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MODELLING OF POLYESTER FABRIC DYEING IN THE PRESENCE OF ULTRASONIC WAVES

Article Highlights

- Non-standard dyeing of PES fabric without carrier is possible by ultrasound
- Continual growth of the amount of exhaustion dye with mass of material is noted
- The Langmuir model shows precise description of experimental data
- Kinetic model of pseudo second-order adequately describes disperse dye – PES fabric system

Abstract

In this paper, modelling of dyeing, i.e., adsorptive behaviour of disperse dyes on polyester fibres under the influence of ultrasound has been considered with the aim of getting data about binding mechanisms, as well as defining the conditions of dyeing with additional energy source without the use of carriers, compounds that increase permeability of the fibres and help dyeing. Dyeing adsorption was conducted under different conditions, and the concentration of dyes, mass of the substrate, recipes and time of dyeing were varied. It was established that ultrasound allows dyeing without carriers, and that the efficiency of dyeing depends on the time of contact, initial concentration of the dye and the amount of absorbent material. Continual growth of the amount of bound dye with the mass of the absorbent was observed. Characteristic plots obtained from confirmed that the Langmuir isotherm model ensures a precise description of polyester dyeing by disperse dye. The dyeing kinetics was remarkably well described by pseudo second-order in regards to the high functionality.

Keywords: adsorption, polyester, disperse dye, ultrasound, Langmuir isotherm, kinetics.

It is known that polyester (PES) belongs to a group of synthetic fibres that possess active spots where dye molecules can be adsorbed. PES contains a great number of ester groups, as well as a certain number of carboxylic groups, which are placed at the ends of chains, such that during the dyeing of this fibre hydrogen bonds with dye molecules will be established. PES has significant hydrophobic character and compact structure, so taking into consideration this kind of fibres behaviour in the dyeing solution, it is necessary to modify the usual dyeing process, i.e. to increase the rates of dye diffusion in the fibres. Generally, the rates of dyeing could be increased by using suitable dyes, changing the fibre structure, changing the conditions of dyeing, etc. [1,2].

The rate of dye diffusion can be intensified by increasing the permeability of the fibres, *i.e.*, increasing the fibre swelling ability. This can be achieved by adding simple organic compounds (with smaller molecules than the dye molecules and with certain affinity towards the fibre) in the dyeing solution. These compounds are termed as carriers: due to their small molecular size they quickly diffuse into the fibre, bind to carboxylic groups and establish hydrogen bridges. Carriers cannot be completely removed from the fibres by washing; therefore, they require special attention due to their toxic and dermatologic effects. On the other hand, the presence of these substances on the fibres adversely affects the fastness of many dyes with light, and in certain cases they influence fibre shrinking as well [3,4].

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Ultrasound in the 20-100 kHz frequency range is used to increase the chemical reaction rate and advance different physical processes, such as cleaning, emulsion, extraction, etc. It can achieve the same or even better results in comparison to already existing techniques under less extreme conditions (*e.g.*, lower temperatures and high chemical concentrations of reactants). Hence, the process of material dyeing using ultrasound is very significant. Observed improvements in ultrasound processes of dyeing generally refer to the phenomenon of cavitation, but some other mechanical influences can occur too, such as dispersion and diffusion [5-7].

This paper strives to explain the ability of dye adsorption into the fibres in aqueous environment with usual auxiliaries according to standard recipes in the presence of ultrasound waves, instead of carriers. The purpose is to successfully perform the process of dyeing of very hydrophobic and crystal fibres under normal pressure and temperature conditions. Consequently, if the dye exhaustion is higher, the amount of dyed wastewater is lower and less harmful to the environment. The inclination was to eliminate the usual supplement – carriers, since it is known that most of these supplements have negative impact on human health and environment. Furthermore, the goal was to explain the polyester dyeing process in new circumstances using a series of experiments, as well as modelling the system and kinetic parameters.

EXPERIMENTAL

As an adsorbent, 100% polyester fabric (polyethylene terephthalate) has been used with the following characteristics: weave – twill ½*S*, warp and weft fineness of 16×2 tex each, warp and weft density of 30 and 22 cm^{-1} and surface mass of 195 g/m^2. The structure of the used disperse dye (adsorbate), C.I. Disperse Blue 79 (DB79), is shown in Figure 1. It is a large molecule, highly energetic dye with good fastness in sublimation and wet treatment. It is suitable for dyeing by exhausting and thermosol procedure, as well as printing synthetic material.

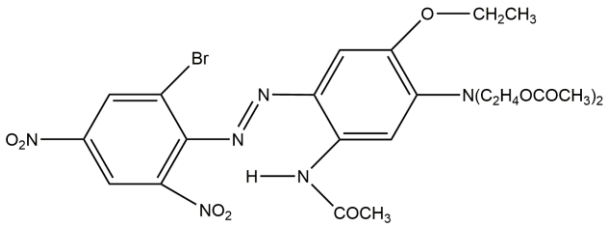

Figure 1. Structure of the used disperse dye, C.I. Disperse Blue 79.

The dyeing process (the method of exhaustion) was performed with the dye bath heated at 60-70 °C with 1.5 g/dm^3 of carrier (Icelan PSN, anionic, on the basis of mixture of different aromatic esters and special emulsifiers, Textilcolor AG, Switzerland) and 1 g/dm^3 of dispersing agent (TC-Dispergator DTS, non-ionic, on the basis of polyglycolether-derivates, Textilcolor AG, Switzerland). The dye bath was adjusted to pH 5 by acetic acid, and, after mixing, the dispersant substance was added, with continual heating to 95 °C. The PES fabric sample was then added and dyed for 60 min. After dyeing completion, the dyed material was washed at 70-80 °C.

Non-standard dyeing was performed under identical conditions, but in the absence of carrier. Instead, an Elac Ultrasonic Laboratory Reactor URS 1000 was used. The frequency of the applied ultrasound oscillations was 140 kHz, while the power was 50 W.

The amount of PES fabric in the dyeing adsorption test was varied from 2 to 6 g, and the used dye solution (constant volume of 0.1 dm^3) were prepared at concentrations of 50, 100, 200, 300 and 400 mg/dm^3 in distilled water. The time of treatment, with constant mixing, was 10, 20, 30, 40, 50 and 60 min. The time of 60 min was taken as equilibrium no significant changes in dyeing adsorption were observed with further treatment.

For determining the concentration of dye in the solution, a Cary 100 Conc UV-Vis Varian spectrophotometer was used (absorption maximum at 550 nm).

The level of dye exhaustion (%) is calculated as [8]:

$$100\frac{c_0 - c}{c_0} \tag{1}$$

where c_0 and c, mg/dm^3, are the initial and final concentration of the solution of dye.

Langmuir isotherm was obtained from the following equation [9]:

$$\frac{c_e}{q_e} = \frac{1}{Q_{max}b} + \frac{1}{Q_{max}}c_e \tag{2}$$

where c_e, g/dm^3, is the equilibrium concentration of dye after finished adsorption; q_e, g/kg, is the adsorbed amount of adsorbate (dye) per mass unit of the adsorbent (fabric); Q_{max}, g/kg, is the maximum amount of adsorbate which can be bound on the adsorbent; b, dm^3/g, is the Langmuir constant.

The amount of adsorbed dye per mass unit of fabric is calculated as [9]:

$$q_e = \frac{(c_0 - c_e)V}{w} \quad (3)$$

where w, kg, is the mass of fabric and V, dm^3, is the volume of the solution from which the adsorption was done.

Lagergren's pseudo first-order equation is usually expressed in the linear form [10]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where q_e and q_t, mg/g, are the capacities of the adsorption in equilibrium and after time t, respectively, and k_1, 1/min, is the rate constant of pseudo first--order adsorption.

The kinetic equation of the pseudo second-order adsorption has the form [10]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2, g/mg·min, is the rate constant of the second-order adsorption.

RESULTS AND DISCUSSION

The chosen dye DB79 is not water-soluble. The solubility depends on the chemical composition and especially on the content of polar and non-polar functional groups. As a typical donor-acceptor chromogen, this dye has two nitro groups and one bromine that pull on electrons, and, to a certain extent, electron-donor ethoxy group, whereas acetylamino and diacetyloxyetilamino groups practically are not suitable donors and acceptors of electrons. In consideration of interaction of the mentioned functional groups, substantivity will occur towards the textile, which is in this case a hydrophobic material.

The inclusion of dispersing agent in the dye bath is a crucial factor in the application of disperse dyes. The hydrophobic tails of the dispersing agent molecules are inside a micelle which, as a consequence, is able to solubilise the disperse dye molecules, thus conferring a higher apparent solubility to the dye [11].

The dye transfers to the fibre from the micelles. As micelles release their dye, they reform and dissolve more dye from the solid particles. Much of the evidence that is available on the subject suggests that in dyed polyester fibres the disperse dyes are present chiefly in the monomolecular state. At the end of the dyeing process, the dye that has been absorbed by the fibre is in a state of dynamic equilibrium with the dye that remains in the bath, and the fraction of the latter that is in aqueous solution must be present in the same state of aggregation as the dye in the fibre [11].

The influence of time or the length of contact between adsorbate and adsorbent on adsorption - dye exhaustion during ultrasound (without carrier), for different initial concentration of disperse dye, is shown by comparative plots in Figure 2. The continuity in changes during time is present, *i.e.*, the longer time carries greater amount of adsorbed dye per mass unit of adsorbent. At lower dye concentrations there is greater dye exhaustion in contrast to higher dye concentrations. Realistically, however, higher amount of dye adsorbed occurs at higher initial dye concentrations.

In other words, for example, dye exhaustion is 72.48% for the concentration of 50 mg/dm^3 and 10 min of adsorption, while dye exhaustion is 57.03% for the concentration of 400 mg/dm^3 and 10 min of adsorption.

Therefore, there is a greater exhaustion at low concentration, but after calculating, real dye adsorption at a lower concentration is: 72.48%×50 mg/dm^3 =

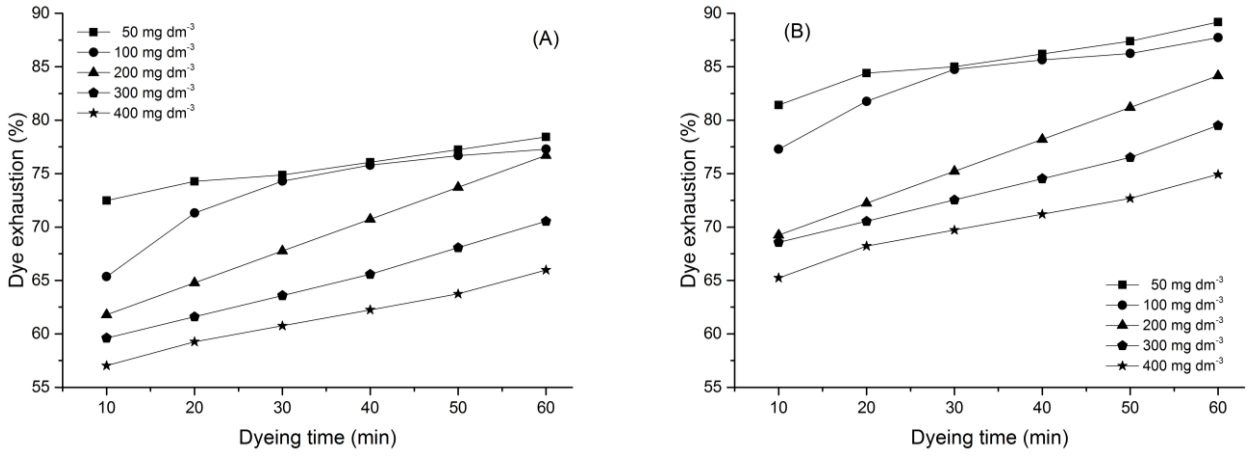

Figure 2. The influence of adsorption time on the percentage of DB79 exhaustion (A - PES, 2 g; B - PES, 6 g).

= 36.24 mg of dye adsorbed on PES fabric; while at higher concentration the amount is: 57.03%×400 mg/dm^3 = 228.12 mg of dye adsorbed on PES fabric;

Linear parts of the curve reflect diffusion in the surface layer, whereas the parts of the plateau on the curve respond to diffusion in pores. The diagram for adsorption on 4 g of PES is not shown, because there are no great differences in the appearance of the curves.

A similar investigation by Olenka *et al.* used the same dye (Disperse Blue 79) for PES dyeing [12]. They implemented the chemical modification of the substrate, instead of using ultrasound, and PES dyeing was performed without carriers. The results of dye exhaustion showed that the best dyeing conditions were to treat the PES for 15 min at 85 °C with *N,N*--dimethylacrylamide as a modifier, followed by a dyeing time of 30 min at 85 °C. These conditions were shown to be suitable for the dye. Photoacoustic spectroscopy allows the determination of the penetration conditions at which the modified PES can absorb more dye of original.

Also, disperse dye exhaustion was analyzed by Choi and Kang [13]. They prepared six nano-disperse dyes using corresponding O/W nanoemulsions in order to dye PES (two type, regular- and micro-fibers). Dye exhaustion using nano dyes resulted in low exhaustion yields of 17-26% on regular polyester fiber and 28-38% on ultramicrofiber polyester. The observed low exhaustion yields of nano-disperse dye can be explained by the solubilization of dye particles into surfactant micelles as well as the high stability of the nanoemulsions, which might reduce the capacity of dye uptake by the fibers. As commercial disperse dyes exhibit exhaustion of 90-95%, these results were extremely lower than conventional disperse dyes. However, in the case of dyeing with nano-dyes prepared on ultramicrofibers, it was observed that microfiber site exhibited higher *K*/*S* values than those of regular polyester site, in the range of 1.5-2.4%, which was promising a possibility for higher efficiency on ultramicrofibers.

Likewise, the potential of ultrasound as a means of enhancing dyeing efficiency was evaluated by Lee and Kim [14]. Changes in the particle sizes of a disperse dye dispersion with ultrasound irradiation are studied using the turbidity concept, and the effect of particle size on the exhaustion rate is also investigated. Ultrasound irradiation of a dye dispersion reduces the particle sizes of disperse dyes, and the exhaustion rate of the dyes on fibers is enhanced by this reduced particle size by the ultrasound pretreatment before dyeing experiments. These results suggest that ultrasound is useful method of accelerating the dyeing rate and increasing dyeing efficiency.

During the dyeing of Disperse Blue 56 with and without ultrasound, as might be expected, increasing the dyeing temperature increased the dye uptake and dyeing rate regardless of ultrasound use [15]. Comparing the dyeing kinetics of Disperse Blue 56 with and without ultrasound, authors did not see a significant increase in dye uptake and dyeing rate for Disperse Blue 56 with ultrasound use. The effect of ultrasound on the dyeing behavior of Disperse Blue 56 on PET fibers was almost non-existent, with little influence on dye absorption and dyeing rate. PET dyeing of Disperse Red 60 with ultrasound irradiation showed a considerable increase not only in the dyeing rate but also in dye uptake. Comparing dyeing with and without ultrasound, dye uptake was higher by some 68 and 6%, respectively, for Disperse Red 60 when dyeing was conducted with ultrasound. Compared with the results for Disperse Blue 56, this demonstrates that ultrasonic energy can have a profound effect on the dye uptake and dyeing rate of more crystalline dyes like Disperse Red 60.

A comparison of dyeing with carrier with or without ultrasound, and dyeing with ultrasound only, are shown in Figure 3 with respect to their dependency on exhaustion dye-time of dyeing. Only data for dye concentration of 400 mg/dm^3 and minimal and maximal amount of PES fabric is shown, since very similar behaviour is observed under other concentrations and 4 g of remaining material mass. The shape of the curves is very much alike for the given concentration and 6 g of PES, whereas for minimal amount of PES (2 g), the curves partly differ.

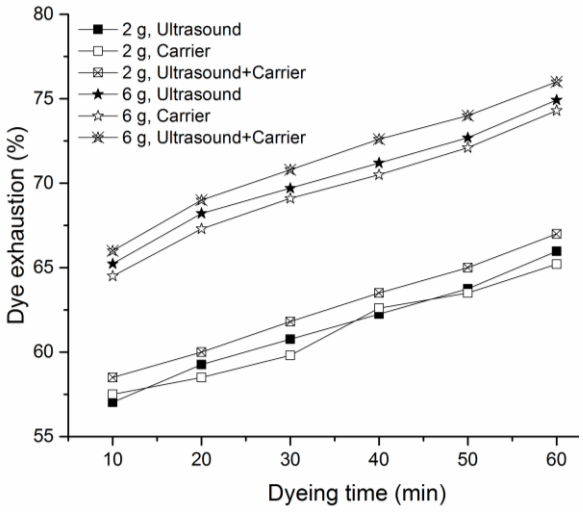

Figure 3. The influence of adsorption-dyeing time on DB79 exhaustion (400 mg/dm^3) in different conditions.

The fact that stands out is that dyeing with ultrasound leads to more exhaustion and binding dye for PES fibres in comparison to dyeing with carrier without ultrasound. It is interesting that the presence of ultrasound in the dye bath with all auxiliaries (including carrier) gives better results, i.e. the biggest DB79 exhaustion on the fibre. This kind of behaviour practically is mapped at all dye concentrations and all amounts of adsorbents. As the amount of adsorbent is increased, dyeing with ultrasound without carrier performs much better in comparison to dyeing with carrier. Nonstandard dyeing with ultrasound, but with carrier, gives the best results of dyeing in all cases. It is associated with the fact that the present carrier, having achieved the ability of swelling, opens the structure of fibres and causes greater dye exhaustion that is helped very much by the present ultrasound.

This proves the positive effect of ultrasound waves on dyeing with and without carrier, which is explained by dispersion (separation of big dye particles into smaller ones), then by degassing (ejection of soluble or trapped air from the capillaries of the fibres), expansion (speeding up the dye molecules to penetrate into PES fibres) and intensive mixing of the dye solution [16].

Aside from the above mentioned, greater dye exhaustion can be observed due to the change in PES fibre crystallinity of PES fibres changes during the ultrasound processing, because of removal of oligomer from the surface and surface layers, and the cavitation of ultrasound dislocating macromolecules among micro crystallites, thus enlarging the amorphous area [5].

In other words, in order to diffuse the molecules of dye properly into the fibres, the free volume must be formed inside the substrate (fibre). The applied ultrasound helps the free volume to be created easily inside the polymer via thermal moving of the chains of molecules and dye molecules, which enter this free area. At the same temperature, thermal moving of molecule chains is directly related to the strength of polymer substrate, *i.e.*, the faster dye diffusion can be achieved in softer and more flexible substrates of polymers, which is partially enabled by using ultrasound waves [5].

Similarly, Saligram *et al.* found that sonication during dyeing brought much more [17]. Namely, ultrasound used in the dyeing of polyester fibres with disperse dyes at low temperature, and results compared with those achievable in conventional dyeing at the boil using a carrier. Dyeing was enhanced in presence of carrier and by pre-swelling the fibres, although the results obtained were not generally as good as those that can be obtained in conventional high-temperature processes. Taking into account the energy conservation aspect, ultrasound appears to be a promising technique for dyeing.

Also, poly(trimethylene terephthalate) (PTT) fabric, a new type of polyester fibre, was dyed with Disperse Red FB by using ultrasonic power by Wang *et al.* [18]. It was shown that the ultrasonic-assisted dyeing could increase the depth of shade in PTT fabric at a lower temperature. The ultrasonic energy can disintegrate the large particles of oligomer on the surface of the PTT fibre to smaller ones and slightly decreases the crystallinity of the PTT fibre, which can reduce the particle size of the disperse dye in the dye solution as well. Moreover, the ultrasonic dyeing of the PTT fabric with a swelling agent can enhance the colour strength of the dyed fabric, thereby reducing the dyeing time as well as saving energy. The effects of ultrasound on the *K*/*S* values of the fabric, the fibre structure and the disperse dye were investigated. The results show that the ultrasonic power increases the *K*/*S* values of the fabric, disintegrates the large particles of oligomer on the surface of poly(trimethylene terephthalate) fibre into smaller ones and reduces the particle size of the dye in solution. The *K*/*S* value of poly(trimethylene terephthalate) fabric dyed using ultrasound is much higher than that without ultrasound, especially at temperatures higher than 60 °C.

In a similar manner, an attempt was made to evaluate the possibility of using ultrasonic techniques for effective low-temperature dyeing of polyester [19]. The ultrasonic dyeing depends strongly on a preswelling process that would be both expensive and difficult to carry out commercially (particularly in terms of health and safety aspects). Performance also depends on the energy levels of the dyes used. The results obtained for the dyes of higher relative molecular mass were much worse than those obtained when using carrier at the boil (although raising the dyeing temperature would be expected to provide notable improvements in depth). Little advantage would be gained over conventional dyeing methods, particularly when carrier was incorporated in the dyebath. An ultrasound dyeing unit with a lower frequency level (around 26 kHz), to generate more pronounced cavitation effects, may have given better results. However, the unit chosen had a frequency rating that was both readily available commercially (38 kHz) and could still be considered operationally viable. The noise levels associated with lower frequency units would be unacceptable in commercial use.

Since it is being established that the dye exhaustion on the polyester is sufficiently good with

ultrasound without carrier, the results of modelling of dyeing – adsorption without carrier but under the influence of ultrasound are given as follows. The results of changing the adsorbed amount of adsorbate on the adsorbent during time, for different initial concentrations of dye during dyeing with ultrasound (without carrier) in relation to the mass of PES fabric, are shown in Figure 4. The continuity in changes with time can be observed, *i.e.*, the longer the time, the greater the amount of the adsorbed dye per mass unit of adsorbent. The highest adsorption occurred at the highest applied concentrations of dye.

Since the total surface area of fibres is higher than the outside surface, the molecules of dye will faster adsorb during dyeing than the present auxiliaries. Since the dynamic equilibrium of the solution deranges because of that, the aggregates of dye will dissolve into molecules and establish equilibrium again in the solution. Adsorption will continue up to the point when the equilibrium between dye concentration in the solution and dye concentration in the fibre is not reached. Since the molecules of dye have the tendency to form aggregates in aqueous solution, ultrasound energy causes degradation of dye aggregates in the solution, decreasing the size of dye particles in dispersion, which is the first pre-condition for better adsorption on the adsorbent [5-7].

Figure 5 represents the interpretation of Langmuir adsorptive isotherm for different amounts of adsorbents, showing the dependency of parameters (c_e/q_e) on the equilibrium dye concentration (c_e) during dyeing with ultrasound (without carriers). From the slope and intercept of the fits, the values of Langmuir constants (Q_{max} and b) were obtained, which are related to the maximum amount of dye that can bind on the fibre, and the free energy of adsorption, respectively.

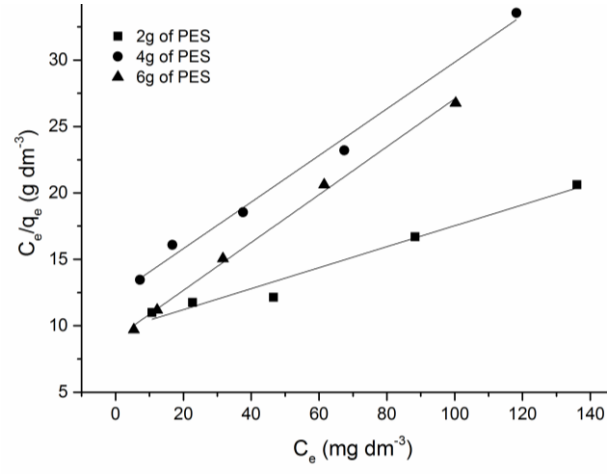

Figure 5. Langmuir adsorption isotherms for DB79 - PES fabric system.

Figure 5 shows that adsorption curves are flat and continual, which leads to saturation during different concentrations on the outer interphase of adsorbent material. Moderate dispersing of data is present which indicates the adequacy of Langmuir isotherm for describing the adsorption equilibrium of the examined systems. This kind of behaviour could be explained by the assumption that the dye in the beginning adsorbs on the outer surface of PES fabric, and after reaching a certain level of saturation, it enters the inner space of PES fibres, when it becomes adsorbed by inner surfaces. After diffusing of dye into pores of the fibres, diffused resistance increases, which leads to a decrease in diffusion rate. By decreasing the concentration of dye in the solution, the diffusion rate becomes constantly lower so the diffusion process reaches an equilibrium state, which completely submits to the law of equilibrium adsorption defined by Langmuir isotherm.

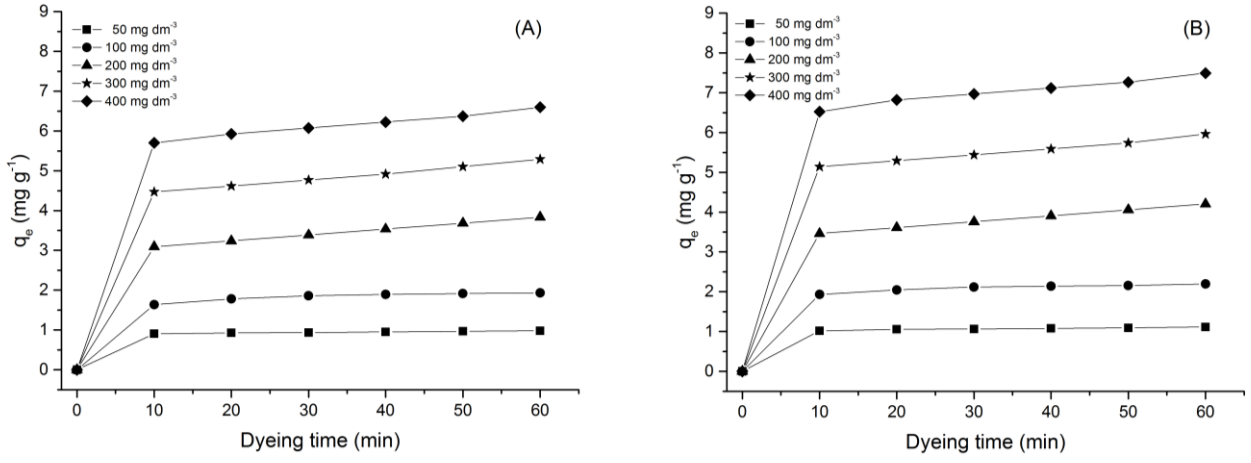

Figure 4. Adsorbed amount of dye DB79 on PES fabric during time of ultrasonic treatment (A - PES, 2 g; B - PES, 6 g).

Table 1 shows the analytical expressions of Langmuir isotherm, values of Langmuir parameters Q_{max} and *b,* and values of coefficient of determination R^2. The coefficient of determination is a relative measure of representability of regression line or measures of usage of Langmuir model.

According to the results for coefficient determination from Table 1, high values (above 0.97) are noted, which means that great percentage of square sums of variables values that deviate from arithmetic mean is explained by regression model. Therefore, in the procedure of determining capacities of dye retaining and affinities of adsorbent to dye, Q_{max} and *b*, respectively, the Langmuir monolayer model fits the experimental data reasonably well and it can be acceptable for adsorption of disperse dye on PES fabric.

The Langmuir model parameters are strongly dependent on the amount of adsorbent: Q_{max} decreases with the increasing of PES amount, whereas the values of other constant, *b,* increase continually with increasing the mass of the material. Higher values of *b* obtained for PES – disperse dye system mean stronger binding of dye.

In the study of Wang *et al.,* the Nernst, Langmuir and Freundlich isotherm models were employed in the fitting of the experimental points using the software Origin [18]. It can be seen that the coefficients of determination (R^2) of the Langmuir isotherm are the highest in the three models, indicating that the Langmuir model is the most effective in simulating the adsorption isotherm of Disperse Red FB onto the PTT fibre. In addition, the adsorption capacities (Q_{max}) of the PTT fibre dyed in the presence of ultrasound are all higher than that of the PTT fibre dyed without ultrasound at three temperatures. This proves the ultrasound-assisting effect on the dyeability of PTT fibre with disperse dye.

Figure 6 shows diagrams with results related to kinetic sorption of DB79 on PES fabric for the applied mass of 2 g of adsorbent and different initial dye concentration during dyeing with ultrasound (without carrier). According to linear forms of pseudo first-order model (Figure 6A), it can be concluded that the rates of adsorption in given experimental conditions, does not describe properly pseudo first-order model for the whole period of sorption, in comparison to the model of pseudo second-order (Figure 6B) which gives functional straight line for all initial concentrations of dye. Based on this, it can be said that, in this particular case, the pseudo second-order model is more usable. Similar behaviour is observed for mass of material of 4 and 6 g, hence those results are not shown in this text.

Tables 2 and 3 show results of kinetic parameters of process of adsorption DB79 on PES fabric (equilibrium rates constant of kinetics for pseudo first--order and pseudo second-order) for the used mass of adsorbent, all initial concentration of dye, as well as values for parameter *q* (calculated – q_{cal} and experimental – q_{exp}).

Table 1. Analytical expressions of Langmuir isotherm with coefficient for DB79 – PES system

Adsorbent, g	Analytical expression	Langmuir's parameters		R^2
	(Langmuir's equations)	Q_{max} / mg g^{-1}	b / dm^3 mg^{-1}	
2	$c_e/q_e = 9.635 + 0.078c_e$	12.67	0.008	0.973
4	$c_e/q_e = 12.295 + 0.175c_e$	5.70	0.014	0.992
6	$c_e/q_e = 9.057 + 0.180c_e$	5.55	0.020	0.997

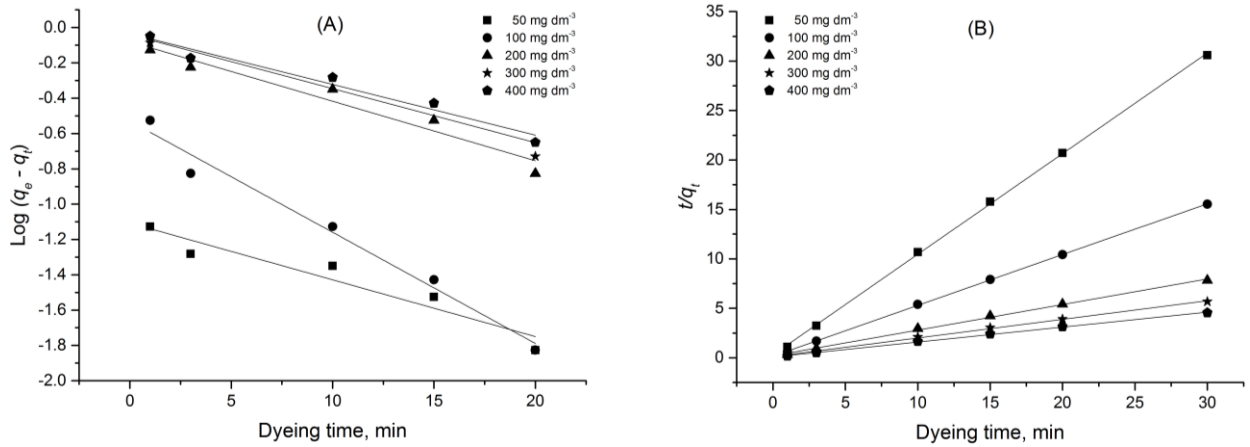

Figure 6. Kinetic of sorption DB79 on 2 g of PES fabric (A - pseudo first-order; B - pseudo second-order).

Table 2. Kinetic parameters of process of adsorption of dye on 2 g of PES fabric (pseudo first-order)

Dye concentration mg/dm^3	$q_{e,exp}$ mg/g	Pseudo first-order		
		k_1 / min^{-1}	$q_{e,cal}$ / mg g^{-1}	R^2
50	0.98	0.074	0.078	0.921
100	1.93	0.145	0.295	0.979
200	3.83	0.078	0.831	0,949
300	5.29	0.070	0.912	0.933
400	6.60	0.066	0.922	0.965

Table 3. Kinetic parameters of process of adsorption of dye on 2 g of PES fabric (pseudo second-order)

Dye concentration mg/dm^3	$q_{e,exp}$ mg/g	Pseudo first-order		
		k_2 / g mg^{-1} min^{-1}	$q_{e,cal}$ / mg g^{-1}	R^2
50	0.98	3.63	0.98	0.999
100	1.93	1.63	1.95	0.999
200	3.83	0.32	3.86	0.998
300	5.29	0.28	5.32	0.998
400	6.60	0.28	6.61	0.999

Although the coefficient of determination R^2 for kinetic model of pseudo first-order is higher than 0.92, completely different values are obtained for the calculated parameter (q_{cal}) in comparison to those for the experimental parameter (q_{exp}). Because of this, adsorption cannot be well described by the kinetic model of pseudo first-order, because in many cases the equation of pseudo first-order does not cover adequately the whole range of contact time, which is confirmed by the results in Table 2.

In contrast, kinetic model of pseudo second-order has in all cases $R^2 \approx 1$, Table 3, by which the complete functionality is achieved and the model can be completely used for describing processes of adsorption of dye on PES fabric. In addition, differences between parameters q_{cal} and q_{exp} for this model are insignificant, i.e. acceptable.

Concentration of dye decreases very fast during initial absorption, before diffusion inside the particles starts to control adsorption kinetics in all cases. Increase of contact time decreases the resistance of borderline layers, and supported by ultrasound waves, it intensifies the mobility of dye during the time of adsorption [20].

In addition, the paper of Carrion-Fité proposes a dyeing process for polyester at low temperatures (40 °C and below) with disperse dyes using a microemulsion prepared by ultrasonic agitation, composed of a small proportion of organic solvent (alkyl halogen) and phosphogliceride as the emulsifier [21]. The kinetics of this dyeing system are determined as a function of temperature with various disperse dyes at different molecular weights. In general, dyes with lower molecular weight have a faster dyeing rate and those with a higher molecular weight have a lower rate. Activation energies range from 20-40 kcal/mol; these values are similar to those achieved in traditional dyeing with a carrier.

CONCLUSIONS

Modelling of disperse dye adsorption, *i.e.*, dyeing of PES fabric was being tested under different conditions without carrier in dye bath, although it is well-known that dyeing of synthetic PES by disperse dye is performed usually in the presence of this chemical and/or in conditions of high pressure and temperature. Usually, the used carriers can show problems in usage for such dyed material or in production itself during dyeing. Use of ultrasound could solve all the drawbacks, having in mind health advantages and economic savings.

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

- non-standard dyeing of PES fabric without carrier is possible by ultrasound in atmospheric conditions;
- the longer the contact time, the higher the amount of dye adsorbed on the material;
- the concentration of dye in solution decreases with the duration of adsorption;
- the continuity of growth in the amount of exhaustion dye with mass of material is noted, *i.e.*, greater adsorption occurs in smaller proportion of bath;
- data obtained from teh Langmuir equation shows that this model enables precise description of experimental data;

The kinetic model of pseudo second-order adequately describes disperse dye – PES fabric system.

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NAUČNI RAD

MODELOVANJE BOJENJA POLIESTARSKE TKANINE U PRISUSTVU ULTRAZVUČNIH TALASA

U radu je razmotreno modelovanje bojenja, odnosno, adsorpciono ponašanje disperzne boje na poliestru (bojenje) pri delovanju ultrazvuka, sa ciljem dobijanja podataka o mehanizmu vezivanja boje i definisanju uslova procesa bojenja ovog sintetičkog vlakna uz dodatni izvor energije bez primene kerijera, jedinjenja koja povećavaju permeabilnost vlakana i pomažu bojenje. Bojenje-adsorpcija je vođena pod različitim uslovima, varirana je koncentracija boje, masa supstrata, receptura i vreme bojenja. Utvrđeno je da ultrazvuk dozvoljava bojenje bez kerijera a efikasnost bojenja zavisi od vremena kontakta, početne koncentracije boje i količine adsorbenta - tkanine. Postoji kontinuitet rasta količine vezane boje sa masom adsorbenta. Karakteristični prikazi dobijeni iz Langmuir-ove izoterme potvrdili su da ovaj model obezbeđuje dovoljno precizan opis bojenja poliestra disperznom bojom. Kinetika bojenja odlično je protumačena pseudo II redom s obzirom na visoku funkcionalnost.

Ključne reči: adsorpcija, poliestar, disperzna boja, ultrazvuk, Langmuir izoterma, kinetika.