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KINETIC STUDY OF POLYESTER DYEING WITH DISPERSE DYE IN A BETAINE-BASED DEEP EUTECTIC SOLVENT

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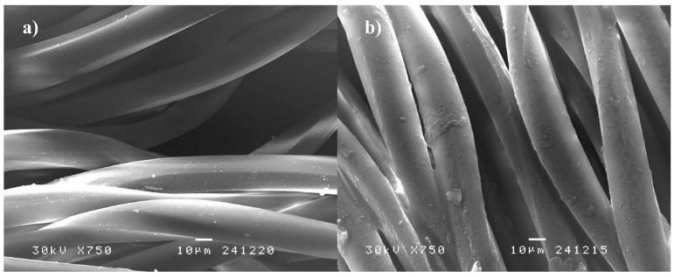
This study investigates the kinetics of polyester fabric dyeing with a disperse dye in a betaine-based deep eutectic solvent (DES). The dyeing process was monitored by measuring the decrease in dye concentration in the dye bath over time under varying initial dye concentrations (200–1000 mg/dm^3) and dyeing times (10–60 min). The adsorption behavior was analyzed using Jovanović, Harkin–Jura, and Temkin isotherm models. The results indicate that dye uptake increases with dyeing time, while the degree of exhaustion decreases with increasing initial dye concentration. Among the applied models, the Harkin–Jura model showed the best fit (R^2 = 0.99), suggesting multilayer adsorption on a heterogeneous surface. The Jovanović model also showed a high correlation (R^2 = 0.98), indicating possible monolayer contributions. SEM analysis confirmed no morphological changes, while TGA confirmed the thermal stability of the dyed fabric, without any degradation behavior occurring.



INTRODUCTION

Polyester, the most widely used synthetic fiber since its commercialization in the 1940s, represents a class of polymers characterized by ester bonds in the main chain, typically synthesized via polycondensation. Due to their low density, chemical resistance, and other advantageous properties, thermoplastic polyesters have found extensive applications in textiles, packaging and biomedical fields.[1,2] Despite these advantages, conventional industrial polyester dyeing presents several limitations. The process often requires high temperatures and pressures, prolonged dyeing times, and the use of potentially toxic auxiliaries, leading to substantial generation of wastewater.[1–3]

For hydrophobic or semi-hydrophobic fibers such as acetate, polyester and nylon, synthetic disperse dyes are commonly used. These dyes inherently exhibit low water solubility, necessitating the use of auxiliaries to enhance their dispersion.[4–6] Commonly used auxiliaries, such as

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leveling and dispersing agents, are often toxic and difficult to remove post-dyeing, posing significant challenges for wastewater treatment.[1,4]

A promising and environmentally friendly alternative involves the use of deep eutectic solvents (DESs) as non-aqueous medium. DESs have emerged as effective substitutes for conventional organic solvents.[1,5] Over recent decades, they have attracted attention in green chemistry due to their simple preparation, lower toxicity, reduced cost, and enhanced biodegradability. DESs typically exhibit melting points lower than those of their individual components and comprise hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD).[7]

The reduction in melting point is primarily attributed to hydrogen bond formation in hydrophilic DESs and van der Waals interactions in hydrophobic DESs. Choline chloride remains the most widely used HBA, although other compounds such as betaines and quaternary ammonium salts have been employed. Among these, betaine has proven to be an excellent alternative to choline chloride. As an organic salt, betaine is non-toxic, cost-effective, readily biodegradable, and derived from renewable sources as a by-product of sugar production. These properties have led to increasing research interest in betaine-based DESs.[8,9]

Although numerous studies have examined dyeing processes involving DESs, most have not focused on adsorption kinetics. The aim of this study is to investigate the adsorption kinetics of disperse dye on polyester fabric using betaine-based deep eutectic solvent. Such analysis provides valuable insights into the rate and mechanism controlling dye adsorption. The dyeing process was carried out without water, at lower temperatures and shorter durations than conventional methods, and without the use of carriers or dispersing agents. In addition, scanning electron microscopy (SEM) was used in order to observe any morphological changes in the fabric samples, while thermogravimetric analysis (TGA) was performed in order to obtain information regarding thermal stability and degradation behavior of the fabric.

RESULTS AND DISCUSSION

1. Adsorption

The influence of the initial dye concentration on the adsorption and exhaustion of disperse dye during polyester fabric dyeing over different time intervals is illustrated in Fig. 1. A clear trend is observed as the initial dye concentration increases: the degree of dye exhaustion decreased in a time-dependent manner. At lower dye concentrations, a larger drop in the percentage of exhausted dye is observed, which becomes less pronounced toward the end of the dyeing process. Shorter dyeing time (10 min) resulted in the lowest exhaustion values, whereas the longest dyeing time (60 min) yielded the highest degree of exhaustion.

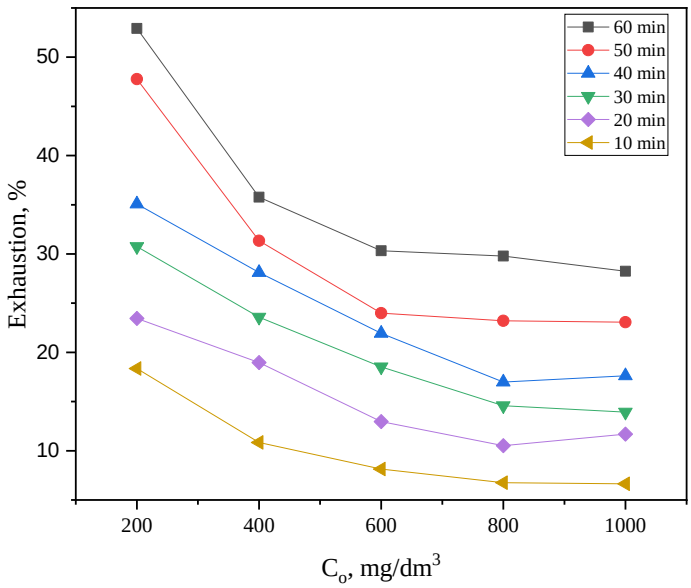

Fig. 1 – The influence of initial dye concentration on the degree of exhaustion of disperse dye during the dyeing of polyester fabric.

As seen in Fig. 2, prolonged dyeing resulted in more pronounced binding of the dye onto the surface of the fabric, *i.e.* greater amount of adsorbed dye per unit mass of adsorbent. The highest initial dye concentration and the longest dyeing time are correlated with the highest dye adsorption onto the fabric.

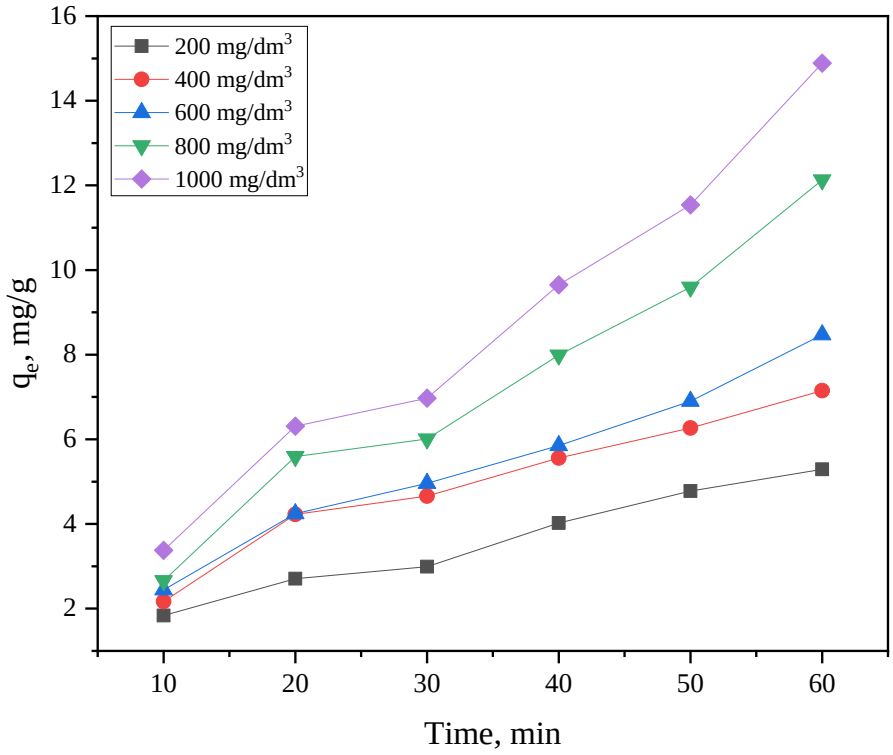

Fig. 2 – Adsorbed amount of disperse dye per unit mass of polyester fabric at different initial dye concentrations.

2. Adsorption isotherms

The adsorption data were fitted using three isotherm models. The results shown in Fig. 3 and Table 1 indicate the applicability of the Temkin model for describing the adsorption process. High coefficient of determination ($R^2 = 0.90$) indicates a good agreement between the experimental data and the model, suggesting that Temkin's model adequately describes the interactions between the adsorbate and the adsorbent in the investigated system. The Temkin model assumes that the heat of adsorption decreases linearly with increasing surface coverage, implying the presence of interactions between adsorbed molecules. The obtained parameters further support this interpretation. The equilibrium binding constant A_T (0.79 L/mg) reflects a moderate affinity of the adsorbate for the adsorbent, while the constant B_T (144.04 J/mol) refers to the heat of adsorption and provides insight into the energy changes occurring during the process.

Table 1

Linear isotherm models and parameters for the disperse dye–polyester fiber system

Model	Analytical model equations	Model parameters		R^2
Temkin	$\ln q_e = 75.9349 + 18.06629 + C_e$	A_T [J/mol] B_T [J/mg]	0.79 144.04	0.90
Jovanović	$\ln q_e = 1.49838 + 0.0017 \cdot C_e$	Q_{max} [mg/g] K_j [L/mg]	4.4744 0.0017	0.98
Harkin-Jura	$\ln q_e = 0.10649 + 0.03584 \cdot C_e$	A_H B_H	27.90 0.11	0.99

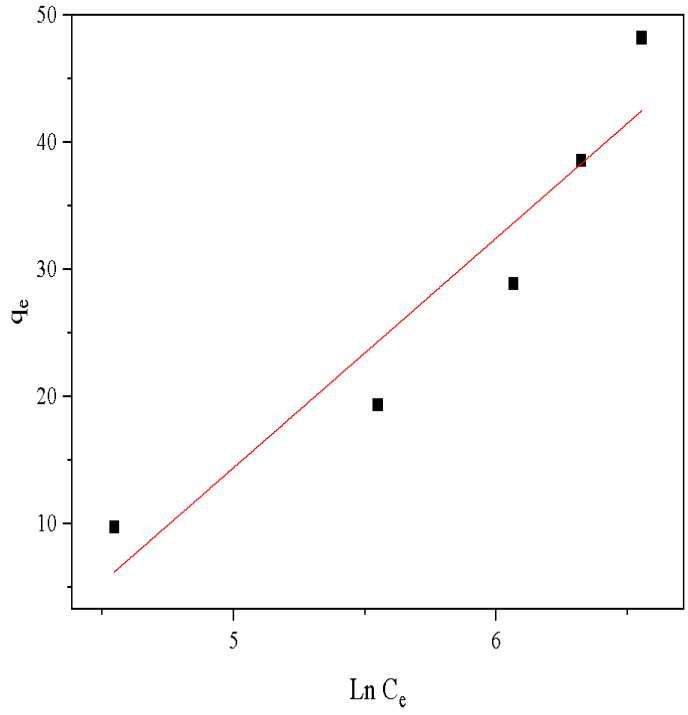

Fig. 3 – Temkin linear regression model for equilibrium dyeing of polyester fabric with disperse dye.

The results shown in Table 1 indicate a very good agreement between the experimental data and Jovanović model, as confirmed by the high coefficient of determination (R^2 = 0.98) (Fig. 4). This value suggests that the model describes the adsorption process in the analyzed system with a high degree of accuracy. The obtained model parameters provide further insight into the adsorption mechanism. The maximum adsorption capacity Q_{max} (4.4744 mg/g) indicates a relatively high capacity of the adsorbent for dye uptake. The equilibrium constant K_j (0.0017 L/mg) reflects the affinity between the adsorbate and the adsorbent. Although its relatively low value suggests weaker individual interactions between the adsorbate and the adsorbent, it is consistent with the observed significant overall adsorption capacity.

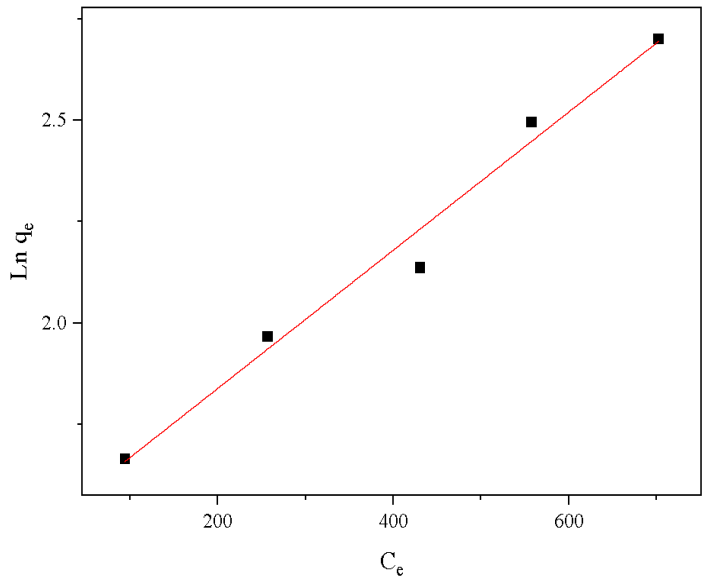

Fig. 4 – Linear regression model of Jovanović for equilibrium dyeing of polyester fabric with disperse dye.

Table 1 and Fig. 5 show the results indicating an excellent agreement between the experimental data and the Harkin-Jura model, as confirmed by very high value of its coefficient of determination (R^2 = 0.99). This value suggests that the model provides a highly accurate description of the adsorption process in the investigated system. The Harkin-Jura model assumes a heterogeneous adsorbent surface and the possibility of forming multilayer adsorption, making it particularly suitable for systems with a non-uniform distribution of energetic sites. The obtained model parameters further elucidate the nature of the adsorption process. The constant A_H (27.90) is related to the thickness of the adsorption layer and the surface energetic characteristics, where its value indicates pronounced interaction between the adsorbate and the heterogeneous surface of the adsorbent. The constant B_H (0.11) reflects the degree of surface heterogeneity and suggests the presence of energetically diverse binding sites. Based on these results, it can be concluded that adsorption occurs on a heterogeneous surface with the formation of multilayer structures.

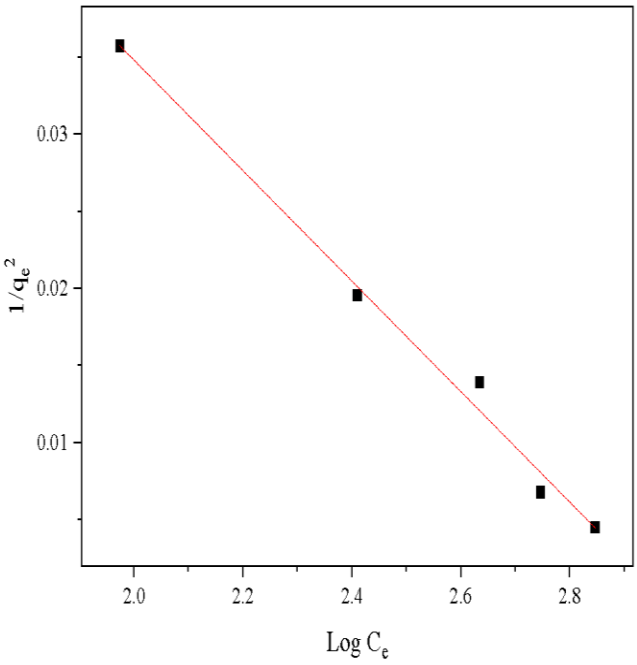

Fig. 5 – Linear regression model of Harkin-Jura for equilibrium dyeing of polyester fabric with disperse dye.

A comparative analysis of the applied isotherm models shows that all models describe the adsorption process to a certain extent, but with different levels of agreement and interpretation of the mechanism. The Temkin model (R^2 = 0.90) suggests the presence of interactions between adsorbed molecules and a non-uniform distribution of binding energies, although it exhibits a somewhat weaker fit compared to the other models. In contrast, the Jovanović model (R^2 = 0.98) demonstrates a significantly improved agreement with the experimental data, indicating that adsorption predominantly occurs via the formation of a monolayer, potentially accompanied by mechanical interactions with the adsorbent surface. The highest level of agreement is achieved by the Harkins-Jura's model (R^2 = 0.99), which indicates that the adsorption is most likely controlled by the heterogeneity of the surface and the formation of multilayer adsorption structures.

3. SEM and TGA analyses

Figure 6 presents SEM images of untreated and DES-dyed polyester fabric sample, dyed at the highest initial dye concentration and for the longest dyeing time. The untreated polyester fabric exhibited a smooth surface, while the DES-dyed samples maintained a comparable morphology. This observation indicated that the dyeing process did not induce any discernible changes to the surface structure of the polyester fabric.

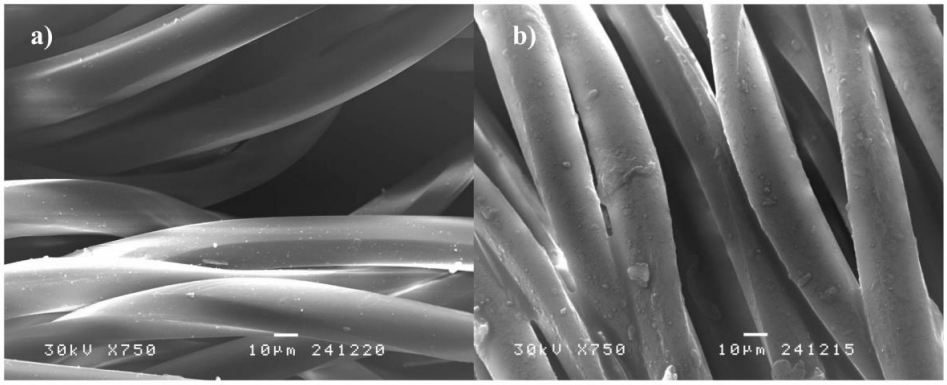

Fig. 6 – SEM images of a) untreated and b) DES-dyed polyester fabric sample.

A comparison of the thermal stability of untreated and DES-dyed sample, dyed at the highest initial dye concentration and for the longest dyeing time, is shown in Fig. 7. The results indicated that the untreated polyester exhibited lower thermal stability compared to the dyed sample. Decomposition of the polyester fibers, involving the cleavage and depolymerization of polyester molecular chains, occurred at temperatures above approximately 370 °C, with the most significant degradation observed around 400 °C, for all samples. At this temperature, the mass residues were 76.636% for the untreated polyester and 81.519% for the DES-dyed polyester. These results suggested that DES-dyeing process enhanced the thermal stability of polyester. Analysis of the mass residues at the final temperature of 600 °C further indicated that the most pronounced degradation occurred in the DES-dyed sample.

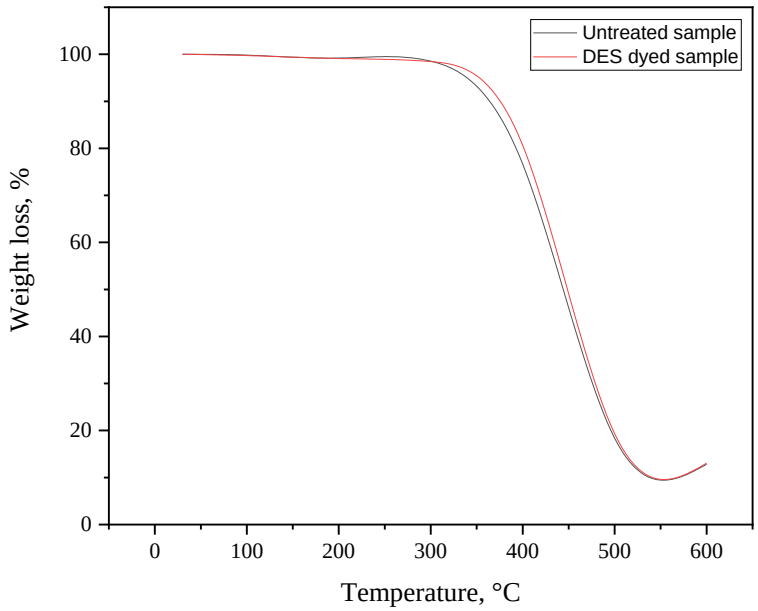

Fig. 7 – TGA of untreated and DES-dyed polyester fabric sample.

EXPERIMENTAL

1. Materials

A 100% untreated polyester fabric (mass per unit area 75 g/m^2) was obtained from Yumco (Vranje, Serbia). A nonionic detergent (Sarabid LDR, CHT GmbH, Tubingen, Germany) was used to wash the raw polyester fabric. Urea (99%, Centrohem, Stara Pazova, Serbia), glycerol (Ph Eur grade, Meilab, Belgrade, Serbia) and betaine hydrochloride (99%, Tokyo Chemical Industry,

Tokyo, Japan) were used for the preparation of the deep eutectic solvent. Sodium hydrosulfite (Centrochem, Stara Pazova, Serbia) and sodium hydroxide (Centrochem, Stara Pazova, Serbia) were used for reductive cleaning. Disperse Violet 26 dye (Hoechst,Frankfurt, Germany) was used for dyeing and its chemical structure is shown in Fig. 8.

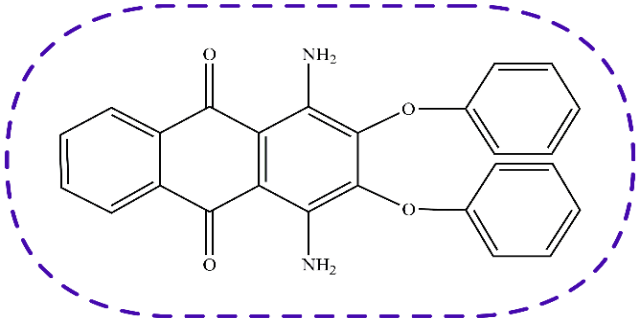

Fig. 8 – Chemical structure of Disperse Violet 26.

2. Preparation of DES

DES was prepared by mixing urea, glycerol, and betaine hydrochloride in a 1:1:1 molar ratio. The mixture was heated at 40 °C under continuous stirring (1100 rpm) until a clear and homogeneous liquid was obtained (approximately 20 min). The prepared DES was stored in a desiccator until use.

3. Washing of raw fabric

Untreated polyester fabric was washed in a 2 g/dm^3 non-ionic detergent at 60 °C for 30 minutes at ratio of 1:30. After washing, the fabric was rinsed and dried at room temperature for 24 h. The dried fabric was cut into 5 × 5 cm samples for dyeing.

4. Dyeing procedure

Dyeing was carried out in the prepared DES without the addition of water or auxiliary chemicals at pH 4. The dyeing temperature was 100 °C, with dyeing time 10, 20, 30, 40, 50 and 60 min. Initial dye concentrations were 200, 400, 600, 800 and 1000 mg/dm^3. After dyeing, the samples were subjected to reductive cleaning (2% sodium hydrosulfite and 2% sodium hydroxide) for 15 min at 60 °C, followed by cold water rinsing and drying in a dryer at 80 °C for 15 minutes.

5. Adsorption process

The degree of dye exhaustion (E%) was calculated using the equation: [10]

$$E(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t [mg/dm^3] are the initial and time-dependent dye concentrations, respectively.

The amount of absorbed dye per unit mass of adsorbent is calculated using the equation:[10]

$$q_t = \frac{C_o - C_t}{w} \times V \; and \; q_e = \frac{C_o - C_e}{w} \times V \quad (2)$$

where *qt* [mg/g] – mass of adsorbed dye per unit mass of dye at time *t*, *qe* [mg/g] – mass of adsorbed dye per unit mass at equilibrium, C_o [mg/dm^3] – initial dye concentration, C_t [mg/dm^3] – dye concentration in the solution at the time of dyeing *t*, C_e [mg/dm^3] – the equilibrium concentration of the dye in the solution, *w* [g] –mass of polyester fabric sample, *V* [dm^3] – volume of solution.

6. Adsorption isotherms (models)

The Temkin isotherm can be expressed by the following equation:[11,12]

$$Q_e = B_T \cdot lnA_T + B_T \cdot lnC_e \quad (3)$$

where Q_e [mg/g] – is amount of adsorbed dye in equilibrium, B_T – adsorption heat constant, A_T - Temkin's binding equilibrium constant, *T* – is the absolute temperature.

The linear form of the Jovanović isotherm is represented by the following equation:[13]

$$lnQ_e = lnQ_{max} - K_J \cdot C_e \quad (4)$$

where Q_e – is amount of adsorbate in the adsorbent at equilibrium [mg/g], Q_{max} – maximum absorption of adsorbate, K_J – Jovanović's constant; C_e [mg/dm^3] – equilibrium concentration of adsorbate in solution.

The mathematical representation of the Harkin-Jura isotherm is given by the following equation:[13]

$$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_H} - \left(\frac{1}{A}\right) log C_e \quad (5)$$

where Q_e – is amount of adsorbate in the adsorbent at equilibrium [mg/g], C_e [mg/dm^3] – equilibrium concentration of adsorbate in solution, A_{HJ} and B_{HJ} are constants of the Harkin-Jura isotherm related to the porosity and heterogeneity of the adsorbent surface.

7. Scanning electron microscopy (SEM)

The surface morphology of untreated and DES-dyed sample was characterized using scanning electron microscopy (SEM). Prior to observation, the samples were sputter-coated with a gold–palladium alloy (85%/15%) under vacuum employing a Fine Coat JEOL JFC-1100 Ion Sputter (JEOL Ltd., Tokyo, Japan). Subsequent imaging was performed with a JEOL Scanning Electron Microscope JSM-5300 (JEOL Ltd., Tokyo, Japan) at a magnification of 750×, an accelerating voltage of 20 kV, and a vacuum level of 1.33 × 10–$^{-5}$ Pa.

8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of polyester fabric samples was performed using a Perkin-Elmer TGA 4000 thermogravimetric analyzer (Norwalk, CT, USA). Approximately 10 mg of each sample was placed in a ceramic crucible, pre-annealed to 900 °C at a heating rate of 40 °C/min. A separate crucible was used for each measurement to ensure consistency. The analyses were conducted under an inert nitrogen atmosphere with a flow rate of 20 mL/min over a temperature range of 30–600 °C, applying a heating rate of 10 °C/min. Initially, the samples were held at 30 °C for 5 min, then heated from 30 to 300 °C, followed by an isothermal hold of 10 min. Subsequently, the temperature was increased to 400 °C under the same conditions and maintained isothermally for an additional 10 min. Finally, the samples were heated to 600 °C before being gradually cooled to room temperature.

CONCLUSIONS

Based on the experimental results and isotherm analysis, the adsorption of disperse dye on polyester fabric is a complex process influenced by both dyeing time and initial dye concentration. The high coefficients of determination, particularly for the Harkin–Jura model (R^2 = 0.99), indicate that adsorption is primarily governed by surface heterogeneity and multilayer formation, while the Jovanović and Temkin models point to monolayer adsorption with additional interactions and energetic non-uniformity. Increasing dyeing time significantly enhances dye uptake, confirming a time-dependent establishment of equilibrium and stronger adsorbate–adsorbent interactions. In contrast, higher initial dye concentrations reduce the degree of exhaustion, likely due to saturation of active sites, although longer dyeing times improve overall efficiency. SEM analysis confirms that dyeing in a DES medium preserves the surface morphology of polyester fibers, while TGA results indicate that the dyed fabric was thermally stable.

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