

DYEING KINETICS OF MULTI-COMPONENT TEXTILE YARN WITH BASIC DYE

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Kinetic analysis of the dyeing process of multi-component textile yarn with a basic dye was performed in this article. The yarn consists of multiple components, specifically three different fibers, with the highest proportion being modal, followed by cotton, and the least being polyamide. Dyeing of the yarn was carried out using a discontinuous method, with the appropriate initial dye concentration and different dyeing times. The aim is to elucidate the dynamic events during the adsorption of dye molecules onto the fibers and their diffusion into the interior. Two kinetic reaction models (Pseudo-first-order and Avrami) and one kinetic diffusion model (Weber-Morris) were used to test the experimental data from the dyeing process. Dyeing multi-component yarn yields satisfactory results, with even coloration of the yarn. The degree of dye exhaustion and the amount of dye on the fibers increase with time, while the initial dye concentration in the solution decreases as the dyeing process progresses. In the linear simulation of the kinetic dyeing parameters, the Avrami reaction model proves to be efficient, while the Weber-Morris model is found to be a very favorable diffusion equation.

Keywords: yarn, basic dye, dyeing, kinetic models.

INTRODUCTION

Textile products made from fiber blends are often found in the market, and they can be either dyed or undyed. The dyeing of fabrics, knits, or yarns made from fiber blends can be performed at various stages of their production. For instance, two or more different fibers can be separately dyed and then mixed to achieve a two-tone or multicolored effect in the final product. In many cases, dyeing blends is done in the form of fabric or

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knits. Dyeing fibers in their loose state is cheaper, but dyeing fabrics or knits is safer and more convenient, especially if these products need to be stored and dyed according to fashion market demands [1].

Dyeing textile materials in the form of fibers, yarns, or fabrics containing different components can be executed in the following ways [2]:

- Dyeing all components in the same shade.
- Dyeing only one component.
- Dyeing all components in different shades.

In practice, the most common scenario is the dyeing of two-component blends, and the most interesting form is dyeing each component with the appropriate dye in a single bath. In this case, dyeing each type of fiber is much better controlled than when both fibers are dyed with the same dye simultaneously. An example of an "ideal" blend for dyeing is a blend of viscose and acetate rayon. Direct dyes, if selected correctly, do not have much affinity for the acetate cellulose rayon, while disperse dyes, which successfully dye acetate cellulose rayon, practically do not dye viscose rayon [3].

Dyeing blends can be carried out using the following methods [4]:

- In a single bath, by dyeing all components in the same bath with one or more suitable dyes.
- In two or more baths, by dyeing each component in a separate bath with the appropriate dye.

Dyeing with basic dyes operates by forming ionic bonds with the fibers, similar to the process of dyeing with acid dyes. Basic dyes are also known as cationic dyes because their structure allows them to dissociate in an aqueous solution, giving a colored cation [5].

This paper presents a comprehensive set of research activities related to the kinetic analysis of the dyeing process of multi-component yarn with a basic (cationic) dye. By analyzing the rate and mechanism of dyeing, this research contributes to the understanding of the sorption process of the basic dye on yarn composed of three different fibers. The goal is to successfully perform the dyeing of multi-component yarn in a single bath and clarify the interactions between dye and fibers.

MATERIALS AND METHODS

In the experimental part of the study, a multi-component yarn was used, consisting of 2.0% Polyamide, 38.0% Cotton, and 60.0% Modacrylic (Figure 1).

Some of the key characteristics of the yarn that should be highlighted include the following: the average fineness is 31.6 tex, the average twist count is 200 twists per meter, the average shrinkage value is 2.6%, and the average thickness is 290 μm .





Figure 1. Appearance of the multi-component yarn before and after dyeing

For dyeing, a basic (cationic) dye, Basic Green 4 (Astrazon Green M) from Huntsman, Switzerland, was used. The structure of this dye is shown in Figure 2.

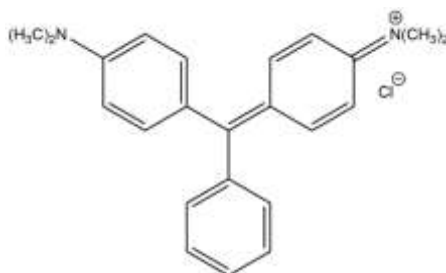


Figure 2. Structure of the green basic dye used

To verify the kinetic parameters of the dyeing process, a batch (discontinuous) process was employed. A fiber sample weighing 0.5 g was dyed in a bath with a constant volume of 0.05 dm³. The dyeing temperature was maintained at a constant temperature of 98 °C, while the dyeing time varied from 10 to 60 minutes, and the dye concentration was kept constant at 100 mg/dm³. In addition to the dye, sodium chloride at 20 g/dm³ and acetic acid at 1 g/dm³ were used as additives in all cases.

To determine the dye concentration in the solution using a calibration curve, absorbance was measured with the Varian Cary 100 UV-VIS Spectrophotometer (measurements were taken at the absorption maximum, 590 nm).

The kinetics of the adsorption of the basic green dye on the yarn were analyzed using the following reaction kinetic models: *Pseudo-first-order* and *Avrami*.

The kinetic data described by the *Pseudo-first-order* model represent the first known equation that describes the rate of sorption based on the adsorption capacity [6]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

Where q_e and q_t are the adsorption capacities at equilibrium (e) and after some time (t), respectively (mg/g), and k_1 is the rate constant of the pseudo-first-order sorption (1/min).



The *Avrami* model defines certain kinetic parameters, such as possible changes in the sorption rate as a function of initial concentration and sorption time, as well as determining the kinetic order of the fraction [7].

$$q_t = q_e \cdot \{1 - \exp[-(K_A \cdot t)]^{n_A}\} \quad (2)$$

where q_t - is the adsorption capacity at time t (mg/g), K_A - is the adjusted kinetic constant (1/min) ^{n_A} , n_A - is the constant related to the sorption mechanism.

In the research, the *Weber-Morris* kinetic diffusion model was used.

The *Weber-Morris* model, also known as the intra-particle diffusion model, is described by the following equation [7]:

$$q_t = k_{WM} \cdot t^{0.5} \quad (3)$$

Where: k_{WM} - is the intra-particle diffusion rate constant (mg/g·min^{-0.5}); t - is the contact time (min)

RESULTS AND DISCUSSION

Information about dyeing kinetics is crucial for determining the optimal operating conditions for a full batch process. The kinetics of sorption can be represented graphically as the uptake-exhaustion of dye over time, and this dependency is known as the kinetic isotherm. The kinetics depend on material factors such as the adsorbent (fibers) and adsorbate (dye), as well as experimental factors like temperature or pH. The results confirm that higher temperatures accelerate the diffusion of dye molecules into the fiber structure, leading to a faster attainment of apparent equilibrium. However, the final adsorption capacity decreases with increasing temperature, which is consistent with the exothermic nature of the adsorption process and the weaker interactions between the dye and the fiber at elevated thermal energy [3, 4].

The diagram in Figure 3 illustrates the dependence of the amount of basic dye in the dye bath and the amount of dye on the yarn over the dyeing time. It can be observed that, as expected, the dye concentration in the bath decreases during the dyeing process in all cases, while longer dyeing times result in a slightly higher amount of adsorbed dye per unit mass of yarn. The adsorption process continues until equilibrium is reached between the dye concentration in the solution and the dye concentration on the fiber. Since dye molecules tend to form aggregates in the aqueous solution, mechanical agitation breaks apart the dye aggregates in the solution and reduces the particle size of the dye in dispersion, which is the first condition for better sorption on fibers.



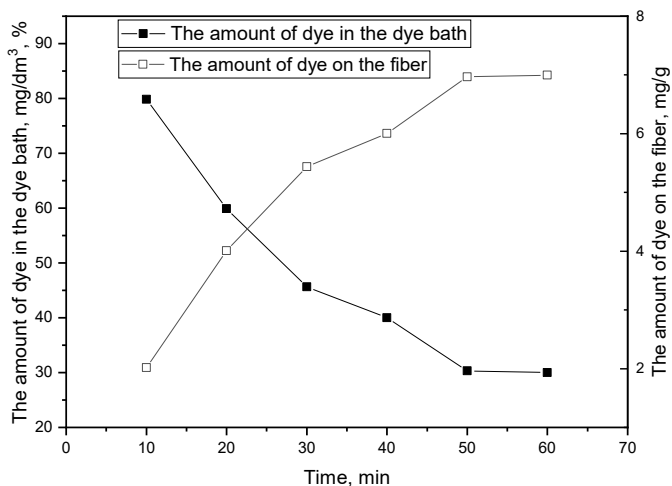


Figure 3. Change in the amount of dye in the dye bath and the amount of dye on the yarn during dyeing

In a similar study, the dyeing of polyamide composite fabric with a cationic dye was conducted, where the success was attributed to the electrostatic interaction between the dye cations and the negatively charged surface of the fabric treated with nanoclay. On the other hand, van der Waals forces can also serve as a means of bonding between the polymer chains and dye cations. The results indicated that the optimal conditions for dyeing polyamide fabric were as follows: pH 7 and a dyeing temperature of 85 °C. The impact of dyeing time (5, 10, 15, 20, 30, and 60 min) on the exhaustion level revealed a significant increase in the dye exhaustion percentage onto the polyamide fabric during dyeing. Under optimal conditions, polyamide fiber achieved an exhaustion of 97%, which was attributed to the swelling and expansion of the nanoclay, facilitating the penetration and distribution of dye molecules within the fabric [8].

Figures 4 and 5 present diagrams for the dye sorption kinetics on fibers, including experimental data points and linear kinetic reaction models: *Pseudo-first-order*, and *Avrami*, for an initial concentration of basic green dye of 100 mg/dm³. According to the fitting curves that match the experimental data points, the *Avrami* equation appeared to be better suited for describing the kinetics of basic green dye sorption (Figure 5), with the fitted curve of this kinetic equation closely following the experimental points. In contrast, based on the curve in Figure 4, the *Pseudo-first-order* model noticeably lags behind and makes a smaller contribution to explaining the sorption kinetics.

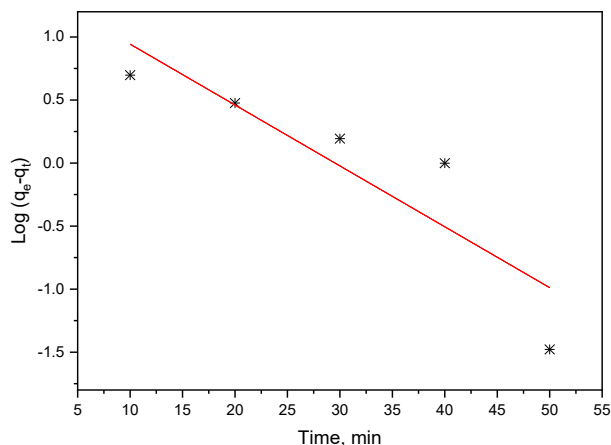


Figure 4. Sorption kinetics of basic green dye according to the *Pseudo-first-Order* kinetic reaction model

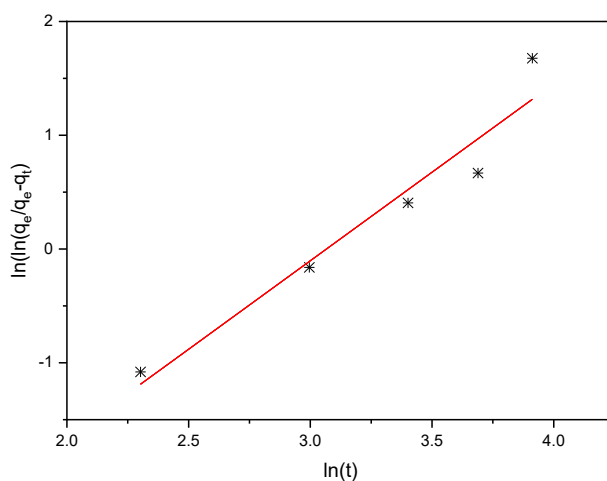


Figure 5. Sorption kinetics of basic green dye according to the kinetic reaction model *Avrami*

To understand the mechanism that controls the entire sorption kinetics, preference is given to kinetic diffusion models or mechanistic (theoretical) models. From a diffusion perspective, to interpret experimental data, it is necessary to identify the steps involved in sorption, described by external mass transfer, diffusion through the boundary layer, and diffusion within particles [8].

Figure 6 shows a dyeing rate diagram with experimental points and the curve of the *Weber-Morris* kinetic diffusion model for an initial concentration of basic dye of 100 mg/dm³. Based on the appearance of the fitting curve, this model describes the dyeing kinetics very well. Considering that the fitting line passes through the coordinate origin,



it can be concluded that diffusion within particles is the dominant phase controlling the rate of sorption. Therefore, diffusion through the film or boundary layer is negligible, while diffusion within particles is practically the only rate-controlling step for dyeing a multi-component yarn with basic green dye.

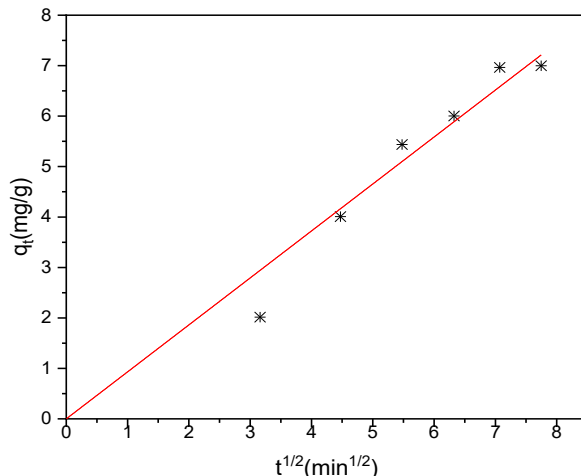


Figure 6. Sorption kinetics of basic green dye according to the diffusion model *Weber-Morris*

Similar kinetic studies are presented in a research paper dealing with the kinetics of adsorption and the thermodynamics of dyeing a copolyester fabric with a basic dye at 80, 90, and 100 °C. The results showed that the *Pseudo-second-order* model proved to be the most favorable and could be used to effectively explain the adsorption kinetics and predict the rate coefficient (k_2) at different temperatures. It was found that the adsorption equilibrium data were in accordance with the *Langmuir* isotherm with high correlation, while the thermodynamic parameters revealed that the dye adsorption on the fabric was a spontaneous, endothermic, and chemisorption process [6].

Table 1 provides numerous values of parameters for kinetic reaction models and the diffusion model for the sorption of a basic dye on yarn. Based on the highest coefficient of determination, the dominance of the *Weber-Morris* kinetic model is confirmed. This model is very suitable and useful since its curve fits the experimental points excellently. Very high statistical parameters of suitability (validity) ($R^2=0.993$) obtained from the *Weber-Morris* model for diffusion and sorption of a basic dye on a multi-component yarn indicate that diffusion within particles is the rate-controlling step for dyeing.

The *Pseudo-first-order* kinetic model proved to be the weakest of the models used ($R^2=0.795$), meaning that the sorption rate cannot be described solely based on the adsorption capacity, and the change in the sorption rate does not depend solely on the initial concentration and reaction time.

The *Avrami* equation was used to verify specific changes in kinetic parameters during dyeing. This model has a high coefficient of determination, $R^2=0.940$. The data suggest



that the dyeing process is limited to surface reaction, and the diffusion of dye molecules is fast ($n_A > 1$). Since it is an exponential equation, n_A as a fractional number is associated with possible changes in the sorption mechanism during dyeing. This model assumes that the distribution of dye molecules on the fiber surface is homogeneous and that sorption occurs at a constant growth rate, as the values of n_A are greater than 1. Therefore, the sorption mechanism is accompanied by multiple kinetic fractions that change during the contact of the dye with different fibers.

Table 1. Numerous values of parameters for kinetic reaction models and diffusion model with statistical parameters.

Analytical expression			
Kinetic model		Parameters	Values
<i>Pseudo-first-order</i>	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303} t$	k_1 (min ⁻¹)	0.11
		R^2	0.795
<i>Avrami</i>	$q_t = q_e \cdot \{1 - \exp[-(K_A \cdot t)]^{n_A}\}$	K_A (min ⁻¹) ^{-n_{AV}}	0.05
		n_A	1.55
		R^2	0.940
<i>Weber-Morris</i>	$q_t = k_{WM} \cdot t^{0.5}$	k_{WM} (mg·g·min ^{-0.5})	0.93
		R^2	0.993

CONCLUSION

Based on the research results, it can be concluded that yarn composed from various types of fibers can be effectively dyed with basic green dye at the boiling temperature in a single bath. The aim is to successfully complete the dyeing process in a single bath to avoid the costs associated with dyeing in multiple baths, considering that each component is dyed separately.

During the dyeing of the yarn, the amount of adsorbed dye and the degree of dye exhaustion continuously increase over time, while the initial concentration of dye in the solution decreases.

The Avrami model exhibited the best agreement with to the experimental data, as it most efficiently describes the complex kinetics of dye adsorption in multicomponent textile yarn, where the process occurs through several simultaneous mechanisms, including rapid surface adsorption and slower intra-fiber diffusion. In comparison, the pseudo-first-order model is overly simplified and cannot capture this complexity. Among the kinetic diffusion models, the Weber–Morris equation is the most favorable for linearly simulating the kinetics of fiber dyeing in multicomponent yarn. According to the Avrami and Weber–Morris models, the distribution of dye molecules on the fiber surface is homogeneous, sorption proceeds at a constant growth rate, and the overall sorption mechanism is governed by intra-particle diffusion.

The results of this study suggest the feasibility of a different approach to the simultaneous dyeing of yarn made from a mixture of fibers in a single bath, therefore enabling greater exhaustion, cost savings, and reduced waste dye after the dyeing process.



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KINETIKA BOJENJA VIŠEKOMPONENTNE TEKSTILNE PREĐE BAZNOM BOJOM

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U ovom radu izvršena je kinetička analiza procesa bojenja višekomponentne tekstilne pređe baznom bojom. Pređa se sastoji od više komponenti, konkretno od tri različita vlakna, pri čemu je najzastupljeniji modal, zatim pamuk, a najmanje poliamid. Bojenje pređe izvedeno je diskontinuiranom metodom, pri odgovarajućoj početnoj koncentraciji boje i različitim vremenima bojenja. Cilj je razjašnjenje dinamičkih dešavanja tokom adsorpcije molekula boje na vlakna i njihove difuzije u unutrašnjost. Za ispitivanje eksperimentalnih podataka dobijenih tokom procesa bojenja korišćena su dva kinetička reakciona modela (pseudo-prvog reda i Avrami) i jedan kinetički model difuzije (Veber-Moris). Bojenje višekomponentne pređe daje zadovoljavajuće rezultate, sa ujednačenim nijansiranjem pređe. Step en iskorišćenja boje i količina boje na vlaknima rastu tokom vremena, dok početna koncentracija boje u rastvoru opada kako proces bojenja napreduje. U linearnoj simulaciji parametara kinetike bojenja, Avramijev reakcioni model se pokazao kao efikasan, dok se Veber-Morisov model istakao kao veoma pogodna difuziona jednačina.

Ključne reči: pređa, bazna boja, bojenje, kinetički modeli.

