

## Industrial Impact via Nanodyeing Technology of Polyester and Nylon-6 Micro-fabrics: Comparative Investigations of Kinetic and Thermodynamic Parameters

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**Abstract:** The possibility of reducing temperature, using less dyestuff, and saving energy of conventional dyeing of polyester and nylon-6 micro-fabrics with a disperse dye via nanodyeing were studied in order to reach higher exhaustion values comparable to those obtained with the conventional ones at different temperatures. The aim was to prepare a nanodisperse dye using dry ball milling and characterize the as-prepared nanodye by transmission electron microscopy and UV-vis spectroscopy. Dyeings of polyester and nylon-6 micro-fabrics were carried out in the temperature range between 70 and 130°C using both Disperse Yellow 42 and its nano-size dye to compare the results. For each dyeing, the exhaustion curves of the dye bath were determined and the better results of dyeing kinetics were obtained in case of nanodyeing. Hence the corresponding dye adsorption rate constants according to pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were calculated. Moreover the diffusion coefficients and activation energies were also evaluated. The partition coefficient and standard affinity at various temperatures were determined for the Disperse Yellow 42 and its nanoscale dye. The corresponding thermodynamic parameters, enthalpy and entropy changes, of conventional and nanodyeing processes were also compared.

**Key words:** Nanotechnology, Polyester, Nylon-6, Micro-fabrics, Disperse dye, Kinetic and thermodynamic parameters.

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### INTRODUCTION

Nanotechnology is a very complex field combining science (biology, chemistry and physics), technology (computer programming), engineering (electronics and design) and math. Nanotechnology can be applied to many areas in textiles. They are used for producing nano-fibers, and nano-composites, and in nanodyeing and nano-finish. Nanodyeing is the application of reduced size dyes that are smaller than 100nm in textile dyeing (Hornyak *et al.*, 2009).

Comprehensive research efforts have been made in the area of disperse dyes that have been used for the dyeing of hydrophobic fabrics (Blacker and Patterson, 2008; Gaffer *et al.*, 2010). Consequently, in the last two decades, the research trends focused their efforts on the application of new technologies (Nahed and El-Shishtawy, 2010) such as nanotechnology, electrochemistry, supercritical carbon dioxide dyeing, plasma, ultrasonic and microwave to modify and develop the dyeability of polyester and nylon fabrics. Polyester is the most hydrophobic of all common fibers and has a highly compact and crystalline structure. For this reason, its aqueous dyeing is carried out at high temperature and high pressure using disperse dyes (Choi *et al.*, 2001); while nylon-6 has a linear polymer structure and is thermoplastic with extent of non-crystalline region in the fiber. These facts make it impossible to apply the disperse dyestuffs by conventional methods resulting in high fabric dyeing efficiency. This impossibility increases in case of dyeing microfibers (Shin and Bide, 2000). Microfibers are typically <1 dtex and enjoy manifold apparel applications owing to their soft handle, high lustre and excellent drapeability (Burkinshaw, 1995). Microfiber has a larger surface area than conventional decitex fiber per unit mass of substrate (Burkinshaw and Son, 2010).

Choi and Kang prepared six nanodisperse dyes using oil/water nanoemulsions and studied the influence of nanodyes on the exhaustion yields of regular and ultramicro-fiber polyester (Choi and Kang, 2006). Set of nanocolorants were successfully prepared by using a modified miniemulsion polymerization process. These nanocolorants exhibited excellent chromatic properties attributed to the nanoscale effects of homogeneous nanocolorants (Hu *et al.*, 2008). In our lab, nano-Disperse Red 60 was successfully prepared via modified miniemulsion polymerization to be applied into micro-polyester (El-sayed *et al.*, 2012). Fang *et al.* once successfully colored the cationized cotton with nanoscale pigment (Fang *et al.*, 2005). Hao *et al.* prepared nanoscale pigment using milling method and investigated the kinetic adsorption properties of this nanoscale pigment on cationized cotton fabrics (Hao *et al.*, 2012). To the best of our knowledge, so far, the preparation of nanodisperse dye by dry ball milling technique has never been studied and applied in a comparative adsorption study onto hydrophobic fabrics.

The purpose of this work was to prepare nanodisperse dye and determine whether nanodyeing could be used to intensify the dyeability of polyester and nylon-6 micro-fabrics with a traditional disperse dye and its nano scale in a comparative study without using chemical auxiliaries. The paper concerns the dyeing mechanism of traditional and nanodisperse dye on both polyester and nylon-6 micro-fabrics by studying the kinetic and thermodynamic adsorption properties and diffusion ability parameters in the dye bath at different temperatures.

### Experimental:

#### Dye and Fabrics:

Disperse Yellow 42 (DY42) was kindly supplied by DyStar. The structure is represented in Fig.1. Woven micro-polyester (0.22 dtex) and micro nylon-6 (0.06 dtex) fabrics were generously supplied by El-Mahalla El-Kobra Company. The fabrics were scoured in aqueous solution with a liquor ratio 1:50 containing 2 g/l nonionic detergent solution (Hostapal, Clariant) and 2 g/l  $\text{Na}_2\text{CO}_3$  at 50°C for 30 min to remove waxes and impurities, then rinsed thoroughly in cold tap water, and dried at room temperature.

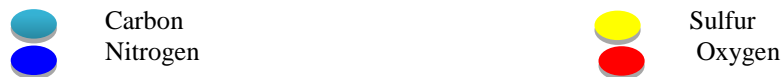
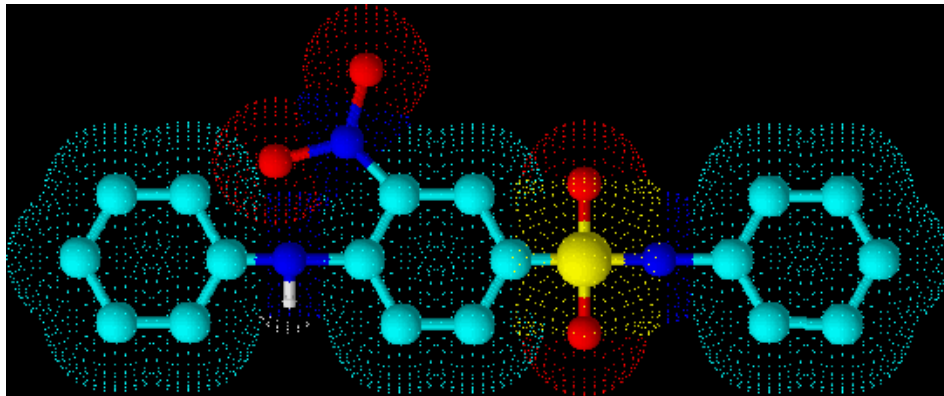


Fig. 1: Structural formulae of DY42 drawn by ACD/ChemSketch.

#### Preparation of Nanodye:

Nano-Disperse Yellow 42 (nDY42) was prepared using ball milling (RETSCH Planetary Ball Mills Type PM 400, Germany). DY42 was charged and dry mixed into 250 ml stainless steel agar with 8 grinding balls, 400 rpm, for 8hrs. The prepared nDY42 was analyzed using JEM-2100 High Resolution Transmission Electron Microscope (HRTEM, JEOL, Japan). Absorption spectra in water were recorded by UV-vis spectrophotometer (Perkin Elmer Lambda 35, USA).

#### Dyeing Process:

To determine the dyeing process behavior of polyester and nylon-6 micro-fabrics with DY42 and nDY42 at different temperatures, 2 g fabric samples were introduced in a flask containing the dye bath of 1, 2, 3, 4% of dye and 2g/l SDS as anionic surfactant for time intervals up to 120 min at 70, 80, 90, 100, and 130°C with 1:50 liquor ratio at pH adjusted to 5.2. At the end of dyeing, the dyed samples were removed, rinsed in tap water and allowed to dry in the open air. The measurements were performed with an UV-vis spectrophotometer.

#### Adsorption Kinetic Modeling:

To evaluate the adsorption kinetics of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics, pseudo-first order (Errais *et al.*, 2011), pseudo-second order (Alver and Metin, 2012), and intra-particle diffusion (Elsherbiny *et al.*, 2012) kinetic models were investigated to fit the experimental data obtained at different temperatures.

$$1^{\text{st}} \text{ order kinetic model} \quad \ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$2^{\text{nd}} \text{ order kinetic model} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$\text{And} \quad h = k_2 q_e^2 \quad (3)$$

intra-particle diffusion model (4)

$$q_t = k_p t^{1/2} + C$$

where  $q_e$  and  $q_t$  are the dye adsorbed per unit weight of fabric ( $\text{mg g}^{-1}$ ) at equilibrium and at any time  $t$ , respectively;  $k_1$  is the rate constant for 1<sup>st</sup> order reaction ( $\text{min}^{-1}$ ),  $k_2$  is the rate constant for 2<sup>nd</sup> order reactions ( $\text{mg g}^{-1} \text{min}^{-1}$ ),  $h$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ );  $k_p$  is rate constant for intra-particle diffusion ( $\text{mg g}^{-1} \text{min}^{-1/2}$ );  $C$  is the intercept of intra-particle diffusion equation ( $\text{mg g}^{-1}$ ).

Different methodologies were suggested to calculate the diffusion coefficient,  $D$  ( $\text{cm}^2 \text{min}^{-1}$ ), of dye into fabric in dyeing process depending on the employed dyeing procedure and the physical shape of material. In this study, the Hill's equation, Eq. 5 (Shoar *et al.*, 2009) was employed to determine the diffusion coefficient of dye into both fabrics. The activation energy of the diffusion was calculated according to Arrhenius's equation, Eq. 6 (Rabiei *et al.*, 2012).

$$\frac{C_t}{C_e} = 4 \sqrt{\frac{Dt}{\pi r^2}} \tag{5}$$

$$\ln D = \ln D_0 - \frac{E}{RT} \tag{6}$$

where  $C_t$  and  $C_e$  represent the dye concentrations in solution at time  $t$  and at equilibrium ( $\text{mg L}^{-1}$ );  $D_0$  is a constant;  $r$  is a radius of the cylindrical fiber (cm);  $E$  is the activation energy ( $\text{kJ mol}^{-1}$ );  $R$  is a gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K).

**Thermodynamic Parameters:**

The partition coefficient,  $K$ , of the dye concentration between the fiber and the dyeing solution was obtained from the adsorption isotherm. The standard affinity of the dye was calculated using the following equation (Rabiei *et al.*, 2012):

$$-\Delta\mu^0 = RT \ln \frac{[D]_f}{[D]_s} = RT \ln K \tag{7}$$

where  $-\Delta\mu^0$  is a standard affinity ( $\text{kJ mol}^{-1}$ ),  $[D]_f$  and  $[D]_s$  are dye concentrations in fiber ( $\text{mg g}^{-1}$ ) and in solution ( $\text{mg ml}^{-1}$ ), respectively.

The dyeing enthalpy change was obtained from the empirical plot of the Clausius-Clapeyron equation, Eq.8, and the enthalpy change can be calculated from the slope of the straight line of Eq. 9. The dyeing entropy change was calculated from the experimental plot of the relation between  $-\Delta\mu^0$  and  $T$ , Eq. 10 (Rabiei *et al.*, 2012).

$$\Delta H^0 = \frac{\delta(\Delta\mu^0/T)}{\delta(1/T)} \tag{8}$$

$$\frac{\Delta H^0}{T} = \frac{\Delta\mu^0}{T} + Const. \tag{9}$$

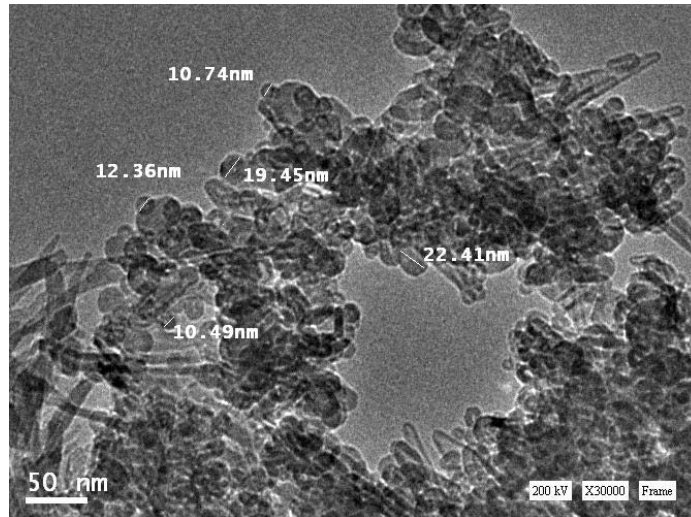
$$-\Delta\mu^0 = T\Delta S^0 - \Delta H^0 \tag{10}$$

where  $\Delta H^0$  is enthalpy change, heat of dyeing, ( $\text{kJ mol}^{-1}$ );  $Const.$  is an integral constant;  $\Delta S^0$  is the change in entropy ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ).

**RESULTS AND DISCUSSION**

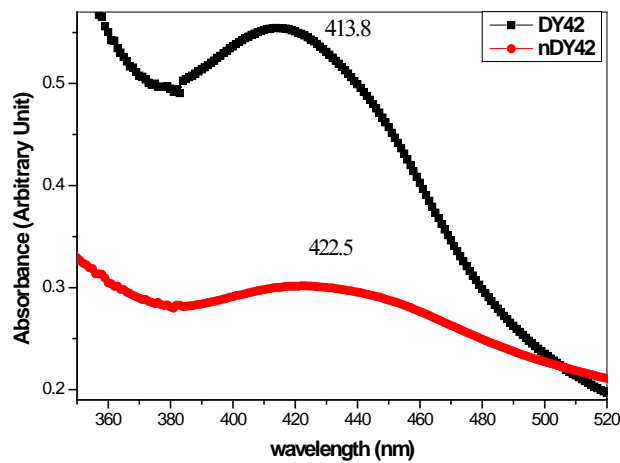
**Characterization of nDY42:**

The transmission electron photograph of the newly prepared nDY42 is presented in Fig.2, where homogeneous spherical nano-particles with average particle size smaller than 25 nm were observed.



**Fig. 2:** Transmission electron photograph of nDY42

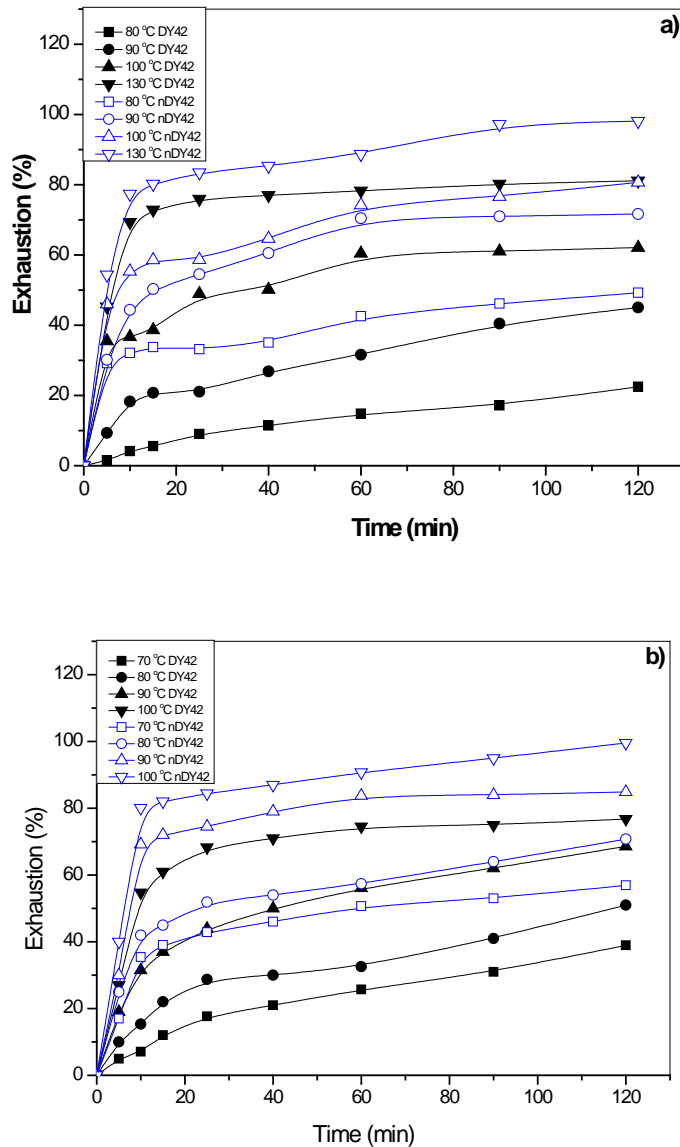
UV-vis absorption spectra were obtained by dissolving DY42 and nDY42 in absolute ethanol. As shown in Fig.3, the hypsochromic shift  $\lambda_{\max}$  422.5 nm of nDY42 than the original  $\lambda_{\max}$  413.8 nm of DY42 confirmed that the absorption energy shifted to higher frequency with decreasing diameter of the dye particles. This was readily observed from the reflected color change of the brilliant yellow of DY42 to yellowish orange of nDY42. Because the nitro diphenylamine-base of DY42 which is a big p-conjugated planar structure, it generates inter molecular p-p\* interaction and leads to molecular stacking (Kim *et al.*, 1999).



**Fig. 3:** UV-vis absorption spectra of DY42 and nDY42.

#### ***Dyeing kinetics:***

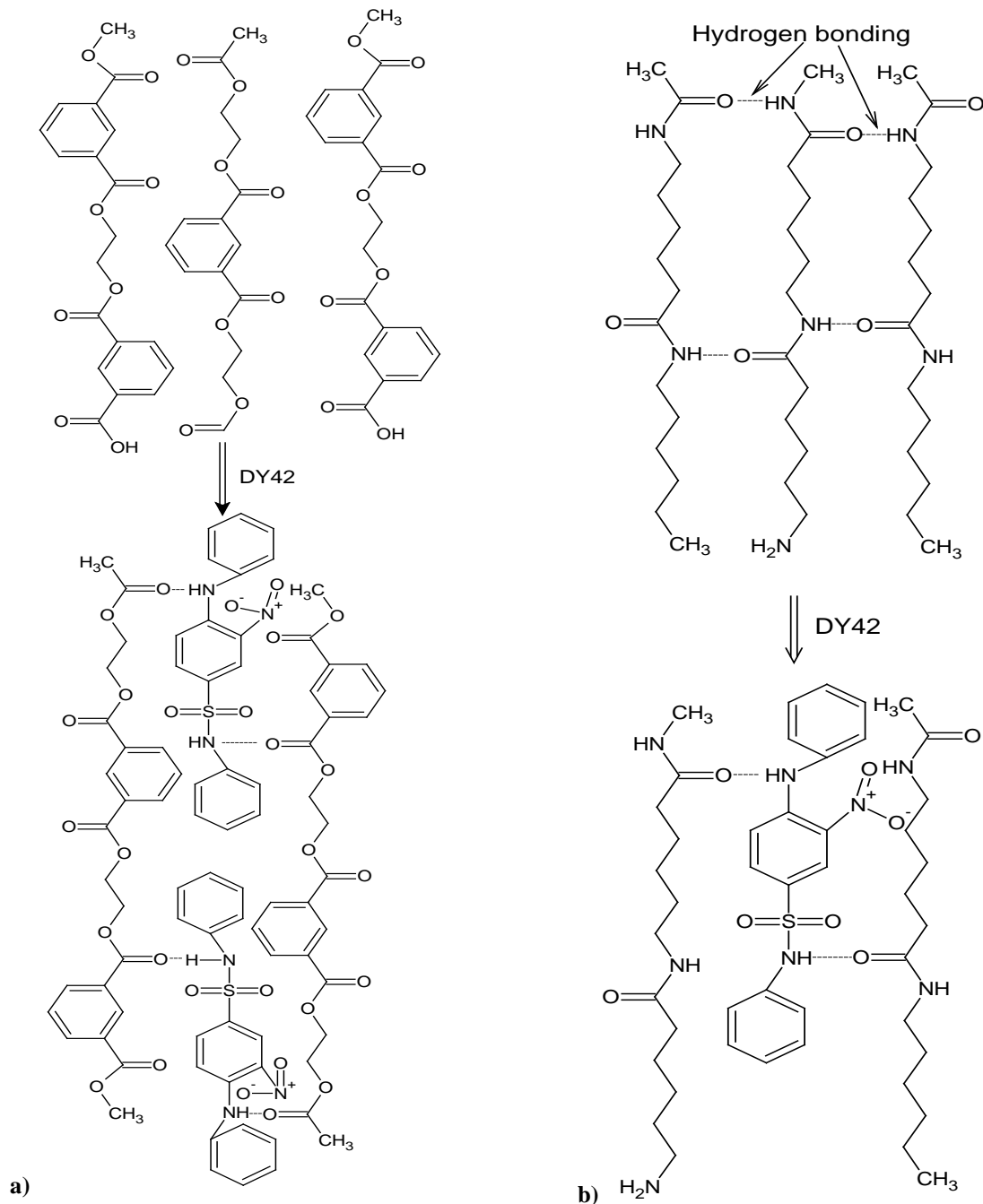
Time-exhaustion isotherms of polyester and nylon-6 micro-fabrics using DY42 and nDY42 are shown in Fig. 4. The figure shows that the dyeability of polyester and nylon-6 samples using nDY42 is generally better than that obtained using DY42. Improvements observed in nanodyeing processes are generally attributed to the smaller particle size of the nanodye, approximately thousand times smaller, and, as a consequence, nDY42 can not only diffuse into the fabric without aggregation on the surface but also penetrate into the fiber pores. Higher temperature resulted in an increase in dye exhaustion onto fabrics; hence, the dye adsorption is an endothermic process.



**Fig. 4:** Time-exhaustion isotherm for dyeing of a) polyester b) nylon-6 micro-fabrics using DY42 and nDY42 [Dyeing conditions: 2%owf; LR 1:50; pH=5.2].

From Fig. 4, it is clear that polyester and nylon-6 micro-fabrics have the lower and higher dyeability at the same temperature, respectively. This may be due to firstly, when considering the chemical structure of DY42 and the fabrics (Fig. 5), the amide group,  $-\text{CO}-\text{NH}-$ , among nylon-6 chains is potentially a bifunctional electron donor with  $2sp^2$  "lone pairs" at the oxygen atom and a  $2pz^2$  "lone pair" at the nitrogen atom and therefore has two possible electron-donating sites to coordinate with the dye molecule. Overlap of  $2pz$  orbitals of the oxygen, carbon, and nitrogen atoms in the planar amide group would reduce the electron density on the nitrogen atom and favor the formation of hydrogen bond between the amine group of the dye and the carbonyl oxygen atom. The terminal group,  $-\text{NH}_2$  on nylon-6 provides the dye sites for dye molecules. Whereas dye bonding with the amide groups in the nylon-6 breaks the intermolecular hydrogen bonds between nylon-6 chains which is schematically shown in Fig. 5. While in case of the nearly planar polyester, the atomic positions in the crystallite indicate that no special forces of attraction exist between the molecules. After dyeing, the interaction between dye and polyester is due to the formation of hydrogen bonds, dipole-dipole interactions, and Van der Waals forces (Gupta *et al.*, 2009). Secondly, the less crystalline structure of nylon-6 [crystallinity values of 50% and 65%-85% for nylon-6 (McIntyre, 2005) and polyester (Timar and Eastop, 2002), respectively]. In addition, the internal structure of polyester fabric during the dyeing process is more rigid than that of nylon-6 that could lead

to less penetration in comparison with nylon-6 fabric. Eventually, the polyester is more hydrophobic than nylon-6.



**Fig. 5:** Simple schematic representation of the possible interactions between DY42 and (a) Polyester (b) Nylon-6 [ACD/ChemSketch]

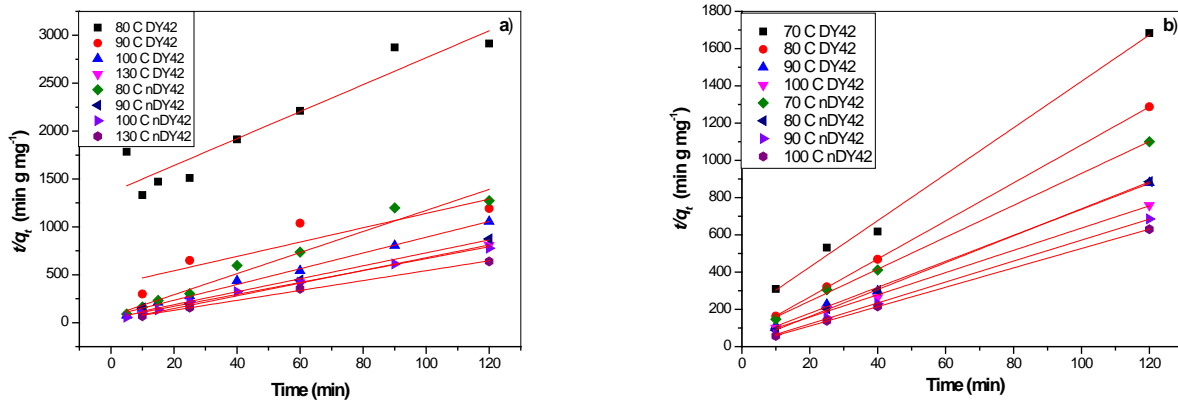
Adsorption kinetics are important from the point of view that it controls the efficiency of the process and the models correlate the adsorbate uptake rate with its bulk concentration. Therefore, the most practical parameters, i.e. dyeing rate constant, diffusion coefficient and activation energy of diffusion were determined for both types of fabrics. The experimental data shown in Fig. 4 can be analyzed using three kinetic models that represented by Eq. 1, 2, and 3 to determine the adsorption kinetics of DY42 and nDY42 on polyester and nylon-6 micro-fabrics at temperature range 70-130°C. The kinetic data of adsorption process towards temperature is given in Table 1 and it is observed that adsorption increases with the increase in temperature. This indicates that the endothermic nature of the process is attributable to the tendency of dye molecules to escape from the bulk phase to solid phase with an increase in temperature of the dyeing bath.

**Table 1:** Kinetic parameters of the dyeing process of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics.

Fabric	Dye	Temperature (°C)	$q_{e,exp}$ (mg g <sup>-1</sup> )	Pseudo 1 <sup>st</sup> order			Pseudo 2 <sup>nd</sup> order				Intra-particle diffusion		
				$k_1 \times 10^2$ (min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$r_1^2$	$k_2$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$r_2^2$	$k_p$ (mg g <sup>-1</sup> min <sup>1/2</sup> )	$C$ (mg g <sup>-1</sup> )	$r_p^2$
Polyester	DY42	130	0.04118	-1.622	0.03961	0.98833	0.01035	0.07107	0.00073	0.99635	0.0041	0.0057	0.9893
		100	0.10072	-1.256	0.0879	0.8329	0.01907	0.13363	0.00255	0.99645	0.0087	0.0009	0.9044
		90	0.11363	-4.425	0.0804	0.92661	0.11894	0.1215	0.01445	0.99521	0.0063	0.0511	0.9049
		80	0.14842	-4.735	0.06186	0.59735	0.43907	0.15074	0.06619	0.99976	0.0025	0.1221	0.8133
	nDY42	130	0.09432	-1.33	0.04046	0.28251	0.15336	0.09089	0.01394	0.99582	0.0034	0.0519	0.6327
		100	0.13723	-6.941	0.10642	0.86515	0.12894	0.14781	0.01906	0.9904	0.0076	0.0653	0.3695
		90	0.15462	-2.856	0.08575	0.8849	0.13483	0.16066	0.02166	0.99452	0.0072	0.0794	0.9472
		80	0.18797	-3.188	0.09406	0.5128	0.19868	0.19347	0.03844	0.99644	0.0049	0.1333	0.9882
Nylon-6	DY42	100	0.07127	-0.05678	0.07473	0.94046	0.06988	0.08026	0.00561	0.99289	0.0050	0.0202	0.8968
		90	0.09323	-0.05933	0.07464	0.93977	0.16224	0.09804	0.01591	0.99996	0.0038	0.0536	0.8490
		80	0.13634	-0.09539	0.15009	0.90384	0.17574	0.14341	0.0252	0.99746	0.0061	0.0760	0.7857
		70	0.15825	-0.0752	0.1535	0.9436	0.15135	0.16751	0.02535	0.99791	0.0074	0.0837	0.8420
	nDY42	100	0.10908	-0.05141	0.09095	0.93147	0.11677	0.11674	0.01363	0.99872	0.0052	0.0540	0.9651
		90	0.13554	-0.09157	0.09912	0.91852	0.41596	0.13838	0.05756	0.99974	0.0029	0.1061	0.8298
		80	0.17509	-0.11251	0.12991	0.89871	0.59583	0.1777	0.10588	0.99974	0.0028	0.1468	0.8136
		70	0.19034	-0.08279	0.08878	0.69501	0.76506	0.19231	0.14713	0.99995	0.0018	0.1703	0.9683

The parameters  $k_1$  and  $q_e$  for the pseudo-first order kinetic model, Eq. 1, can be determined from the slope and intercept of a straight line of  $\ln(q_e - q_t)$  versus  $t$  and the values are given in Table 1. The values of the correlation coefficient  $r_1^2$  for the pseudo-first order model changed in the range 0.2825–0.9883. Furthermore, the values of  $q_e$  are not in agreement with the experimental  $q_{e,exp}$ . This suggests that the adsorption of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics did not follow the pseudo-first order kinetic model, and it is not a diffusion-controlled phenomenon.

For the pseudo-second order kinetic model, Eq. 2, the  $q_e$  and  $k_2$  values can be obtained from the slopes and intercepts of plots of  $t/q_t$  versus  $t$  which are illustrated in Fig. 6. The correlation coefficients  $r_2^2$  of linear plots at different temperatures are higher than 0.9904, which suggest that the adsorption of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics follows the pseudo-second order kinetic model. Besides, it is well consistent between the values of  $q_e$  and the experimental  $q_{e,exp}$ . Therefore, it can be concluded that pseudo-second order equation is better in describing the adsorption kinetics of both DY42 and nDY42 onto polyester and nylon-6 micro-fabrics. The pseudo-second order model suggests that the adsorption depends on the adsorbate as well as the adsorbent and involves chemisorption process in addition to physisorption. The chemisorption might be the rate limiting step where valency forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate (Xiong *et al.*, 2010). The parameters are listed in Table 1.

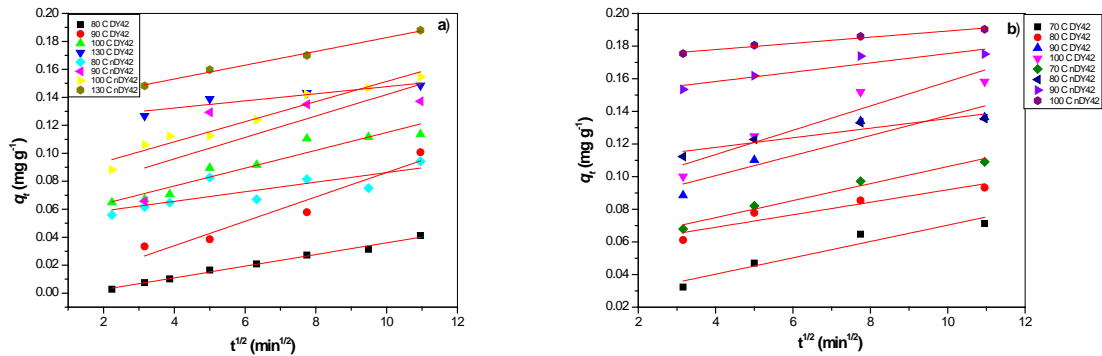


**Fig. 6:** Pseudo-second order adsorption kinetics of DY42 and nDY42 onto a) polyester b) nylon-6 micro-fabrics at various temperatures. [Dyeing conditions: 2%owf; LR 1:50; pH=5.2].

In order to investigate the mechanism of the dyeing of DY42 and nDY42 onto polyester and nylon-6micro-fabrics, an intra-particle diffusion based mechanism has been studied. The plot of  $q_t$  vs.  $t^{1/2}$  is shown in Fig. 7.



According to Eq. 4, the intra-particle diffusion rate constant  $k_p$  and  $C$  are given in Table 1. If intra-particle diffusion is only involved in the adsorption process, then the plot will result in a linear relationship, passing through the origin; if not, the boundary layer diffusion controlled the adsorption to some degree (Cheung *et al.*, 2007). As seen in Fig. 7, the plots were firmly linear over the whole time range but with slightly deviation from the origin; this indicates that the intra-particle diffusion is not only rate controlling step, but also some other processes may control the rate of dye adsorption (Mahmoud *et al.*, 2012; Kousha *et al.*, 2012). It was concluded that the dyeing adsorption mechanism was predominantly intra-particle diffusion but there was also a dependence on pore size as the dye diffuses through macro-pore and micro-pore of fabrics. The  $C$  value is obtained from intercept and gives an indication of the thickness of the boundary layer. The larger  $C$  shows greater boundary layer effect (Kismir and Aroguz, 2011). The values of  $C$  are between 0.0009 and 0.1703 over the whole temperature range, this indicates that boundary layer effect may slightly control the dyeing rate.



**Fig. 7:** Intra-particle diffusion kinetics of of DY42 and nDY42 onto a) polyester b) nylon-6 micro-fabrics at various temperatures. [Dyeing conditions: 2% owf; LR 1:50; pH=5.2].

The dyeing process is a solid/liquid phase process, which proceeds by the movement of the dye molecules from liquid phase to the solid surface of the fabric by virtue of their affinity, and then diffusion takes place inside the fabric. Therefore, the first process would be a fast adsorption controlled process where the dye molecules get into the fabric, the second slow process which is diffusion controlled, starts to take place. For the dye molecules to diffuse into the fabric, it is expected that the free volume could be formed within the fabric. This free volume is regarded as the void being temporarily formed within the fabric by the thermal movement of molecular chains and the dye molecules penetrate into this empty space (Weigmann *et al.*, 1977; Kamel *et al.*, 2005). According to Hill's equation, Eq. 5, the diffusion coefficients were calculated by plotting  $\frac{C_t}{C_e}$  versus  $t^{1/2}$

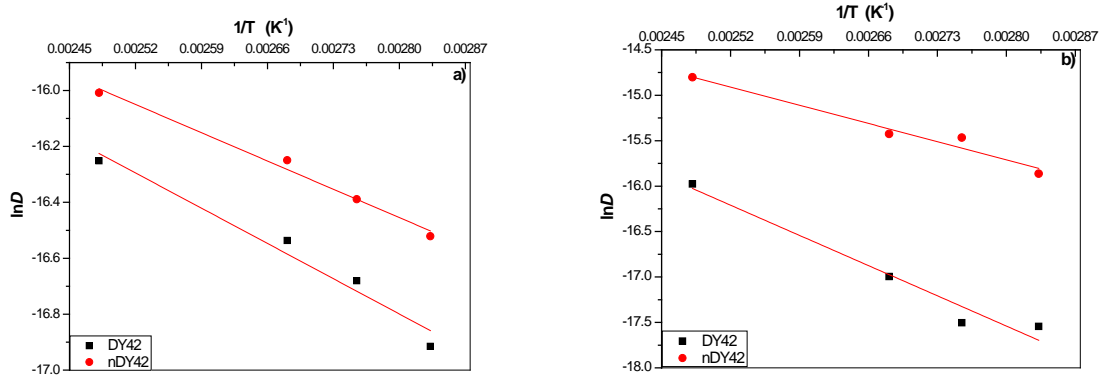
for the early stage of dyeing. As can be seen, Table 2, as the temperature of dyeing increases, the diffusion coefficient also increases which means the capability of fabrics to hold dye molecules within its polymeric matrix at higher temperatures. Also, the diffusion coefficients of nDY42 onto polyester and nylon-6 micro-fabrics are higher than that of DY42 for all temperature range. Because of the particles size reduction of nDY42 (<25 nm), it can easily diffuse and incorporate into the swelled polymeric matrix of fabrics in addition to the surface adsorption.

The activation energy of the diffusion of DY42 and nDY42 was calculated by Eq. 6 from the linear relationship of  $\ln D$  against  $1/T$  for both micro-fabrics, Fig. 8. The activation energy of the diffusion,  $E$ , explains the dependence of diffusion coefficient on the dyeing temperature and also represents the energy barrier that a dye molecule should overcome to diffuse into the polymer chains (Alan, 1989; Kim *et al.*, 2005). The activation energy of diffusion of DY42 onto polyester and nylon-6 micro-fabrics (3.587 and 39.503 kJmol<sup>-1</sup>, respectively) is significantly higher than that of nDY42 (2.887 and 23.790 kJmol<sup>-1</sup>, respectively). This means the activation energy of diffusion of DY42 is lowered by 19.7% for micro-polyester and 39.7% for micro nylon-6 using nDY42. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ mol<sup>-1</sup>, while higher activation energies (40–800 kJ mol<sup>-1</sup>) suggest chemisorption (Nollet *et al.*, 2003). The diffusion coefficient and activation energy results for dyeing of polyester and nylon-6 micro-fabrics using both DY42 and nDY42 are demonstrated in Table 2. Considering these values are in the typical activation energy range for physisorption, one can conclude that DY42 and nDY42 adsorbed onto polyester and nylon-6 micro-fabrics are mainly physically.



**Table 2:** Diffusion coefficient and activation energy of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics at various temperatures.

Fabric	Dye	$D \times 10^8$ ( $\text{cm}^2 \text{min}^{-1}$ )					$E$ ( $\text{kJmol}^{-1}$ )
		70 °C	80 °C	90 °C	100 °C	130 °C	
Poly	DY42	--	4.5055	5.6999	6.5796	8.7543	3.5878
	nDY42	--	6.6817	7.6292	8.7708	11.215	2.8777
Nylon-6	DY42	1.966	2.5004	4.1569	11.515	--	39.5036
	nDY42	12.896	19.209	19.99	37.319	--	23.7901



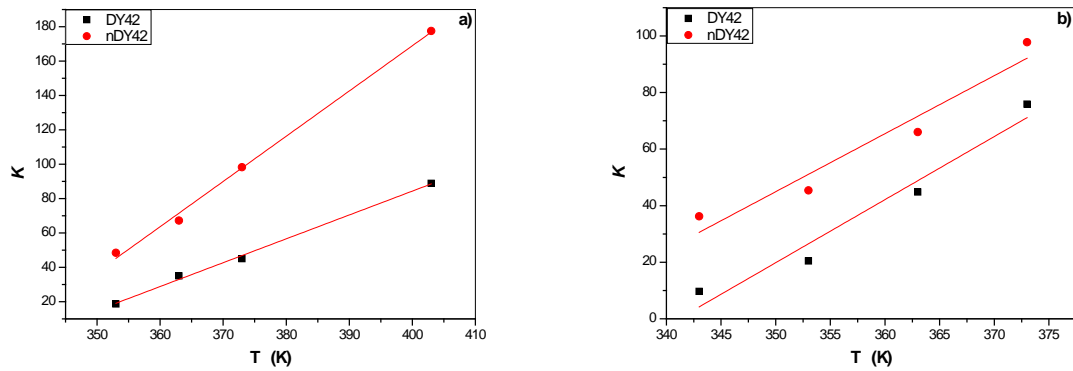
**Fig. 8:** Relation between  $\ln D$  and  $1/T$  for determination of activation energy of dye diffusion on to a) polyester b) nylon-6 micro-fabrics.

**Dyeing Thermodynamics:**

The thermodynamic parameters are depicted in Table 3. Fig. 9 shows that as the temperature increases, the partition coefficient of dye increases for both micro-fabrics. This indicates again that the adsorption of dye towards micro-polyester and nylon-6 fabrics is well known as an endothermic reaction process, resulting higher dyeing temperature gives a positive effect on the thermodynamic adsorption. The most basic thermodynamic parameter is the standard affinity,  $-\Delta\mu^0$ , of the dye in dyeing solution towards fiber substrate. This parameter was defined as a difference between the chemical potential of the dye in the fiber and the chemical potential of the dye in the dyeing solution. This value measures the tendency of the dye to move from its standard state of the solution to its standard state of the fiber (Vickerstaff, 1954). From Table 3, it was noticed that the differences between the standard affinity of dye molecules towards micro-polyester and nylon-6 fabrics are due to the differences in the chemical structures and physical properties of fabrics. Also, a significant increase in the standard affinity values of nDY42 onto micro-polyester and nylon-6 fabrics than that of DY42. This reflects that the tendency of nDY42 molecule to move from its standard state in the dye bath to its standard state in the micro-fabrics is significantly higher than that of DY42.

**Table 3:** Thermodynamic parameters for the adsorption of DY42 and nDY42 onto polyester and nylon-6 micro-fabrics at various temperatures.

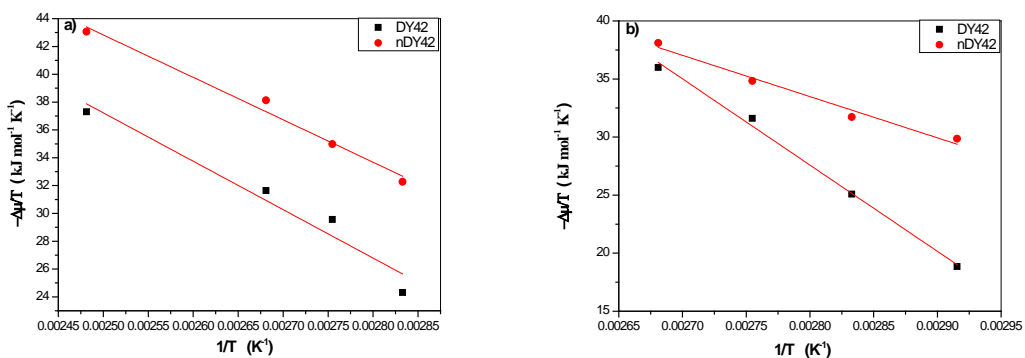
Fabric	Dye	$K$					$-\Delta\mu^0$ ( $\text{kJ mol}^{-1}$ )					$\Delta H^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^0$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )
		70 °C	80 °C	90 °C	100 °C	130 °C	70 °C	80 °C	90 °C	100 °C	130 °C		
Poly	DY42	--	18.611	35.010	44.981	88.858	--	8.580	10.730	11.803	15.034	+34.806	-0.122
	nDY42	--	48.489	67.175	98.195	177.550	--	1.139	12.697	14.224	17.353	+30.507	-0.118
Nylon	DY42	9.644	20.422	44.789	75.862	--	6.463	8.853	11.474	13.424	--	+74.267	-0.235
	nDY42	36.252	45.378	66.021	97.763	--	10.239	11.196	12.645	14.211	--	+35.527	-0.133



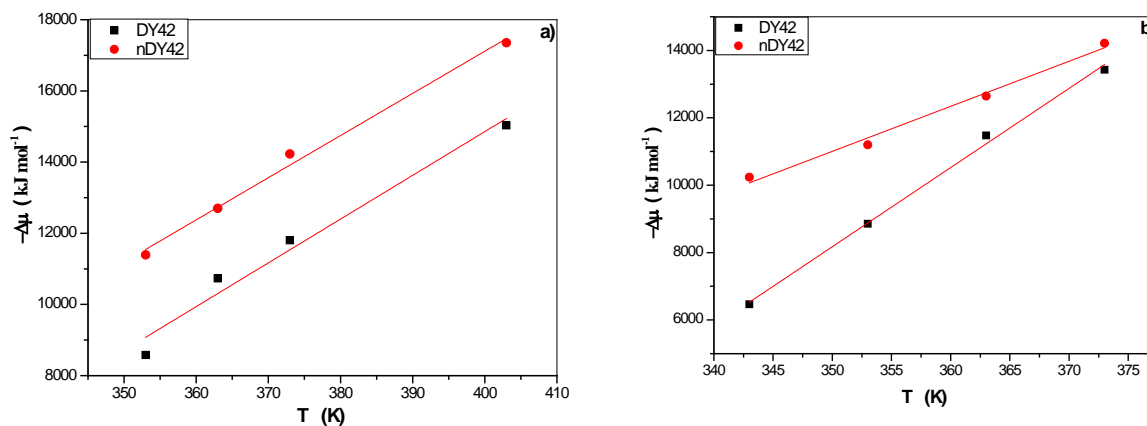
**Fig. 9:** Partition coefficient relation at different dyeing temperatures for DY42 and nDY42 onto a) polyester b) nylon-6 micro-fabrics.

The enthalpy change,  $\Delta H^0$ , means the amount of the released thermal energy when dye molecules are adsorbed onto fabric. In addition, the enthalpy change is considered as the measure of the adsorption strength of dyes (Trotman, 1984). Adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy change. It is accepted that if magnitude of enthalpy change is less than  $84 \text{ kJ mol}^{-1}$ , the adsorption process is physical in nature. However, the chemisorption process takes place in range from 84 to  $420 \text{ kJ mol}^{-1}$  (Errais *et al.*, 2011). As can be seen from Fig. 10, the enthalpy changes,  $\Delta H^0$ , were determined as  $+34.806$  and  $+30.507 \text{ kJ mol}^{-1}$  for DY42 and nDY42 onto micro-polyester fabric while their corresponding values onto micro nylon-6 were  $+74.267$  and  $+35.527 \text{ kJ mol}^{-1}$ , respectively. All magnitudes of enthalpy change indicate that the adsorption is physical in nature. In addition to the adsorption of DY42 and nDY42 had a positive  $\Delta H^0$  value that confirmed again the endothermic nature of the overall dyeing processes.

Meanwhile, the entropy change,  $\Delta S^0$ , shows the extent of the reduced freedom of dye molecules after the completion of dyeing and represents the entropy difference of the dye molecules within the fiber (Kim *et al.*, 2007). According to Fig. 11, the values of entropy changes are  $-0.122$  and  $-0.235$  for DY42 onto micro-polyester and nylon-6 fabrics, respectively, while the corresponding changes in entropy values for nDY42 are  $-0.118$  and  $-0.133$ . The decrease in the entropy values may explain the decrease in randomness after the nanodyeing process, Table 3. The entropy change shows negative values in dyeing process, because adsorbed dyes become more ordered within fiber molecules than dyeing solution. Therefore, the value of the entropy change can be regarded as the measure of immobility of dyes within the fiber (Kongkachuichay *et al.*, 2002; Alkan *et al.*, 2004).



**Fig. 10:** Relationship between  $\frac{-\Delta\mu^0}{T}$  and  $\frac{1}{T}$  on enthalpy change for DY42 and nDY42 onto a) polyester b) nylon-6 micro-fabrics.



**Fig. 11:** Relationship between  $-\Delta\mu^0$  and  $T$  on entropy change for DY42 and nDY42 onto a) polyester b) nylon-6 micro-fabrics.

### Conclusion:

Comparing the results, micro-polyester and micro nylon-6 nanodyeing process with the prepared nDY42 at different temperatures can be regarded as an eco-friendly alternative to traditional dyeing without adding polluting auxiliary agents. For example, at 100°C the exhaustion values for polyester and nylon-6 micro-fabrics using nDY42 are 80.7 and 99.5% which corresponding to 62.1 and 76.7% using DY42, respectively; while at 90°C, the exhaustion values are 71.6 and 84.8% using nDY42 which corresponding to 55 and 68.5% with DY42, respectively. That means less dyestuff is required which in turn reduces the waste water pollution. In this way, great energy has been saved due to the lower process temperature involved to reach higher dyeability using nDY42. The positive effect of nanodyeing process was investigated by the evaluation of some kinetic parameters and confirmed by saving over 19 and 39% activation energies for micro-polyester and micro nylon-6, respectively. In conclusion, the dyeing process is determined to be endothermic with a physical in nature which further supported by the partition coefficient and standard affinity trends and the positive values of the enthalpy change. Finally the work is currently underway to investigate more in depth of the adsorption isotherm and fastness properties of dyeing processes.

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