Modeling of polyester fabric dyeing after proteolytic enzyme pre-treatment

D. M. Djordjevic[1*], R. P. Krstic[1], M. G. Kodric[1], S. P. Djordjevic[2]

[1]*University of Nis, Faculty of Technology in Leskovac, Serbia*
[2]*Higher Technlogical and Artistic Professional School Leskovac, Serbia*

This paper investigates modeling of dyed fabrics made of 100% polyester fibers with disperse dye, after pre-treatment with the proteolytic enzyme papain. The aim of the enzyme pre-treatment is to modify the surface of fibers in order to influence the sorption properties and the possibility of dyeing polyester fabric without carriers in atmospheric conditions. Based on the examination results of the polyester fabric, it was determined that the water absorption, and the wetting rates improve to a great extent after treatment with papain enzyme. Langmuir isotherm, among the equilibrium models, proved to be the best for the description of the process of enzyme-modified polyester dyeing with disperse dye, adsorption occurred at a limited number of definitely localized spots on the fiber, and the adsorbed layer was monomolecular.

Keywords: polyester, papain enzyme, dyeing, disperse dye, modeling, isotherms.

INTRODUCTION

Polyester (PES) fibers (usually polyethylene terephthalate) belong to a group of synthetic fibers with active spots where dye molecules can be located (attached, integrated). PES fibers have an expressed hydrophobic character and compact structure, which makes the dyeing process more difficult, leading it towards extreme conditions. The alternative is to modify these fibers or to modify the usual dyeing process, that is to increase the rate of dye diffusion into fibers [1, 2].

For simpler dyeing of PES fibers, various pre-preparation methods are used. Thus, hydrolytic modification of the surface of polyester materials (treatment with different alkalis) is mentioned in order to obtain a better appearance, touch and simpler dyeing.

Furthermore, enzymes are increasingly being used in this field, as ecological and nature-friendly products [3]. Enzymes used to improve the hydrophilicity of polyester fiber include lipases, polyesterases, cutinases and papain [4, 5]. Among them, papain has a wide specificity by showing the activity of amidases and esterases [4, 5].

Papain, also known as papaya proteinase I, is the cysteine protease enzyme (EC 3.4.22.2) found in the papaya species, *Carica papaya* and *Vasconcellea cundinamarcensis*. It was discovered that the enzyme is localized in the papaya bark and that it is collected from cut unripe papaya fruit as raw latex. Papain is primarily used as amidase in textile processing, and not as esterase. There are few papers analyzing the possibility of papain modifying polyester fabric in order to improve its hydrophilicity by hydrolysis of ester bonds [6, 7].

The purpose of the paper is to clarify the adsorption ability of a disperse dye for PES fibers pre-modified with the usual additives according to the standard dyeing recipe, without the use of carriers. The aim is to simplify the dyeing of polyester fibers with the help of nature-friendly enzymes, to eliminate additives (carrier) and to dye at lower temperatures and atmospheric conditions. The modeling of polyester dyeing with selected isothermal models will explain the expediency of pre-preparation of polyester by enzyme papain.

EXPERIMENTAL

For pre-treatment and later dyeing, polyester fabric (100% polyethylene terephthalate) kindly offered by the textile company Yumco (Vranje, Serbia) was used, with the following characteristics: warp and weft fineness per 17×2 tex, warp and weft density of 35 and 29 threads/cm and surface mass of 235 g/m^2.

Before dyeing sample preparation was performed, i.e. pre-treatment of polyester with the commercial enzyme. The used enzyme commercial papain (Sigma-Aldrich, USA) had the following characteristics: enzyme origin–papaya latex, *Carica Papaya*, crude powder, 1.5-10 units/mg, mol. wt. 21 kDa.

Besides the enzyme, the polyester treatment bath consisted of a buffered solution and an activator (ethylenediamine-tetra acetic acid). Tris buffer solution (pH 8), a mixture of tris(hydroxy- methyl) aminomethane (Centrohem, Serbia) and hydro-

chloric acid (Centrohem, Serbia) were used in the following ratio: 100 cm^3 of 0.1 M tris (hydroxymethyl) aminomethane + 58.4 cm^3 of 0.1 M hydrochloric acid, while ethylenediamine-tetra acetic acid (Centrohem, Serbia) was used at a concentration of 5% (owf). It is a relatively inexpensive strategy for immobilizing enzymes on polyester fabric by supporting functionalization with ethylenediamine.

Samples of polyester fabric were treated in a bath with active ingredients, that is the ratio of liquid and textile was 40:1, the bath temperature was 40°C, and the processing time was 120 min. The concentration of the enzyme papain for polyester processing was 65% (owb).

All polyester treatments with papain enzyme were carried out in a Linitest laboratory device. After processing, enzyme inactivation was performed, PES fabric samples were immersed in hot water (90°C) and held for 15 minutes.

The following test methods were used for checking the effects of enzymatic hydrolysis: change in mass (based on the differences in mass before and after processing); water absorption power-capillarity (ISO 18695:2007: a test specimen (polyester fabric) is immersed vertically, partly in water and after a certain time (1 min) measure the height of the part of the tube above the surface of the water which is wetted by water penetration); water absorption power-absorption (ISO 18696:2006: the mass of the test specimen is measured before immersion in water, then the tube is immersed in water and after 1 min the mass of the wet tube is measured. The amount of water remaining on the test tube after squeezing is calculated as a percentage); scanning electron microscopy (SEM) on a Jeol JCM 5300 type apparatus; wetting time (AATCC TM27-2013: a test specimen is padded in a water solution of a rewetting agent and dried. A drop of water is then carefully deposited on the taut surface of the specimen and the time required for a specular reflection of the water is recorded as the rewetting time), mechanical characteristics (ISO 5081).
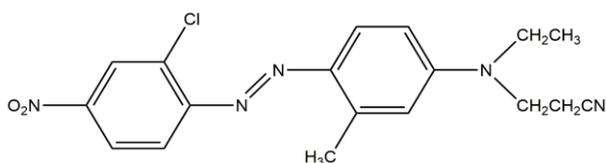

Figure 1. The structure of the disperse dye C.I. Disperse Red 65 (using the ChemBioDraw Ultra 14.0 software).

The applied dye belongs to the class of mono azo dyes, and it has a small molecule suitable for a polyester. The dyeing process (the exhaustion method) was realized in a 98°C bath, without added carriers, the bath pH was 5. First, a dispersant is added to the bath, then the dye and finally the PES textile sample. Dyeing-adsorption begins and ends at 98°C at the predicted time.

The dyeing-adsorption test itself was performed in such a way that the mass of PES fabric was constant (1 g), the dyeing bath had a constant volume (100 cm^3), the concentration of disperse dye ranged from 10 to 100 mg/dm^3, while the processing time, with continuous stirring on a bath shaker (135 rpm), ranged from 5 to 60 minutes.

UV-VIS spectrophotometry and Cary 100 Conc UV-VIS apparatus, Varian (maximum absorption at 490 nm) were used to determine the dye concentration in the solution.

The amount of adsorbed disperse dye per unit mass of modified polyester fabric [8] (adsorption capacity at time t or at equilibrium time) was calculated using the following formula:

$$q_{t,e} = \frac{(C_o - C_{t,e}) \cdot V}{w} \qquad (1)$$

where: C_o (g/dm^3) is the initial dye concentration; $C_{t,e}$ (g/dm^3) is the dye concentration at time t or at equilibrium time; w (kg) fabric mass and V (dm^3) is the solution volume from which adsorption was performed.

Langmuir adsorption model [9] is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \left[\frac{1}{b \cdot Q_o}\right] \cdot \frac{1}{C_e} \qquad (2)$$

where: Q_0 (mg/g) is the adsorption capacity, b (dm^3/mg) is the adsorption energy.

The isothermal equation *Harkins-Jura* [9] is expressed as:

$$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \cdot \log(C_e) \qquad (3)$$

where B_{HJ} and A_{HJ} are *Harkins-Jura* model constants.

The *Temkin* isotherm [9] is represented by the following equation:

$$q_e = B_T \cdot \ln(K_T) + B_T \cdot \ln(C_e) \qquad (4)$$

where: K_T (dm^3/mg) and B_T are *Temkin* constants, the first of which is the adsorbate-adsorbent interaction, and the other one is related to the heat of adsorption b_T (J/mol).

RESULTS AND DISCUSSION

In the enzyme processing mode in a wet environment, the substrate, i.e. polyester fabric, undergoes appropriate changes, primarily on its surface. Considering the high degree of crystallinity, compactness and strength of these fibers, it is very unlikely that these treatments would affect the internal structure of the fibers.

The confirmation of events on the polyester surface after enzyme treatment can be seen through a micrograph of fibers from the PES fabric recorded with a magnification of several thousand times. Figure 2 shows surface micrographs of untreated and papain enzyme-treated PES fibers. The untreated sample has a cleaner morphology, while the micrograph of the processed sample shows changes on the surface of the fibers in the form of surface stratification, peeling, deposits, which are not present on the untreated sample.
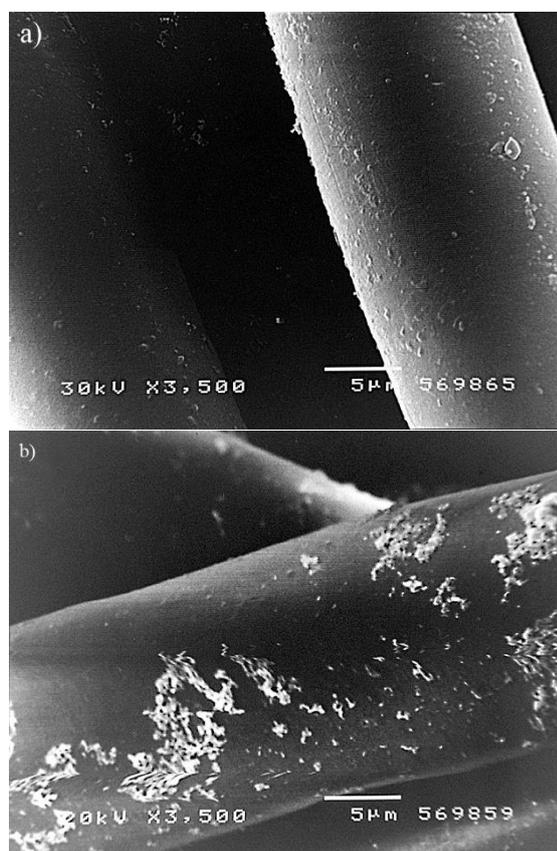

Figure 2. Micrographs of PES fiber samples in the enzyme treatment mode. a) untreated sample; b) sample treated with papain enzyme

A similar behavior was observed in the paper of Kardas *et al.* [10], where the tests performed by SEM showed differences in the appearance of the fiber surface before and after modification of poly(ethylene terephthalate) fibers from the point of view of changes in their surface structure in terms of its micro-topography. The tests performed by SEM showed differences in the appearance of the fiber surface before and after modification (smoothing or increased roughness), depending on the type of enzyme preparation, lipase or esterase used.

The first thing that can be noticed after the modification of polyester is the loss in mass due to the hydrolysis of the fiber surface (up to 2.1%) caused by the action of papain enzymes, Table 1.

Table 1. Comparative results of the examined parameters of PES fabric in the papain enzyme treatment mode

Examined parameter	Values of results	
	Untreated sample	Treated sample
Loss of mass, %	0	2.1
Capillarity, warp direction, mm	0	14
Absorption, %	127	141
Wetting time, s	290	13
Breaking strength, warp direction, daN	149	140
Breaking elongation, warp direction, %	40	43

The following fiber properties on which enzymatic hydrolysis can have a significant effect are those that improve wetting: water penetration, water adsorption or wetting, Table 1. Water penetration in the direction of the warp threads is far higher (14 mm) in comparison to the untreated fabric (0 mm). The absorption of water by PES fabric confirms that the treated samples give better results, about twenty percent higher than the untreated sample.

The papain enzyme treatment improves the surface wetting ability of hydrophobic PES fibers. Such an improved wettability was attributed to the increasing number of polar groups, surface deformation, increased surface roughness of the material, etc. According to Table 1, the untreated sample of PES fabric has by far the slowest wetting of 290 s; in processed samples the average time of wetting is 13 s.

Mechanical properties, breaking strength and elongation, show a change, strength decreases and elongation increases slightly, which is a direct consequence of surface modification of fibers by the papain enzyme.

The influence of time of contact between adsorbate (dye) and adsorbent (PES fiber modified with papain enzyme) on the change of dye concentration (dashed line of curves) and adsorption capacity (full line of curves) is shown in the diagram in Figure 3. There is continuity in the changes of adsorption capacity (q_t) over time, i.e. longer dyeing time causes a higher amount of adsorbed dye per unit

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mass of adsorbent, reaching a maximum at 60 min. During dyeing, the concentration of the disperse dye (C_t) decreases evenly, initially faster and then slower, reaching a minimum at the equilibrium time.
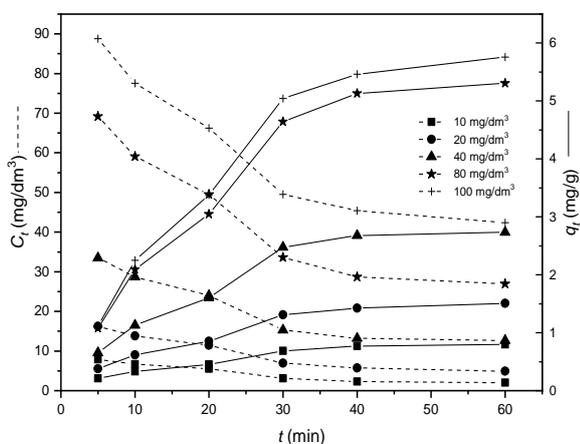

Figure 3. The influence of adsorption time on the change in the initial dye concentration and adsorption capacity

Linear regression was used to determine the best fitted isotherm, while the least squares method was used for finding the parameters.

The diagram in Figure 4 represents a linear interpretation of the *Langmuir* adsorption isotherm. There is a slight scattering of the measured values around the fitted curve, which indicates the adequacy of the *Langmuir* isotherm to describe the adsorption equilibrium of the tested system.

According to the results of this empirical model for a specific system, it is assumed that adsorption occurred only at a limited number of definitively localized sites on the fiber, and the adsorbed layer consisted of only one molecule of dye (monolayer adsorption).
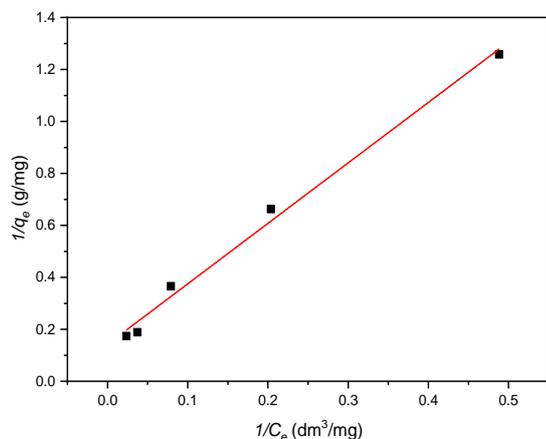

Figure 4. *Langmuir* adsorption isotherm for the system of disperse dye–PES.

Similar conclusions were made by other researchers examining the dyeing of polyester fiber, where the application of the *Langmuir* isotherm proved to be an excellent model for explaining the dyeing-sorption of the disperse dye [11].

The diagram in Figure 5 illustrates the *Harkins-Jura* model. It is noted that the fitting curve passes far from the experimental points, which leads to the conclusion that this isotherm cannot be accepted for the description of dyeing modified polyester with disperse dye. In the specific case, according to the presented *Harkins-Jura* isotherm, there is no multilayer adsorption, polyester fibers do not represent a heteroporous material and there is no heterogeneous pore distribution on the adsorbent-fiber surface.

This confirms the applicability of the *Langmuir* isotherm, which implies monolayer adsorption, and therefore there is no multilayer adsorption that dominates in the *Harkins-Jura* model.
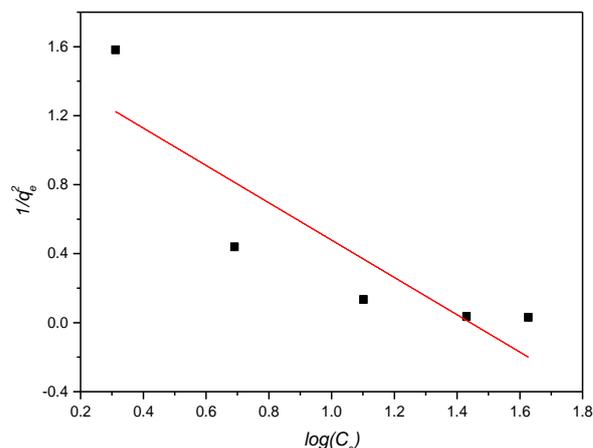

Figure 5. *Harkins-Jura* adsorption isotherm for the system of disperse dye–PES.

The diagram in Figure 6 represents the *Temkin* isotherm of adsorption, the linear regression curve fits relatively well the experimental points. According to this model, the heat of adsorption of all molecules of the disperse dye on the surface of PES fibers decreases linearly with increasing degree of coverage and adsorption is characterized by a uniform distribution of binding energy of molecules on the surface of the adsorbent.

Table 2 shows the analytical expressions of the used *Langmuir, Harkins-Jura,* and *Temkin* models with numerous values of characteristic constants, i.e. isotherm parameters. Also, the value of the statistical parameter is given, the coefficient of determination R^2, on the basis of which the validity is evaluated, i.e. the applicability of the models used.
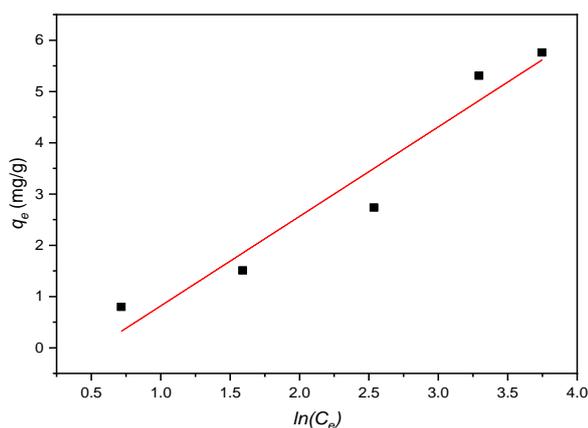
Figure 6. *Temkin* adsorption isotherm for the system of disperse dye–PES

According to the results, the leading *Langmuir* isotherm with the highest value of R^2 (0.992), is followed by the *Temkin* and *Harkins-Jura* models (0.940 and 0.782, respectively). The *Langmuir* parameter, adsorption energy, b, related to the apparent energy (surface energy) of sorption, has a relative value of 0.06 dm^3/mg, i.e. low surface energy in the system, which indicates a more probable connection between disperse dyes and PES fibers.

The characteristics of the *Langmuir* isotherm can also be expressed by a dimensionless constant, the equilibrium parameter R_L. From the values for b

(Table 2) and the highest initial concentration of disperse dye (100 mg/dm^3), the parameter R_L was calculated to be between 0 and 1, i.e. it is 0.14, on the basis of which it can be concluded that it is an isotherm suitable for describing a specific dyeing process.

In the process of determining the dye retention capacity and affinity of the dye adsorbent, the *Langmuir* monolayer model adequately covers the experimental data and may be absolutely acceptable for adsorption of the applied disperse dye on enzyme-treated PES fabric. On the other hand, the *Harkins-Jura* model is not acceptable for a specific system due to the much lower value of R^2. According to the results of the *Temkin* model, it seems that adsorption is characterized by a uniform distribution of binding energies, and the heat of adsorption of all molecules in the layer decreases linearly with coverage due to the adsorbate-adsorbate interaction. The value of heat of adsorption (b_T) for the observed system is 1.77 kJ/mol, which indicates a weak interaction between the dye and the fibers, and the process of interaction was manifested by physical adsorption (physi-sorption). It is a fact that the typical range of binding energy for the ion exchange mechanism (chemi-sorption) is between 8 and 16 kJ/mol [12].

Table 2. Analytical expressions and parameters of the used models for the description of adsorption of the disperse dye for the modified PES fiber.

Model	Analytical expression of the model	Model parameters		R^2
Langmuir	$\dfrac{1}{q_e} = 0.14 + 2.33 \cdot \dfrac{1}{C_e}$	Q_0 (mg/g)	7.03	0.992
		b (dm^3/mg)	0.06	
		R_L	0.14	
Harkins-Jura	$\dfrac{1}{q_e^2} = 1.56 + 1.08 \cdot \log(C_e)$	B_{HJ}	1.44	0.782
		A_{HJ}	0.92	
Temkin	$q_e = -0.93 + 1.75 \cdot \ln(C_e)$	K_T (dm^3/mg)	0.59	0.940
		B_T	1.75	
		b_T (kJ/mol)	1.77	

CONCLUSIONS

Modification of the surface of polyester fibers by the papain enzyme has led to an improvement in the hydrophilicity of the highly hydrophobic and crystalline fiber. In addition to the influence on the sorption characteristics, there is also positive influence on the ability to dye polyester material. Micrograph of the processed PES sample shows changes on the surface of the fibers in the form of

surface stratification, which are not present on the untreated sample.

Modeling of disperse dye adsorption, i.e. dyeing of PES fabric was tested under different conditions without carriers in the dyeing bath. It was found that adsorption depends on the time of contact, the initial concentration of the dye, as well as on the fact that it is a monolayer adsorption on a homogeneous surface. The value of heat of adsorption indicates a weak interaction between the dye and the fibers, and

the process of interaction was manifested by physical adsorption (physi-sorption).

The results of this study suggest the possibility of different approaches in the dyeing process with polyester-disperse dye, all in favor of greater efficiency and cost-effectiveness, as well as environmental protection.

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