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Miniemulsion of Nanoencapsulated Dye for Highly Efficient Polyester Dying

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IN THIS work dispersed red- 153dyewas converted to nano scale using mini emulsion polymerization. The particle size and zeta potential was investigated by dynamic light scattering. Dyeing of polyester fabrics was carried out to coated polyester fiberwith (PEG6000 + SORBITOL) and non-coated polyester (original) fabric before dying process in the temperature range 50-135^{o}C and compared with the polyester fabrics coated and non-coated before dying process with the same dyes in normal size by detect their k\s values. Kinetic study for the dying process was carried out for the nano and normal dye and different fastness properties (washing, light and rubbing) for all dyed fabric were carried out.

Keywords: Miniemulsion polymerization, Dye encapsulation, Polyester, Coated, Non-coated.

Introduction

Nanotechnology has converted more powerful and impressive than any other fields because it's working to improve direction and develop technology in many applications. Especially, there are many products depend on nanotechnology in textiles, for example, nanofiber for oil-water separation and visual fiber [1]. Textile manufacturing is also researching the importance of nanotechnology in numerous applications [2]. Disperse dyes are water heater compounds without any charge on their sites so these compounds are slightly water-soluble it's commonly crystalline with the variety in their particle size [3]. The disperse dye is grinding in the existence of a dispersing agent [4], disperse dye is somewhat soluble in water so it's employed for dyeing artificial fiber such as polyester, acrylic, and nylon which classified as hydrophobic fiber.

Disperse dyes are applied in aqueous dispersions in which the rates of its particle size are on average between 800~1,000 nm. In the traditional dyeing process, disperse dye is utilized for dyeing polyester fiber at 135°C and for dyeing Nylon fabrics at 100°C [5]. This temperature is too high and request a lot of energy, so if particle size minimized to nano size it would lead to reduce energy by the way reduce temperature and amount of dye that consumed during dyeing process. There are several methods to convert dispersed dye to nano, one of these methods is nanoemulsion.

Nanoemulsions are very little distribution of oil in water droplets on the regular scale in size 100 to 600 nm [6]. Another method to convert disperses dye to nano is polymer-encapsulation, polymerization methods have several kinds such as:Dispersion polymerization [7], soap-

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free emulsion polymerization [8], suspension polymerization [9], emulsion polymerization [10]. Mini emulsion polymerization is a fitting process to mix dyes of low water solubility to polymer nanoparticles [11,12].

It is an aqueous diffusion of comparatively settled oily droplets preparation by a system of oil/water with surfactant blind with low water-insoluble compound by ultra-sonication or homogenization, so-called hydrophobic whose functionality responsible for restricting decaying of droplet [13]. The specifications of the mini emulsion polymerization are encapsulated of nanoparticles which can be taken out via instantly to dispersing the hydrophobic particles and nucleating all the droplets in miniemulsions [14]. A property that describes mini emulsion polymerization is their droplet have high stability doesn't change in size, composition or size distribution upon polymerization [15]. So, our trail included the preparation of nano colorant that is sparingly monomer-soluble dye to produce great stability of colloidal diffusion with smaller particle size and higher monomer conversion of nano colorant [11].

Polyester fiber which dying with disperse dye at temperature 135^{o}C this temperature is high soIn this work, we aimed to minimized these temperature with high values of k\s by use changed miniemulsion polymerization for the preparation nano colorant particles and applied this nano colorant on polyester fabric, The particle size, zeta potential and dyeing behavior of the encapsulated dyes at several temperature were studied.

Materials and Methods

Materials

Scoured and bleached 100% polyester fabric (114 gm.\m^2) was supplied by El-Mahalla El-Kobra Company, commercial disperse dyes C.I RED 153 were supplied by OH YOUNG INDUSTERIAL CO., LTD. KOREA, Styrene (St), BA methacrylic acid, KPS (Potassium per sulfate), SDS (sodium dodecyl sulfate),glacial acetic and CETAB (cetyl tetra ammonium bromide)supplied by sigma Aldrich , acid non-anionic surfactant (TISSOCYL CFD CONC) from ZSCHIMMER &, SCHWARZ GERMANY, PEG6000 from ADVENT CHEM. (INDIA) and sorbitol from ADVENT CHEM. (INDIA).

Methods

Encapsulation of dye in copolymer

In 250 ml a round reactor 100 ml (solid content) of (BA/St 1:1) with KPS (0.78 mmol) as initiatorand SDS (1.56 gm) as anionic surfactant to prepared copolymer mini-emulsion was sonicated with 1 wt% (weight percentage calculated referred to the solid content of the mini-emulsion) of dye at room temperature for 30 min. the size of the silica NPs in the mini-emulsion was investigated using Particle size analyzer. The results indicate that the diameter of the encapsulated dye is homogenized distribution.

Sample preparation

Was prepared by using 100% polyester (PET) woven fabric with 114g/m^2 and a thickness of (0.25) mm. The PET woven fabric was soaped with hot water at 50°C with non-anionic surfactant (TISSOCYL CFD CONC) from ZSCHIMMER & SCHWARZ GERMANY to be freed from surface impurities and spinning oil .

Coating procedure

A 12 grams of PEG6000 from ADVENT CHEM. (INDIA) mixed with 6 grams of sorbitol from ADVENT CHEM. (INDIA) [18] and 1grame of CTAB dissolve this in 70 ml water then put fabric in this solution and then coating process take place in dying machine at 135^{o}C 40^{o}C minutes,rinsing in water at 60 for 5 minutes then dried at 100^{o}C in drying oven [16].

Dyeing procedure

Dyeing bath was prepared by adding 10ml of nano and normal disperse dye and 1ml of acetic acid in 100ml water then dyeing at several temperature 50,60,70,80,90,135 [3] , in a dyeing machine (DaeLim Starlet-3) MODEL: DL-6000 PLUS for 30 minutes.

Measurements and Analysis

Color measurement

The visible absorption spectra of the dye solutions were measured using a Shimadzu UV-Vis spectrophotometer. The colorimetric analysis of the dyed samples was performed using a Hunter Lab Ultra Scan R PRO spectrophotometer. was applied to measure the colour strength samples in terms of KubelkaMunkeunction. This was signified as K⁄S values at the highest wavelength ʎ= 510 nm, the relative colour strength (K/S values) was assessed using the following equation:

$$k/_{s} = \frac{(1-\mathbf{R})2}{2\square} \quad (1).$$

Where R = decimal fraction of the reflectance of the dyed fabric, K = absorption coefficient and S = scattering coefficient [17].

Fastness properties

Fastness properties of dyed polyester fabrics using nano and normal dye are shown in Table 3, the results indicate good to very good fastness properties of the dyed samples using nano and normal disperse dyes.

Colour fastness to washing

The colour fastness to washing was determined according to the AATCC Test method 61- 1975 using Launder-Ometer. The specimens (5 × 10 cm) were sewed between two similar pieces of bleached cotton fabric and wool fabric. The composite specimen was immersed into an aqueous solution containing 5 g/L soap and 2 g/L sodium carbonate using a material to liquor ratio 1:50. The bath was thermostatically adjusted to 95^{o}C. The test was run for 45 min. at 42 rpm. The samples were then removed, rinsed twice in 100 ml bath of water at 40^{o}C for one minute with occasional stirring or hand squeezing ,souring in 100 ml of 0.014% solution of acetic acid for one minute at 27^{o}C, rinsing again for one minute in 100 ml water at 27^{o}C followed by drying. Evaluation of the wash fastness was established using the Gray Scale reference for colour change [18].

Colour fastness to rubbing (crocking)

The colour fastness to crocking was determined according to the AATCC test method 8 - 1977. [34]. This test is designated for determining the degree of colour which may be transferred from the surface of the coloured fabric to other surface by rubbing. A coloured test specimen fastened to the base of a Crock Meter was rubbed with white crock test cloth under controlled conditions [19].

Dry Rubbing Test

The test specimen was placed flat on the base of the Crock Meter. A white testing cloth was mounted on the finger of the crock meter. The covered finger was lowered onto the test specimen and caused to slide back and forth 20 times by making ten complete turns at a rate of one turn/second. The evaluation was done using the Gray Scale for staining.

Wet Rubbing test

The white test sample was thoroughly wetted out in distilled water to a 65% wet pick up. The procedure was run as before. The white test samples were then air dried before evaluation.

Color Fastness to Light

Color fastness to light was determined according to AATCC test method (16A-1988). The evaluation was established using the blue scale as reference of color change [20].

Particle size

Dynamic light scattering (DLS) instrument (PSS, Santa Barbara, CA, USA), using the 632 nm line of aHeNe laser as the incident light with angel 90^{o} and Zeta potential with external angel 18.9^{o}. Nanomaterial Investigation Lab., Central Laboratory Network (CLN), National Research Centre (NRC).

Scanning Electron Microscope

The surface morphology of coated with (peg6000+ sorbitol) and non-coated (original) polyester fabric which dyed with nano and normal dye was examined by high resolution scanning electron microscopy (SEM Quanta FEG 250 with field emission gun, FEI Company – Netherlands).

Results and Discussion

The particle size Intensity-Gussian distributions are shown in **Figure (1).** The distributions are present with bell shape character with narrow poly dispersity index 0.478 for modified nano-encapsulated dye. The mean diameter was 87.5 nm for modified nano-encapsulated dye.

Table (1) Illustrated the particle size and zeta potential of modified nano-encapsulated dye. Average zeta potential for PS-BA nano-encapsulated dye 6.52 mV that indicated nice stability of dispersed dye in aqueoussolution. In addition, the Average mobility of charged modified nano-encapsulated dye is 0.45 which pointed to nice particle movement between the electrodes according to the viscosity and refractive index of medium.

Figure (2) and Table (2) shows k/s values of nano disperse dyed sample and normal dyed samples.The values were comparable for nano dyed samples and normal dyed samples at several temperature 50, 60,70,80,90,135.

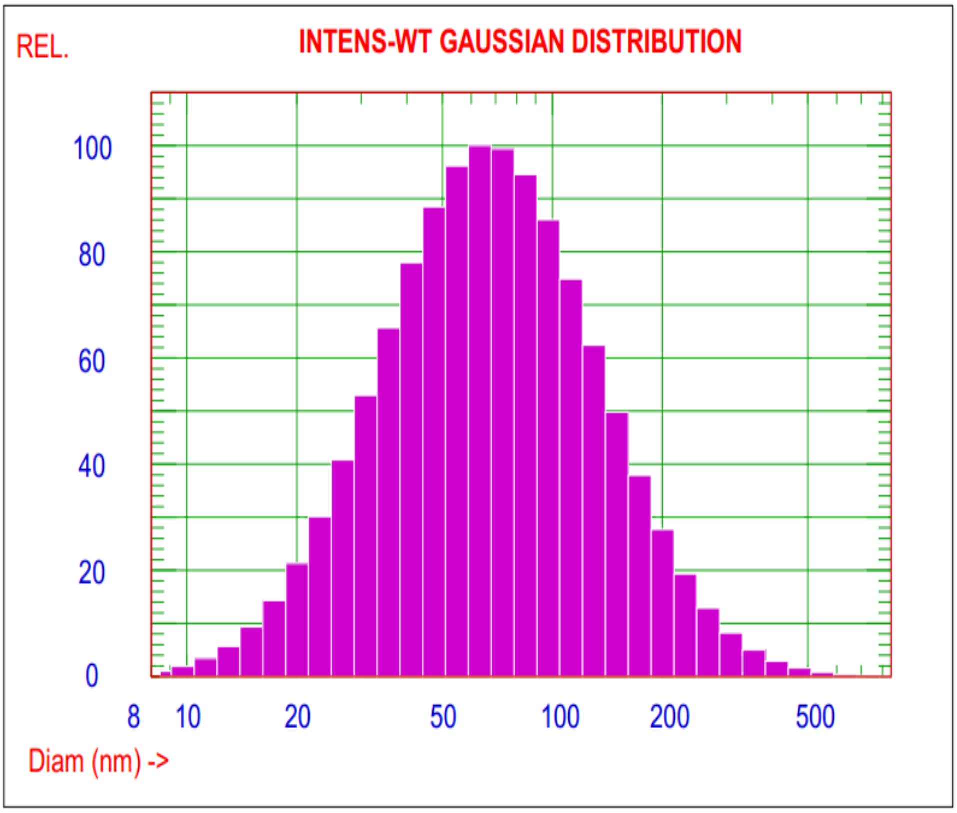


Fig. 1. Particle size distribution of nano-encapsulated dye .

TABLE 1. Shows the particle size and zeta potential with relative indices .

Particle size	Mean diameter, nm	Standard deviation	Chai square	Variation PDI
PS-PBA-dye	87.5	56.8	326	0.478
Zeta potential	Avg. zeta potential, mV	Cell current, mA	Avg. mobility, M. U.	Frequency shaft, Hz
PS-PBA-dye	6.52	0.43	0.45	1.67

TABLE 2. Color values of nano disperse and normal dye without coating and without additives at several temperatures.

Temp.	k/s of Nano dye	k/s of Normal dye
50 °C	0.71	0.67
60 °C	0.74	0.91
70 °C	3.61	3.70
80 °C	15.80	8.39
90 °C	17.36	10.31
135 °C	24.19	10.89

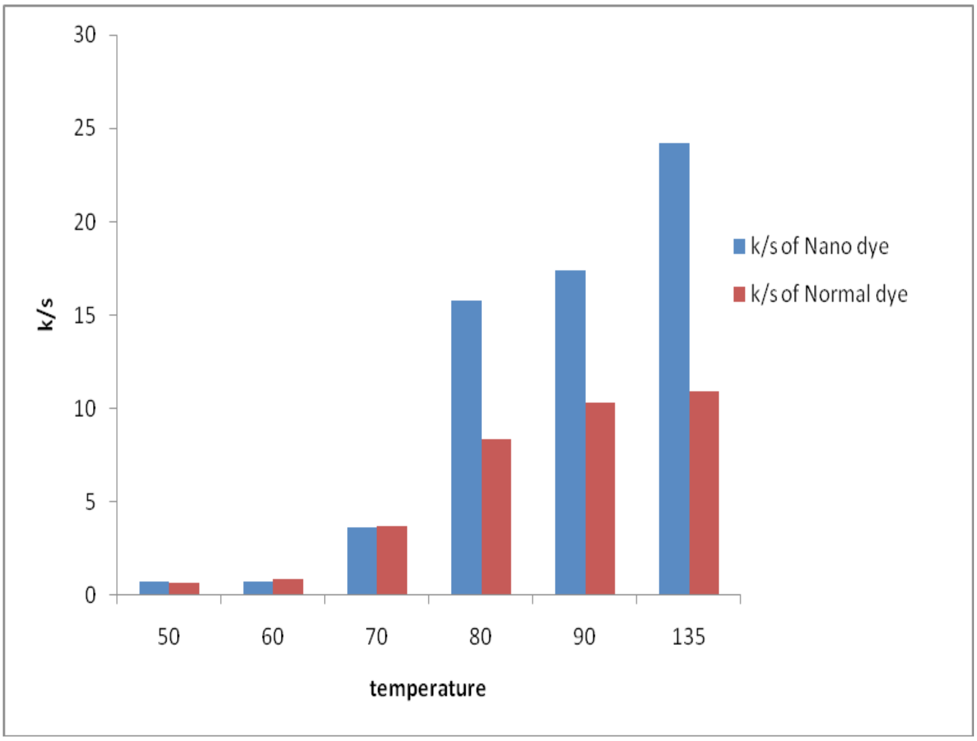


Fig. 2. Color strength of nanodisperse and normal dye without coating at several temperatures.

Figure (2) and Table (2) shows the K/S values of the nano disperse dyed samples and that of normal dyed samples. The values were comparable at different temperatures taken for the study. The k/s of nano dye showed the highest value (24.19) at 135°C while value of k/s for normal dye was (10.89) at the same temperature, this results from the nano colorant particles which obtained by use changed mini emulsion polymerization which minimized dye particle to 87.5 nm while the pores of polyester fiber in the range of 1 to 10 microns which increase the penetration of dye molecules in the polyester fabric so increased k/s values of dyed samples by nano disperse dye than the others samples which dyed by commercial dye in normal size.

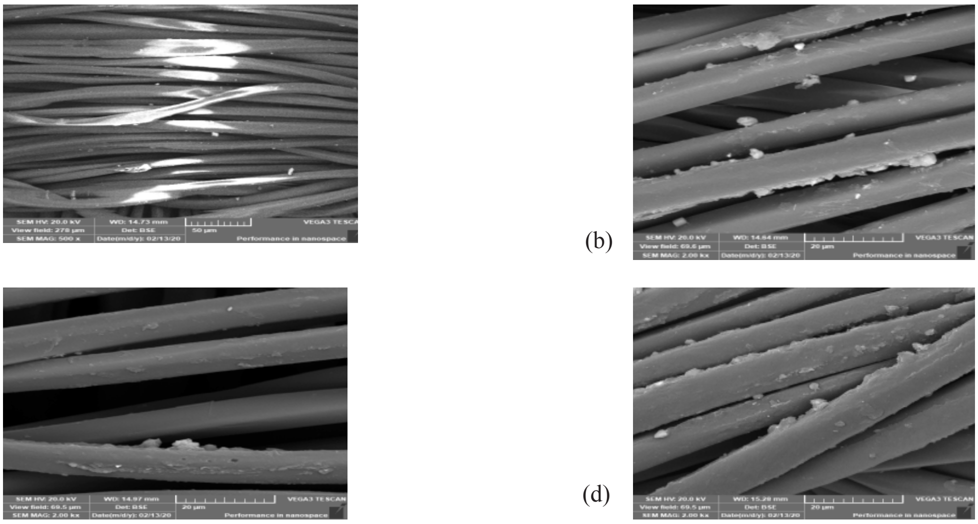
Scanning electron microscope (SEM)

The surface morphology of the normal dyed polyesters fabric (a), nano polyester dyed fabric (b) and the coated polyester with normal and nano disperse dye (c),(d) were examined under electron microscope (SEM) shown in **Figure (3).**

The normal dyed fiber was observed clear and smooth under microscope as seen in Figure3a, for fiber dyed by nano dye were uniformly integrated with the surface of polyester fabric as shown in Figure3b, this holds true in case of c and d.

Figure (4) and Table (4) shows k/s of nano disperse dye and normal dye with and without coating at different temperature. The k/s of nano dye with coating to fiber before dying showed the highest value (25.3) at 135°C while k/s of nano disperse without coating to fiber showed (24.19) at 135°C While the highest value of k/s of normal dye showed at 90 °C (14.06) with coating to fiber before dye and then the values of k/s decrease with increase temperature but the values of k/s of normal with coating to fiber before dye is higher than without coating at different temperature this may be attributed to the normal dye and nano dye formed hydrogen bond with the layer formed by coating fiber with PEG6000+ sorbitol l+ CTAB [21], so increase hydrophilicity of fiber by the way increase the k/s value Fig. (4), but with increase temperature k/s of normal and nano dyed polyester fabric shows decrease in normal dyed sample and in nano dye showed not higher difference than non-coated dyed samples this was because of the hydrogen bond decrease with increasing temperature so decrease dye uptake by the way decrease k/s values [21].

The thickness after coating increase from (0.25) mm to (0.35) mm this was because of formation layer on the surface of the fiber.



(a) (b) (c) (d)

Fig. 3.(a) The surface morphology of the normal dyed polyesters fabric, (b) the surface morphology of the nano dyed polyesters fabric. (c) The surface morphology of normal dyed coated polyester fabric. (d) The surface morphology of nano dyed coated polyester fabric.

TABLE 4. k/s values of nano disperse dye and normal dye with and without coating.

Temperature	k/s of nano dye without coating	k/s of normal dye without coating	k/s of nano dye with coating	k/s of normal dye with coating
50 °C	0.71	0.67	1.09	0.62
60 °C	0.74	0.91	1.13	0.65
70 °C	3.61	3.70	5.06	3.61
80 °C	15.80	8.39	19.76	10.31
90 °C	17.36	10.31	24.78	14.06
135 °C	24.19	10.89	25.30	11.46

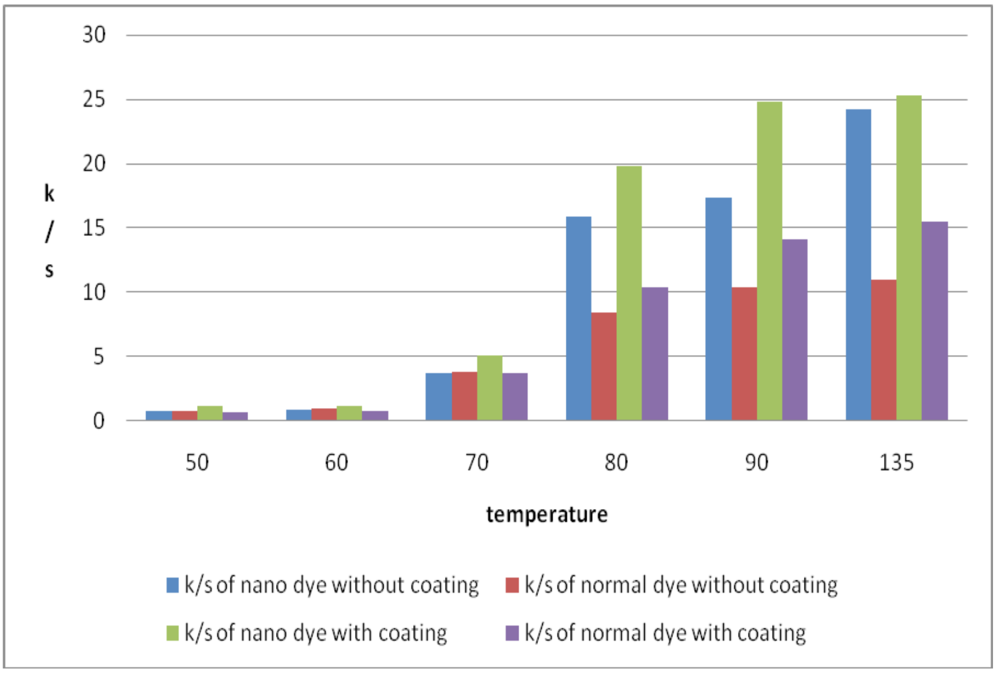


Fig.4. k/s of nano disperse dyed sample and normal dyed samples with and without coating before dying process.

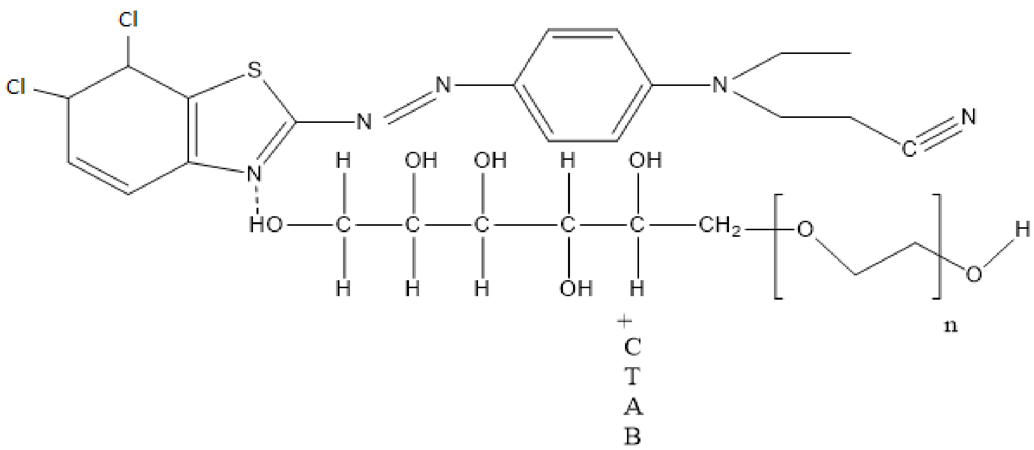


Fig. 5. schematic structures of polyethylene glycol reacts with sorbitol and disperse red 153.

Kinetics of dyeing

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.

It is known that the rate of any process means a change in one of the starting materials that takes place in the process or the product that obtained per unit time.

Applying this definition in the dyeing process can be regarded as the change in the dye-uptake per unit time [22]. Time- dye uptake isotherms of nano dye and normal dye are shown in Figure (6).

The figure shows that the dye uptake values of nano dyed samples are generally better than those of normal dyed samples.The isotherm of two dyes started to be differentiated for each other to show better dye up take of nano dye in comparison with normal dye.

The data in **Figure (4)** can be analyzed by using general form of first order rate Eq. (1)

$$\frac{\mathbf{Af - At}}{\mathbf{Af - A0}} = \mathbf{e}^{-\mathbf{Kt}} \qquad (2).$$

Where At is the absorbance at time t, A0 is the initial absorbance, Af is the final absorbance, t is the reaction time and k are the reaction rate. Since the absorbance of solution is directly related to the concentration by Beer Lambert law, Eq. (2) can be rewritten in terms of dye-uptake to give Eq. (3):

$$\frac{Qf - Qt}{Qf - Q0} \quad e^{-kt} \qquad (3).$$

Where Qt is the dye-uptake at time t, Q0 is the dye uptake at zero time, and Qf is the final dye-uptake, t isthe dyeing time and k is the dyeing rate. Taking the logarithm of Eq. (3) would lead to Eq. (4) and since Qf is known, Qt_Qf can be calculated.

$$\ln[Qf\text{-}Qt]=\ln[Qf\text{-}Q0]\text{-}kt \qquad (4).$$

Aplot of ln [Qt_Qf] versus time is expected to be linear with a slope of _k and an intercept of ln [Q0_Qf] if the reaction is first order. Fig. 5 shows the plot ofln [Qt_Qf] asa function of time for dyeing of polyester with nano and normal dye.

The linear fitting of Eq. (4) holds indeed and the values of dyeing rate constants could be obtained as listed in Table (5).

The time of half dyeing t1/2, which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, is estimated either from each isotherm directly **(Figure 4)** and/or from the following equation:

$$T\ 1/2= \ln {}^{2}/_{k} \qquad (5).$$

The values of half dyeing t1/2 are given in Table (3). The rate constant of dyeing polyester fabrics dye is clearly increased with nano dye in comparison with normal dye.Also the value of t1/2 are clearly short than for samples dyed by nano dye in comparison with those dyed by normal dye.

Fastness properties

Fastness properties of coated and non-coated dyed polyester fabrics using nano and normal disperse dye are shown in

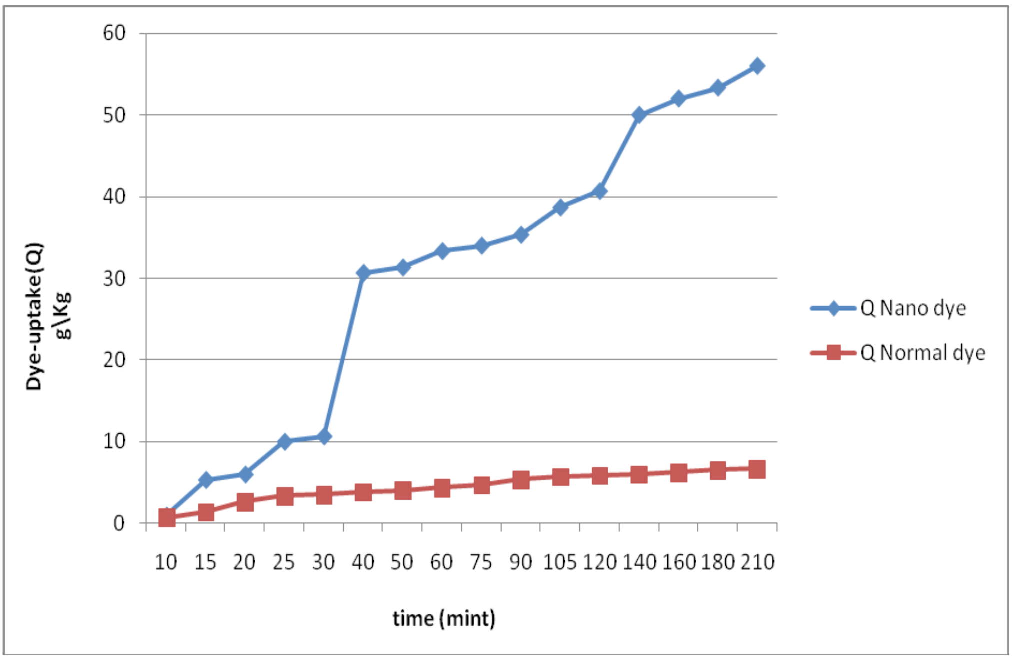


Fig.6. Dyeing rates of nano and normal dye.

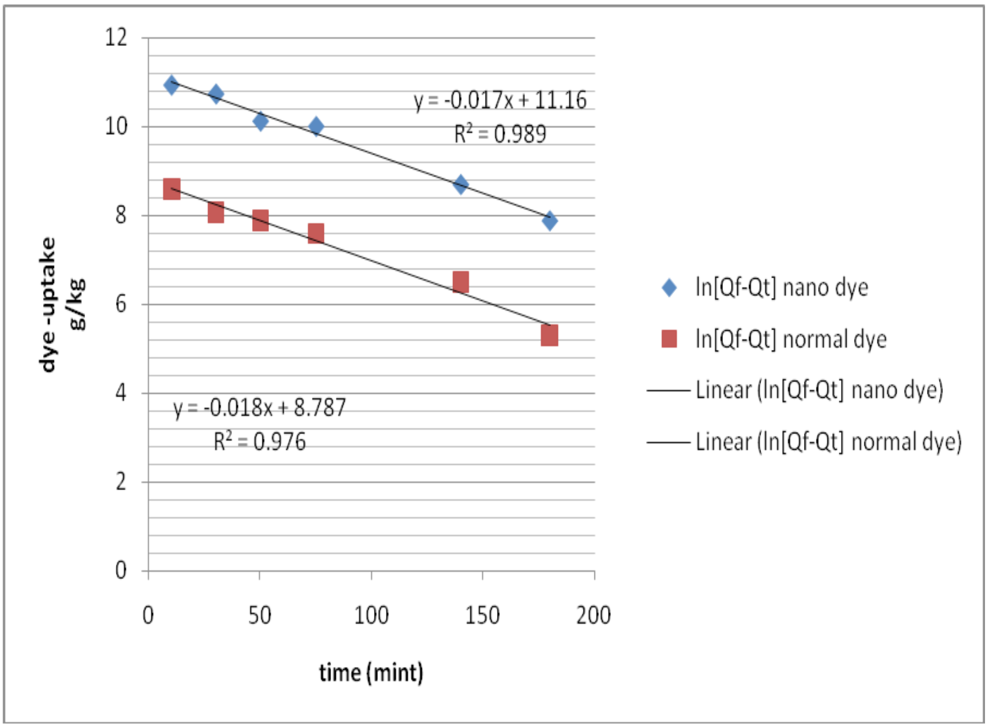


Fig. 7. Dyeing rate for nano and normal dye.

TABLE 5. Dyeing rate constantk, times of half dyeing t1/2, and amount of final dye uptake by polyester fabrics using nano and normal dye.

K×100		T1/2 (min)		Qf (g/kg)	
Na	No	No	Na	No	Na
1.6	1.5	46.2	43.32	6.66	56

TABLE 6. The results indicate good to very good fastness properties of the dyed samples using both nano dye and normal dye.

Temperature of dyeing	Normal.					Nano.				
	Washing fast.		Rub fast.		Light.	Washing fast.		Rubbing fast		Light
	St.	Alt.	wet	dry		St.	Alt.	wet	dry	
80 without coating	3-4	3-4	2-3	2-3	4	3-4	3-4	3-4	3-4	5
80 with coating	3-4	3-4	3	3-4	3-4	3-4	3-4	3-4	3-4	5
90 without coating	3-4	3-4	3-4	3-4	4	3-4	3-4	3	3	5-6
90 with coating	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3	3-4	5-6
135 without coating	4	4	4-5	4-5	4-5	3-4	3-4	3-4	3-4	6
135 with coating	4	4	4-5	4-5	4-5	4-5	4-5	3-4	3-4	6

St.: Staining on cotton.
Alt.:alteration.

Conclusion

This study shown the values of k\s for nano disperse dye higher than that of normal dye when dying of polyester fabric also the coating operation increase the value of k\s for normal and nano dying, the Dye in nano size proved effectiveness in the dye-uptake of polyester fabric, the enhanced K/S was about 60% more than dyeing by using normal dyes it's also shows decrease in temperature which polyester fabric dying at 135 ^{o}C in this study we dyed polyester fabric at several temperature and K\S shows higher values at 80 ^{o}C to the polyester dyed sample which dyed with nano dye than the other dyed at 135 ^{o}C with normal dye. Fastness properties of the dyed fabric of nano disperse dye showed higher value than that of samples dyed with normal dye and the coated fabric showed higher fastness properties than the non-coated fabric.

References

1. http://www.dicros.co.jp/e/textile03.html.

2. Joshi, M., and Bhattacharyya, A. Nanotechnology – a new route to high-performance functional textiles. *Textile Progress, 43(3), 155–233* (2011). .

3. Kale, R., Pratap,A., Kane, P., and Gorade, V., Dying OfNylon Fabric Using Nano emulsion. *Indian J.Sci.Res*. 14 (2): 257-261.(2017).

4. Al-Etaibi, A., El-Apasery, M. and Al-Awadi, N., The effect of dispersing agent on the dyeing of polyester fabrics with disperse dyes derived from 1,4-diethyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile. *European Journal of Chemistry* 4 (3):240-244 (2013).

5. Choi J. H and Kang M. J., Preparation of Nano disperse Dyes from Nano emulsions and their Dyeing Prop. *On ultra-micro fibers polyester fiber and polymers*, 7 (2): 169-173 (2006).

6. Yukuyama.M., Ghisleni. D., Pinto.T., Bou-Chacra..N., Nanoemulsion. Process selection and application in cosmetics – a review, *Int. J. Cosmet. Sci*. 38 (1):13–24. (2015).

7. Cho.Y., Hwan Shin.C. and Han.S., Dispersion Polymerization of Polystyrene Particles Using Alcohol as Reaction Medium.*Springeropenjournal*, 11 (46): 1-9 (2016).

8. KiChang.L., Hun Seung.C., Jeong. Mi.,Soap-Free Emulsion Copolymerization of Styrene with COPS.*Journal of Adhesion and Interface,* 15 (3): 93-99 (2014).

9. Guan, D., Li, J., Sun, G., and Zhai, X.Some Reflections On Styrene Suspension Polymerization Experiment Teaching. *IOP Conference Series: Materials Science and Engineering, 473(2019*).

10. Shahriar S., Extending the Limits of Emulsifier-Free Emulsion Polymerization to Achieve Small Uniform Particles, *RSCAdvances journal*, 5 (72),58549-58560(2015).

11. Galila M. El-sayed, M. M. Kamel, N. S. Morsy, F. A. and Taher., Encapsulation of Nano Disperse Red 60 via Modified Miniemulsion Polymerization. I. Preparation and Characterization, *Journal of Applied Polymer Science*, 125 (2): 1318-132(2012).

12. Jansen, T., Meuldijk, J., Lovell, A.and van Herk, A. On the miniemulsion polymerization of very hydrophobic monomers initiated by a completely water-insoluble initiator: thermodynamics, kinetics, and mechanism.*Journal of Polymer Science Part A: Polymer Chemistry,* 54(17), 2731–2745 (2016). .

13. Zhao, Y., Liu, J., Chen, Z., Zhu, X., and Möller, M.Hybrid nanostructured particles via surfactant-free double miniemulsion polymerization. *Nature Communications*, 9(1), 1-9 (2018). .

14. Ronco, I., Minari, J., and Gugliotta, M., Particle Nucleation UsinDifferentInitiators In TheMini emulsions Polymerization Of Styrene . *Brazilian Journal of Chemical Engineering, 32(1), 191–200*(2015).

15. Li, J., Fan, J., Cao, R., Zhang, Z., Du, J., and Peng, X., Encapsulated Dye/Polymer Nanoparticles Prepared via MiniemulsionPolymerization for Inkjet Printing. *ACS Omega, 3(7), 7380–7387(*2018*).*

16. Takke, V., Behary, N., Perwuelz, A., and Campagne, C., Surface and adhesion properties of poly(ethylene glycol) on polyester(polyethylene terephthalate) fabric surface: Effect of air-atmospheric plasma treatment. *Journal of Applied Polymer Science, 122(4), 2621–2629.* (2011).

17. Wang, L. D. Zhang, H. Su, Z. P. Zhang, G. H. Li, G. W. Meng, J. Zhang, Y. W. Wang, J. C. Fan, and T. Gao, Phys. Lett. A, 281, 59 (2001).

18. AATCC, Technical Manual, Method 8 (1989), 68 (1993), 23–25.

19. AATCC, Technical Manual, Method 36 (1972), 68 (1993).

20. AATCC, Technical Manual, Method 16 A (1988), 68 (1993), 33–48.

21. Tang .X., Michael J., and Lynne S. T., The Effect of Temperature on Hydrogen Bonding in Crystalline and Amorphous Phases in Dihydropyrine Calcium Channel Blockers, *Pharmaceutical Research* 19: (4),485-490 (2002).

22. Kamel, M., Helmy.M., Mashaly. H., H., and Kafafy, H., Ultrasonic assisted dyeing: Dyeing of acrylic fabrics *C.I.* Astrazon Basic Red 5BL 200%. *UltrasonicsSonochemistry*, *17(1), 92–97* (2010).