

The Isotherms, Kinetics, and Thermodynamics of Acid Dye on Nylon6 with Different Amounts of Titania and Fiber Cross Sectional Shape

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ABSTRACT

The adsorption of acid dye on nylon6 yarns with different amounts of Titania (0.03% and 0.3% wt.) and the rate of adsorption with various fiber cross-sectional shapes (circular and triangular) were studied. According to results, dye adsorption rates in yarns increase by changing the cross-sectional shape from circular to triangular and by decreasing the amount of TiO₂. The rates of dyeing were calculated at different temperatures, values of activation energy, standard affinities, entropies, and enthalpies. The results indicate that increasing the temperature leads to decreases in the values of partition ratio and affinity. Moreover, from the analysis of the thermodynamics of dyeing, the enthalpic and entropic terms were found to be negative. It was noted that the adsorption of acid dye on nylon6 was an exothermic process. The adsorption isotherm was tested by fitting the adsorption data with Langmuir, Freundlich, Redlich–Peterson, and Dubinin–Radushkevich isotherms. Results show that the adsorption isotherm of acid dye on nylon6 is Langmuir type.

INTRODUCTION

Nylon was successfully made by W. H. Carothers (DuPont Co.) in 1930. He used hexamethylene diamine and adipic acid monomers by condensation polymerization to obtain nylon6, 6 polyamide. After spinning, the first synthetic fiber of nylon6, 6, which had elasticity and dyeability, was invented. In 1938 Schlack of Germany made a nylon6 fiber. He used α -amino caproic acid chloride salt as the catalyst and reacted it with α -caprolactam to produce nylon6. It is well known that the presence of amino

end groups (AEG) in nylon fibers imparts substantivity towards various classes of anionic dye, namely acid dyes, direct dyes, mordant dyes and reactive dyes; of these dye classes, acid dyes, predominate commercially. It is widely held that the substantivity of such anionic dyes, under acidic conditions, towards nylon6 is based mainly on electrostatic forces of interaction operating between anionic (typically sulfonate) groups in the dye and the protonated, terminal amino groups in the fiber; the adsorption of anionic dyes on nylon is thus considered to be site-specific [2-7]. The substantivity of anionic dyes towards nylon fibers can be modified by altering the concentration of amino end groups in the substrate. By increasing the AEG content, dye-fiber substantivity is enhanced; such anionic-dyeable variants are commonly referred to as low, standard, deep or ultra-deep, depending on AEG content [2, 3]. Much attention has been focused on the effects of structure on the dyeability of nylon6 fibers [8-12]. They found that the physical and chemical structures have a predominant effect in dye sorption. They showed that the uptake of acid dye is affected by the morphology of the nylon-6 fibers. An open amorphous and a low crystallinity phase results in a large number of amino end-groups in the fiber being accessible to the acid dye. Thus both chemical affinity and segmental mobility are important for acid dye pick-up. Several parameters affect the properties of melt spun yarns (like Nylon6), including the spinneret's cross-section and additives [13, 14]. Cross-sectional shape is one of the most important morphological features of fibers, which largely determines the mechanical, thermal and optical

properties. These fiber properties also affect the properties of yarns and fabric. The round fiber cross section is the most common shape manufactured by synthetic fiber producers. However, a round cross-section is not always preferred in fiber applications. Other shapes have emerged for a variety of reasons, such as performance, comfort, pilling propensity, bulkiness, tactility, and processing [17, 18]. The first attempt was to mimic the gloss of expensive silk fibers by changing the cross section to a trilobal shape. Then, various types of specialized sections were developed with specific orifices, such as conventional slits, combinations of circle and slit, and hollow shapes. A non-circular cross-sectional shape of fiber has properties, including bending stiffness, coefficient of friction, softness, appearance, and handle, different from those of cylindrical fibers with a circular cross section [19-22]. Many researchers have studied the effects of polyester fiber cross-sectional shapes on fiber properties. These studies investigated the mechanical properties and handle of the woven fabrics composed of polyester staple fiber, and subsequently, could examine the abrasion resistance of the produced fabrics [20, 26, 15].

One of the most common additive agents in the textile industry's spinning process is Titanium dioxide, which is used for matting and gloss reduction of synthetic fibers [1, 28]. There is a growing interest in the development of composites consisting of organic polymers and Titania (TiO₂), based on positively perceived characteristics including mechanical performance, thermal properties, biodegradability, and optical properties [27, 28]. The added amount depends on the desired degree of matting (*Table I*).

TABLE I. Different amount of TiO₂ for matting.

TiO ₂ -content (%)	Type of yarn
< 0.03	Super bright
0.03-0.05	Bright
0.15-0.35	Semi dull
0.45-1.00	Dull
> 1-4%	Full dull

TiO₂ exists in both crystalline and amorphous forms. In the case of delustering, the crystalline form does not exist. There are three crystalline phases of TiO₂: anatase, rutile, and brookite. Anatase and rutile are both tetragonal in structure and are used in fiber production, while the brookite structure is orthorhombic. Rutile pigments are only used in polypropylene fibers, but anatase pigments are used

in nylon and other synthetic fibers [1].

The adsorption of acid dye C.I. Acid Blue 62 by yarns produced using identical manufacturing conditions but with different yarn cross-section and amounts of TiO₂ were investigated in this paper.

EXPERIMENTAL

Materials

Nylon6 yarns, produced in a previous study [29] were used (*Table II*). Before being used, the yarns were treated with a solution containing 2 g/l non-ionic detergent, 1 g/l sodium carbonate at 70°C for 30 min and L : G 50 : 1. Then, the yarns were thoroughly washed with water and air dried at room temperature. Other materials used in this study were acid Blue 62 and sulphuric acid. Sulphuric acid was supplied by Merck and Telon Blue RR 01(acid blue 62) was supplied by Dystar (*Figure 1*).

TABLE II. Specification of produced yarns.

Sample	Fiber cross section	TiO ₂ (%)	Yarn density (denier)	Spinneret hole number	Crystallinity %
1	O	0.03	40	10	28.20
2	Δ	0.03	40	10	26.34
3	O	0.3	40	10	30.64

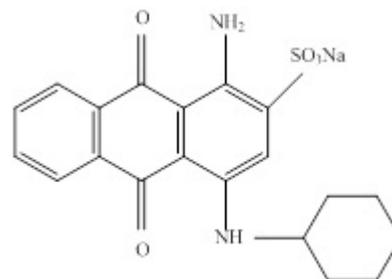


FIGURE 1. C.I. Acid Blue 62.

Instrumentation

A Jenway 6505 UV-Visible spectrophotometer was used for absorbance measurements using quartz cells of 1 cm path lengths. A pH meter (Jenway 3510) was used to measure the pH values of the dyeing bath. A shaker bath equipped with a thermostat (SDL-D403/1- 3) operated at 100 rpm, was used to study the adsorption and kinetics of acid dye onto nylon6 samples. The morphological properties of the samples were observed by a scanning electron microscope (LEO 440i, Leo Electron Microscopy, (Cambridge, England). The samples were coated with gold and observed under 20keV accelerating voltage.

Dyeing Methods

Dyeing nylon6 samples was carried out in a dye bath containing different dye solutions, temperatures (60 to 90 °C), times (5–240 min), different pHs (3–7), and dye materials (100– 350 mg dye in 100 ml water) with L: G 100: 1. The dyed samples were rinsed with cold water and dried at ambient temperature.

Kinetic Studies

One gram of nylon6 sample was dyed with acid dye at 60°, 80°, and 90°C and pH 3 at different times, keeping the L: G 100: 1 and an initial dye concentration of 270 mg/L. The quantity of dye adsorbed on nylon6 samples were estimated using the following Eq. (1):

$$q_t = \frac{(c_0 - c_t)V}{W} \quad (1)$$

Where, q_t is the quantity of dye adsorbed on nylon6 samples (mg/g nylon6) at any time, C_0 and C_t are the initial and dye concentrations (mg/L) after dyeing time t , respectively. V is the volume of dye bath (l) and W is the weight of nylon6 sample (g). The maximum absorbance for Acid Blue 62 was 640 nm. The calibration curve of this dye was accordingly plotted in order to be used for the determination of the concentration of an unknown solution.

For dyeing each sample, the absorbance of dye solution was monitored until it became constant. Then, the equilibrium concentrations of dye in the residual bath and the dye uptake were calculated using the calibration curve. Subsequently, using the different points obtained between the times of 5 to 240 minutes, the dyeing rate of acid dye was plotted.

Equilibrium Studies

One gram of nylon6 sample was dyed with different dye concentrations at 60°, 80°, and 90°C, pH 3 for 120 min. The quantity of dye adsorbed on nylon6 samples at equilibrium were calculated using the following Eq. (2):

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (2)$$

Where, q_e is the quantity of dye adsorbed on nylon6 samples (mg/g nylon6) at equilibrium, C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), respectively. V is the volume of dye bath (ml) and W is the weight of nylon6 sample (g).

RESULTS AND DISCUSSION

The Effect of Dye Bath pH

The pH is an important factor that controls the adsorption of acid dyes from aqueous solution onto different samples [3]. The effect of pH 3–7 on the adsorption of acid dye onto nylon6 was studied because nylon6 is commonly dyed in acidic solutions. *Figure 2* shows that the highest adsorption Value of dye is obtained at pH=3. The effect of pH can be attributed to the surface of nylon6 fiber, and the correlation between dye and nylon6 fiber. Because it is widely held that the substantivity of such acid dyes, under acidic conditions, towards nylon6 is based on electrostatic forces of interaction operating between anionic (typically sulfonate) groups in the dye and the protonated, terminal amino groups in the fiber. By decreasing pH, the adsorption of dye on nylon6 increases [3]. According to these results, the pH of dye bath in all experiments was fixed at 3.

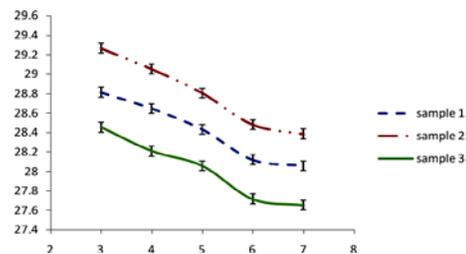


FIGURE 2. Effect of pH on adsorption of acid dye on different nylon6 yarn. Dyeing conditions: initial dye concentration 300 mg/L, L: G 100:1, temperature of dyeing 60 °C, and time of dyeing 120 min.

Rate of Dyeing

Determining the equilibrium time is one of the most important characteristics of acid dyeing on nylon6. According to the results presented in *Figure 3*, the dye adsorption increases with increasing of time up to 120 minutes of dyeing.

Longer time had no influence on dye adsorption. This means that the dye adsorption reached its equilibrium at each temperature at 120 minutes. The results show that temperature is an important factor in adsorption and slightly increases by decreasing the temperature.

It is clear that the adsorption of acid dye on nylon6 was controlled by an exothermic process. As shown in *Figure 3*, q_t values obtained increase as the time increases to 120 min and afterwards the q_t remains constant. This means that dyeing for 120 min gives a high q_t value. Therefore, time of dyeing was set at 120 min, which was later on used for isotherm studies.

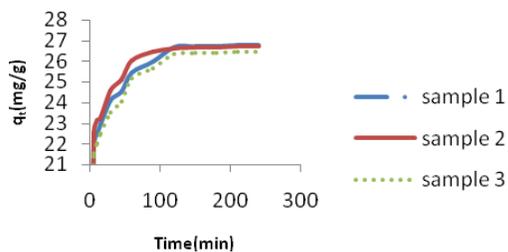
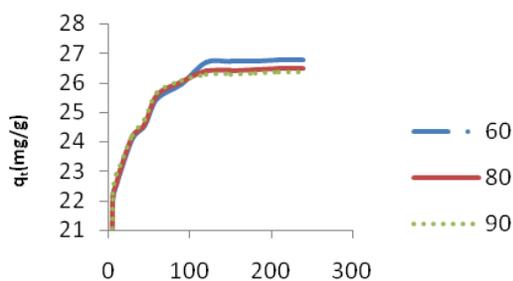
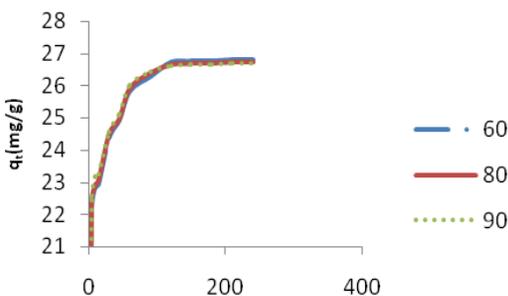


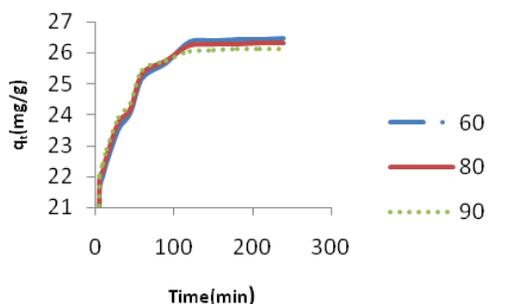
FIGURE 3. Effect of time of different nylon6 dyeing with acid dye Dyeing conditions: initial dye concentration 270 mg/L, L: G 100:1, pH=3, and temperature of dyeing 60 °C.



a)



(b)



(c)

FIGURE 4. Effect of time and temperature of different nylon6 dyeing with acid dye Dyeing conditions: initial dye concentration 270 mg/L, L: G 100:1, and pH=3. (a) Sample 1 (b) Sample 2 (c) Sample 3.

Scanning Electron Microscopy (SEM)

Fiber cross-sectional shapes were observed by SEM. As shown in *Figure 5a and 5b* two cross sections (circular and triangular) were selected. Fibers cross sectional area and perimeter were calculated by MATLAB software and the results are presented in *Table III*. According to *Table III* cross sectional area for all samples was approximately the same. On the other hand, their perimeters were clearly different (*Table III*). According to our observations, the adsorption rate is directly related to the contact area of the fiber; thus, triangular samples with a larger perimeter had more total contact area. Therefore the triangular cross-section has more rate of adsorption than the other samples. These results verify the behavior observed for samples, as explained in former sections (rate of dyeing).

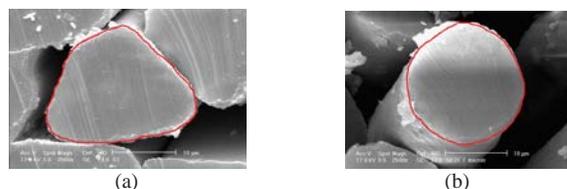


FIGURE 5. SEM micrograph for nylon6 fiber with different cross sectional shapes (a: triangular, b: circular).

TABLE III. Area and perimeter for different cross sectional shapes.

Cross sectional shape	Area (μm^2)	Perimeter (μm)
circular	298	55
triangular	300	63

Adsorption Isotherms

Generally, the capacity of surface for a particular solute involves the interaction of three properties: the concentration, C_e , of the solute in the fluid phase, the concentration, q_e , of the solute in the solid phase, and the temperature, T , of the system. If T is kept constant, C_e and q_e can be graphed to represent the equilibrium. Such a plot gives an adsorption isotherm. An adsorption isotherm is the equilibrium relationship at constant temperature, of the concentration of the solute in the fluid and the concentration adhered to the surface. The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Such adsorption isotherms may be used for scaling-up batch type processes with moderate success. In this research, to describe the relation between the amount of acid dye adsorbed on nylon6 and the amount of dye in residual dyeing bath, Langmuir, Freundlich, Dubinin—Radushkevichand, Redlich—Peterson models were used.

Langmuir Isotherm Model

This model can be described by the following form [30]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (3)$$

Where q_e is the quantity of dye adsorbed on nylon6 samples (mg/g nylon6) at equilibrium, C_e is the equilibrium dye concentrations in residual dyeing bath (mg/L) and k_L (L/mg) and q_m (mg/g) are the Langmuir constants. The model assumes that adsorption occurs on a homogenous adsorbent surface of identical sites that are equally available and energetically equivalent with each site carry equal numbers of molecules and no interaction between adsorbate molecules [30].

From the *Table IV*, it was observed that the Langmuir isotherm could be linearized to at least four different types [31]. The Langmuir constants k_L , and q_m values can be calculated from the plot between C_e/q_e versus

C_e , $1/q_e$ versus $1/C_e$, q_e versus q_e/C_e , and q_e/C_e versus q_e for type 1, type 2, type 3, and type 4 Langmuir isotherms, respectively. *Table IV* show the predicted isotherm constants (k_L and q_m) and the corresponding R^2 values. From the *Table IV*, it was observed that the isotherm parameters obtained from the four linearized Langmuir isotherm were different. Type 1 Langmuir isotherm was found to be the best fitting linearized Langmuir expression with coefficient of determination of approximately 1. Therefore the results were taken from Longmuir equation type 1. Correlation coefficients are near to 1 which means that experimental data fitted this model well. According to the results, it can be seen that temperature increases led to decreased adsorption of dye on nylon6 samples and it means that adsorption of acid dye on nylon6 samples are exothermic. Also, results show that k_L and q_m values increased with decreasing temperature and it can be seen from the q_m values that the nylon6 samples have a maximum affinity for acid dye at lower temperature. Besides,

TABLE IV. Langmuir isotherm and its linear forms.

Langmuir Isotherm	Linear form	Plot
Type1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{k_L q_m}$	C_e/q_e vs. C_e
Type2	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$ $\frac{1}{q_e} = \frac{1}{k_L q_m C_e} + \frac{1}{k_L q_m}$	$1/q_e$ vs. $1/C_e$
Type 3	$q_e - q_m = \frac{q_e}{k_L C_e}$	q_e vs. q_e/C_e
Type4	$\frac{q_e}{C_e} = k_L q_m - k_L q_e$	q_e/C_e vs. q_e

TABLE V. Calculated Langmuir isotherm parameters by different linear method.

samples	1 Temperature(°C)			2 Temperature(°C)			3 Temperature(°C)		
	60	80	90	60	80	90	60	80	90
Langmuir Adsorption isotherm									
Type1									
q_m	31.55	31.25	30.21	32.895	32.89	32.68	30.21	29.94	29.586
K_L	1.848	1.435	1.350	1.754	1.470	1.380	1.324	1.250	1.138
R^2	1	0.9998	0.9998	0.9999	0.9998	0.9998	1	0.9999	0.9999
Type2									
q_m	30.96	30.49	29.91	32.154	31.95	31.85	29.85	29.59	29.33
K_L	2.045	1.790	1.790	2.020	1.770	1.640	1.510	1.410	1.235
R^2	0.9974	0.9865	0.9884	0.9911	0.9931	0.9935	0.9903	0.9893	0.9923
Type3									
q_m	30.87	30.378	29.386	32.22	31.916	31.785	29.749	29.494	29.283
K_L	2.064	1.821	1.810	2.015	1.770	1.650	1.530	1.430	1.249
R^2	0.9958	0.9793	0.9807	0.9855	0.9865	0.9875	0.9855	0.9837	0.9867
Type4									
q_m	30.904	30.54	29.52	32.089	32.04	31.82	29.85	29.61	29.375
K_L	2.055	1.783	1.770	2.045	1.747	1.630	1.511	1.403	1.232
R^2	0.9958	0.9793	0.9807	0.9855	0.9865	0.9875	0.9855	0.9837	0.9867

that maximum adsorption is observed in the sample containing 0.03% Titania and triangular cross section. The dye showed highest adsorption on the nylon6 yarn with 0.03wt% TiO₂ and triangular cross section compared to other samples. There are two main reasons for this fact. First: by changing the cross section from circular to triangular, the specific area of contact between fibers and dye increases, therefore dye absorption improves. Second: TiO₂ particles are nucleation agents and hence by addition in the amount of these particles, crystallinity increases (verified by DSC results) and dye adsorption decreases as a result [3].

For a Langmuir type adsorption process, the influence of the isotherm shape on whether adsorption is “favorable” or “unfavorable” can be classified by a term “ R_L ” a dimensionless constant separation factor [32].

$$R_L = \frac{1}{1+kC_0} \quad (4)$$

Where R_L is a dimensionless constant separation factor, C_0 the initial concentration of dye solution (mg/L), and k is the Langmuir constant (L/mg), the parameter R_L indicates the shape of the isotherm

accordingly. *Table VII* depicts the values of R_L . The magnitude of the exponent R_L gives an indication of the favorability of adsorption. According to *Table VI*, Values $0 < R_L < 1$ represent favorable adsorption conditions.

TABLE III. Values of separation factor R_L .

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

Freundlich Isotherm Model

The Freundlich isotherm assumes that the adsorption occurs on heterogeneous surface at sites with different energy of adsorption and with non-identical adsorption sites that are not always available [32, 33]. Mathematically it is characterized by the heterogeneity factor ‘ $1/n$ ’.

$$q_e = k_F C_e^{1/n} \quad (5)$$

TABLE IVI. Calculated different isotherm parameters by linear method.

Samples	1 Temperature(°C)			2 Temperature(°C)			3 Temperature(°C)		
	60	80	90	60	80	90	60	80	90
Adsorption isotherm									
Langmuir									
q_m	31.55	31.25	30.21	32.895	32.89	32.68	30.21	29.94	29.586
K_L	1.848	1.435	1.350	1.754	1.470	1.380	1.324	1.250	1.138
R_L	0.0015	0.002	0.0023	0.0016	0.0019	0.0021	0.0022	0.0023	0.0025
R^2	1	0.9998	0.9998	0.9999	0.9998	0.9998	1	0.9999	0.9999
Freundlich									
K_F	19.21	18.499	18.03	19.72	19.06	18.74	17.76	17.45	16.99
N	6.057	5.942	6.440	5.280	5.120	5.140	6.150	6.180	6.140
R^2	0.888	0.9214	0.9374	0.9013	0.9228	0.9233	0.9209	0.9251	0.9278
D-R									
B	7×10^{-8}	8×10^{-8}	8×10^{-8}	7×10^{-8}	7×10^{-8}	8×10^{-8}	1×10^{-7}	1×10^{-7}	1×10^{-7}
E	2.672	2.500	2.500	2.672	2.672	2.500	2.236	2.236	2.236
q_s	29.157	28.890	28.270	29.900	29.640	29.540	28.380	28.143	27.870
R^2	0.9898	0.9815	0.9848	0.9823	0.9775	0.9794	0.9876	0.9842	0.9827
R-P									
K_r	31.55	31.25	30.21	32.895	32.89	32.68	30.21	29.94	29.586
a_r	0.244	0.474	0.510	0.033	0.461	0.560	0.660	0.730	0.840
G	1.5407	1.2729	1.2289	0.8104	1.3268	1.2384	1.1404	1.1035	1.056
R^2	0.968	0.9915	0.9954	0.9941	0.9866	0.9928	0.9975	0.9982	0.9992

Where K_F is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. The Freundlich model can be represented by the linear form as follows:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \quad (6)$$

Therefore, K_F and $1/n$ can be determined from the linear plot of $\ln q_e$ against $\ln c_e$. The K_F and n values are listed in *Table VII*. Results show that increases temperature led to decreases K_F and which means that adsorption of acid dye on nylon6 fibers is an exothermic process. Correlation coefficients are below 0.95 and means that experimental data are not fitted to this model. The values of correlation coefficients are lower than the other four isotherms values. In all cases, the Freundlich equation represents the poorer fit of experimental data than the other isotherm equation.

Redlich–Peterson Isotherm Model

The formula of Redlich–Peterson isotherm model can be represented by Eq. (7) [32, 34]:

$$q_e = \frac{k_r c_e}{1 + a_r c_e^g} \quad (7)$$

Where K_r is the modified Langmuir constant, a_r and g are the constants. For simplicity, $K_r = K_L$ [32]. This model can describe the adsorption process over a wide range of concentrations. It has a linear dependence on concentration in the numerator and an exponential function in the denominator. a_r and g can be estimated from the slope and the intercept of the linearised form of Redlich–Peterson equation, respectively.

$$\ln \left(\frac{k_r c_e}{q_e} - 1 \right) = g \ln c_e + \ln a_r \quad (8)$$

The a_r and g values are listed in *Table VII*. The correlation coefficients of this model are above 0.98. However, the regression coefficients obtained by Langmuir is higher than Redlich–Peterson. This means that experimental data does not fitted to the Redlich–Peterson model as well as Langmuir model.

Dubinin-Radushkevich Isotherm Model

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich [35].

$$q_e = q_s \exp(-B^2) \quad (9)$$

Where q_s is D-R constant and B can be correlated:

$$B = RT \ln \left(1 + \frac{1}{c_e} \right) \quad (10)$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2B}} \quad (11)$$

The determined values of E are presented in *Table VII*. The Langmuir, Freundlich and Redlich–Peterson isotherms constants do not give any information concerning the chemical or physical properties of the sorption. But the calculated mean energy of

TABLE VI. Values of the Pseudo First Order and Pseudo Second Order Models for Adsorption of acid dye on different nylon6 yarns.

Samples	Temperature (°C)	$q_{e,exp}$ (mg/g)	K_1 (min ⁻¹)	Pseudo first-order		Pseudo second-order		
				q_e (mg/g)	R^2	K_2 (min ⁻¹)	q_e (mg/g)	R^2
1	60	30.871	0.022	5.325	0.988	0.012	27.174	0.999
	80	30.841	0.029	5.404	0.978	0.015	26.738	0.999
	90	29.900	0.035	5.439	0.970	0.018	26.599	0.999
2	60	32.254	0.028	5.511	0.985	0.014	27.100	0.999
	80	32.223	0.033	5.728	0.976	0.016	27.027	0.999
	90	32.028	0.037	5.742	0.972	0.018	26.954	0.999
3	60	29.854	0.024	5.659	0.977	0.012	26.809	0.999
	80	29.543	0.027	5.432	0.969	0.014	26.667	0.999
	90	29.174	0.032	5.267	0.965	0.017	26.385	0.999

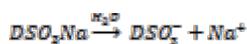
Adsorption, E , from the D-R isotherm, gives information about the chemical or physical properties of the sorption. The mean adsorption energy was found to be in the range of 0.9- 4 kJ/mol, which are in the energy range of physical adsorption reactions.

Calculated Dubinin-Radushkevich constants for the adsorption of acid dye on nylon6 samples are shown in *Table VII*. The correlation coefficients of this model are above 0.97. However, the regression coefficients obtained by Langmuir and Redlich-

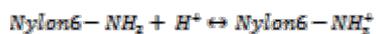
Peterson are higher than D-R. This means that experimental data does not fitted to the D-R model as well as Langmuir and Redlich-Peterson.

Adsorption Mechanism

By considering the adsorption of acid dyes onto the surface of samples, different mechanisms may be involved such as ionic attraction between anionic sulphonate group(s) of dissolved dye molecules and the cationic amino groups of protonated samples. The possible mechanisms of the adsorption process of nylon6 samples and acid dye are discussed: In aqueous solution, the acid dye is first dissolved and the sulphonate groups of acid dye (D-SO₃Na) is dissociated and converted to anionic dye ions.



Also, in the presence of H⁺, the amino groups of nylon6 samples (-NH₂) were protonated.



The adsorption process then proceeds due to the electrostatic attraction between these two counter ions:



Amino End Groups

To present another explanation for the decrease in dye adsorption by increasing the amount of TiO₂, amino end groups for samples were obtained [36]. As shown in *Table IX* samples with a same amount of TiO₂ showed very little difference in the amino end groups which could be because of the difference in cross sectional shapes. But, this difference in the samples with different amount of TiO₂ was clearly obvious. This may be due to the generated changes in fibers relative to the changes in the amount of TiO₂.

TABLE IX. Amount of Amino end groups for different samples.

sample	Cross section	Amount of TiO ₂ (%)	Amount of Amino end groups (mmol/kg)
1	O	0.03	52
2	Δ	0.03	54
3	O	0.3	46

Kinetics of Adsorption

To investigate the mechanism of adsorption process of acid dye on nylon6 samples pseudo- first- order and pseudo- second-order models were used. These models are two of the most commonly models used to describe the sorption of dyes on textile fibers.

Pseudo-First-Order

A simple kinetic analysis of adsorption is the Lagergren equation, a pseudo-first-order equation, describes the kinetics of the adsorption process as follows Eq. (12) [37]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (12)$$

Where, k₁ is the rate constant of pseudo-first-order adsorption (s⁻¹), and q_e and q_t is the amount of dye adsorbed on nylon6 samples (mg/g nylon6) at equilibrium and at time t. In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption. After definite integration by applying the initial conditions q_t=0 at t=0 and q_t= q_t at t=t, Eq. (13) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

Linear plot features of ln (q_e - q_t) against t for dyed nylon6 samples were achieved and the k₁ and q_e values calculated from the slope and intercept of these lines are summarized in *Table VIII*.

Pseudo-Second-Order

The pseudo-second-order kinetic model is another important model to investigate kinetic of adsorption of dye on textile materials and it is based on adsorption equilibrium capacity and can be expressed as Eq. (14) [37]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (14)$$

Where, k₂ is the rate constant of pseudo-first-order adsorption (g nylon6/mg min). Integrating Eq. (15) and applying the initial conditions, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

The pseudo-second-order rate constant k₂ and q_e calculated from slope and intercept of plotted t/q_t against t. The values of k₂ and q_e are listed in *Table VIII*. The correlation coefficient (R²) for both of kinetics models are shown in *Table VIII*. The correlation coefficient of pseudo-first-order and pseudo-second-order both close to 1. However, the q_e, adsorption capacity, is in accord with experimental results and pseudo-second-order model. Therefore, it can be concluded that the adsorption kinetic of acid dye on nylon6 fitted by pseudo-second-order.

Activation Energy

The amount of dye adsorbed at equilibrium at different temperatures, (60, 80 and 90 °C,) were utilized to evaluate the thermodynamic parameters for the dyeing nylon6 samples with acid dye. The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by the following Arrhenius-type relationship eq. (16) [38]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (16)$$

Where, E_a is the Arrhenius activation energy of adsorption, A is the Arrhenius factor, R is gas constant, and T is temperature (K). When $\ln k_2$ is plotted against $1/T$ (Figure 6), a straight line with slope E_a/R is obtained. The values of E_a , A , and the correlation coefficient (R^2) are listed in Table VII. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physical sorption processes usually have energies in the range of 5–40 kJ/mol, whereas higher activation energies (40–800 kJ/mol) suggest chemical sorption [37]. The result of Table X for dyeing of nylon6 samples with acid dye at different temperatures (60, 80 and 90 °C), considering that these values are in the typical activation energy range for physical sorption.

TABLE XI. Thermodynamic Parameters (ΔH° , $\Delta\mu^\circ$, ΔS°) for the Adsorption of acid dye by nylon6.

Samples	Temperature (°C)	K	$\Delta\mu^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R^2
1	60	3.06	-3.09	-10.14	-21.20	0.99
	80	2.43	-2.60			
	90	2.27	-2.48			
2	60	4.59	-4.22	-11.94	-23.18	0.99
	80	3.64	-3.79			
	90	3.18	-3.49			
3	60	1.94	-1.84	-4.24	-7.16	0.95
	80	1.84	-1.79			
	90	1.69	-1.59			

Where, R is the gas constant, T is the absolute temperature (K), and K is the partition ratio. The values of partition ratio (K) and standard affinity ($-\Delta\mu^\circ$) were obtained from Figure 6 and are presented in Table XI. It can be observed from Table XI that the standard affinity and partition ratio decrease as temperature increases. Values of standard affinity ($-\Delta\mu^\circ$) are negative, confirming that the adsorption of acid dye onto nylon6 samples is spontaneous and thermodynamically favorable. The more negative values of $\Delta\mu^\circ$ imply a greater driving force to the adsorption process. As the temperature increases, the $\Delta\mu^\circ$ values decrease, indicating less driving force and hence resulting in lesser adsorption capacity at higher temperatures.

TABLE X.VI Activation Energy (E_a) for the Adsorption of acid dye by nylon6.

Sample	E_a (kJ/mol)	R^2
1	13.63	0.98
2	8.43	0.95
3	14.60	0.93

Standard Affinity, Enthalpy and Entropy

The data for dyeing equilibrium is generally reported as the standard affinity of dyeing ($-\Delta\mu^\circ$). Therefore, the standard affinity ($-\Delta\mu^\circ$) were determined by using following eq. (17) [38]:

$$-\Delta\mu^\circ = RT \ln k \quad (17)$$

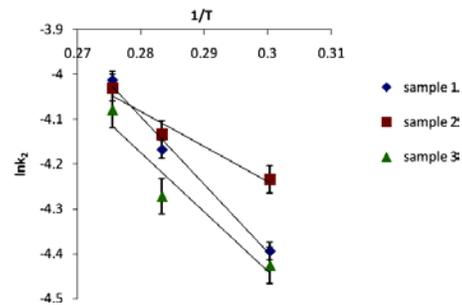


FIGURE 6. Relation between $\ln k_2$ and $1/T$ for dyeing of different nylon6 yarns with acid dye.

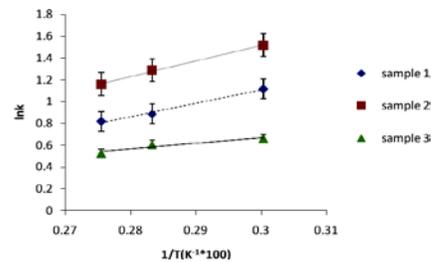


FIGURE 7. Relation between $\ln k$ and $1/T$ for dyeing of different nylon6 yarns with acid dye.

Standard enthalpy (ΔH°) and entropy (ΔS°) were determined from the Van't Hoff equation, [38]:

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (18)$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln k$ against $1/T$ as shown in Figure 7. The values of ΔH° and ΔS° are listed in Table XI. The values of ΔH° are negative, indicating that the adsorption process is exothermic in nature. The negative values of ΔS° indicate greater order of reaction during adsorption of acid dye on nylon6 surface.

CONCLUSION

The adsorption isotherm, thermodynamics, and kinetic study of adsorption of acid dye on nylon6 yarn with different amount of Titania and different cross sectional shape were studied. The results show that adsorption is dependent on the pH, temperature, amount of Titania, and cross sectional shape. Results show that the adsorption isotherm of acid dye on nylon6 is Langmuir type. The partition ratio (K), the standard affinity ($\Delta\mu^\circ$), the heat of dyeing (ΔH°), and entropy of dyeing (ΔS°) were determined. It is noted that the adsorption of acid dye on nylon6 is an exothermic process. Rate of dye adsorption improved and increased by changing the cross sectional shape from circular to triangular. This higher rate of adsorption is related to higher fiber perimeter which is based on different fiber cross sectional shapes. Besides, the increase in dye adsorption is due to change in the crystallinity of the yarns (verified by DSC results) by decreasing the amount of TiO_2 respectively.

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