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EQUILIBRIUM MODELING OF ACRYLIC DYEING WITH CATIONIC DYES

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Abstract: *This article presents a complex set of research activities related to the sorption analysis of the process of dyeing acrylic fibers with cationic dyes to clarify the complex events during the adsorption of dye molecules for fibers and their diffusion into the interior. Typical acrylic fibers were used for dyeing with cationic blue dye. The fiber samples were dyed in a constant bath, the initial dye concentration and dyeing time were varied. The results reveal that the degree of dye exhaustion on acrylic increases as the initial concentration of dye increases. A longer time carries a higher degree of exhaustion, the same happens with the amount of adsorbed dye per unit mass of the acrylic. Isothermal linear modeling of the dyeing process gives results according to which the Langmuir model best covers the experimental points, thus confirming the existence of monolayer dye adsorption, with a uniform distribution of adsorption heat and affinity over the homogeneous fiber surface. The Freundlich and Hill–de Boer isotherm models give somewhat weaker results for the interpretation of equilibrium acrylic dyeing.*

Key words: *acrylic fibers, cationic dye, dyeing, isotherm models, dye exhaustion.*

1. INTRODUCTION

Acrylic fibers are widely used in the textile industry for the production of various textile materials and products. Acrylic fibers have a small amount of anionic centers, so they can be easily dyed with dyes that have a positive charge, i.e. cationic dyes. Cationic dyes bind to acrylic fiber by ionic bonds and are by far the most important class of dyes used for these fibers. In terms of performance, acrylic fibers are very similar to wool, they have a number of excellent properties, such as good elasticity, softness and voluminousness. Acrylic fiber textiles usually exhibit bright color, good light fastness, excellent antibacterial properties and insect resistance. Depending on the use, acrylic fibers can be processed into pure products or mixed with other fibers. Acrylic-based fabrics are widely used in clothing, home textiles and decoration [1].

When the acrylic fiber comes into contact with the cationic dye, a high mutual affinity occurs. They combine rapidly with the anionic groups of acrylic fibers, which usually results in uneven adsorption and poor even properties.

In addition to the rapid adsorption of dyes on the surface of acrylic fibers, it is also important how the dyes diffuse into the interior of the fiber. Under normal conditions, there are not enough gaps, ie. the intermolecular space in the fibers is very small, so cationic dyes hardly diffuse into the acrylic fibers. Usually, this problem is solved by increasing the dyeing temperature. A lot of water and energy is consumed during dyeing. The problem of poor evenness is solved by adding surfactants to the dye bath. All of this puts an additional burden on the quality and quantity of waste water, making treatment more difficult. To meet the demands of cleaner production, new highly efficient and environmentally friendly dyeing techniques are being tested [2].

Acrylic fibers have a pronounced molecular structure, a well-developed crystalline region, small cavities and a hydrophobic surface. All this makes it difficult to dye with high molar mass dyes, which is why acrylic fibers are mostly dyed at temperatures above 95 °C. The glass transition temperature (Tg) of acrylic fibers plays an important role in the dyeing of these fibers. At temperatures lower than Tg, the diffusion of dye molecules into the fibers is difficult due to the regular structure, at temperatures higher than Tg the thermoplasticity and mobility of segments of the polymer chains increases and facilitates the diffusion of dye molecules into the fibers. Therefore, a further increase in temperature causes an increase in the adsorption of dye on acrylic fibers [3].

Finishing textile material by dyeing, from a theoretical and practical point of view, is a very complex procedure. Practically speaking, textile dyeing is the pinnacle of finishing, which gives the textile material a final, visually improved, and commercially usable product appearance. When dye molecules enter the fiber, their movement is restricted not only due to the influence of physical bonding forces but also due to the molecular structure and physical properties of the fibers [4].

Important factors in the dyeing process are the chemical composition and structure of the fiber. Dyeing systems are complex, multi-component and largely determined by the relationship between fiber properties and dye properties. Determining a direct and precise correlation between the chemical structure of the fibers and the chemical structure of the dye cannot be fully achieved, considering the complexity of the fibers as a substrate, the complexity of the dye structure, and the large number of parameters that act in the dyeing process [5].

Studio research in the field of textile dyeing has always been a challenge for researchers because it is a very interesting, always current, and perspective-innovative area of textile technology. Every new knowledge in this area, in addition to the efficiency for which it was first designed, implies a review of the background, ie. the consequence of the application of new technologies on the environment and therefore environmental protection [6].

This paper presents a complex set of research activities related to the sorption analysis of the process of dyeing acrylic fibers with cationic dyes to clarify the dynamic and therefore very complex events during the adsorption of dye molecules for fibers and their diffusion into the interior. Understanding these activities will facilitate the understanding of dyeing conditions and the definition of specific parameters decisive for the achievement of even dyeing, as well as high dye exhaustion.

2. EXPERIMENTAL PART

2.1 Materials and Methods

In the experimental part of the work, acrylic fibers (Lebanteks, Serbia) with basic properties were used: fineness 2.5 dtex, breaking strength 10 cN, and breaking elongation 22%. Cationic dye C.I.Basic Blue 41 (Textilcolor, Switzerland), molecular formula $C_{20}H_{26}N_4O_6S_2$, and molar mass 482.57 g/mol, was used for dyeing.

The dye used belongs to the mono azo class of dyes, it is a dark purple powder, soluble in water, and it is used for dyeing acrylic and wool fibers, knitted fabrics, fabrics, carpets, etc.

The dyeing-adsorption test was performed in such a way that a 0.5 g acrylic sample was dyed in a constant volume solution of 50 cm^3, with different dye concentrations (10, 20, 30, 40, 50, and 60 mg/dm^3). Distilled water was used in all dyeing cases. The dyeing time was 10, 20, 30, 50 and 60 min. The equilibrium time of dyeing is 60 min, namely, it has been shown that with longer dyeing there are no significant changes in the degree of exhaustion of this dye. The aqueous dye solution also contained electrolyte Na_2SO_4 (10%), while the dyeing temperature was 95 °C, in an acidic medium, pH 4.5.

UV-VIS spectrophotometry and a Cary 100 Conc UV-VIS device, Varian (absorption maximum at 590 nm) were used to determine the concentration of the dye in the solution.

The degree of dye exhaustion [7] is calculated using the equation:

$$Exhaustion\ degree = \frac{C_0 - C_t}{C_0} \cdot 100\ \ (\%) \quad \textbf{(1)}$$

where: C_0 and C_t (mg/dm^3) - initial and dye concentration at time t.

The amount of adsorbed dye [8] was obtained through the forms:

$$q_t = \frac{C_0 - C_t}{w} \cdot V \qquad \text{and} \qquad q_e = \frac{C_0 - C_e}{w} \cdot V \quad \textbf{(2)}$$

where: q_t (mg/g) - mass of adsorbed dye per unit mass of fibers in dyeing time t; q_e (mg/g) - mass of adsorbed dye per unit mass of fibers in equilibrium; C_e (mg/dm^3) - equilibrium concentration of the dye in the solution; w (g) - fiber mass and V (dm^3) - volume of dyeing solution.

The Langmuir linear isotherm [9] was used to quantitatively describe the adsorption:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b \cdot q_m} \cdot \frac{1}{C_e} \quad \textbf{(3)}$$

where: q_e - adsorption capacity (mg/g); C_e - equilibrium concentration of adsorbate in solution (mg/dm^3); q_m - the maximum amount of adsorbate on the sorbent (mg/g); b - the ratio of adsorption rate constant and adsorbate desorption rate constant (dm^3/mg).

The Freundlich model is represented by the following linear equation [10]:

$$ln\, q_e = ln\, K_F + \frac{1}{n} ln\, C_e \quad \textbf{(4)}$$

where: K_F $(mg/g)\cdot(dm^3/mg)^{(1/n)}$ and n - constants characteristic of the observed system: cationic dye, acrylic and water.

The Hill–de Boer linear equation was used to describe the case of mobile sorption with lateral interaction between adsorbed dye molecules [11]:

$$ln\left[\frac{C_e \cdot (1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = ln\, K_1 - \frac{K_2 \cdot \theta}{R \cdot T} \quad \textbf{(5)}$$

where: K_1 - Hill–de Boer constant (dm^3/mg); θ - fractional (partial) coverage; R - universal gas constant (kJ/mol·K); T - temperature (K); K_2 - energy constant of interaction between adsorbed molecules (kJ/mol).

3. RESULTS AND DISCUSSION

The influence of initial dye concentration on dye exhaustion and amount of adsorbed cationic dye during standard dyeing, for different times, is given by diagrams in Figure 1 and 2. There is continuity in the changes during the growth of the initial dye concentration. With the increase in dye concentration, the degree of dye exhaustion from the dyeing bath decreases, and the amount of

adsorbed dye increases. With the increase in the concentration of the dye in the solution, initially, there is a slightly weaker decrease in the percentage of exhausted dye, but at the end of the dyeing, after C_0=50 mg/dm^3, this decrease would be more intense, for each dyeing time, from 10 to 60 min. The longest dyeing time causes the highest degree of exhaustion and the highest amount of dye adsorbed by the fibers.

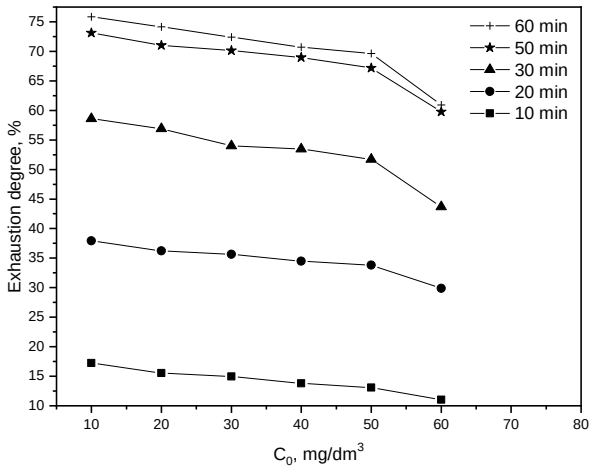

***Fig. 1**: Degree of dye exhaustion vs initial dye concentration*

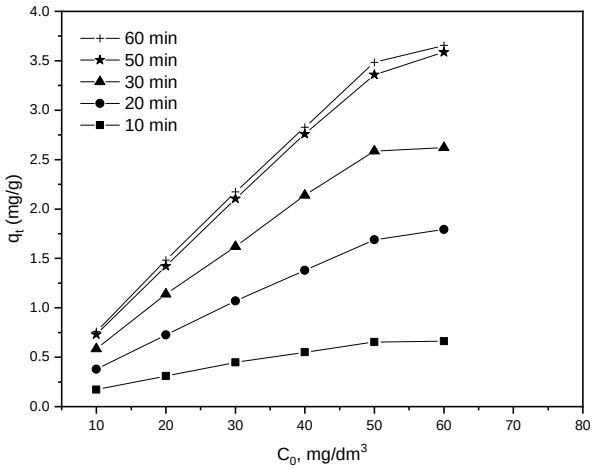

***Fig. 2**: Degree of the amount of adsorbed cationic dye vs initial dye concentration*

Figure 3 gives a comparative representation of the mentioned Langmuir models, through linear fitting of experimental data. The high functionality of the variables is noticeable in the diagrams, which indicates the fact that the Langmuir adsorption isotherm can be taken seriously in consideration of the explanation of the sorption of cationic dye on acrylic fibers. The fitted curves pass through the experimental points with a slight deviation.

The parameters of Langmuir sorption model, as well as the values of the coefficients of determination R^2, are given in Table 1.

According to the values of R^2, from tab. 1, it can be seen that the adsorption of blue cationic dye on acrylic has very high values (0.998), which assumes the absolute functionality and acceptability of the monolayer sorption model for the description of the equilibrium dyeing.

The equilibrium parameter, R_L, lies between 0 and 1, i.e. the value is 0.29, which means that the adsorption of the cationic dye is suitable for acrylic (tab. 1).

Once a dye occupies a site, no further adsorption can take place at that site; intermolecular attractive forces decrease rapidly as the distance increases. There is no interaction between dye molecules adsorbed on neighboring sites, adsorption on the surface is localized, which means that the adsorbed molecules are present at specific and localized sites [12].

According to the visual inspection of the linear regression line from the diagram in Figure 4, it is observed that the Freundlich model covers the experimental points very well, ie. the position of the regression line is very close to the ideal position of the fitted curve that follows the closest path to the experimental points.

The results from Table 1 confirm that $n > 1$, that is, $1/n < 1$, ($1/n = 0.73$), which shows that the dye adsorbs well under the given test conditions. Values of the parameter n close to unity indicate a reduced intensity of adsorption and represent a guide in which direction and in which way the dyeing process should be conducted [13].

Also, according to the data from Table 1, it is noted that the coefficient of determination of the Freundlich isotherm (0.968) is weaker compared to the one obtained for the Langmuir expression, which means that it is a good but not the best functionality.

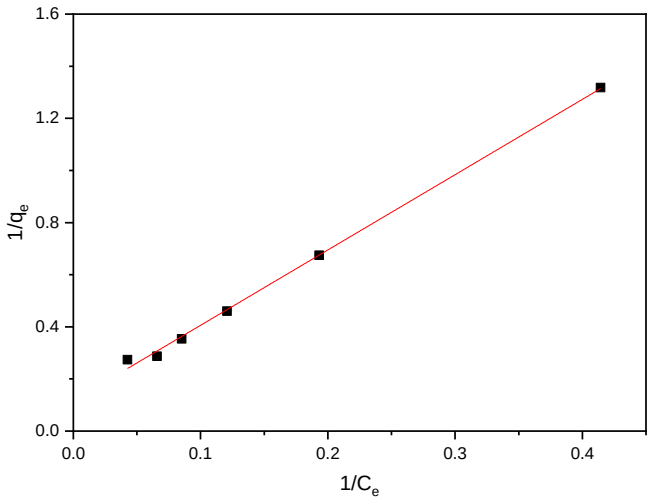

***Fig. 3**: Langmuir linear regression models for equilibrium dyeing of acrylic fibers*

The existence of mobile sorption with lateral interactions between adsorbed dye molecules was verified using the Hill–de Boer equation. The graphical representation of this model is done through the diagram in Figure 5 and obviously, the linearity of the fitted curve is present about the experimental points.

More specifically, quantitative analysis, through the data given in tab. 1 and the amount of the statistical parameter (R^2=0.907), confirms a good result, with the indication that the results of this isotherm cannot be accepted for the dominant description of coloring. There is the presence of lateral interactions between cationic dye molecules on the surface of acrylic fibers.

Given that the parameter K_2 has a positive value and a high value, it means that there is an attraction between adsorbed dye molecules, otherwise there would be repulsion [11].

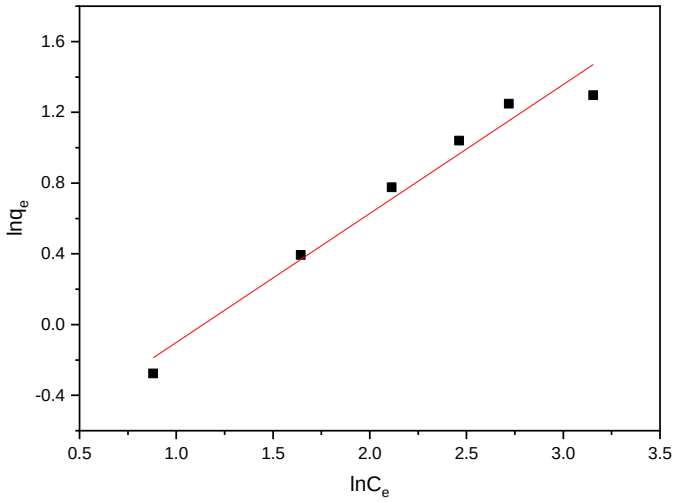

***Fig. 4**: Freundlich linear regression models for equilibrium dyeing of acrylic fibers*

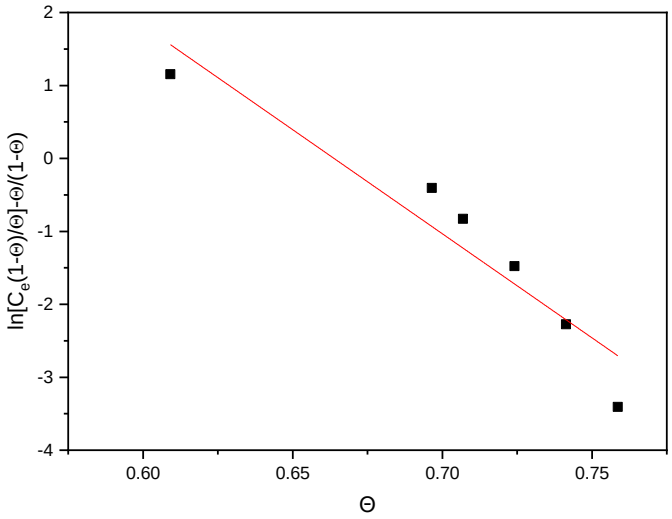

***Fig. 5**: Hill de Boer linear regression models for equilibrium dyeing of acrylic fibers*

Table 1: *Analytical expressions of linear isotherms with coefficients for the cationic dye–acrylic fiber system*

Model	Analytical expression	Model parameters		R^2
Langmuir	$\frac{1}{q_e} = \frac{1}{8.54} + \frac{1}{0.34} \cdot \frac{1}{C_e}$	q_m, mg/g	8.54	0.998
		b, dm^3/mg	0.04	
		R_L	0.29	
Freundlich	$ln\, q_e = -0.84 + 0.73 \cdot ln\, C_e$	K_F, (mg/g)·(dm^3/mg)$^{(1/n)}$	0.43	0.968
		n	1.37	
Hill-de Boer	$ln\left[\frac{C_e \cdot (1-\Theta)}{\Theta}\right] - \frac{\Theta}{1-\Theta} = 18.95 - 28.92 \cdot \Theta$	K_1, dm^3/mg	$5.9 \cdot 10^{-9}$	0.907
		K_2, kJ/mol	88.49	

5. CONCLUSIONS

When dyeing, one should be very careful when designing the final form, given that the textile material is a very complex system with a large number of variable parameters. According to the results of the research on the dyeing of acrylic fibers, the results that could be accepted and used more can be singled out.

By modeling the dyeing process, data is obtained that connect the concentration of dye, temperature, the presence of electrolytes, and the efficiency of the achieved dyeing on acrylic, that is, the amount of waste dye left in the bath after dyeing.

The process of dyeing acrylic fibers with a typical representative of cationic dyes of various concentrations gives good results at 95 °C. The degree of dye exhaustion on acrylic increases during the increase of the initial dye concentration. A longer time carries a greater degree of exhaustion. At lower initial dye concentrations, a higher percentage of exhaustion occurs and this trend is maintained mostly throughout the dyeing process. A larger amount of dye in the solution or a longer dyeing time results in a slightly larger amount of adsorbed dye per unit mass of the adsorbent.

Isothermal linear modeling of the dyeing process gives results according to which the Langmuir model best covers the experimental points, followed by the Freundlich model, and finally the Hill-de Boer isotherm. In the specific case of dyeing, the existence of monolayer dye adsorption is confirmed, with a uniform distribution of adsorption heat and affinity over a homogeneous surface.

REFERENCES

[1] Z. Zhang, A. Yuan, H. Wang, L. Zhu, H. Xu, C. Zheng, *"Effects of solvent properties on cationic dyeing process of acrylic yarn"*, Korean J. Chem. Eng., vol. 31, pp. 719-723, 2014.

[2] M. Naeimi, M. G. Afjeh, A. A. Gharehaghaji, F. Zeighami, *"Dyeing Behavior of Polyacrylonitrile Nanofibers: Physicochemical Parameters of Dyeing with Basic Dye in Comparison with Regular Polyacrylonitrile Fibers"*, Fibers Polym., vol. 18, pp. 1724-1733, 2017.

[3] A. Hou, H. Chen, Y. Xu, X. Yang, Y. Zhang, K. Xie, A. Gao, *"Rapid and environmental-friendly continuous gel-dyeing of polyacrylonitrile fiber with cationic dyes"*, J. Cleaner Prod., vol. 274, pp. 122935, 2020.

[4] V. Frunze, M. Irovan, *"Innovative Bio-Dyeing Techniques For The Promotion Of Traditional Motifs"*, Annals Of The University Of Oradea Fascicle Of Textiles, Leatherwork, vol. 24, pp. 45-50, 2023.

[5] A. Singh, J. Sheikh, *"Synthesis of a Novel Cationic Dye to Impart Mosquito-Repellent and UV Protection to an Acrylic Fabric"*, ACS Omega. vol. 8, pp. 10214−10224, 2023.

[6] E. F. C. Chauque, L. N. Dlamini, A. A. Adelodun, C. J. Greyling, J. C. Ngila, *"Electrospun polyacrylonitrile nanofibers functionalized with EDTA for adsorption of ionic dyes"*, Phys. Chem. Earth., vol. 100, pp. 201–211, 2017.

[7] L. Chirila, E-C. Mitran, I. Dumitrescu, E. Perdum, O. G. Iordache, D. Stefanescu, M. Pislaru, I. Mancasi, *"Effect Of Brasi-Color Dye On Uv Protection Of Bamboo Knitted Fabrics"*, Annals Of The University Of Oradea Fascicle Of Textiles, Leatherwork, vol. XIX, pp. 31-36, 2018.

[8] A. A. Adeyi, S. N. A. Md Jamil, L. C. Abdullah, T. S. Y. Choong, *"Adsorption of Malachite Green Dye from Liquid Phase Using Hydrophilic Thiourea-Modified Poly (acrylonitrile-co-acrylic acid): Kinetic and Isotherm Studies"*, J. Chem., vol. 2019, pp. 1–14, 2019.

[9] S. Sombatdee, S. Saikrasun, *"Structures and dyeing performances of polyethyleneimine-carbamate linked bamboo viscose fibers dyed with lac"*, Text. Res. J., vol. 90, pp. 179-193, 2020.

[10] B. Noroozi, G. A. Sorial, *"Applicable models for multi-component adsorption of dyes: A review"*, J. Environ. Sci., vol. 25, pp. 419–429, 2013.

[11] N. Ayawei, A. N. Ebelegi, D. Wankasi, "Modelling and Interpretation of Adsorption Isotherms", J. Chem., vol. 2017, pp. 1–11, 2017.

[12] C. Qin, R-C. Tang, G. Chen, *"Preparation of Fluorescent Acrylic Fabrics"*, presented at the International Conference on Dyeing and Finishing EXCO, Daegu, Korea, March 13, 2009.

[13] A. Haji, A. M. Shoushtari, M. Abdouss, *"Plasma activation and acrylic acid grafting on polypropylene nonwoven surface for the removal of cationic dye from aqueous media"*, Desalin. Water Treat., vol. 53, pp. 3632-3640, 2015.