Kragujevac J. Sci. 44 (2022) 37–43.
doi: 10.5937/KgJSci2244037N

UDC 677.494.675: 547.556.33
Original scientific paper

EQUILIBRIUM SORPTION OF REACTIVE DYE ON POLYAMIDE

Milena M. Nikodijević*, Dragan M. Đorđević

University of Niš, Faculty of Technology, Republic of Serbia,
Bulevar oslobođenja 124, 16000 Leskovac, Serbia
*Corresponding author; E-mail: nikmilena94@gmail.com

(Received October 5, 2021; Accepted December 12, 2021)

ABSTRACT. The equilibrium sorption of dyeing polyamide 6.6 fabric with reactive dye is presented in this paper. Polyamide is a chemical fiber obtained from synthetically produced polymers, while reactive dyes are most often sulfonated azo compounds: which are derived from bendisidine and its derivatives. The solution in a constant volume contained dye concentrations of 5, 10, 15, 20, 30, 40 and 50 mg/L. The samples were dyed at temperatures of 40, 60 and 98°C. A spectrophotometer (Cary 100 Conc UV-VIS, Varian) was used to measure the absorbance of aqueous dyed solutions and to calculate the unknown dye concentration in the solution and to construct a calibration curve. The degree of dye exhaustion and the amount of absorbed dye were calculated. Two models of adsorption isotherms were used: *Freundlich* and *Florry-Huggins*. The high functionality of the variable was observed in the *Freundlich* model.

Keywords: polyamide, dyeing, sorption, reactive dye

INTRODUCTION

Polyamides are reinforced polymer composites that should meet increasingly stringent environmental requirements due to different fiber composition and matrix. With the development of the polymer fiber industry, there is a significant incentive to explore the possibility of high efficiency of polymer fiber that can be used to strengthen polymer matrices of identical or similar composition (GONG and YANG, 2009).

Polyamide is well known for its high performance. Due to their good durability, polyamide fibers are widely used in the clothing industry. In the family of polyamide fibers, polyamide 6.6 fibers have relatively better mechanical properties and this fibers are used in the production of tires, airbags, and body armor (IREMONGER and WENT, 1996).

Polyamide 6.6 fiber is used to successfully achieve a new high-volume fraction of polymer fiber/polymer composites by hot compression process. During hot compaction, the surface of the fiber is partially melted to form the temperature of the matrix, which resulted in obtaining glass at low temperature (HINE and WARD, 2006).

Reactive dyes provide high humidity (better than cheaper direct dyes), but their use is not always possible due to difficulties in achieving uniformity of dye. The stability of chlorine is slightly lower than direct dyes, as well as the stability of light in extreme conditions (HARFI and HARFI, 2017).

Reactive dyes are the only textile dyes designed to form a covalent bond with the material during the dyeing process with reactive dyes allowing for a wide range of shades of good light fastness and excellent washing resistance when cotton is dyed. Such properties allow this type of dye to reach the quality market (FAROUK and GAFFER, 2013).

Reactive dyes used for dyeing cellulose, but increasingly used for wool and polyamide. The first commercial of reactive dyes for dyeing cotton were based on the dichloro-s-triazine reactive group (GAO and CRANSTON, 2008).

In this paper, the equilibrium sorption of reactive dye during dyeing on polyamide 6.6 fabric was investigated. The aim of the research is to expand the spectrum of dyes that can be used to dye polyamide, as well as to model the equilibrium sorption of reactive dye when dyeing polyamide fabric.

MATERIALS AND METHODS

In the experimental part, 100% raw polyamide 6.6 fabric (Jumko, Vranje) was used. The longitudinal mass of the warp is 10.85 tex, and of the weft is 11.11 tex. The surface mass of the fabric is 96 g/m^2. The dyeing was performed in erlenmeyers in which samples of polyamide 6.6 fabric in a solution of citric acid and reactive dye were placed. pH of solution was 4. The erlenmeyers were heated for 60 minutes. The amount of citric acid was 5 g/mL. The used dye is Reactive Brown 18 (Sparrowings, Gujarat, India). The samples were dyed with different concentrations of dye: 5, 10, 15, 20, 30, 40, 50 mg/L. The temperature at which the samples were dyed was 40, 60 and 98°C. Conventionally, high temperatures are used for dyeing polyamides, i.e. 80°C and above, however, in this study, both 40 and 60°C were used to test the dyeing efficiency at lower temperatures compared to conventional dyeing. After dyeing, the absorbance of the cooled solution was measured at the maximum wavelength for the dye, using a spectrophotometer (Cary 100 Conc UV-VIS, Varian). The absorption maximum for the dye used is 470 nm. Also, a calibration curve was made to determine the unknown dye concentration during dyeing.

The degree of dye exhaustion was calculated using the form (TAYEBI *et al.*, 2015):

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

where: C_0 and C_t (mg/L), initial and dye concentration at time *t*.

The amount of absorbed dye per unit mass of adsorbent (absorption capacity) was obtained using equation [9]:

$$q_t = \frac{C_0 - C_t}{w} \times V \quad and \quad q_e = \frac{C_0 - C_e}{w} \times V \quad (2)$$

where q_t (mg/g), mass of absorbed dye per unit mass at dye time *t*; q_e (mg/g), mass of absorbed dye per unit mass in equilibrium, C_o (mg/L), initial dye concentration; C_t (mg/L), dye concentration in solution at dyeing time *t*, C_e (mg /L), equilibrium dye concentration in solution; *w* (g), mass of sample and *V* (dm^3), volume of dyed solution.

The most important multilayer adsorption isotherm for heterogeneous surfaces is the *Freundlich* adsorption isotherm, the linear form of this isotherm is expressed as (NETHAJI *et al.*, 2013):

$$log\ q_e = log\ K_F + \frac{1}{n}\ log\ C_e \quad (3)$$

where K_F (g/L) is the *Freundlich* constant, and *n* (g/L) is the Freundlich exponent, C_e (mg/L) is the dye concentration in the solution after dyeing.

The *Florry-Huggins* model is shown by the following equation (LATIF *et al.*, 2018):

$$log\left(\frac{\theta}{C_e}\right) = log\, K_{FH} + \alpha_{FH} log\,(1-\theta) \quad (4)$$

α_{FH} is the number occupied by sorption sites, and K_{FH} is the adsorption equilibrium constant, C_e is the concentration of dye in the solution after dyeing (mg/L), θ - the degree of surface coverage by the membrane. The values of K_{FH} and α_{FH} can be obtained from the cross section and slope of the graphs (θ/C_e) in relation to log (1-θ). The equilibrium constant K_{FH} can be used to calculate the Gibbs free energy for the sorption process.

RESULTS AND DISCUSSION

Figure 1 shows a graph, the degree of dye exhaustion at all concentrations, for different temperatures. At lower concentrations of dye solution, at the beginning there is a slightly larger drop in the percentage of exhausted dye, and at the end of dyeing this drop was somewhat milder. At the highest dyeing temperature, ie. 98°C, the highest degree of dye exhaustion occurs. As the temperature rises, the degree of dye exhaustion increases, which is to be expected. At a temperature of 40°C, there is a sharp drop in the degree of dye exhaustion at an initial dye concentration of 40 mg/L. At a temperature of 60°C, the degree of dye exhaustion is balanced, however, at an initial dye concentration of 40 mg/L, there is a sharp drop in the degree of dye exhaustion at all temperatures, where the curve is the steepest.

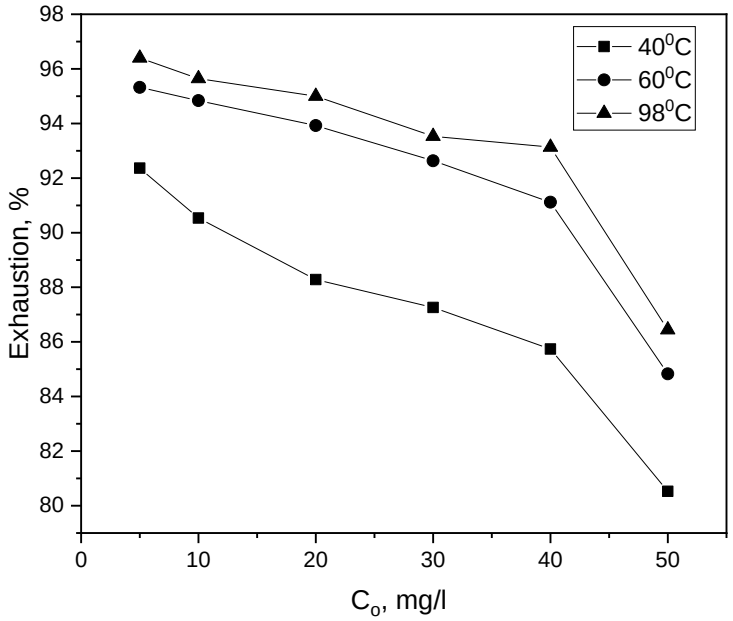

Figure 1. Influence of initial dye concentration on the degree of dye exhaustion during dyeing of polyamide 6.6 fabric

The results of the change in the adsorbed amount of adsorbate (dye) on the adsorbent (fabric) for different initial concentrations and temperatures are shown at the graph, in figure 2. There is continuity in the changes during the growth of the initial concentration and temperature, ie. a higher amount of dye in solution or a higher dyeing temperature contribute to a higher amount of adsorbed dye per unit mass of adsorbent, ie. at the highest initial dye concentrations and the highest dyeing temperature, the highest adsorption occurs.

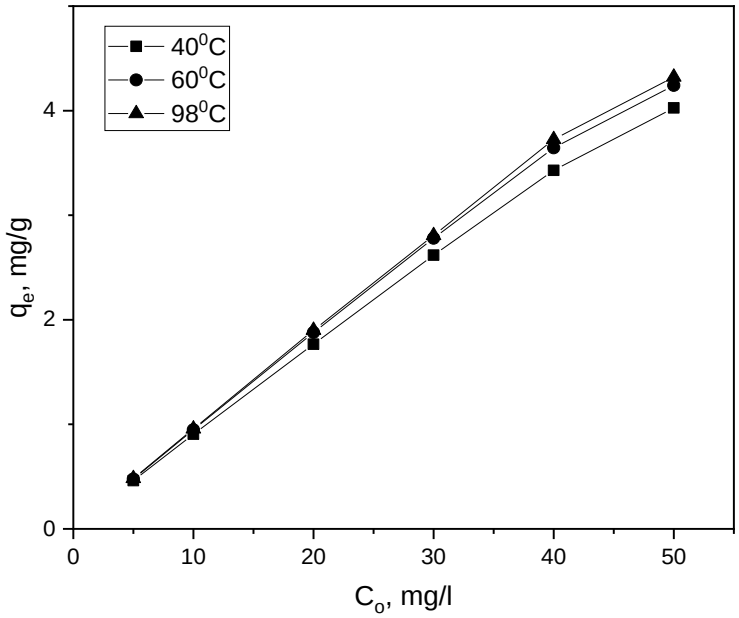

Figure 2. Adsorption capacity of polyamide 6.6 fabric during dyeing in relation to the initial concentration and temperature

The graph in figure 3 represents the *Freundlich* adsorption isotherm for dyeing polyamide 6.6 fabric at different temperatures. The values of *Freundlich* constants can be determined from these graphs, ie the slope and the section of the functional line.

Under the given experimental conditions, this graph depicts the high (R^2 = 0.990 - 40°C), (R^2 = 0.969 - 60°C), (R^2 = 0.960 - 98°C) functionality of the variables, which indicates the fact that the *Freundlich* adsorption isotherm may have an advantage in use in explanations for certain dye adsorption on fabric. The highest value of the coefficient of determination is suitable for temperatures of 40°C, i.e. R^2 = 0.990. According to this graph, there is no scattering of experimental data around the ideal fitting curve, which indicates *Freundlich's* adequacy for describing the adsorption equilibrium of the reactive dye-polyamide fabric system.

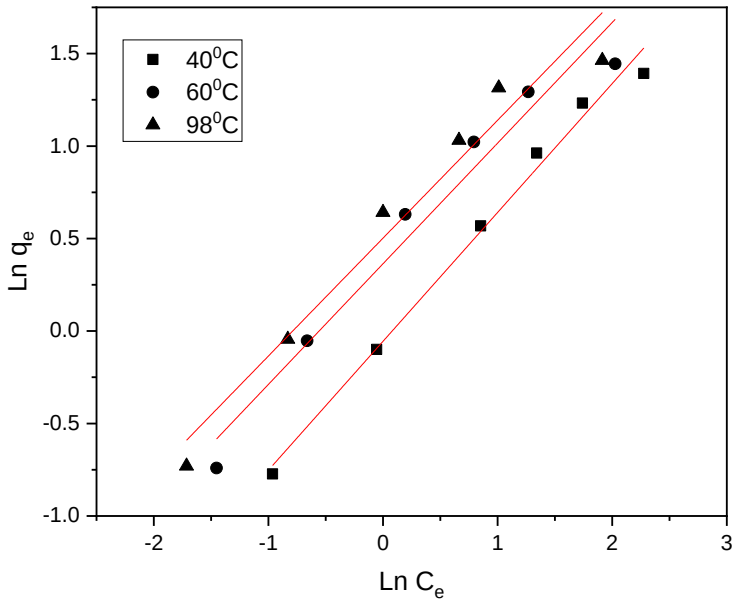

Figure 3. Graphic representation of a linear *Freundlich* model for dyeing polyamide 6.6 fabric at different temperatures

Florry-Huggins theory is based on a simple lattice model that can be used for nonideal solutions. In this model, the sizes of the lattice sites are chosen to be equivalent to the size of the solvent molecules. It is also assumed that the molecules in the solution have the same size. Therefore, either the solution or the solvent molecule can occupy one place at a given time. The increase in entropy due to the mixing of solvent and solute gives ΔSm which can be obtained by the *Boltzmann* relation: $\Delta Sm = k \ln \Omega$, where k is the *Boltzmann* constant, and Ω gives the total number of ways of arranging n_1 solvent molecules and n_2 dissolved molecules. In this study, the *Flory-Huggins* model was selected to take into account the characteristic surface coverage of the substrate molecule and the surface solvent molecule (DILL *et al.*, 2010).

Thus, the major source of entropy associated with mixing polymers should be translational or the fact that the whole polymer chain can access more configurations by being moved from a sample of pure polymer into a polymer blend or a solvent. In this light, we can view the whole chain as a large molecule gains translational entropy by having more locations to place its center of mass as we had in the regular solutions theory. This is equivalent to the entropy of an ideal gas (VERMA and MISHRA, 2010).

Figure 4 shows the *Florry-Huggins* isotherm for dyeing polyamide 6.6 fabric at different temperatures. This graph shows the high functionality of the variables (R^2 = 0.936 - 40°C), (R^2 = 0.797 - 60°C) and (R^2 = 0.792 - 98°C) *Florry-Huggins* constants were determined based on the slope and the section and evaluated the suitability of the model for describing the adsorption process of the used dye on polyamide 6.6 fabric. The highest value of the coefficient of determination is noticeable when dyeing polyamide fabric at 40°C, i.e. R^2 = 0.936.

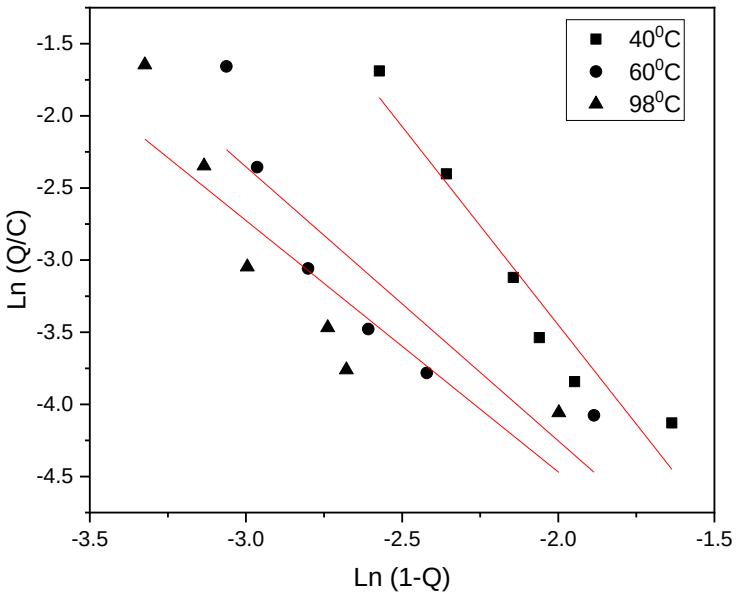

Figure 4. Graphic representation of a linear *Florry-Huggins* model for dyeing polyamide 6.6 fabric at different temperatures

Table 1 shows the values, adsorption parameters, analytical expressions of adsorption isotherms, and values of the coefficient of determination R^2. According to the results from table 1, a high value of the coefficient of determinism is observed, which indicates a large percentage of the sum of the squares of the deviation of the value of the variable from the arithmetic mean.

The *Freundlich* equation often provides an adequate description of adsorption data over a limited concentration range. In addition to the homogeneous surface, the *Freundlich* equation is also suitable for a very heterogeneous surface, which indicates multilayer adsorption. A value of *n* higher than 1 (n>1) indicates that adsorption takes place at a low concentration, but an increase in the adsorbed amount becomes less significant at a higher concentration and vice

versa. The higher the value of K_F, means the higher the intensity of adsorption (VERMA and MISHRA, 2010).

The *Flory-Huggins* isotherm model, which relates to the degree of surface coverage characteristics of the adsorbate on the adsorbent, can express the feasibility and spontaneous nature of the adsorption process. In this respect, the degree of coverage area, where K_{FH} and α_{FH} are an indicator of its equilibrium constant and model exponent.

Positive K_{FH} values (0.00013 for 40°C, 0.0003 for 60°C, 0.0003 for 98°C) are an indicator of feasible and spontaneous adsorption. Negative values of α_{FH} (-2.75 for 40 °C, -1.90 for 60°C, -1.74 for 98 °C) (Table 1) imply that the *Flory-Huggins* model can't be used to describe data on adsorption.

Table 1. Analytical expressions of linear isotherms with coefficients for the reactive dye system - polyamide 6.6 fabric

Models	Temp. (°C)	Analytical equations of the model	Model parameters		R^2
Freundlich	40	$ln\ q_e = +0.70\ ln\ C_e$	K_F n	0.94 1.43	0.990
	60	$ln\ q_e = +0.65\ ln\ C_e$	K_F n	1.44 1.53	0.963
	98	$ln\ q_e = +0.64\ ln\ C_e$	K_F n	1.65 1.57	0.960
Florry-Huggins	40	$ln\ \frac{\Theta}{C_0} = -2.75\ ln\ (1-\Theta)$	K_{FH} α_{FH}	0.00013 -2.75	0.936
	60	$ln\ \frac{\Theta}{C_0} = -1.90\ ln\ (1-\Theta)$	K_{FH} α_{FH}	0.0003 -1.90	0.797
	98	$ln\ \frac{\Theta}{C_0} = -1.74\ ln\ (1-\Theta)$	K_{FH} α_{FH}	0.0003 -1.74	0.792

CONCLUSIONS

Dyeing PA 6.6 fabric with reactive dye in laboratory conditions gives good results at a temperature of 40, 60 and 98°C. The best results were obtained when the dyeing was performed at a temperature of 98 °C. By increasing the concentration of dye when dyeing PA 6.6 fabric with reactive dye, the degree of dye exhaustion decreases, the highest temperature gives the highest degree of dye exhaustion, and this is maintained throughout the dyeing process. A higher amount of dye in solution or a higher dyeing temperature contribute to a higher amount of adsorbed dye per unit mass of adsorbent, ie. at the highest initial dye concentrations and the highest dyeing temperature, the highest adsorption also occurs.

The *Freundlich* linear isotherm is efficient in simulating the adsorption isotherm of Reactive Brown 18 choose the adequate composition of the bath and the method of dyeing, to work out the dyeing phase in order to achieve a better dyeing of the polyamide 6.6 fabric.

References:

[1] DILL, K. A., BROMBERG, S., STIGTER, D. (2010): Molecular driving forces: statistical thermodynamics in biology, chemistry, physics, and nanoscience. 2nd Edition, *Garland Science* doi: 10.4324/9780203809075

[2] EL HARFI, S., EL HARFI, A. (2017): Classifications, properties and applications of textile dyes: A review. *Applied Journal of Environmental Engineering Science* **3** (3): 312-230. doi: 10.48422/IMIST.PRSM/ajees-v3i3.9681

[3] FAROUK, R., GAFFER, H. E. (2013): Simultaneous dyeing and antibacterial finishing for cotton cellulose using a new reactive dye. *Carbohydrate polymers* **97** (1): 138-142. doi: 10.1016/j.carbpol.2013.04.037

[4] GAO, Y., CRANSTON, R. (2008): Recent advances in antimicrobial treatments of textiles. *Textile research journal* **78** (1): 60-72. doi: 10.1177/0040517507082332

[5] GONG, Y., YANG, G. (2009): Manufacturing and physical properties of all-polyamide composites. *Journal of materials science* **44** (17): 4639-4644. doi: 10.1007/s10853-009-3708-0

[6] HINE, P. J., WARD, I. M. (2006): Hot compaction of woven nylon 6, 6 multifilaments. *Journal of applied polymer science* **101** (2): 991-997. doi: 10.1002/app.22771

[7] IREMONGER, M. J., WENT, A. C. (1996): Ballistic impact of fibre composite armours by fragment-simulating projectiles. *Composites Part A: Applied Science and Manufacturing* **27** (7): 575-581. doi: 10.13140/2.1.2202.3044

[8] LATIF, Z., FAZAL, A., CHOUDHARY, M. A., AHMAD, Z., MIRZA, M. A. (2018): Validation of Flory-Huggins Model for Phenol Adsorption by Parthenium Hysterophorus in A Batch System. *Applied Chemical Engineering* **1** (2): 1-9. doi: 10.24294/ace.v1i2.432

[9] NETHAJI, S., SIVASAMY, A., MANDAL, A. B. (2013): Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *International Journal of Environmental Science and Technology* **10** (2): 231-242. doi: 10.1007/s13762-012-0112-0

[10] TAYEBI, H-A, YAZDANSHENAS, M.E., RASHIDI, A., KHAJAVI, R., MONTAZER, M. (2015): The Isotherms, Kinetics, and Thermodynamics of Acid Dye on Nylon6 with Different Amounts of Titania and Fiber Cross Sectional Shape. *Journal of Engineered Fibers and Fabrics* **10**: 97-108. doi: 10.1177/155892501501000110

[11] VERMA, V. K., MISHRA, A. K. (2010): Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon. *Global NEST Journal* **12** (2): 190-196. doi: 10.30955/gnj.000638