

EQUILIBRIUM SORPTION OF DIRECT DYE ON POLYAMIDE

ORIGINAL SCIENTIFIC PAPER

Milena Nikodijević✉, Dragan Đorđević

DOI: 10.5281/zenodo.6371191

RECEIVED
2021-10-06ACCEPTED
2021-11-11Faculty of technology, University of Niš, Serbia
✉ nikmilena94@gmail.com

ABSTRACT:

In this paper, the equilibrium sorption of dyeing polyamide 6.6 fabric with direct dye is presented. Polyamide is a chemical fiber obtained from synthetically produced polymers, while direct dyes are most often sulfonated azo compounds: which are derived from bendisidine and its derivatives. Samples of 100% raw polyamide 6.6 fabric were used in the experiment. The direct used dye is called Solophenyl blue 4GL. The samples were dyed at different dye concentrations: 5, 10, 20, 30, 40, 50 mg/l. The temperature at which the samples were dyed was 40, 60 and 98 °C. Citric acid was added to the dye solution to achieve a certain pH of the solution. A spectrophotometer (Cary 100 Conc UV-VIS, Varian) was used to measure the absorbance of aqueous stained 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: *Langmuir* and *Harkins-Jura*. The high functionality of the variable was observed in the *Langmuir* model.

KEYWORDS: polyamide, dyeing, sorption, direct dye

INTRODUCTION

Polyamides (PA) or nylons were among the first synthetic polymers used for fiber applications. Polyamide fibers are used for a variety of different applications ranging from textiles and carpets to reinforcement of tires. PA's are polymers where the repeat units are held together by an amide linkage. PA can be classified into aromatic polyamides and aliphatic polyamides. Aliphatic PA's consist of only aliphatic chains whilst aromatic PA consist of aromatic rings in the main chain. Most of the aliphatic PA's are synthesized by either condensation polymerization or ring opening polymerization. Aromatic PA's are difficult to synthesize using diacids and diamines due to the lower reactivity of aromatic amines compared to aliphatic amines, and therefore aromatic PAs are usually made from diamine and diacid chloride [1-4].

Polymer blends are a class of polymeric systems, which can allow obtaining "new" materials with a suitable range of properties, with a relatively good performance/cost ratio. Unfortunately, when chemically different polymers are blended, incompatibility leads to a final product with poor properties, often worse than those of the corresponding neat polymers [5, 6].

In order for direct dye to be used for dyeing, it must be possible to change the solubility of the

compound, and groups may be included which will make the agent soluble in water. The type of interaction, whether physical or chemical, will depend on the groups on the dye molecules and in the fiber chains. Direct dyes are synthesized with sulfonic acid groups to give them solubility in water, separating and giving sodium cations. This allows the dye to bind to the chains in the fiber, often through intermolecularly hydrogen bond. They are used in dyeing in an aqueous solution containing sodium chloride. Salt reduces the electrical repulsive forces between the negative charge on the fiber surface and the type of anionic dyes [7, 8].

Most direct dyes are azo compounds, which often contain two or three azo groups. Azo groups have the potential to form hydrogen bonds with hydroxyl groups in polyamide. Vital substituents of direct dyes are said sodium sulfonate group, $-\text{SO}_3\text{Na}$, bound to benzene or naphthalene rings. It is a sulfonate group that gives most direct dyes the solubility property in water which is very important for dyeing. Dyes containing these groups ionize into sodium cations and dyed sulfonate anions that are positively and negatively charged [9].

In this paper, the equilibrium sorption of direct dye on polyamide 6,6 fabric was investigated. The aim of the research is to expand the spectrum of polyamide dyes.

MATERIALS AND METHODS

In the experimental part, 100% raw polyamide 6,6 fabric (Jumko, Vranje) was used. The dyeing was performed in Erlenmeyer in which samples of polyamide fabric in a solution of citric acid and direct dye were placed. The Erlenmeyers were heated for 60 minutes. The amount of citric acid was 5 g/ml, pH = 3. The dye used is Solophenyl blue 4GL (Huntsman, Texas, United States), whose chemical structure is shown in figure 1.

The used dye has practically 3 azo groups, one benzene ring, three naphthalene nuclei, four sulfonate groups, there is also an aniline residue attached to naphthalene. Active places for binding, ie. contact, in molecules, are negatively charged hydrophilic sulfonate groups, as well as electron donor and acceptor groups. The active groups in the polyamide structure are the amino, carboxyl and amide groups. When immersed in an acidic aqueous solution, PA fibers receive a positive charge (amino, amide groups) which are then neutralized by dye anions (sulfonate groups).

The samples were dyed at different dye concentrations, as follows: 5, 10, 20, 30, 40, 50 mg/l. The temperature at which the samples were dyed was 40, 60 and 98 °C. Upon completion of dyeing, the solution was cooled and absorbance was measured using a spectrophotometer (Cary 100 Conc UV-VIS, Varian). The absorption maximum for the used dye is 580 nm. Also, a calibration curve was made to determine the unknown dye concentration during dyeing.

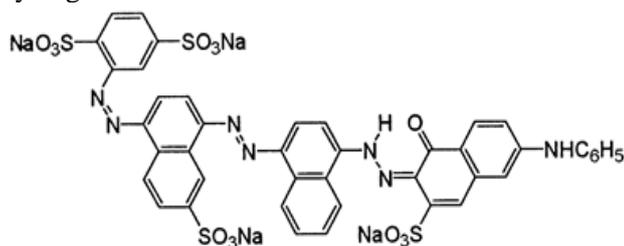


Figure 1. Chemical structure of Solophenyl blue 4GL

The degree of dye exhaustion was calculated using the form [10]:

$$\text{Degree of dye exhaustion} = \frac{C_0 - C_t}{C_0} \times 100(\%) \quad (1)$$

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]:

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

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_0 (mg/l), initial dye concentration; C_t (mg/l), dye concentration in solution at dye time t , C_e (mg / l), equilibrium dye concentration in solution; w (g), mass of sample and V (dm^3), volume of dyeing solution.

The *Langmuir* equation is applicable to a homogeneous surface where the adsorption of each adsorbate molecule has the same sorption activation energy. The linear form of this isotherm is represented by equation [11]:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left[\frac{1}{b \cdot Q_0} \right] \cdot \frac{1}{C_e}$$

where C_e is the equilibrium dye concentration (mg/g), q_e is the equilibrium amount of adsorbed dye (mg/g), Q_0 is the maximum single layer coating capacity (mg/g), b is the adsorption energy.

The *Harkin-Jura* (H-J) isotherm model assumes the possibility of multilayer adsorption on the surface of an adsorbent having a heterogeneous pore distribution. Mathematically, this model can be expressed by equation [11]:

$$\frac{1}{q_e^2} = B / A - \left(\frac{1}{A} \right) \log \log C_e$$

where B and A are *Harkin-Jura's* constants.

RESULTS AND DISCUSSION

The effect of initial dye concentration on adsorption – the degree of dye exhaustion when dyeing polyamide 6.6 fabric with direct dye, at different temperatures, is given in figure 2. There is continuity in changes during the growth of initial dye concentration. As the concentration increases, the degree of dye exhaustion decreases.

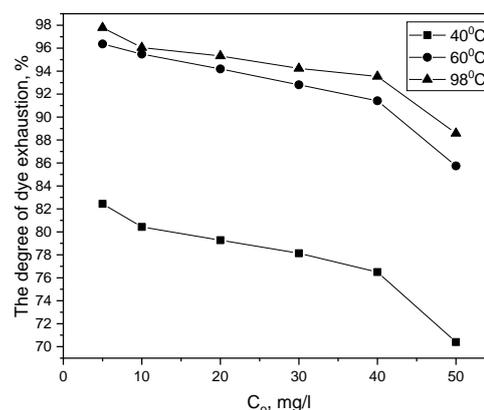


Figure 2. Influence of initial dye concentration on adsorption – the degree of dye exhaustion

At lower concentrations of dye in the 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 higher degree of dye exhaustion occurs. As the temperature rises, the degree of dye exhaustion increases, which is to be expected because is this conventional dyeing for polyamide fibers. 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.

The diagram in figure 3 shows the results of the change in the adsorbed amount of adsorbate (dye) on the adsorbent (polyamide 6.6 fabric) for different initial concentrations and temperatures. As the initial dye concentration increases, the dye absorption on the polyamide 6.6 fabric increases sharply. The curve is steeper at the highest applied dye concentration applied. As the initial dye concentration in the solution increases, better dye absorption occurs on the polyamide 6.6 fabric.

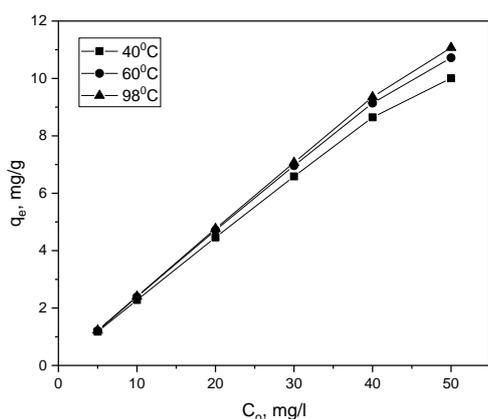


Figure 3 Adsorbed amount of direct dye per unit mass of PA 6.6 fabric in relation to the initial concentration for different times

Figure 4 shows the *Langmuir* isotherm for different dyeing temperatures, which is derived under the assumption of surface heterogeneity with uneven heat sorption distribution on the surface. From this diagram, the high functionality of the variables ($R^2 = 0.980$ - 40 °C), ($R^2 = 0.996$ - 60 °C) and ($R^2 = 0.966$ - 98 °C) is noticeable. Based on the slope and section, the *Langmuir's* constants were determined, and the suitability of the model for describing the adsorption process of the used dye on polyamide 6.6 fabric was evaluated through them.

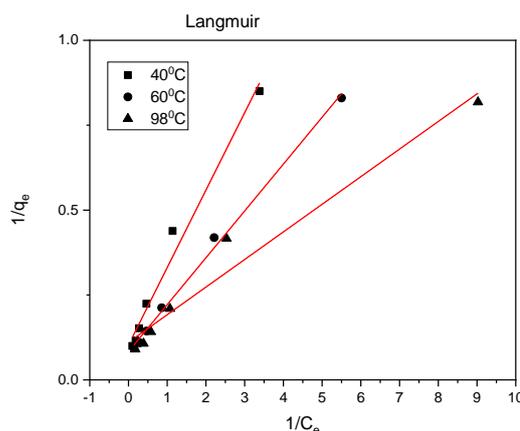


Figure 4 Graphical representation of the linear shape of the *Langmuir* adsorption isotherm for dyeing polyamide 6,6 fabric at different temperatures

By analyzing the isothermal data by fitting it, one comes across different isothermal equations by finding a suitable model that can be used to control the dyeing process. In the given research, the *Harkin-Jura* isothermal model was used for fitting experimental points with the help of OriginPro software.

In the *Harkin-Jura* model, multilayer adsorption at a relatively large distance from the surface is not noticeable. The diagram in figure 5 presents *Harkin Jura* isotherms for dye adsorption on the adsorbent. The high functionality of the variables is not noticeable, ie. $R^2 = 0.779$ for 40 °C, $R^2 = 0.707$ for 60°C and $R^2 = 0.769$ for 98°C, so based on this diagram, *Harkin Jura's* constants were determined, as well as the coefficient of determination over which the inadmissibility of this model for describing was assessed. The process of adsorption of the used dye on the adsorbent-fabric at different temperatures (figure 5).

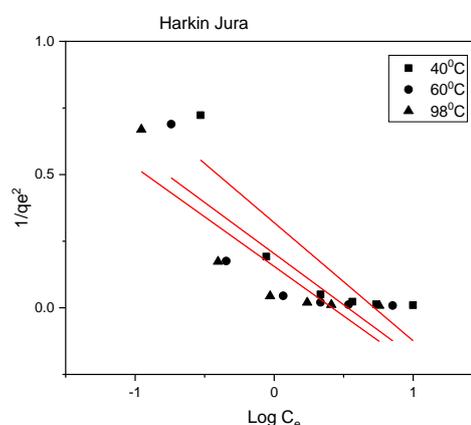


Figure 5 Graphic representation of *Harkin Jura* adsorption isotherm for dyeing polyamide 6.6 fabric at different temperatures

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 determination 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.

Q_o and b are Langmuir constants. The maximum adsorption capacity Q_o increases with temperature, thus increasing the mobility of the dye ion. This led to a higher chance of direct dye being adsorbed on the adsorbent, resulting in an increase in its adsorption capacity in increasing pore size or activating the adsorbent surface area. The observed linear relationship is statistically significant (at the 95% confidence level) which proves high R^2 values (which are closest to 1). This indicates the applicability of the *Langmuir* isotherm.

The adsorption energy b varies with increasing temperature. In general, the parameter b usually has

the value 1. This parameter is a measure of the heterogeneity of the system and a more homogeneous system would have b value approaching one, a more heterogeneous system would have a value of b approaching zero. The value of R_L indicates the shape of the isotherms that should be unfavorable ($R_L < 1$), linear ($R_L = 1$), favorable ($0/R_L/1$) or irreversible ($R_L = 0$).

The *Harkin Jura's* constants A and B were calculated from the linear ratio $1/q^2e$ and $\log C_e$, and the values of the constants are presented in table 1. The value of the coefficient of determination for Solophenyl blue 4GL is $R^2 = 0.779$ for 40 °C, $R^2 = 0.707$ for 60 °C and $R^2 = 0.769$ for 98 °C, which indicates that the model is poorly adapted to the obtained data. The model showed that there is no heterogeneous pore distribution. Constant A increases with increasing temperature and constant B decreases with increasing temperature. This explains the heterogeneous nature of both adsorbents.

Table 1. Analytical expressions of linear isotherms with coefficients for the system Solophenyl blue 4GL - polyamide 6.6 fabric

Models	Temperature (°C)	Analytical equations of models	Parameters of models		R^2
<i>Langmuir</i>	40	$\frac{1}{q_e} = 0.10 + 0.23 \cdot \frac{1}{C_e}$	Q_o	9.75	0.980
			b	0.45	
			R_L	0.04	
	60	$\frac{1}{q_e} = 0.08 + 0.14 \cdot \frac{1}{C_e}$	Q_o	11.98	0.996
			b	0.60	
			R_L	0.03	
	98	$\frac{1}{q_e} = 0.11 + 0.08 \cdot \frac{1}{C_e}$	Q_o	9.04	0.966
			b	1.36	
			R_L	0.01	
<i>Harkin Jura</i>	40	$\frac{1}{q_e^2} = 0.32 + 0.44 \log \log C_e$	B	0.72	0.779
			A	2.25	
	60	$\frac{1}{q_e^2} = 0.20 + 0.38 \log \log C_e$	B	0.53	0.707
			A	2.61	
	98	$\frac{1}{q_e^2} = 0.15 + 0.37 \log \log C_e$	B	0.42	0.769
			A	2.69	

CONCLUSION

Based on the obtained experimental results, it was concluded that the addition of citric acid to the dye solution results in better dye adsorption on the polyamide 6,6 fabric, given the bonds established in the interactions of (+) and (-) charged functional groups.

The dyeing process at a higher temperature gives better results than at a lower temperature. As the concentration increases, the degree of dye exhaustion per unit mass of adsorbent (polyamide) decreases. At the highest applied dye concentrations and the highest temperature, the highest dye adsorption occurs.

The *Langmuir* isotherm is effective in simulating isothermal adsorption of brown direct dye on a polyamide 6.6 fabric. It was found that staining - adsorption depends on the temperature and the initial dye concentration.

REFERENCES

- [1] Allcock H R., et al. (2003). *Polymer Chemistry*, 3rd edn, Prentice Hall, Upper Saddle River, NJ.
- [2] Murthy, N. S. (2006). Hydrogen bonding, mobility, and structural transitions in aliphatic polyamides. *Journal of Polymer Science Part B: Polymer Physics*, 44(13), 1763-1782.
- [3] Kotek, R., Jung, D., Tonelli, A. E., & Vasanthan, N. (2005). Novel methods for obtaining high modulus aliphatic polyamide fibers. *Journal of Macromolecular Science Part C: Polymer Reviews*, 45(3), 201-230.
- [4] Vasanthan, N. (2009). Polyamide fiber formation: structure, properties and characterization. *Handbook of Textile Fibre Structure*, 232-256.
- [5] La Mantia, F. P., Ceraulo, M., Mistretta, M. C., Botta, L., & Morreale, M. (2019). Compatibilization of polypropylene/polyamide 6 blend fibers using photo-oxidized polypropylene. *Materials*, 12(1), 81.
- [6] La Mantia, F.P.; Morreale, M.; Botta, L.; Mistretta, M.C.; Ceraulo, M.; Scaffaro, R. Degradation of polymer blends: A brief review. *Polym. Degrad. Stab.* 2017, 145, 79–92.
- [7] Parvinzadeh, M., & Najafi, H. (2008). Textile softeners on cotton dyed with direct dyes: reflectance and fastness assessments. *Tenside Surfactants Detergents*, 45(1), 13-16.
- [8] Haberer, P., & Bereck, A. (2002). Silicone softeners part 2. *Rev. Prog. Color*, 32, 125-137.
- [9] Ishegbe, E., Bello, K. A., & Kogo, A. A. (2014). Synthesis and application of direct dyes derived from terephthalic and isophthalic acids on cotton fabrics. *Journal of Polymer and Textile Engineering*, 1, 50-58.
- [10] 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.
- [11] Amin, M. T., Alazba, A. A., & Shafiq, M. (2015). Adsorptive removal of reactive black 5 from wastewater using bentonite clay: isotherms, kinetics and thermodynamics. *Sustainability*, 7 (11), 15302-15318.

THIS PAGE OF
TECHNOLOGICA ACTA
INTENTIONALLY LEFT BLANK