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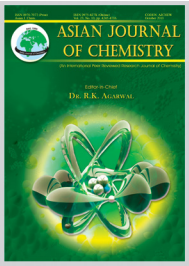

Use of Ultrasonic Energy in Dyeing of Microfiber

NIGAR MERDAN[1,*] and YUSUF INANICI[2]

[1]Istanbul Commerce University, Faculty of Engineering and Design Department, 34840 Küçükyali, Istanbul, Turkey
[2]Marmara University, Technical Education Faculty, 81040 Goztepe, Istanbul, Turkey

*Corresponding author: E-mail: nmerdan@iticu.edu.tr

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In recent years, dyeing kinetics in dyeing of polyamide microfiber become more important in recent years due to its use in textile industry and its functional features, with C.I. reactive yellow 39, C.I. reactive red 84 and C.I. reactive blue 69 was studied and conventional dyeing method and the method in which ultrasonic energy is used were compared from the point of view of dye uptake %, dyestuff amount, which moves away during washing, fixation %, significant rate, half-dyeing time, standard affinity and diffusion coefficient. Also, the samples, which had been dyed by using conventional and ultrasonic methods, were compared with washing, light, perspiration and rubbing fastness as well as the values of ΔE*, ΔL*, Δa* and Δb*, which were obtained from colourimetric measurements.

Key Words: Ultrasonic method, Conventional method, Dye uptake %, Polyamide microfiber, Reactive dyestuff.

INTRODUCTION

The use of ultrasonic energy in wet processes of textile is useful from the point of view of process time, saving in energy and chemicals and increased product quality. Mass transfer increases from liquid to solid as a result of cavitation, which occurs on solid/liquid interface[1]. The matters such as homogeneity and ultrasonic pressure distribution, transducers' position, the way for passing the fabric through the machine and bath temperature are highlighted in machinery design for usability of ultrasonic energy in industrial scale[2]. It was reported that washing fastness is better in the method in which ultrasonic probe is used in final washing of reactive dyeing[3]. Sonication has positive effect on dyeing and fastness features in dyeing cellulose fibers with reactive dyestuff[4,5].

Sonication has no effect on the fiber's T_g value, dyeing rate and dye adsorption in PES dyeing with disperse dyes[6] more adsorption occurs in dyeing PA ve PA/Lycra mixture fabrics with reactive dyestuff by ultrasonic method. However dyeing has no effect on fastness features[7,8], colour fastness is better in dyeing Nylon 6 with reactive dyestuff, diffusion is better due to de-aggregation in dyestuff molecules and ultrasonic energy may have effect on dyestuff-fiber covalent bond fixation[9].

Microfibers are manufactured for especially sport, fashionable and functional wear in recent years due to their waterproof and air-permeable features[10]. Polyamide microfiber and mixtures consisting of this fiber and natural fibers will have a certain importance in the future.

Reactive dyestuffs have different reactivity characteristics due to the reactive groups, which are borne by them. Substantive characteristics of a dyestuff are different also depending on chromophore group of the dyestuff. Reactive dyestuff containing triazine ring produce covalent bond with -OH groups in cellulose through substitution. The dyestuff, which were used in this study and whose reactive group is sulfato ethyl sulfone, are turned into vinyl sulfone, which has high reactivity, in basic media and produce ether bond with the fiber. Bi-functional reactive dyestuffs containing vinyl sulfone- monochlorotriazine structure are bound to form covalent bond with cellulose fiber's functional groups according to both of nucleophilic substitution and addition mechanisms. These reactive groups in dyestuff molecules have effect on dyeing reaction rate, stability of the bond between fiber and dyestuff and fastness of dyed stuff[11,12].

EXPERIMENTAL

The details of dyestuffs, which used in this research are given below:

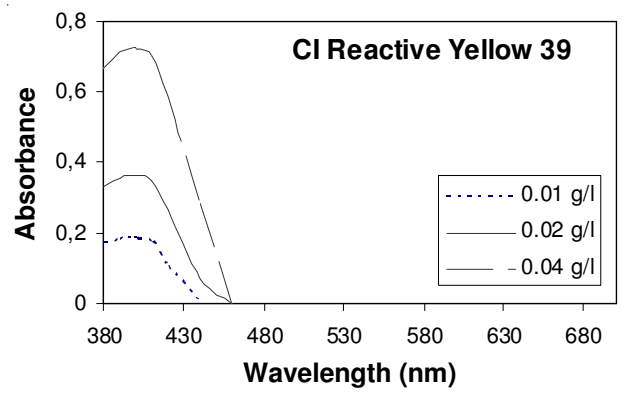
Colour index no	Trade name	Chromophore structure	Reactive group
C.I. reactive yellow 39	Lanasol yellow 4G-CGy	Azo	α-Bromo acryl amide
C.I. reactive red 84	Lanasol red 6G-CGy	Anthraquinone	α-Bromo acryl amide
C.I. reactive blue 69	Lanasol blue 3G-CGy	monoazo	α-Bromo acryl amide

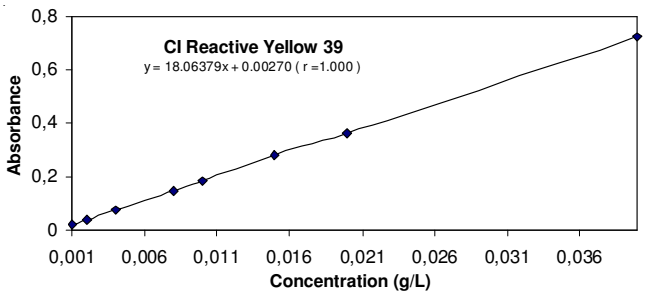
Air-jet textured yarn, which had been manufactured from 184/195 dtex numbered polyamide microfiber, was used in the study (Tactel-ICI). Diameter of the yarn 162 µm and diameter of the fiber is 10.26 µm. Ultimate strength of the yarn is 25 cN/tex and its breaking elongation rate is 46 %.

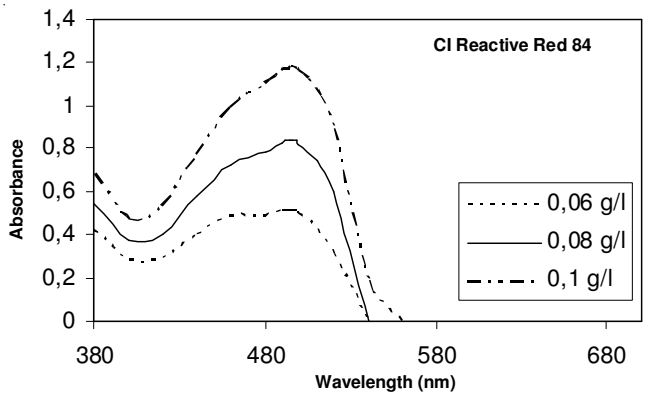
Devices: Schimadzu UV-1200 UV-visible spectrophotometer; Sonifier 250 (branson) ultrasonic probe; Colourgen colour measuring device.

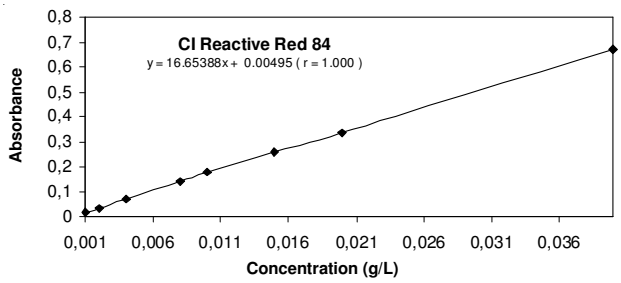
Spectrophotometer measurements: First, 1 g L^{-1} of stock dyestuff solutions were prepared to determine dyestuffs λ_{max} values and then, these stock solutions were diluted in 100 mL flasks and as a result, dyestuff solutions were precisely obtained with densities of 0.01, 0.02 and 0.04 g L^{-1} for C.I. reactive yellow 39 and C.I. reactive blue 69 and with densities of 0.06, 0.08 and 0.1 g L^{-1} C.I. for C.I. reactive red 84. Distilled water, which was used in diluting solutions, was considered as blind bath and spectrophotometer measurements were completed within 380-780 nm. λ_{max} values for each dyestuff were determined from wavelength-absorbance graphics obtained from these measurements. As seen in Fig. 1, the dyestuffs' maximum absorption values are λ_{max} = 398 nm for C.I. reactive yellow 39, λ_{max} = 495 nm for C.I. reactive red 84 and λ_{max} = 603 nm for C.I. reactive blue 69. To obtain calibration lines of the dyestuffs, additional 0.001, 0.002, 0.004, 0.008, 0.01, 0.015, 0.02 and 0.04 g L^{-1} diluted dyestuff solutions were prepared from 1 g L^{-1} of stock dyestuff solutions, which had been prepared separately for each dyestuff and absorbance values of these solutions were obtained from spectrophotometer measurements at 398 nm for C.I. reactive yellow 39, 495 nm for CI reactive red 84 and 603 nm for C.I. reactive blue 69. Calibration (wavelength-absorbance) lines were obtained with the help of these values (Fig. 1).

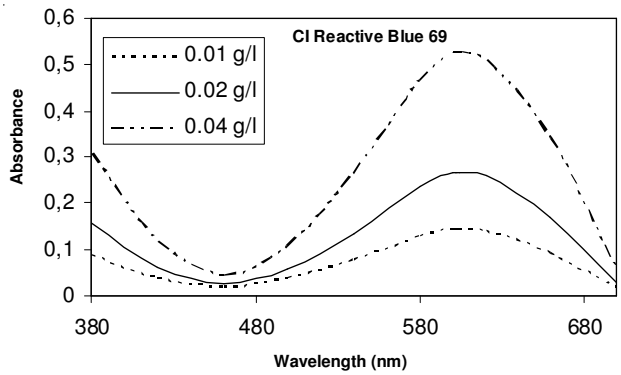
Dyeing: In dyeing processes by using ultrasonic energy, Sonifier 250 (Branson) ultrasonic probe was used as sonication source. The device's output control tune was brought to 4 and 1/ 4 probe tip was used. The device's duty cycle tune was held











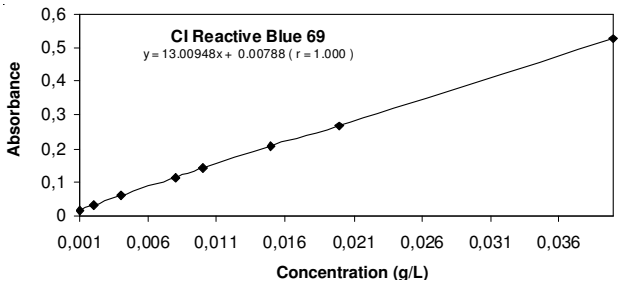


Fig. 1. Wavelength-absorbance curves and calibration lines

at hold and the process was performed by immersing tip of the probe into the dye bath until 1 cm. Sonication power decreases during work with ultrasonic probe at temperatures above 80 ºC[13].

It was understood in pre-tests that repeatability of a dyeing can be ensured only in long bath ratios. Therefore, present study's working temperature was specified as 70 ºC and the bath ratio was specified as 1:600. Material weight was specified as 1.5 g in all dyeing process.

Microfiber material was dyed with the reactive dyestuffs, according to dyeing conditions given in Table-1 by using conventional and ultrasonic methods. Dyeing was started at 40 ºC and the work was continued at 40 ºC for 10 min and

TABLE-1
DYEING CONDITIONS

Liquor ratio	1:600
Sodium sulfate calcine	40 gL^{-1}
Dyestuff	1 %
pH	5.5 (with acetic acid)
Time	70 min
All ingredients were added at the beginning of the process except pH adjustment	

then, temperature of the bath was raised to 70 ºC in 20 min. The work was continued at this temperature for 20 min and then, the bath's pH value was brought to acidic, 5.5 and the work was continued for more 20 min at the same temperature. Washing conditions applied in the dyeing process was given in Table-2.

TABLE-2
WASHING CONDITIONS

	ºC	t (min)	Washing bath	Volume of the bath
1st washing	30	10	Distilled water	75 mL
2nd washing	70	10	1 g/L Foryl 100 (Türk-Henkel) non-ionic washing agent	75 mL

Determining adsorption % and the dyestuff amount moved away during washing: In determining time-dye uptake % curves, 5 mL of samples were collected from the dyeing bath from the beginning of the dyeing process at 0, 10th, 20th, 30th, 40th, 50th, 60th and 70th min and absorbance values for these samples were determined by spectrophotometer measurements performed in the wavelength in which the dyestuffs achieved maximum absorbance. The absorbance values were used in the calibration equation to find dyestuff concentrations in the float at the minutes mentioned above and dye uptake % values were calculated with the help of these data (eqn. 1). Dye uptake % values were used to form the curves for dye uptake % *versus* time (Fig. 2).

$$\text{Adsorption \%} = [(c_1-c_2)/c_1] \times 100 \quad (1)$$

where, c_1 = initial concentration, g L^{-1}; c_2 = concentration at 10th min of the process, g L^{-1}.

Dyestuff amount transferred to washing floats during the washing processes after dyeing process was found according to eqn. 2.

$$\text{Dyestuff amount in washing bath (g)} = (c \times V)/1000 \quad (2)$$

where, V: volume of dyeing bath, mL; c: dyestuff concentration in washing bath, g L^{-1}.

Fixation %: Dyestuff amount fixed to the material was calculated by finding the difference between the dyestuff amount in the fiber at the maximum dye uptake % value of the dyestuff and total dyestuff amount moved away during washing process and the result was used in calculating fixation % values for the three dyestuffs used in the study.

Half dyeing time: Time required for that a fiber adsorbs half of the maximum dyestuff amount, which is absorbed by it, is called half-dyeing time. This is also important like significant rate, for that the fiber adsorbs the dyestuff properly irregularity risk increases in dyeing processes as the half-dyeing time is shortened. Half-dyeing time may be determined with the help of adsorption % curve of the relevant dyestuff.

Standard affinity: Standard affinity is required for dyeing processes in combination and dyestuffs, which are close to each other, is suitable for such processes. Standard affinity values of these three dyestuffs were calculated for this fiber according to eqn. 3 for further studies[14].

$$-\Delta\mu^o = R \times T \times [\ln[D]_\phi/[D]_\sigma] \quad (3)$$

where, $-\Delta\mu^o$ is standard affinity (kJ mol); R is gas constant (8.315 J mol K); T is absolute temperature (K); $[D]_\phi$ is the dyestuff on the fiber (g kg) and $[D]_\sigma$ is the dyestuff in the dye float (gL).

Diffusion coefficient : Diffusion rates of dyestuffs should be close to each other in combined dyeing processes. Diffusion coefficients of the dyestuffs used in this study were calculated according to eqn. 4 at their half-dyeing time[14].

$$D = 0.04919 \times (l^2/t_{1/2}) \quad (4)$$

where, D is diffusion coefficient (cm^2/s); l is the diameter of the fiber (cm) and $t_{1/2}$ is the half-dyeing time (s)

Fastness of the dyed material: The standards of TS 1008 EN ISO 105-B02 in light fastness tests of the dyed material, TS EN 20105-C01 in washing fastness tests, TS 717 EN ISO 105-X12 in friction fastness tests and TS 398 pr EN ISO 105-E04 in perspiration fastness tests were used. The blue scale was used in evaluation of light fastness while the grey scale was used in evaluation of other fastnesses[15-18].

Colorimetric measurements: Per cent reflectance values of the dyed samples were measured by using colourgen colour measurement device and Dyematch computer program. In the measurements, the samples, which had been obtained by the conventional method were considered standard and D/65 light source was used with an angle of 10º. Eqn. 5 was employed in calculating colour values according to CIE Lab system[19].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (5)$$

Three coordinates, L*, a* and b* can be calculated by using tristimulus values which are used to define a colour and the axes of a* and b*, which are perpendicular to each other and intercept at the neutral point and L* axis, which is perpendicular to the plane formed by these axes, are made base. Different shades of a colour take place on a line extending outside from the neutral point inside the plane formed by the axes of a* and b*.

Positive $L^*_{sample} - L^*_{standard}$ value means that the sample is lighter than the standard while a negative value shows that the sample is darker than the standard. A negative a* value shows that the colour is closer to green than the standard, while a positive value means that the colour is closer to red than the standard. A negative b* value shows that the colour has more blue gradations than the standard does while a positive shows more yellow gradations compared with the standard.

RESULTS AND DISCUSSION

Adsorption % and fixing: Fig. 2 shows curves for the fibers dyed by the conventional and ultrasonic methods time *versus* dye uptake %. In ultrasonic method, dyestuff amount transferred to the fiber is higher by 0.4 % for C.I. reactive yellow 39 compared with that dyed by the conventional method. Dyestuff amount transferred to washing bath after dyeing is higher by 56.5 % for C.I. reactive yellow 39 in ultra-

sonic method (Fig. 2). Considering dyestuff amounts moved away during washing process, dyestuff amount fixed to the fiber is 95.2 % in the conventional method and 93.5 % in ultrasonic method for CI reactive yellow 39. Fixing is higher in the fiber dyed by using the conventional method by 1.79 %.

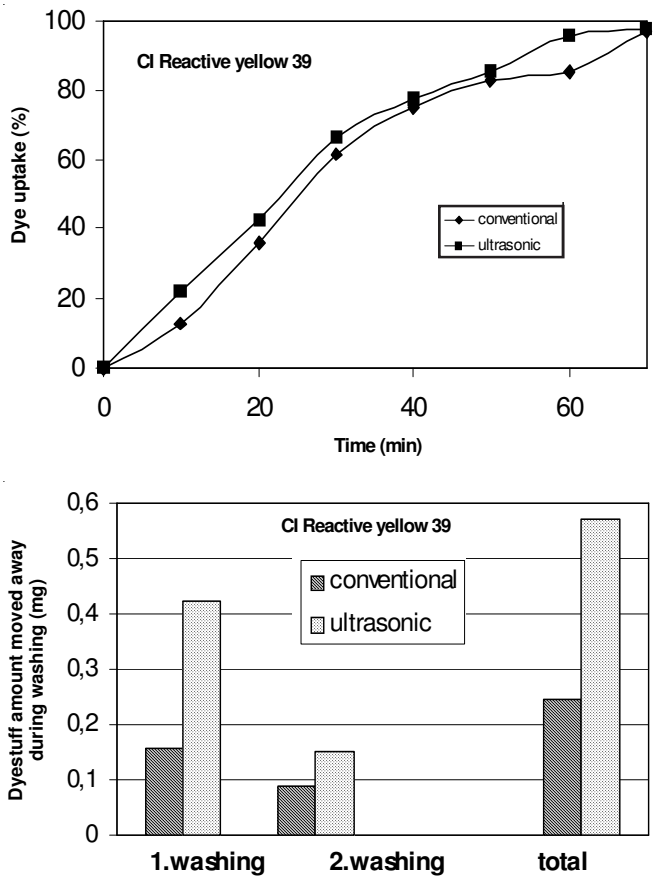
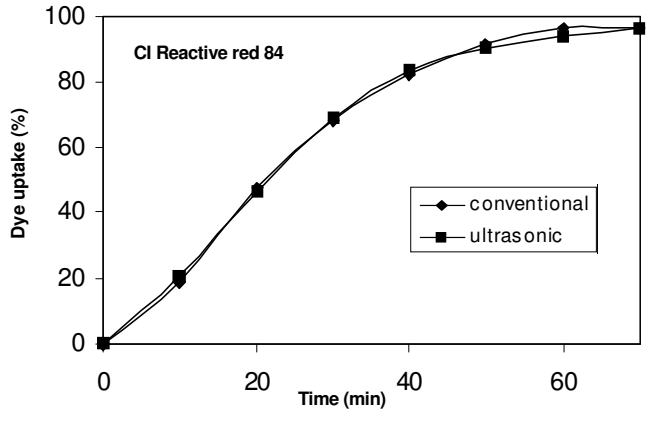


Fig. 2. Curves for adsorption % and dyestuff amounts moved away during washing depending on time for CI reactive yellow 39

It was determined that 0.1 % less dyestuff was transferred to the fiber dyed by ultrasonic method for C.I. reactive red 84. In the same method, 47 % less dyestuff was transferred to washing bath during washing process after dyeing for C.I. reactive red 84 (Fig. 3). Considering dyestuff amounts moved away during washing process (Fig. 3), dyestuff amount fixed to the fiber is 93 % in the conventional method and 94 % in ultrasonic method for C.I. reactive red 84. Fixing is higher in the fiber dyed by using ultrasonic method by 1 %.



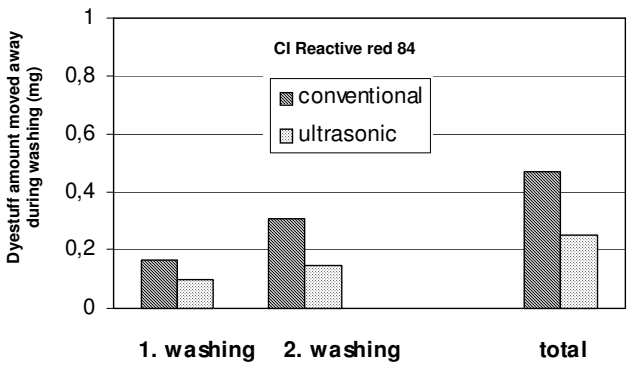


Fig. 3. Curves for adsorption % and dyestuff amounts moved away during washing depending on time for CI reactive red 84

Fig. 4 shows the curves for dye uptake % and dyestuff amounts moved away during washing depending on time in the conventional and ultrasonic methods for C.I. reactive blue 69. In ultrasonic method, dyestuff amount transferred to the fiber is higher by 0.4 % for C.I. reactive blue 69 compared with that dyed by the conventional method. Dyestuff amount transferred to washing float after dyeing is lower by 36 % for C.I. reactive blue 69 in ultrasonic method (Fig. 4). Considering dyestuff amounts moved away during washing process, dyestuff amount fixed to the fiber is 88.9 % in the conventional method and 89.8 % in ultrasonic method for C.I. reactive blue 69. Fixing is higher in the fiber dyed by using ultrasonic method by 1 % (Fig. 4).

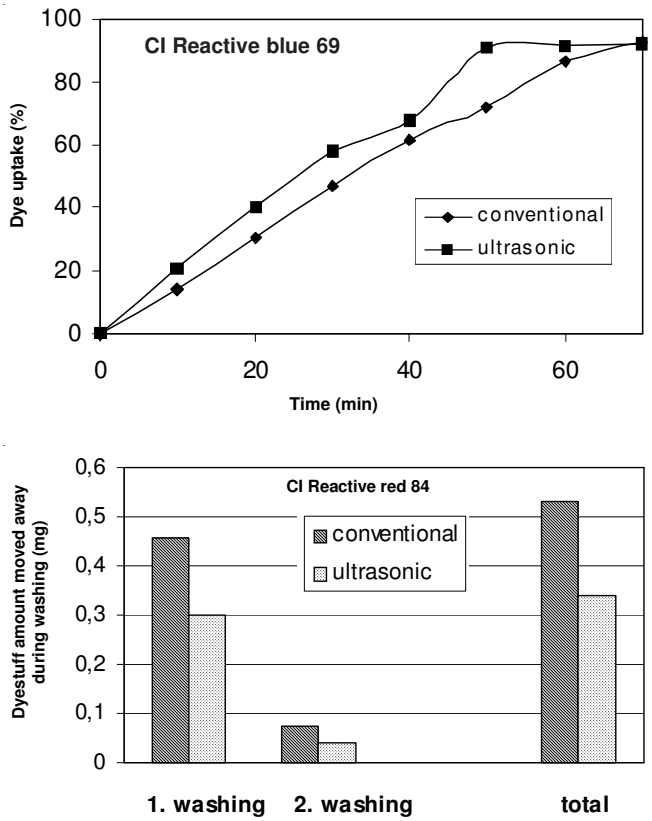


Fig. 4. Curves for adsorption % and dyestuff amounts moved away during washing depending on time for CI reactive blue 69

Half dyeing time-standard affinity and diffusion coefficient: Half-dyeing time for C.I. reactive yelllow 39 ($t_{1/2}$) was

TABLE-4
FABRICS' FASTNESS VALUES

Washing				Light		Rubbing				Perspiration							
c		u		c	u	c		u		c				u			
cc	s	cc	s			w	d	w	d	cca	sa	ccb	sb	cca	sa	ccb	sb
C.I. Reactive Yellow 39																	
4	4	4	4	8	8	5	5	5	5	5	5	4	5	5	5	5	4-5
C.I. Reactive Red 84																	
4	5	4	5	8	8	5	5	5	5	4	5	4	3	4	5	4	5
C.I. Reactive Blue 69																	
5	4-5	5	4-5	8	8	4-5	5	5	5	4	5	4	5	5	5	4	4

c: conventional; u: ultrasonic; cc: colour change; s: staining; w: wet d: dry; cca: colour change acidic; ccb: colour change basic; sa: staining acidic; sb: staining basic

calculated as 24.88 min in the conventional method while it was 22.49 min in ultrasonic method. Standard affinity values, which were also obtained by using adsorption % values for the dyed fibers, ($-\Delta\mu^o$) was found as 28.07 kJ mol for the conventional method and 28.47 kJ mol for the ultrasonic method. Diffusion coefficient (D) values, which were also obtained by using adsorption % values for the dyed fibers, are 3.46×10^{-11} cm^2 sec for the conventional method and 3.83×10^{-11} cm^2 sec for the ultrasonic method.

Half-dyeing time for C.I. reactive red 84 ($t_{1/2}$) was calculated as 20.15 min in the conventional method, while it was 20.86 min in ultrasonic method. Standard affinity values, which were obtained by using adsorption % values for the dyed fibers, ($-\Delta\mu^o$) was found as 27.47 kJ mol for the conventional method and 27.39 kJ mol for the ultrasonic method. Diffusion coefficient (D) values, which were also obtained by using adsorption % values for the dyed fibers, are 4.27×10^{-11} cm^2 sec for the conventional method and 4.13×10^{-11} cm^2 sec for the ultrasonic method.

Half-dyeing time for C.I. reactive blue 69 ($t_{1/2}$) was calculated as 29.43 min in the conventional method while it was 23.38 min in ultrasonic method. Standard affinity values, which were obtained by using adsorption % values for the dyed fibers, ($-\Delta\mu^o$) was found as 25.41 kJ mol for the conventional method and 25.25 kJ mol for the ultrasonic method. Diffusion coefficient (D) values, which were also obtained by using adsorption % values for the dyed fibers, are 2.93×10^{-11} cm^2 sec for the conventional method and 3.68×10^{-11} cm^2 sec for the ultrasonic method.

Fastness: It was determined that ultrasonic energy has no effect on fastness of fabrics dyed with C.I. reactive yellow 39, C.I. reactive red 84 and C.I. reactive blue 69 in comparison with the conventional method (Table-4).

Colour values: In fabrics dyed with C.I. reactive yellow 39, colour distinction occurred between the samples dyed by the conventional method and ultrasonic method ($\Delta E^* = 7.77$). Colour of the sample dyed by ultrasonic method is a bit lighter ($\Delta L^* = 0.6$). Colour of the sample dyed by ultrasonic method became closer to red ($\Delta a^* = 0.52$) while blue gradations increased in the sample compared with that dyed by the conventional method ($\Delta b^* = -7.73$) (Fig. 5).

In fabrics dyed with CI reactive red 84, colour distinction occurred between the samples dyed by the conventional method and ultrasonic method ($\Delta E^* = 2.57$). Colour of the sample dyed by ultrasonic method is darker ($\Delta L^* = -1.57$). Darkening improved distinctions in colour gradation. Colour

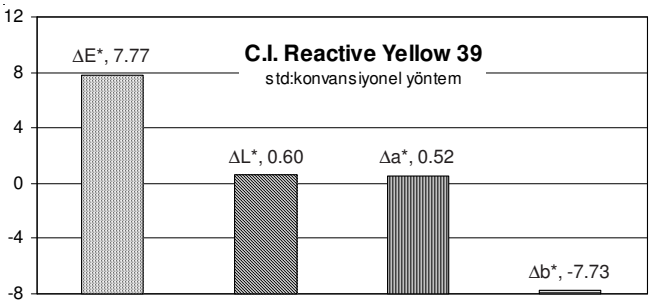


Fig. 5. ΔE^*, ΔL^*, Δa^* and Δb^* values for CI reactive yellow 39

of the sample dyed by ultrasonic method became closer to red ($\Delta a^* = 1.59$) while blue gradations increased in the sample compared with that dyed by the conventional method ($\Delta b^* = -1.26$) (Fig. 6).

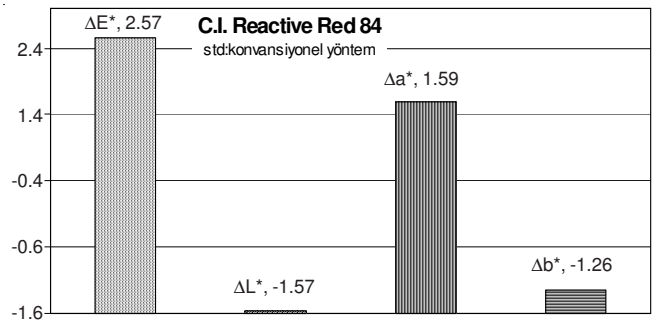


Fig. 6. ΔE^*, ΔL^*, Δa^* and Δb^* values for CI Reactive Red 84

Colour distinction between the samples dyed by ultrasonic and the conventional methods for CI reactive blue 69 is in the interval of the accepted values ($\Delta E^* = 0.76$, the accepted value $\Delta E^* = 1$). Colour of the sample dyed by ultrasonic method is a bit lighter ($\Delta L^* = 0.47$). Colour of the sample dyed by ultrasonic method became closer to red ($\Delta a^* = 0.52$) while yellow gradations increased in the sample compared with that dyed by the conventional method ($\Delta b^* = -7.73$) (Fig. 7).

Conclusion

In this study, dyeing kinetics was studied in dyeing polyamide microfiber with the dyestuff of C.I. reactive yellow 39, C.I. reactive red 84 and C.I. reactive blue 69. It was concluded that the method, which employs ultrasonic energy, may ensure more cost-effective dyeing processes because the method requires less dyestuff and chemicals due to its positive effects on fixation % values of dyestuff. It is believed that ultrasonic method is an alternative method from the point of view of

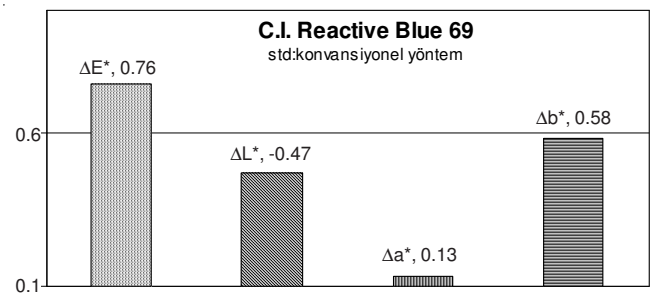


Fig. 7. ΔE*, ΔL*, Δa* and Δb* values for CI Reactive Blue 69

cost and the environment because the use of ultrasonic energy allows better protection with less matter.

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