both structures are present in the crystalline region of the wool and largely determine the behavior of its fiber. One is alpha-keratin and the other is beta-keratin. When stretched, wool acquires a beta-keratin structure [1].

Wool is a natural fiber of animal origin i.e. the soft hair of sheep fur. Conventional dyeing of wool fabric is strictly controlled by the boiling temperature, which can adversely affect the mechanical properties affecting carding, spinning and weaving [2].

Dyeing with acid dyes is done at low pH. Acid dyes are most often used for dyeing wool [3].

Acid dyes belong to the group of synthetic dyes that are produced the most. More than half of the world's annual production includes these dyes [4-6].

Alcohols are organic compounds. Their structure is similar to water [7].

Alcohols are weak acids. They can be used as solvents because of the hydroxyl groups that make the alcohol molecule polar [7].

The paper shows the influence of pre-treatment with alcohol on the dyeing of wool fibers. The goal of the research is the development of a new procedure for dyeing wool fiber with acid dyes with a special reference to pre-treatment with alcohol and the advantages of the pre-treatment with them.

Materials and methods

In the practical part, raw and pre-treated wool fibers were used. Samples of wool fiber were washed in Sarabid (1g·L^{-1}) for 30 minutes at 40 °C, then dried at room temperature for 24 h and set aside for further processing. After drying, the wool fibers are treated in n-pentanol at room temperature at a bath ratio of 1:50, for 30 minutes.

Dyeing of the treated fibers was done with the acid dye Supramin Blau, the structure of this acid dye is presented in Figure 1. The temperature of dyeing was 60 °C and the concentrations of used dye were 100, 200, 300, 400 and 500 mg·L^{-1} and the scale of the dyeing bath was 1:50. Dyeing time was 5, 10, 20, 30, 40, 50, 60 minutes. The addition is HCOOH, to achieve pH=3. The spectrophotometer was used to measure the absorbance at the adsorption maximum for the acid dye Supramin Blau i.e. λ = 590 nm.

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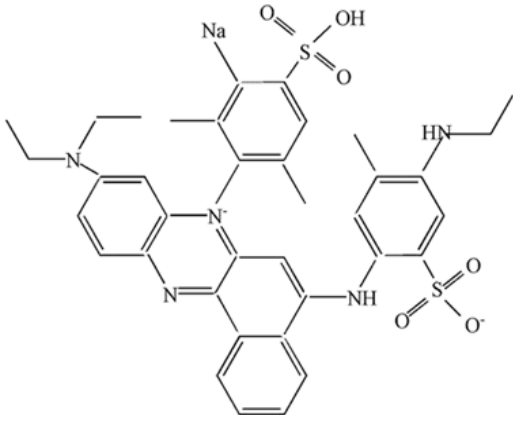


Figure 1. The chemical structure of Supramin Blau acid dye

Equation 1 was used to calculate the degree of dye exhaustion [8]:

$$E = \frac{c_0 - c_t}{c_0} \times 100\ (\%) \quad \text{.....(1)}$$

where: C_0 and C_t (mg·l^{-1}) are the initials and the concentration of dye at a time is *t*.

Equation 2 was used to calculate the adsorption capacity was calculated using equation [8]:

$$q_t = \frac{C_0 - C_t}{w} \times V \text{ and } q_e = \frac{C_0 - C_e}{w} \times V \quad \text{.....(2)}$$

where: *w* (*g*) is the mass of wool and *V* (dm^3) is the bulk of the dye bath, q_t (mg·g^{-1}) is adsorbed dye per unit mass per dyeing time *t*; C_o (mg·l^{-1}) is the concentration of dye at the start, q_e (mg·g^{-1}) is the adsorbed dye per unit mass in equilibrium, C_t (mg·l^{-1}) is the concentration of dye in the dye bath at the dyeing time *t*, C_e (mg·l^{-1}) is the equilibrium concentration of dye in the dye bath.

Equation 3 was used to calculate the linear form of the *Elovich* model [9]:

$$q_t = (1/\beta) \cdot ln(\alpha \cdot \beta) + (1/\beta)\, ln\,(t) \quad \text{.....(3)}$$

where: *α* is the speed at the start of adsorption (mg·g^{-1}min^{-1}), *β* represents surface coverage and activation energy for chemisorption (g·mg^{-1}).

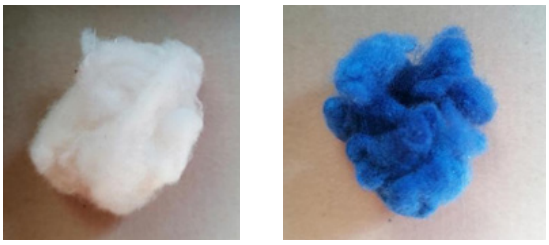
Equation 4 was used to calculate the *Weber-Morris* model [10]:

$$q_t = k_d \cdot t^{1/2} + C \quad \text{.....(4)}$$

where: k_d – is the constant for intraparticle diffusion (mg·g^{-1} min$^{1/2}$), and *C* – is the axis intercept (mg·g^{-1}).

Results and discussion

Figure 2 shows (a) a wool fiber sample pre-treated with n-pentanol and (b) a dyed wool fiber sample pre-treated with n-pentanol.



(a) (b)

Figure 2. The appearance of the wool fiber after pre-treatment with alcohol (a) and after the dyeing of pre-treated wool fiber (b)

The results of the influence of dyeing time on the degree of exhaustion and adsorption capacity for raw and wool pre-treated with n-pentanol at 60 °C at the lowest concentration of dye 100 mg·l^{-1} are shown in Table 1. Changes were observed with increasing concentration of dye at the start. The degree of dye exhaustion for raw wool is around 78-84%, while for wool pre-treated with n-pentanol these values are around 96-99%. Better results of degree of exhaustion, as well as higher values of acid dye adsorption capacity, were observed for wool pre-treated with n-pentanol. As the values of the initial dye concentration increase, thus, the values of adsorbed dye on raw and pre-treated wool with n-pentanol also increase.

Table 1. The effect of the concentration of dye at the start on the degree of dye exhaustion and adsorption capacity of Supramin Blau during the dyeing of raw and pre-treated samples of wool fibers with n-pentanol (T=60 °C, t=60 min)

C_o, mg·l^{-1}	*E*, %		q_e, mg·g^{-1}	
	Raw wool	Wool treated with pentanol	Raw wool	Wool treated with pentanol
100	78.65	96.37	4.03	9.24
200	80.50	98.05	8.05	16.10
300	81.77	98.91	12.26	21.79
400	84.37	99.24	16.87	29.84
500	84.75	99.80	21.19	37.86

The results of the influence of dyeing time on the degree of dye exhaustion and adsorption capacity of acid dye for raw and pre-treated wool with n-pentanol at 60 °C at the lowest concentration of dye 100 mg·l^{-1} are shown in Table 2. By increasing the value of the concentration of dye at the start, the degree of dye exhaustion increases as well. The shortest time shows the lowest degree of dye exhaustion, while at the longest time of dyeing wool, the highest degree of exhausted dye per unit mass of fibers occurs. Wool pre-treated with n-pentanol shows higher values of degree of exhaustion which are noticeable compared to raw wool. Higher values of acid dye adsorption capacity during wool dyeing are visible in wool previously pre-treated with alcohol. A longer dyeing time brings higher values of adsorbed dye on the wool fiber. The pre-treatment process of wool with alcohol removal of surface lipids impedes dye penetration between overlapping cuticle cells.

Table 2. The change in the degree of dye exhaustion and adsorption capacity of Supramin Blau during dyeing of raw wool and wool pre-treated with *n*-pentanol (T=60 °C, C_0=100 mg·l^{-1})

Time, min	*E*, %		q_e, mg·g^{-1}	
	Raw wool	Wool treated with pentanol	Raw wool	Wool treated with pentanol
5	19,.82	64.92	0.99	1.20
10	25.71	70.80	1.28	3.16
20	43.35	87.08	2.17	5.51
30	53.16	90.18	2.66	6.88
40	62.96	91.37	3.15	8.26
50	70.80	92.33	3.54	8.65
60	78,65	94.37	3.93	9.24

The *Elovich* equation is used in chemical adsorption processes and is acceptable, regarding the assumption of surface heterogeneity. In chemical reactions involving surface adsorption without desorption, the rate decreases with increasing time due to surface coverage [11].

The results of the *Elovich* model for acid dye adsorption on wool fiber pre-treated with n-pentanol are shown in Figure 3. It can be noted that the linear fitting curves show a good fit with the *Elovich* model (R^2>0.94) demonstrating that the adsorption of acid dye on wool fiber can be described using this model. This confirms the chemical adsorption on the active areas on the fiber surface.

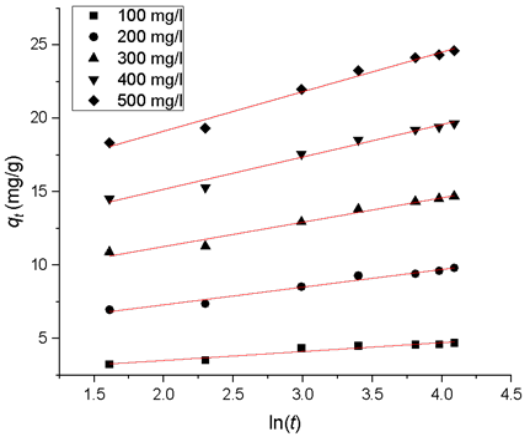


Figure 3. *Elovich* model for acid dye adsorption on wool fiber pre-treated with n-pentanol at different initial dye concentrations

The results of *Elovich* parameters for the adsorption of Supramin Blau acid dye on the wool fiber and parameters α and *β*, which represent the adsorption rate at the start, and the surface coverage are shown in Table 3. The coefficient of determination R^2 is high for all concentrations of dye at the start. These results indicate that dye adsorption is controlled by intra-particle diffusion.

Table 3. *Elovich* constants for acid dye adsorption on wool fiber pre-treated with *n*-pentanol

C_0 (mg·l^{-1})	α (mg·g^{-1}min^{-1})	*β* (g·mg^{-1})	R^2
100	6.25	0.43	0.940
200	13.31	0.20	0.974
300	21.60	0.12	0.975
400	29.24	0.09	0.981
500	37.35	0.07	0.983

The first phase, which lasts for 30 minutes, includes the diffusion of the dye molecules that takes place in the solution to the outer surface of the fiber and the diffusion of the dye molecules through the boundary layer to the surface of the wool fibers. This can be attributed to the immediate use of the most readily available adsorption sites on the surface of the wool fibers.

The second phase, which lasts from 30 to 60 minutes, includes the adsorption of the dye, which takes place gradually. The third phase represents the equilibrium period, during which the diffusion slows down [12, 13].

The results of the *Weber-Morris* kinetic model for adsorption of acid dye onto wool fibers pre-treated with n-pentanol are shown in Figure 4. The coefficient of determination has a value of (R^2>0.87). The preference is given to the *Elovich* model due to the higher values of the coefficient of determination.

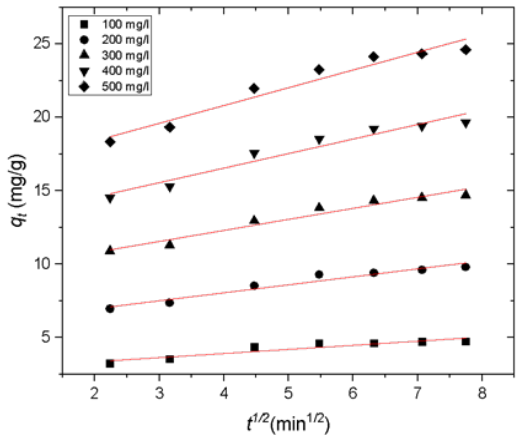


Figure 4. *Weber-Morris* kinetic model for acid dye adsorption onto wool fiber pre-treated with n-pentanol

The results of the parametres of the *Weber-Morris* model for the adsorption of Supramin Blau onto wool fiber pre-treated with n-pentanol are shown in Table 4. The results show that intra-particle diffusion is not the only factor that determines the speed. The *Weber-Morris* model shows the first linear part that arises due to the influence of the branch layer, and the second part appears due to the influence of diffusion within the particles [14].

Table 4. *Weber-Morris* parametres for adsorption of Supramin Blau onto wool fiber pre-treated with n-pentanol

C_0 (mg·l^{-1})	k_i (mg·g^{-1}min$^{1/2}$)	C (mg·g^{-1})	R^2
100	2.80	0.28	0.872
200	5.88	0.54	0.948
300	9.30	0.75	0.953
400	12.59	0.99	0.947
500	15.97	1.21	0.949

Conclusion

According to the results of the research on the dyeing of wool fibers with acid dye, the most significant results can be singled out:

The pre-treatment with n-pentanol yields showed much better results in the degree of dye exhaustion compared to those samples of wool fiber. The degree of dye exhaustion and the adsorption capacity were increased for the wool pre-treated with n-pentanol compared to wool without pre-treatment with n-pentanol

The longest time shows the greatest degree of dye exhaustion. With the increase in the concentration of dye, initially, there is an increase in the value of the exhausted dye and this trend is maintained constantly until the end of the dyeing process.

At the highest used concentrations of dye at the start and the longest dyeing time, the highest adsorption occurs.

It can be observed that the linear fitting curves show a good fit with the *Elovich* model (R^2>0.94) demonstrating dyeing on wool fiber samples can be described using this model, which means that the adsorbent-fiber surface is energetically heterogeneous, as well as the chemisorption of the acid dye on the wool fiber.

The coefficients of determination in the *Weber-Morris* model have lower values (R^2>0.87), so the *Elovich* model is preferred. This dyeing process at a lower temperature has been applied in industry.

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Izvod

PREDNOSTI BOJENJA VUNENIH VLAKANA NA 60 °C NAKON PREDHODNE MODIFIKACIJE ALKOHOLOM

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Ovaj istraživački rad opisuje prednosti bojenja vunenih vlakana na 60 °C nakon predobrade alkoholom. Vuna je prirodno vlakno. Ovo vlakno se može bojiti kiselim, metalkompleksnim i drugim bojama. Kisele boje su rastvorljive u vodi i najčešće se koriste za bojenje vune, svile i najlona. U radu su korišćena vunena vlakna 100% hemijskog sastava. Vuneno vlakno je prethodno obrađeno alkoholom (n-pentanol) na temperaturi od 60 °C tokom 30 minuta. Prethodno obrađena vunena vlakna su obojena bojom Supramin Blau - kisela boja. Vreme bojenja uzoraka vunenih vlakana iznosilo je 5, 10, 20, 30, 40, 50 i 60 minuta. Proces bojenja vunenih vlakana kiselom bojom na 60 °C pokazao je veći stepen iscrpljenosti i kapaciteta adsorpcije kada je vuna prethodno obrađena n-pentanolom u poređenju sa vunom koja nije prethodno obrađena n-pentanolom. Uočeno je konstantno povećanje stepena iscrpljenosti boje na prethodno obrađenom vunenom vlaknu tokom povećanja početne koncentracije boje. Duže vreme bojenja za prethodno obrađenu vunu dovodi do većeg iscrpljivanja boje. Modeli Weber-Morris i Elovich su primenljivi za opisivanje toka adsorpcije jer postoji vrlo malo rasejanja oko idealne krive, tako da funkcionalne prave linije veoma dobro pokrivaju većinu tačaka.

Ključne reči: vuna, alkohol, bojenje, predobrada