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Modelling of Dyeing of Modified Polyester at Lower Temperature by Ultrasound

Modeliranje barvanja modificiranega poliestra z ultrazvokom pri nižji temperaturi

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Abstract

This article discusses the process of polyester dyeing through the modelling process, i.e. the ability of adsorption of dyes for chemically modified polyester fibres of knitted fabrics in aqueous environment in the presence of ultrasound waves, at lower temperature and without carrier. Previous processing before dyeing, i.e. the alkali-alcohol hydrolysis with ultrasound, changes the surface morphology, decreases the mass and thickness of knitted fabric, improves the sorption features, capillarity and absorption of water, and wetting. The process of dyeing a modified polyester knitted fabric in the presence of ultrasound at lower temperature gives much better results than dyeing without ultrasound and it is very close to the standard process of dyeing a raw sample at higher temperature. By modelling the system, it has been found that the *Freundlich* non-linear and linear isotherm are the most efficient in simulating the isothermal adsorption of disperse dye on polyester knitted fabric, whereas *Langmuir* and *Nernst* give weaker results.
Keywords: dyeing, polyester, disperse dye, ultrasound, modelling, Langmuir isotherm, Freundlich isotherm, Nernst isotherm.

Izvleček

Članek obravnava modeliranje procesa barvanja poliestra, tj. sposobnost adsorpcije barvil v pletivih iz kemično modificiranih poliestrskih vlaken v vodnem mediju v prisotnosti ultrazvoka, pri nižji temperaturi in brez barvalnega pospešila (carrierja). Predobdelava pred barvanjem, tj. alkalno-alkoholna hidroliza z ultrazvokom, je spremenila morfologijo površine vlaken, zmanjšala maso in debelino pletiva, izboljšala sorpcijske lastnosti, kapilarnost in absorpcijo vode ter omočljivost. Barvanje modificiranega poliestrskega pletiva v prisotnosti ultrazvoka pri nižji temperaturi je dalo veliko boljše rezultate kot barvanje brez ultrazvoka in je postopek zelo podoben standardnemu postopku barvanja surovega vzorca pri višji temperaturi. Z modeliranjem sistema je bilo ugotovljeno, da sta Freundlichovi nelinearna in linearna izoterma najučinkovitejši pri simuliranju izotermne adsorpcije disperznega barvila na poliestrskem pletivu, medtem ko izotermi Langmuirja in Nernstona dajeta slabše rezultate.
Ključne besede: barvanje, poliester, disperzno barvilo, ultrazvok, modeliranje, Langmuirjeva izoterma, Freundlichova izoterma, Nernstova izoterma

1 Introduction

A polyester (PES) fibre has a compact structure made by multiple stretching and thermic processing; extremely hydrophobic character; high electronegative potential and small number of functional groups capable of reaction with ions and dye molecules. All these features limit the choice of dyes and make the process of dyeing this fibre to be even harder. [1].

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PES fibres can be dyed in all stages of production: as a fibre, in band and filament shape, yarn, fabric or knitted fabrics. The following dyeing methods should be mentioned: batch process (exhaustion), semi-continual and continual process. Batch method of dyeing can be done at boiling water temperature in the presence of carriers, today known as intensifiers; and at higher temperature (130 °C) with increased pressure or the so-called HT (high temperature) method which is mostly in use [2, 3].

Ultrasound with the frequency range of 20–100 kHz is mostly used for increasing the rate of chemical reactions and improving the physical processes, such as cleaning, emulsification, degassing and others. The uses of ultrasound enables quicker processes and reaching the same or better results via already existing techniques in less extreme conditions; for example, lower temperature and lower chemical concentrations. For these reasons, the processes of textile dyeing with ultrasound can be very interesting. The improvements which have been noticed in dyeing the textile with ultrasound are mostly assigned to the phenomenon of empty cavities, with mechanical effects which appear: dispersion, degassing and diffusion [4, 5]. The effects of ultrasound on enhanced mass transfer, shortened reaction cycles, improved reaction yield, increased surface area between the reactants and synthesis and deposition of nanoparticles have been widely reported [6–8]. All these benefits have arisen from acoustic cavitation in liquid media regarded as the formation, growth and collapse of bubbles. Extreme heat has been released through bubbles collapse creating hot spots [9]. The first major steps in introducing a sonochemical method as a technique for surface modification of various substrates were made in 1996 [10] with the use of ultrasound for enhanced surface modification of polyethylene by hydrogen peroxide and persulfate salts as oxidizing agents under mild condition. Sonochemistry has been applied for surface modification causing weight loss, increased roughness and decreased contact angle [10].

On the other hand, nowadays hydrolytic modification of the surface of polyester materials is more and more used for obtaining different, better appearance and touch. It has been shown that polyethylene terephthalate has good conditions for modification by processing with alkalis, such as sodium hydroxide (NaOH). The reaction with NaOH is saponification of polyethylene terephthalate, and the products of reactions are sodium-terephthalate and ethylene-glycol. It is an irreversible reaction, which shows that in case of greater mass loss than wanted, it is not possible to fix the material. It is often called peeling of polyester because by measuring the diffraction of X-rays, it has been proved that the alkali hydrolysis appears only on the surface of fibres, whereas the inner morphological structure of fibres stays unchanged [11, 12].

This work tends to contribute to the explanations of polyester dyeing through the modelling process, i.e. the abilities of adsorption of dyes for chemically modified PES fibres in aqueous environment in the presence of ultrasound waves, at lower temperature without carrier. The goal is to successfully perform dyeing of a hydrolysed hydrophobic fibre in less extreme conditions, i.e. the goals are related to achieving better potential for dye adsorption of chemically modified PES fibres in aqueous environment in the presence of ultrasound waves, at lower temperature without carrier. Also, if the exhaustion of dye is large enough, there will be less dyed wastewater and less harm to the environment.

2 Experiment

In the experimental part of this research, a raw, undyed 100% polyester (polyethylene terephthalate) knitted fabric has been used which is common in practice with the following characteristics: interlacement interlock, fineness of yarn 9.4 tex, course count 15 cm^{-1}, wale count 16 cm^{-1} and surface mass 140 g/m^2.

Before dying, a knitted fabric had been processed by the alcohol solution (ethanol) of sodium hydroxide 80 g/l for 30 minutes, Liquor ratio has been 1:130 while the temperature of the process has been 20 °C at the beginning and 50 °C at the end of the treatment (the temperature rises spontaneously due to the action of ultrasound). During this process, the solution with the substrate (knitted fabric) has been exposed the whole time to ultrasound waves of 200 kHz and power of 50 W (apparatus Elac Ultrasonic Laboratory Reactor URS 1000).

Dyeing of this modified PES knitted fabric has been performed by disperse dye C.I. Disperse Red 60, molecular formula $C_{20}H_{13}NO_4$ and molar mass of 331.32 g/mol, at 80 °C, without carriers, in ultrasound reactor Elac Ultrasonic Laboratory Reactor URS 1000. The frequency of the applied ultrasound oscillations has been 200 kHz whereas the power has been 50 W. The structural formula of the applied dye is shown in Figure 1.

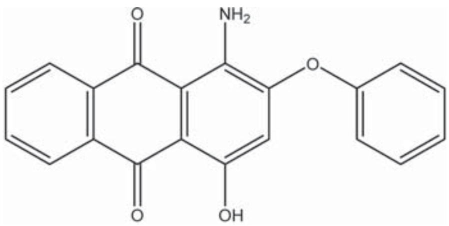

Figure 1: Structure of the applied disperse dye C.I. Disperse Red 60

Precisely, the test of dyeing-adsorption has been performed in the way that 1.5 g of the mass sample of the PES knitted fabric has been dyed in the solution of constant volume of 150 cm^3; dye concentration has been 50, 100, 200 and 400 mg/dm^3. In these cases of dyeing, distilled water has been used. The time of dyeing with constant effect of ultrasound has been 12, 24, 36, 48 and 60 min. Equilibrium time has been 60 min because it has been shown that with longer dyeing, there are no significant changes in the level of dye exhaustion. Aqueous solution of the dye has had the dispersing agent (CHT Dispersing agent SMS), 1.5 g/l and formic acid (pH = 4.5), whereas the temperature of the dye has been 80 °C.
For checking the effects of alkali hydrolysis, the following methods have been used: the change of mass (based on the mass differences before and after the process); the power of water absorption –capillarity, ISO 811:1981; the power of water absorption, ISO 18696:2006; the thickness of fabric, ISO 5084:1977; the time of wetting, AATCC TM27-2013.
For determining the concentration of dye in the solution, the UV-VIS spectrophotometry and apparatus Cary 100 Conc UV-VIS, Varian (absorption maximum on 495 nm) have been used.
The dye exhaustion [13] has been calculated via equation:

$$\textit{Dye exhaustion} = \frac{C_0 - C_t}{C_0} \cdot 100\ (\%) \qquad (1),$$

where, C_0 is an initial dye concentration and C_t [mg/dm^3] is a dye concentration in time t. The amount of the adsorbed dye in equilibrium [13] obtained via equation:

$$q_e = \frac{C_0 - C_e}{w} \cdot V \qquad (2),$$

where, q_e [mg/g] is a mass of the adsorbed dye per mass unit of the knitted fabric in equilibrium, C_0 [mg/dm^3] is an initial dye concentration, C_e [mg/dm^3] is an equilibrium dye concentration in the solution, w [g] is a mass of the knitted fabric and V [dm^3] is a volume of the solution for dyeing.
Langmuir isotherm [13] has been shown via the following equations:

$$q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \text{ and } \frac{C_e}{q_e} = \frac{1}{Q_{max} \cdot b} + \frac{1}{Q_{max}} C_e \qquad (3),$$

where, q_e [mg/g] is an adsorbed amount of the adsorbate (dye) per mass unit of the adsorbent (knitted fabric), Q_{max} [mg/g] is a maximum amount of the adsorbate which can bind to the adsorbent and b [dm^3/mg] is a ratio of the constant of adsorpion rate and constant of desorption rate of adsorbate.
Freundlich model is presented by following equations [13]:

$$q_e = K_F \cdot C_e^{1/n} \text{ and } lnq_e = lnK_F + \frac{1}{n} \ln C_e \qquad (4),$$

where, K_F [(mg/g)·(dm^3/mg)$^{(1/n)}$] and n are the constants characteristic for the observed system: adsorbent, adsorbate and solvent.
Nernst adsorption isotherm [13] is defined like:

$$q_e = K \cdot C_e \qquad (5),$$

where, K [dm^3/g] is a coefficient of the division of dye between fibres and dyebath or coefficient of the equilibrium distribution.

3 Results and discussion

3.1 Alkali-alcoholic hydrolysis of PES knitted fabric

As all other esters, polyester is also faintly stable to alkalis; the process in a slightly alkali solution increases the porosity of fibres, and with the increase of temperature and concentration of alkali dyebath, the level of its hydrolysis increases. In harsh conditions, the complete degradation of fibres appears. By increasing the porosity of surface fibres, the sorption and diffusion of dye into the fibre speeds up which for example reduces the dyeing process [14].

The first thing noticed after modification of polyester is mass loss due to the hydrolysis of the surface of PES fibres caused by the reaction of alkali. The obtained results confirm that the alkali-alcohol process of PES knitted fabric causes certain percentage of mass loss, Table 1. The hydrolysis in the presence of ultrasound waves leads to the greatest mass loss of PES fibres (10.7%) than the same process without ultrasound (6.3%), as expected.

Similar results in the change of mass are noticed for example after previous processing of PES textile by microwave radiation [15]. Namely, the samples of PES fabric treated with 1% solution of caustic soda in the presence of microwave radiation have shown the mass loss of approximately 5.2%. It is established that with increasing of concentration of the alkali, the velocity of hydrolysis increases. Generally, when polyester fabric is treated in the solution of NaOH with conventional heating, the mass of fabric does not decrease fast. However, with microwave radiation, certain fabric shows greater mass loss in shorter time, which indicates that microwave radiation increases the velocity of hydrolysis on the surface of fibres [15].

The feature 'thickness" of a textile product can be in direct relation to the mass changes of a knitted fabric, i.e. an insignificant change in the thickness of a knitted fabric due to alkali hydrolysis is noticed, i.e. the processed samples have lower values of this tested parameter, approximately 1–2% in comparison to the unprocessed sample. Essentially, the mass loss of a knitted fabric leads to its smaller thickness, which happens here, but it should be noted that this tested parameter is affected by deformation or contraction of fibres, i.e. the phenomena like swelling and shortening of fibres, which is manifested as a shrinking of the fibers in the end.

Water penetration along horizontal and vertical column is pretty much equal, regarding that the density is almost equal in all directions so the influence of density and capillaries is excluded. Namely, it is known that capillarity (water penetration) is better in the direction with greater density of yarn which creates the system of capillaries of smaller diameters, which is more suitable for spontaneous water flow. This explanation is not important for the actual case regarding a knitted product whose basic constructive unit is loom and not interlacement from crossed threads (yarns) under right angle as in a woven product. It should be pointed out that the unprocessed sample of knitted fabric almost does not show water penetration through its structure, i.e. the capillarity in both directions is 2.5 mm, whereas in the processed samples, it is from 25/20 mm to 32/30 mm (vertical/horizontal) for the hydrolysis with and without ultrasound, respectively, Table 1.

Also, similar use of ultrasound waves, the sono-alkali hydrolysis of PES fabric, leads to the mass loss, decreasing the fibre diameter because of tearing the ester chains of polyester bonds inside the structure of fibres and creating micro pores on the surface of the fabric. On the other hand, this alkali hydrolysis with ultrasound increases the number of polar functional hydroxyl and carboxyl groups on the surface of fibres. The effect of ultrasound energy in the process is recognized by decreasing the thickness of border layer between the fabric surface and alkali solution by removing the mass of gas trapped in inter-fibres and intra-yarn through the effect of degassing [16].

Water absorption of PES knitted fabric confirms that the processed samples which go to the direction of increasing this tested parameter have better results. The results are better by 20% (the sample hydrolysed without ultrasound) and 25% (the sample hydrolysed with ultrasound) in comparison to the unprocessed sample, Table 1. In constellation of structural parameters, density and linear mass of yarn, construction of knitted fabric, as well as the surface effects of modification, the explanation for certain phenomena in PES knitted fabric related to all tested sorption properties should be sought.

The wettability of the surface is directly connected to the surface energy, so the energy stable surface has lower ability of wetting. Materials with lower wettability (less hydrophilic, i.e. hydrophobic), such as polyester, have weaker ability of dyeing and lower resistance to soiling. The treatment of alkali can be a good and recognizably efficient means for improving the surface wettability of hydrophobic polymer surfaces. This improved wettability is ascribed to increasing amount of polar groups, surface deformation, increased roughness of the surface of the material etc. [15].

According to Table 1, it can be noticed that the modified-hydrolysed samples of knitted fabric wet faster. The unprocessed sample of PES knitted fabric has the slowest wetting, 360 s; the best results, i.e. the most hydrophilic surface of fabric and then the fastest wetting is obtained by the hydrolysis in the presence of ultrasound waves, 9 s.

Table 1: Some properties of PES knitted fabric after alkali-alcohol hydrolysis

Sample	Mass loss [%]	Thickness [mm]	Water absorption [%]	Capillarity [mm]		Wetting time [s]
				Wale	Course	
Untreated	–	0.94	330.6	2.5	2.5	360
Hydrolysis without ultrasound	6.3	0.93	395.2	25	20	11
Hydrolysis with ultrasound	10.7	0.92	412.9	32	30	9

3.2 The effects of ultrasound on dyeing of PES knitted fabric

As far as dyeing of PES fibres is concerned, according to the experiences of examiners, it can be said that there is a contribution of ultrasound to the process of dyeing which is usually explained by the appearance of dispersion (departing of greater particles of dye into smaller ones, regarding the fact the molecules of dye have the tendency to form aggregates), degassing (expulsion of solved or trapped air from capillaries in the fabric), diffusion (moving of dye molecules to the inside of fabric and fibres) and strong agitation (mixing) of dye solutions [5, 17].

Furthermore, for the analysis of the process of dying of PES fibres, the temperature of glass crossing is very important, which is mostly between 67–80 °C in polyester [1]. Taking this into consideration, without precise checking of the used fabric sample, dying of the modified PES knitted fabric is done at the upper limit of that crossing, at 80 °C. The level of dye exhaustion in dyeing of the hydrolysed knitted fabric with ultrasound is much greater than in the similar sample dyed without ultrasound, Table 2, which represents excluded contribution to this additional source of energy, i.e. ultrasound waves. For example, at lowest and greatest initial concentration (50 mg/l and 400 mg/l), the level of exhaustion after one-hour dyeing of the hydrolysed PES knitted fabric with ultrasound waves at 80 °C, are 80.81% and 62.87%, respectively which is very close to the standard way of dyeing of the raw PES knitted fabric at higher temperature (at 100 °C, in the presence of carrier and without ultrasound), where the level of exhaustion is slightly higher, 81.69% and 62.87%, respectively. When the same methods of dyeing the raw and previously modified knitted fabric (at 80 °C) without ultrasound are compared, the values for the level of exhaustion are different, for example 61.09% and 70.54%, respectively (for initial concentration of dye 50 mg/l), which indirectly shows the significant influence of previous alkali alcohol hydrolysis of PES fibres.

These results can confirm the fact that ultrasound changes the surface morphology of PES fibres in the direction of increasing the porosity (during previous processing in alkali-alcoholic solution), decreases the size of dye particles so that more individual molecules of disperse dye are present in water, and there are real chances that the applied ultrasound increased the size of amorphous areas in fibres, which

Table 2: The level of exhaustion of dye on PES knitted fabric during different methods of dyeing

Dye recipes (exhaustion method)	Dye concentration [mg/l]	Dye exhaustion [%]
Dyeing of raw PES knitted fabric **without ultrasound** (standard procedure from the dye manufacturer: 100 °C, Sarapol GFD 2 g/l, CHT Dispergator SMS 1.5 g/l, pH = 4.5, 60 min)	50	81.69
	400	62.87
Dyeing of raw PES knitted fabric **without ultrasound** (80 °C, CHT Dispergator SMS 1.5 g/l, pH = 4.5, 60 min)	50	61.09
	400	43.57
Dyeing of hydrolysed PES knitted fabric **without ultrasound** (80 °C, CHT Dispergator SMS 1.5 g/l, pH = 4.5, 60 min)	50	70.54
	400	52.47
Dyeing of hydrolysed PES knitted fabric **with ultrasound** (80 °C, CHT Dispergator SMS 1.5 g/l, pH = 4.5, 60 min)	50	80.81
	400	61.65

gives the possibility to greater number of dye molecules to diffuse into PES fibres of knitted fabric.

It is known that the increase of temperature influences the increase of molecule vibrations, in the polymer chain of fibres and the dye itself as well, which significantly eases the diffusion of dye into the fibre [5]. The applied ultrasound, according to the effects which it produces on PES fibres, should compensate the high temperature of dyeing (100 °C or 130 °C). Of course, regarding the structure, PES fibres can be significantly sensitive to the change of temperature, but practically insensitive to the change of temperature of dyeing which is proved by the results of certain testing [16, 18]. On the other hand, the probability is higher that the fibres will be sensitive to the reaction of ultrasound waves the consequence of which can be a large amount of dye molecules inside the fibres.

3.3 Modelling of dyeing of PES knitted fabric

Modelling of textile dyeing is a procedure that can lead to interesting conclusions about the fiber sorption mechanism, as well as give guidelines for optimized dyeing. The results related to modelling the dyeing of hydrolyzed PES knitwear in the presence of ultrasonic waves will be presented in the next section of the text.

Isothermal adsorption is of essential significance for investigation of the process of dyeing at lower temperature (80 °C). The analysis of isothermal data by their fitting via different isothermal equations is an important step towards finding the right model which can be used for controlling the process of dyeing. In this investigation, isothermal models of *Langmuir, Freundlich* and *Nernst* have been used, and for fitting of experimental points software OriginPro (USA).

Figure 2 gives comparable display of isothermal models of *Langmuir, Freundlich* and *Nernst* through nonlinear fitting of experimental data. The parameters of models obtained from nonlinear regression are listed in Table 3. Coefficient of determination ($R^2 = 0.998$) in *Freundlich* isotherm is the highest of the three models, which confirms the fact that this model is the most efficient in nonlinear simulating of isothermal adsorption of disperse dye on PES knitted fabric, which can be noticed at visual review of nonlinear curves in the diagram in Figure 2. Then, *Langmuir* model follows, also with high R^2 (0.988), and then in the end, *Nernst* which has the lowest coefficient of determination ($R^2 = 0.930$). The coefficient of determination is a relative measure of representativeness of regression line or measure of using these models.

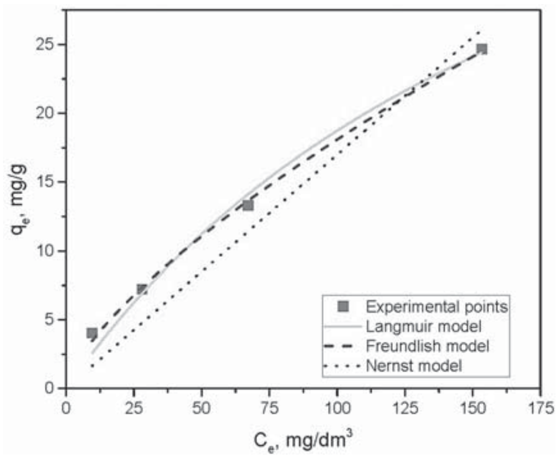

Figure 2: Fitted equilibrium data of adsorption for Nernst, Langmuir and Freundlich nonlinear models of ultrasound dyeing of modified PES knitted fabric

Based on the results from Table 3, it is confirmed that *Freundlich* model is dominant, according to the cover of experimental points, $R^2 > 0.99$, even though other nonlinear models are not left behind. From the applied nonlinear models, *Nernst* showed to be the weakest.

Table 3: Analytic equations of nonlinear isotherms with coefficients for the dye-PES knitted fabric system

Isotherm	An analytic expression of a nonlinear model	Model parameters		R^2
Langmuir	$q_e = \dfrac{0.28 \cdot C_e}{1 + 0.0049 \cdot C_e}$	Q_{max} [mg/g]	56.615	0.988
		b [dm³/mg]	0.0049	
Freundlich	$q_e = 0.692 \cdot C_e^{1/1.41}$	K_F [(mg/g)·(dm³/mg)$^{(1/n)}$]	0.692	0.998
		n	1.41	
Nernst	$q_e = 0.170 \cdot C_e$	K [dm³/g]	0.170	0.930

Besides these nonlinear models, a linear model should also be checked, so the diagrams in Figures 3–5 show linear interpretation of all three isotherms of dyeing. According to the diagrams in Figure 3, *Langmuir* adsorption isotherm shows dependence on parameters (C_e/q_e), in comparison to the equilibrium dye concentration (C_e), at dyeing of hydrolysed PES knitted fabric with ultrasound. From this diagram, i.e. inclination and segment of functional line, obtained by the method of fitting, the values of *Langmuir* constants are determined, Q_{max} and b, which relate to maximum amount of dye which can bind to the fibre and free energy of adsorption, respectively. In the diagram (Figure 3) can be seen that dissipation of data is present, which shows inadequacy of *Langmuir* isotherm for describing adsorption equilibrium of the tested system.

Freundlich and *Nernst* models (Figures 4 and 5) give better results, namely there is a better fitting of experimental data.

On the other hand, in similar work, dyeing of a knitted fabric made of PES filaments by disperse yellow and orange without dispersing agent, after the hydrolysis in the solution of sodium hydroxide, shows a significant deviation of *Nernst* adsorption isotherm in describing of dyeing and excellent behaviour of *Langmuir* model which significantly corresponds to the experimental data (coefficient of correlation is 0.99) [19].

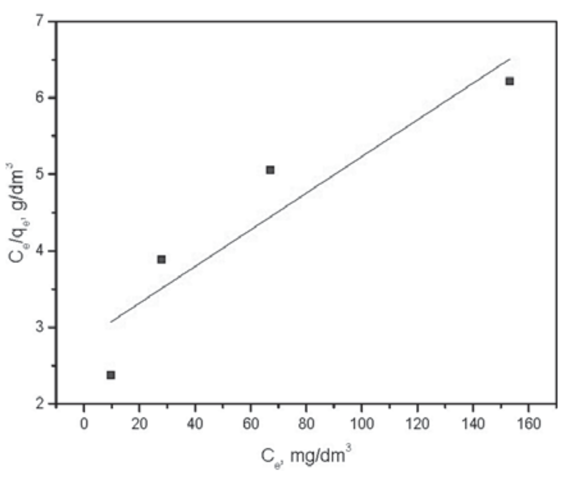

Figure 3: Linear form of Langmuir adsorption isotherm for the dye-PES knitted fabric system

Freundlich isotherm, Figure 4, is obtained with the assumption that heterogeneity of the surface with uneven distribution of heat of sorption through surface exists. From this diagram, high functionality of variables can be seen. Based on inclination and segment, *Freundlich* constants are determined, and via them the valued suitability of this model for describing the process of adsorption of the applied dye on the PES knitted fabric.

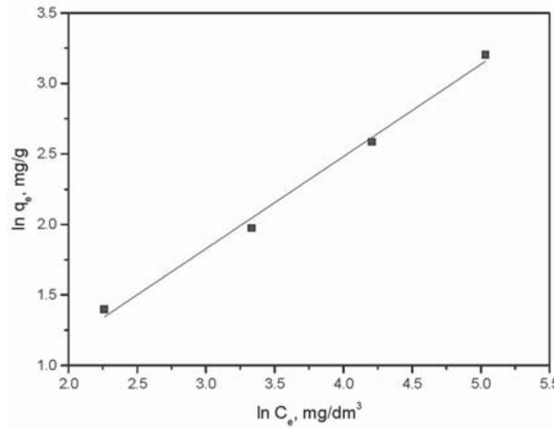

Figure 4: Linear form of Freundlich adsorption isotherm for the dye-PES knitted fabric system

Linear distribution of *Nernst* type is frequently used as a reference for isothermal adsorption of textile dye on polyester [13]. According to the diagram in Figure 5, it is noticeable that there is relatively less dissipation of experimental data in comparison to the curve of fitting, so this model, along with *Freundlich*, belongs to the top model which can describe dyeing of PES knitted fabric by disperse dye using linear method. The advantage is in actual case given to *Freundlich* model.

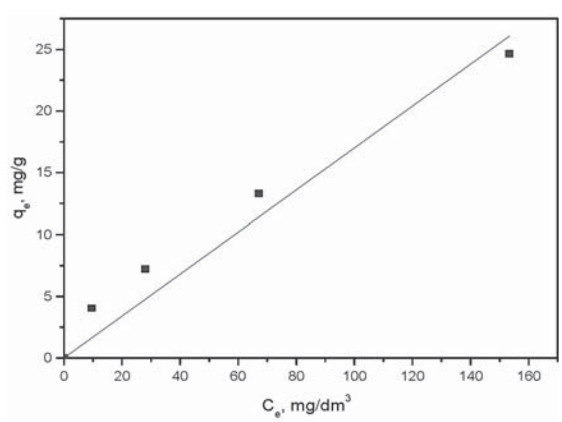

Figure 5: Linear form of Nernst adsorption isotherm for the dye-PES knitted fabric system

Table 4: Analytical equation of linear isotherms with coefficients for the dye-PES knitted fabric system

Isotherm	An analytic expression of a linear model	Model parameters		R^2
Langmuir	$C_e/q_e = 2.838 + 0.024 \cdot C_e$	Q_{max} [mg/g]	41.75	0.867
		b [dm^3/mg]	0.0084	
Freundlich	$lnq_e = -0.134 + 0.654 \cdot C_e$	K_F [(mg/g)·(dm^3/mg)$^{(1/n)}$]	0.874	0.994
		n	1.529	
Nernst	$q_e = 0.170 \cdot C_e$	K [dm^3/g]	0.170	0.980

In Table 4, analytical equations of linear adsorption isotherms are shown, as well as the values of adsorption parameters, and the values of coefficient of determination R^2.

The results for the coefficient of determination in Table 4 can confirm, as seen in the pictures, the high value (>0.99) for *Freundlich* isotherm, which means that a large percentage of the amount of square deviation of variable values form arithmetic middle is analysed by this regression model. So, in the method of determining *Freundlich* constants, K_F and n, *Freundlich* model significantly covers experimental data and it can be acceptable for adsorption of disperse dye on PES knitted fabric.

K_F, one of *Freundlich* constants, is used as a relative measure of the adsorption capacity, the greater value of K_F shows greater adsorption capacity. Other *Freundlich* constant, n, is an empirical parameter which changes with the level of heterogeneity, indicating the level of nonlinearity between capacities of accepting dye and concentration of non-adsorbed dye and it relates to the distribution of bonded ions on the surface of adsorbent. Generally, $1/n<1$ illustrates that the adsorbate is favourably adsorbed on the adsorbent, adsorption capacity rises, and new positions for adsorption appear, the greater the value n, the stronger the intensity of adsorption.

4 Conclusion

The alkali hydrolysis of PES knitted fabric in alcohol medium is a relatively simple method for modification of the surface of polyester fibres, i.e. textile material from these fibres, with the effects which can be significant for dyeing. It is shown that dyeing in the presence of ultrasound increases the dye exhaustion on the modified PES knitted fabric at lower temperature.

Based on the obtained experimental results, the following conclusions can be made:

- The alkali-alcohol hydrolysis with ultrasound decreases the mass and thickness and fixes sorption properties, capillarity and absorption of water and wetting of PES knitted fabric as well.
- The process of dyeing of modified PES knitted fabric in the presence of ultrasound at lower temperature gives good results, much better than dyeing without ultrasound and it is very close to the standard process of dyeing of raw sample at higher temperature.
- The level of exhaustion of dye in dyeing of hydrolysed knitted fabric with ultrasound is higher than in the same method of dyeing without ultrasound, which represents exclusive contribution of this additional source of energy.
- The levels of dye exhaustion in dyeing of raw and previously modified knitted fabric without ultrasound are significantly different, they are much better in hydrolysed samples, which indirectly shows the significant influence of previous alkali-alcohol hydrolysis of PES fibres.
- Freundlich nonlinear isotherm is the most efficient in simulating isothermal adsorption of disperse dye on PES knitted fabric.
- Freundlich linear equation shows that this model enables a sufficiently precise description of experimental data nevertheless the advantage is given to a nonlinear model.

The results of this work based on these effects indicate the possibility of different approach in the process of dyeing the polyester by disperse dye for the benefit of greater exhaustion, economy and protection of the environment.

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