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Original scientific paper

MODELING OF DISPERSE DYE ADSORPTION ON MODIFIED POLYESTER FIBERS

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The results of the research on the ability of adsorption of dye on polyester fibers at a temperature of 98 °C are presented in this paper. The fibers were previously modified in aqueous solutions of NaOH, KOH or $Al(OH)_3$. Typically, the dyeing of the fibers takes place at high temperatures and under pressure in the presence of the carrier. Previous processing before adsorption-dyeing, alkali hydrolysis, changes the surface morphology of polyester fibers. Based on dye exhaustion results, it was found that the dye adsorption on modified polyester fibers (degree of exhaustion 18.2 %, for a dye concentration of 200 $mg \cdot dm^{-3}$ and adsorption time of 5 min) has been bigger than adsorption to unmodified fibers (degree of exhaustion 10 %, for a dye concentration of 200 $mg \cdot dm^{-3}$ and adsorption time of 5 min). The five-parameter nonlinear model of Fritz-Schlunder is the most efficient in simulating isothermal adsorption of disperse dye on polyester fibers (the correlation coefficient is 0.995). Other adsorption models, Dubinin-Radushkevich, Marczewski-Jaroniec and Hill give poorer results and cannot be used to explain the adsorption of the disperse dye for polyester fibers (the correlation coefficients are 0.891, 0.922 and 0.973, respectively).

Keywords: adsorption, polyester, disperse dye, nonlinear modeling.

INTRODUCTION

The synthetic fiber sector is continually exploring new areas to diversify products and give them new properties. Thus, in recent years, great advances have been made in the development of fibers derived from polyester and, for the first time, its consumption has now surpassed the consumption of cotton, the most used natural fiber (1).

Polyethylene terephthalate (PET) fiber, which is a type of polyester (PES) fiber, is the most widely used synthetic fiber due to its good physical and chemical properties. It is also well known that PET fiber is dyed using disperse dyes at high temperatures of 120-130 °C, owing to its hydrophobic nature and highly compact molecular structure (2).

It is known that most polyester textile materials are dyed in high-temperature (HT) conditions. However, it may occasionally occur circumstances in which the use of HT conditions is undesirable, and other methods must be used. These circumstances are, for example, the presence of other fibers mixed with polyesters that are unstable in high-temperature conditions or the need to achieve a brighter color of textile. Some other factors

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may also occur in response to the increasing customer demands from textile production (3).

The fact is that the polyester fiber has a very compact and crystalline structure and is extremely hydrophobic. For this reason, its aqueous dyeing is carried out at high temperature and high pressure using disperse dyes. The dyeing of the polyester can be represented by several successive processes such as dissolving and dispersing the disperse dye, transferring dissolved dye from the aqueous solution to the surface of the fibers, diffusing and adsorbing the dye on the surface of the fibers, and diffusing from the surface to the inside of the fiber. Thus, it should be added that it is very well known that additives affect the processes of dyeing. (4).

Nowadays hydrolytic modification of the surface of polyester materials is more and more used for obtaining different and better appearance. It has been shown that polyethylene terephthalate has good conditions for modification by processing with alkalis. The reaction with NaOH is saponification 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 the peeling of polyester because by measuring the diffraction of X-rays, it is proved that alkali hydrolysis appears only at the surface of fibers, and the inner morphological structure of fibers stays unchanged. Treatment of fabrics with alkali leads to the decrease of fiber diameter and exposure of the new surfaces and hence the fabric properties will change (5-8).

This work tends to contribute to the explanations of dye adsorption on polyester fibers through the modeling process, i.e. abilities of dye adsorption at chemically modified PES fibers in aqueous alkaline solution, at a temperature of 98 °C without a carrier. The aim is to successfully perform the dye adsorption or dyeing of alkaline hydrolyzed hydrophobic fiber in less extreme conditions. Also, if the exhaustion of dye is large enough, there will be less colored wastewater and less harm to the environment.

EXPERIMENT

Raw, undyed 100 % polyester (polyethylene terephthalate) fibers have been used which is common in practice with the following characteristics: length 90 mm, fineness 1.5 dtex, tenacity 51.7 $cN \cdot tex^{-1}$, elongation at break 34.5 %.

Before dyeing 1 g of the PES fibers have been modified by water solution (50 dm^3) of NaOH, KOH and $Al(OH)_3$ for 30 min, fibers: liquor ratio has been 1:50 while the temperature of the process has been 60 °C.

Dyeing of this modified PES fibers has been performed by disperse dye C.I. Disperse Blue 81, molecular formula $C_{14}H_9BrN_2O_4$ and molar mass of 349.14 $g \cdot mol^{-1}$, at 98 °C, without carriers. According to its molecular structure, the dye is classified into anthraquinones and is shown in Figure 1.

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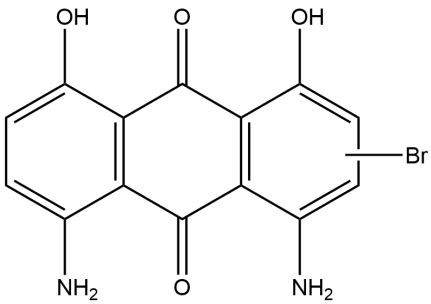

Figure 1. Structure of the applied disperse dye C.I. Disperse Blue 81 (by software ChemBioDraw Ultra 14.0)

The test of dyeing-adsorption has been performed in the way that 1 g of fibers have been dyed in the solution of a constant volume of 0.1 dm^3 on a shaker with a turn of 120 rpm; dye concentration has been 50, 100, 150 and 200 $mg \cdot dm^{-3}$. The time of adsorption–dyeing has been 5, 10, 20, 40 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. The aqueous solution of the dye has had the dispersing agent (Dispersant SP, Achitex Minerva, Italy) 1.5 $g \cdot dm^{-3}$ and formic acid (pH=4.5), whereas the temperature of the dye has been 98 °C.

For determining the concentration of dye in the solution, UV–VIS spectrophotometry and apparatus Cary 100 Conc UV–VIS, Varian (absorption maximum on 630 nm) have been used.

The dye exhaustion (9) or degree of exhaustion has been calculated via equation:

$$Dye\ Exhaustion = \frac{C_0 - C_t}{C_0} \cdot 100\ (\%) \quad [1]$$

where: C_0 and C_t ($mg \cdot dm^{-3}$) are the initial and dye concentration in time t.

The amount of the adsorbed dye (9) obtained via equation:

$$q_e = \frac{C_0 - C_e}{w} \cdot V \quad [2]$$

where: q_e ($mg \cdot g^{-1}$), the mass of adsorbed dye per mass unit of fibers in equilibrium; C_e ($mg \cdot dm^{-3}$), equilibrium dye concentration in the solution; w (g), the mass of fibers and V (dm^3), the volume of solution for dyeing.

The Dubinin–Radushkevich (D-R) isotherm can be applied for the estimation of apparent free energy and the characteristics of adsorption (10).

The Dubinin–Radushkevich equation defined by the following equation:

$$q_e = q_{mDR} \cdot \exp\left[-K_{DR} \cdot \left(R \cdot T \cdot \ln(1 + \frac{1}{C_e}) \right)^2 \right] \quad [3]$$

where K_{DR} is the Dubinin–Radushkevich isotherm constant related to the adsorption energy ($mol^2 \cdot kJ^{-2}$), q_{mDR} is the theoretical isotherm saturation capacity ($mg \cdot g^{-1}$), R is the gas constant (8.314 $J \cdot mol^{-1}\ K^{-1}$) and T is the temperature (K).

Hill (H) has proposed an isotherm model from the non-ideal competitive adsorption model to define different adsorbate binding on a homogeneous surface of adsorbent (10).

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This isotherm model undertakes that the adsorption is basically a cooperative manifestation, including the ligand-binding capability at one site onto the macromolecule, influencing various binding sites onto the same macromolecule.

The Hill isotherm can be represented as follows:

$$q_e = \frac{q_{mH} \cdot C_e^{n_H}}{K_H + C_e^{n_H}} \quad [4]$$

If n_H is greater than 1, this isotherm indicates positive cooperativity in binding, n_H is equal to 1, it indicates non–cooperative or hyperbolic binding and n_H is less than 1, indicating negative cooperativity in binding.

Marczewski–Jaroniec (M–J) isotherm (10) which is as well recognized as the four-parameter general Langmuir equation is recommended based on the suppositions of local Langmuir isotherm and the adsorption energies distribution in the active sites.
Marczewski–Jaroniec isotherm is expressed as follows:

$$q_e = q_{mMJ} \cdot \left(\frac{(K_{MJ} \cdot C_e)^{n_{MJ}}}{1 + (K_{MJ} \cdot C_e)^{n_{MJ}}} \right)^{\frac{m_{MJ}}{n_{MJ}}} \quad [5]$$

The parameter n_{MJ} and $m_{MJ,}$ characterize the heterogeneity of surface, can vary from 0 to 1. This isotherm reduces to Langmuir isotherm for the value of both n_{MJ} and m_{MJ} equal to 1, to Langmuir-Freundlich isotherm for n_{MJ} equal to m_{MJ} connected with the symmetrical quasi-Gaussian energy distribution and to the Toth isotherm for m_{MJ} equal to 1 corresponding to asymmetrical quasi-Gaussian energy distribution. The parameter m_{MJ} describes the spreading of the distribution in the path of higher adsorption energies, while n_{MJ} describes this spreading in the path of lesser adsorption energies.

Fritz-Schlunder (F-S) have proposed a five-parameter empirical expression which can represent a broad field of equilibrium data (9):

$$q_e = \frac{q_{mFS} \cdot K_1 \cdot C_e^{m_1}}{1 + K_2 \cdot C_e^{m_2}} \quad \text{with } m_1 \text{ and } m_2 \leq 1 \quad [6]$$

where q_e is the adsorbed amount at equilibrium (mg·g^{-1}), C_e the equilibrium concentration of the adsorbate (mg·dm^{-3}), q_{mFS} the Fritz-Schlunder maximum adsorption capacity (mg·g^{-1}) and K_1, K_2, m_1, and m_2 are the Fritz-Schlunder parameters.

RESULTS AND DISCUSSION

Alkali hydrolysis leads to the greatest mass loss of PES fibers (9-11.0 %). Physical characteristics vary slightly, the tenacity falls slightly (5-10 %), and elongation at break shows a small increase (3-6 %), all compared to untreated samples of PES fibers.

The level of dye exhaustion in the dyeing of alkali hydrolyzed PES fibers has shown in Figure 2. The results are shown only for the previous treatment of fiber with potassium hydroxide since this pre-treatment showed the best results of the degree of exhaustion compared to pre-treatment with sodium or aluminum hydroxide.

These results can confirm the fact that alkali pre-treatments change surface morphology of PES fibers, increasing the porosity (during the previous process in alkali solution), decreases the size of dye particles so that more individual molecules of disperse

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dye are present in water, and there are real chances that the applied alkali increased fibers permeability, which gives the possibility to a greater number of dye molecules to diffuse into PES fibers (11).

In the process of dyeing of raw PES fibers, i.e. in the disperse dye adsorption process for PES fibers, the degree of dye exhaustion ranges from 10 % (18.2 % for KOH modified PES fibers) to 60 % (69.9 % for KOH modified PES fibers) for an initial dye concentration of 200 mg·dm^{-3} at the time of dyeing 5 and 60 min.

Isotherm adsorption is of essential significance for investigation of the process of dyeing at a temperature of 98 °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 (12).

In this investigation, nonlinear isothermal two-, three-, four- and five-parameter models, i.e. D-R, H, M-J and F–S equation have been used. For the fitting of experimental points, a "trial-and-error" non-linear regression method has used, which is implemented using Microsoft Excel software (12).

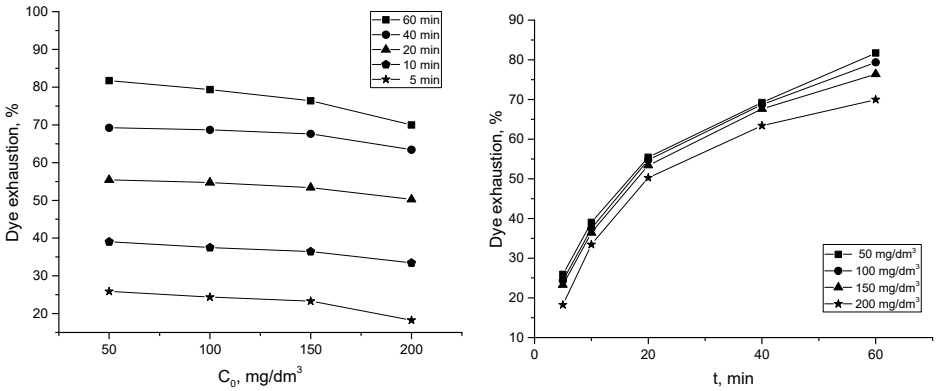

Figure 2. The level of exhaustion of dye on PES fibers during a different time and initial concentrations

This software was used to compare and optimize isotherms using optimization to minimize the residual sum of squares error (SSE) or maximize the coefficient of determination (R^2) between the experimental and the modeled values.

Figure 3 gives a comparable display of isothermal models of D-R, H, M-J and F-S through the nonlinear fitting of experimental data. Parameters of models obtained from nonlinear regression are listed in Table 1. SSE (0.26) and R^2 (0.995) in five-parameter F-S isotherm is the highest of the four models, which confirms the fact that this model is the most efficient in nonlinear simulating of isothermal adsorption of disperse dye on PES fibers, which can be noticed at a visual review of nonlinear curves in a diagram of Figure 3. Then, three-parameter H model follows, also with high SSE (1.48) and a smaller R^2 (0.973), then four-parameter M–J model which has poorer statistical parameters, SSE (4.32) and R^2 (0.922) and finally, two-parameter D-R with the worst results (SSE=6.09 and R^2=0.891). F-S, as five-parameter isotherm is dominant, according to the cover of

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experimental points, even though the other nonlinear models are not far away, especially H model.

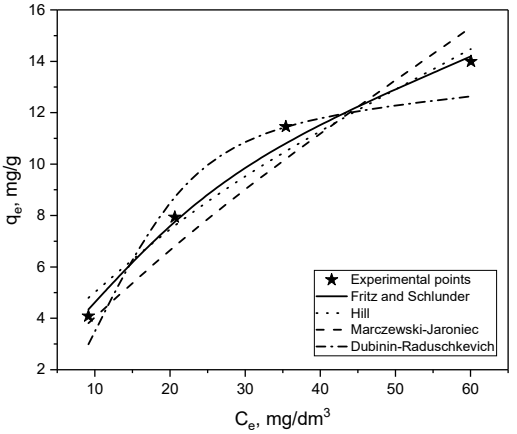

Figure 3. Nonlinear adsorption isotherms during PES fibers dyeing

Table 1. Analytic equations of nonlinear isotherms with coefficients for the system dye-PES fibers

An analytic expression of a nonlinear model	Model parameters		SSE	R^2
Dubinin–Radushkevich: $q_e = 13.12 \cdot \exp\left[-1.4 \cdot 10^{-5} \cdot \left(3084.5 \cdot \ln(1+\frac{1}{C_e})\right)^2\right]$	q_{mDR}, mg/g	13.12	6.09	0.891
	K_{DR}, mol^2/kJ^2	$1.4 \cdot 10^{-5}$		
Hill: $q_e = \frac{3.3 \cdot 10^6 \cdot C_e^{0.59}}{2.5 \cdot 10^6 + C_e^{0.59}}$	q_{mH}, mg/dm^3	$3.3 \cdot 10^6$	1.48	0.973
	n_H, –	0.59		
	K_H, –	2.5 10^6		
Marczewski–Jaroniec: $q_e = 1.3 \cdot 10^{-6} \cdot \left(\frac{\left(1.3 \cdot 10^{-5} \cdot C_e\right)^{0.05}}{1+\left(1.3 \cdot 10^{-5} \cdot C_e\right)^{0.05}}\right)^{-35}$	q_{mMJ}, mg/g	$1.3 \cdot 10^{-6}$	4.32	0.922
	K_{MJ}, dm^3/mg	$1.3 \cdot 10^{-5}$		
	n_{MJ}, –	0.05		
	m_{MJ}, –	-1.75		
Fritz–Schlunder: $q_e = \frac{0.59 \cdot C_e^{0.86}}{1+7.8 \cdot 10^{-5} \cdot C_e^{2.14}}$	q_{mFS}, mg/g	0.35	0.26	0.995
	K_1, –	1.71		
	K_2, –	$7.8 \cdot 10^{-5}$		
	m_1, –	0.86		
	m_2, –	2.14		

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CONCLUSION

It is shown that dye adsorption of alkali modified fibers has increased, the dye exhaustion grows in comparison with the raw sample.

The five-parameter nonlinear model of F-S is the most efficient in simulating isothermal adsorption of disperse dye on PES fibers.

Other adsorption models, D-R, H, and M-J give poorer results and can not be used to explain the adsorption of the disperse dye for PES fibers.

The results of this work achieved by these effects indicate the possibility of a 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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