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Adsorption behavior of disperse orange 30 on polyester fabric

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Abstract: In this study, the adsorption behavior of disperse orange 30, including the adsorption isotherms, Kinetic adsorption and thermodynamic parameters on polyester products at different temperatures (90, 100, 110 ° C) were examined. To determine Adsorption Equation type, Nernst, Langmuir and Freundlich Adsorption Isotherms were used. Results indicate that the most Correlation Coefficient value belongs to Nernst's Adsorption Isotherms. To determine Kinetic adsorption equation type, pseudo first order and pseudo second order equations were used. And studies attribute the best and highest Correlation Coefficient value to the pseudo second order equation. Thermodynamic parameters such as enthalpy, entropy and standard affinity were studied; negativity of these parameters is the evidence of adsorption process's being exothermic.

Keywords: Polyester, Disperse dye, Adsorption isotherm, Kinetics, Thermodynamics.

Introduction

Polyesters are polymers which contain an Ester group in their chain. Polyesters are produced through chemical reaction of Dialcohol and Dicarboxylic acids [1, 2]. Fibers prepared from these compounds, due to their crystalline structure, have low water adsorption and are paler in color. Thus, for dyeing them we use the following methods: 1 – using dyeing materials with low molecular size 2 – applying high temperature and 3 - using swelling agents. The Most commonly used method is the application of high temperature [2-8]. Dye adsorption process in textile products is very complex and requires more detailed studies. To study this process, Adsorption isotherms and thermodynamic parameters are used. Adsorption isotherms which are commonly used include Nernst, Langmuir and Freundlich Adsorption Isotherms, each used in describing behavior of different dye adsorption For example, to describe the adsorption behavior of acid dyes on nylon, Langmuir adsorption isotherm and to describe the adsorption behavior of direct dyes on cotton products, Freundlich adsorption isotherm are used [9-14]. Kinetic Equations in determining adsorption were very various and some of them may include pseudo first order and pseudo second order equations and intraparticle diffusion equation [15, 16]. Variables such as enthalpy difference (ΔH°), entropy (Δs°), and Affinity ($\Delta \mu^{\circ}$) are used in determining Thermodynamic parameters values, with which, it can be determined whether the adsorption process is exothermic or endothermic [12].

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Results and discussion

Effect of pH on color adsorption

The pH is an important factor that controls the adsorption of dyes from aqueous solution onto polyester samples. Therefore, the effect of pH on the adsorption of disperse dye on polyester was studied in range of 3–6 because of normal polyester dyeing at this range. Figure **1** shows that the dyeing pH has a considerable effect on the adsorption of disperse dye on polyester yarns. It can be seen that the highest adsorption Value of dye is obtained at pH=4.5. Thus, this pH value was used for later investigations.

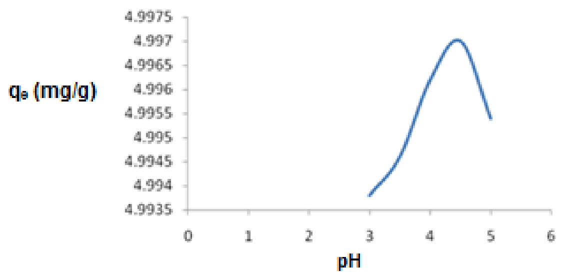

Figure 1: Effect of pH on dye adsorption.

Rate of dyeing (effect of time)

Determining of equilibrium time is one of the most important characteristics which represent the adsorption of disperse dye on polyester. According to Figure **2**, the dye adsorption increases with increasing of time to 120 min of dyeing for polyester samples. Longer time has no influence on dye adsorption. This means that the dye adsorption reaches to equilibrium for different temperatures. As it is shown in Figure **2** q_e values obtained increases as the time increases to 120 min and afterwards the q_e remains constant. This means that dyeing for 120 min give a high q_e value. Therefore, time of dyeing was set at 120 min.

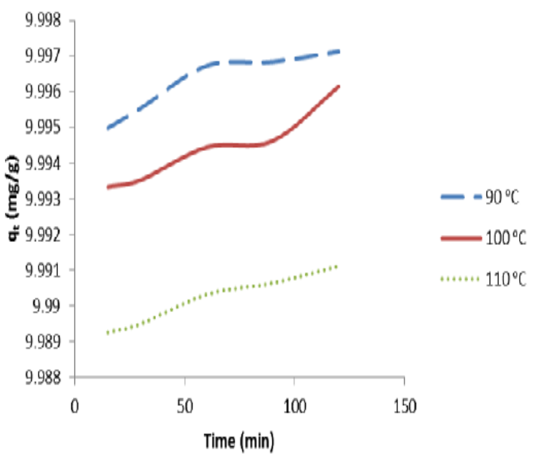

Figure 2: Effect of time on color adsorption at different temperatures.

Effect of concentration on color adsorption

Generally, the capacity of an adsorbent for a particular adsorbate involves the interaction of three properties: the concentration, C_e, of the adsorbate in the fluid phase, the concentration, q_e, of the adsorbate 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 shows the equilibrium relationship at constant temperature, of concentration in the fluid and the adsorbed quantity. 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, for describe the relation between the amount of disperse dye adsorbed on polyester and the amount of dye in residual dyeing bath at different temperatures (90, 100 and 110 °C), Langmuir, Freundlich and Nernst models were used.

Langmuir Adsorption isotherm

Langmuir Adsorption isotherms are one of the most successful isotherm and model for real systems. This isotherm can be applied to cases in which the number of positions in the sorbent is limited and also when in each position of the adsorption, only a single molecule is adsorbed. So according to this theory, a certain amount of substance can be adsorbed and after reaching the saturation point (the point after which there is no possibility of adsorption), the increase in self-adsorbed material will not result in increase in adsorption. Langmuir adsorption isotherms relationship is defined as:

$$q_e = \frac{QbC_e}{1+bC_e} \qquad (1)$$

The linear relationships are also given by:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \qquad (2)$$

Where, Q (mg/g) is the maximum amount of dyes adsorbed on unit weight of samples, C_e (mg/L) concentration of the dye in dye bath at the point of equilibrium, q_e (mg/g) the amount of dyes adsorbed on each gram of sample at equilibrium point and b (ml/mg) is Langmuir constant, which is related to tendency of the adsorbent material. The following reported figures (Figure **3**) present, $1/q_e$ diagram against $1/C_e$ for dyed samples. The values of Q and b are obtained, respectively, from the ordinate origin and the coefficient of lines angles for different temperatures. Results show that, as the temperature rate rises, the adsorption process decreases, and that shows the adsorption process is exothermic. Correlation coefficients are below 0.95 and means that experimental data not fitted to this model. The values of correlation coefficients are lower than the other two isotherms values. In all cases, the Langmuir equation represents the poorer fit of experimental data than the other isotherm equation.

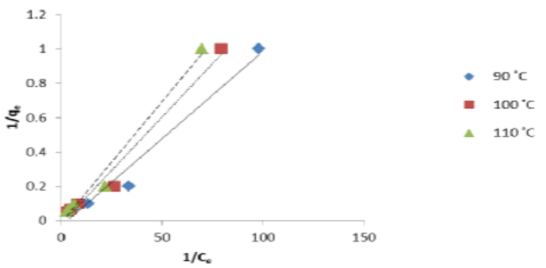

Figure 3: Langmuir adsorption isotherms at different temperatures.

Freundlich Adsorption isotherm

Another important adsorption isotherm, which is important in studying the dyeing behavior of textile fibers, is Freundlich adsorption isotherm. This type of isotherm can be applied to dye adsorption in unlimited situations. In fact, this type of adsorption isotherm is used for levels which have non-homogeneous surface energy. In these adsorption isotherm, at first, dye adsorption increases quickly, as the initial concentration increases, and after occupying a considerable number of adsorption positions in the fiber, the adsorption speed declines. Freundlich adsorption isotherm equation is defined as:

$$q_e = Q_f C_e^{1/n} \qquad (3)$$

Where (mg/g) Q_f is the maximum amount of dyes adsorbed on unit weight of fiber and 1/n represents the adsorption intensity. Linear relationship of the isotherms is also defined as:

$$\ln q_e = \ln Q_f + 1/n \ln C_e \qquad (4)$$

Values of Q_f and 1/n are obtained by plotting $\ln q_e$ diagram against $\ln C_e$ (Figure **4**).

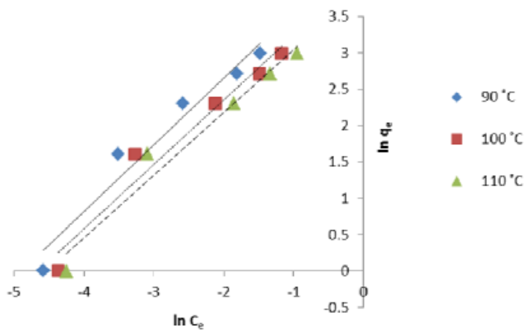

Figure 4: Freundlich adsorption isotherms at different temperatures.

According to the results obtained from the Freundlich adsorption equation, as shown in the figure **4**, one can understand that low coefficient values does not rummage the aptness or prove the inaptness of Freundlich adsorption isotherms in describing the adsorption behavior of disperse orange 30 on polyester products.

Nernst Adsorption isotherms

Nernst adsorption isotherm equation is defined as:

$$q_e = KC_e \qquad (5)$$

Where: q_e, is the concentration of dye in fiber at equilibrium (g/L), C_e, concentration of dye in the dye bath at the time of equilibrium (g/L) and K is the maximum amount of dyes adsorbed on unit weight of fiber (mg/g).

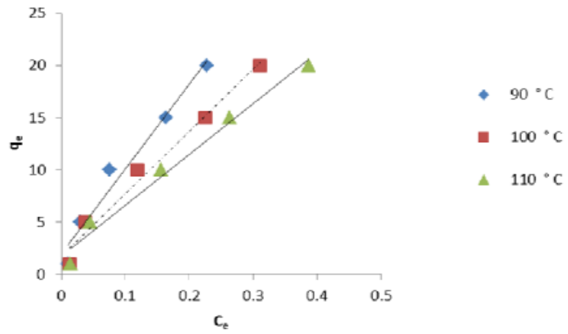

Figure 5: Nernst Adsorption isotherms for dyed samples at different temperatures.

Table 1: Nernst equation constants for dyed samples at different temperatures.

Temperature (°C)	90	100	110
K	81.0910	59.7640	48.6210
R^2	0.9676	0.9802	0.9820

Results show that (Figure **5** & Table.**1**), as the temperature rate rises, the value of K decreases. And this is because, the adsorption process of disperse orange 30 on polyester samples is an exothermic process. Moreover, according to the correlation coefficient values, it can be understood that Nernst adsorption isotherm is the best equation to describe the adsorption behavior of disperse orange 30 on polyester samples.

Adsorption Kinetics

Generally, there are many models for investigating kinetics of chemical reactions. Some of them include the pseudo first order model, pseudo second order model, and intraparticle diffusion equation. Usually the first and second models are used for investigating the adsorption kinetics of dyeing fibers with a dye.

Pseudo-first order model

This model is a simple model for investigating the kinetics of dyeing fibers with dyes. In this equation, the average values of speed constant (k_1) of disperse dye adsorption by polyester sample is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (6)$$

Where, k_1 is the speed constant in pseudo first order model (min^{-1}) and q_t and q_e, respectively, indicate the amount of dyes adsorbed at time t and at equilibrium time (mg/g). After definite integration by applying the initial conditions q_t=0 at t=0 and $q_{t=}$ q_t at t=t, eq. (7) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

Linear plot feature of ln ($q_{e\_}$ q_t) against t for dyed polyester samples were achieved and the k_1 and q_e values calculated from slope and intercept of these lines (Figure **6**). Results show that, as the temperature rate increases, the values of $K_1$and q_e drop. They also indicate that, due to low correlation coefficient value, the pseudo first order kinetic model can't be an applicable one for adsorption kinetics.

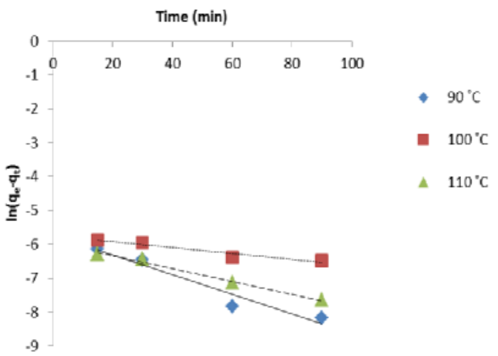

Figure 6: pseudo first equations for dyed samples at different temperatures

Pseudo second order model

This is another model for investigating dyeing kinetics of fibers. In this equation the average value of speed constant (K_2) of disperse dyes adsorptions by polyester fibers, is given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (8)$$

Where, k_2 is the rate constant of pseudo-first-order adsorption (g /mg min). Integrating eq. (8) and applying the initial conditions, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \qquad (9)$$

Values of K_2 and q_e, which are respectively obtained from, the angle coefficient and ordinate origin of lines, were calculated for different temperatures. Results show (Figures **7-9**) that as the temperature rate rises, values of K_2 and q_e drop. Moreover, the high value of correlation coefficient shows that this model is capable of being used to describe adsorption kinetics.

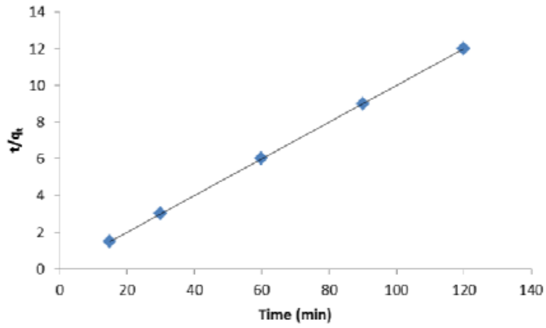

Figure 7: the pseudo second order model for dyed samples at the temperature, 90 °C

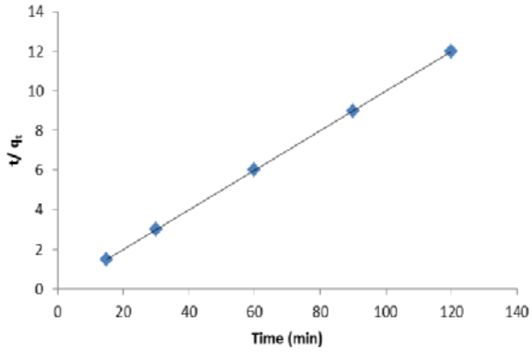

Figure 8: the pseudo second order model for dyed samples at the temperature, 100 °C

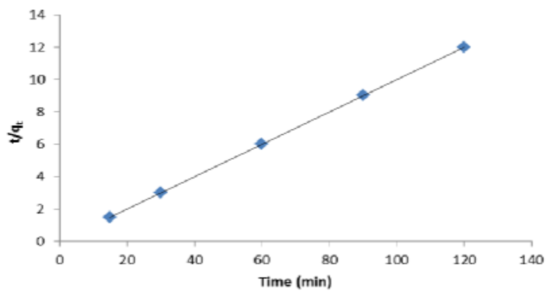

Figure 9: the pseudo second order model for dyed samples at the temperature, 110 °C

Thermodynamic parameters

To investigate thermodynamic parameters of adsorption, parameters such as enthalpy difference (ΔH°), entropy (ΔS°) and standard Affinity ($\Delta\mu^\circ$), were used. The data for dyeing equilibrium is generally reported as the standard affinity of dyeing, $\Delta\mu^\circ$. Therefore, the standard affinity ($\Delta\mu^\circ$) was determined by using following eq. (10);

$$\Delta\mu^\circ = -RT\ln K \quad (10)$$

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 ($\Delta\mu^\circ$) are presented in Table 2. It can be observed from Table 2 that the standard affinity and partition ratio decrease as temperature increase. In Figure **10**, to determine the heat of dyeing (ΔH°) and entropy of dyeing (ΔS°), lnk against 1/T was plotted and enthalpy and entropy were calculated by eq. (11).

$$\ln K_2 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

Where, R is the gas constant, T is the absolute temperature (K), K_2 is the pseudo second order model constant, ΔH° is the heat of dyeing, and ΔS° is the entropy of dyeing. The values of ΔH° and ΔS° are listed in Table 2. As the data above shows, all the parameters, enthalpy, entropy and standard affinity, have negative values which indicates that this process, dyeing polyester sample using disperse orange 30, is an exothermic process.

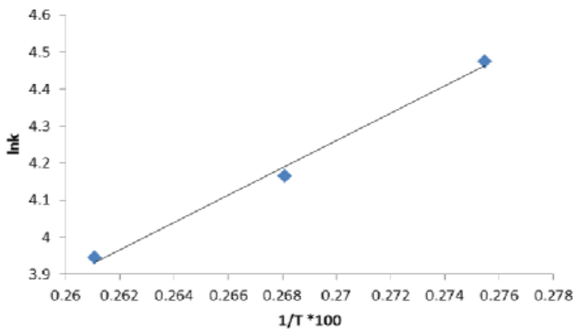

Figure 10: 1/T against lnk plotted to determine Thermodynamic parameters

Table 2: Thermodynamic parameters obtained values

ΔS°	ΔH°	$\Delta\mu^\circ$	K	Temperature (°C)
		-4.13	3.93	90
-30.73	-4.56	-3.85	3.46	100
		-3.63	3.12	110

Conclusion

In this study, polyester samples were dyed using disperse orange 30, and to determine the type of adsorption isotherms, Langmuir, Freundlich and Nernst adsorption equations were used. Results showed that the highest correlation coefficient belongs to Nernst adsorption isotherm. To determine the dominant Kinetic equations in adsorption process, pseudo first order and pseudo second order kinetic equations were used. Results showed that, the best fit belongs to pseudo second order equation. According to the results obtained from thermodynamic parameters of adsorption, enthalpy, entropy and standard affinity, it was observed that the adsorption process of disperse orange 30 on polyester samples is an exothermic process.

Experimental

Materials

The Polyester fabric used in these experiments is a product of Mazandaran Textile Factory. The desired fabric has a 29 weft density, and a 19 warp density and a weight of 428.85 gr/m^2. The dye used in these experiments is the C.I. Disperse Orange 30 (Figure **11**), with the commercial/trade name Dianix classic orange 30 SR, which were purchased from Dystar Company. The dye was used without any purification process and with its commercial degree of purity. Other used chemicals, including non-ionic detergent, sulfuric acid were purchased from Merck Co.

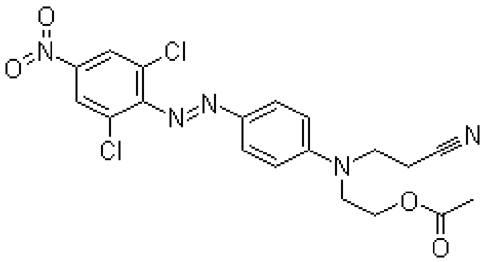

Figure 11: structure of C. I. Disperse Orange 30

Instrumentation

A Jenway 6505 UV-Visible spectrophotometer was used for absorbance measurements using quartz cell of 1 cm path length. A pH meter (Jenway 3510) was used to measure the pH values of the dyeing bath. For dyeing samples, Shadow Dyeing Machine, model Lab Dyer-8RC, purchased from Yazd textile Company, was utilized. The mentioned device has 12 cylinders with a capacity of 200 cc. In this device, it is possible to raise the temperature to 130 °C with precision tolerance of ± 1 °C. It is worth noting that the device's rpm was 70 (revolutions per minute).

Methods

At first, to prepare the samples, a polyester fabric was immersed(entered) into a solution containing 2 grams of non-ionic detergent and one gram of sodium carbonate per liter and then was heated up to 70 °C temperature within 80 minutes. Then the samples were washed and dried respectively. Dyeing polyester samples were carried out in a dye bath containing different dye solution, Temperatures (90, 100, 110 °C), times (5–180 min), and dye materials (10, 50, 100, 150, 200 mg dye in 100 mL water) with L: G 100: 1. The dyed samples were rinsed with cold water and finally dried at ambient temperature.

Kinetic studies

One gram of polyester sample was dyed with disperse dye at 90, 100, and 110 °C and pH 4.5 at different times, keeping the L: G 100: 1 and an initial dye concentration of 100 mg/L. The quantities of dye adsorbed on polyester samples were estimated using the following eq. (12):

$$q_t = \frac{(c_0 - c_t)v}{w} \quad (12)$$

Where, q_t is the quantity of dye adsorbed on polyester samples (mg/g) 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 polyester sample (g). The dye concentrations graph for standard solution versus absorbance at 640 nm wavelength, at where the maximum absorbance was reached, was prepared and used to determine the concentration of an unknown solution. For each dyeing, the absorbance of dye solution was monitored until it was unchanged. Then, the equilibrium concentrations of dye in the residual bath and the dye uptake were calculated using the standard graph. Subsequently, the dyeing rate of disperse dye on polyester was plotted.

Equilibrium studies

One gram of polyester sample was dyed with different dye concentrations (10, 50, 100, 150, 200 mg dye in 100 mL water) at 90, 100, and 110 □C, pH 4.5 for 120 min. The quantities of dye adsorbed on polyester samples at equilibrium were estimated using the following eq. (13):

$$q_e = \frac{(c_0 - c_e)v}{w} \quad (13)$$

Where, q_e is the quantity of dye adsorbed on polyester samples (mg/g) 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 polyester sample (g).

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