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Monochlorotetrazinyl Reactive Dyes: Application to Cotton Fibres

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By the reaction of tetrazine and triazine groups with the chromophores of three different dyes (reactive blue 4, orange 1 and red 2), monochlorotetrazinyl and dichlorotriazinyl reactive dyes were synthesized. Dyeing yield were examined by applying to cotton fibre with these dyes at different temperatures. Exhaustion and fixation rates (%) were determined by analysis of the washing waters containing waste dye. On comparing the results showed that the exhaustion and fixing efficiencies of monochlorotetrazinyl dyes were lower than those of dichlorotriazinyl dyes although they were generally close to each other.

Key Words: Triazine, Tetrazine, Reactive dye, Exhaustion, Fixation.

INTRODUCTION

Reactive dyes are widely used in the dyeing of cellulosic fibres, unlike other textile dyes, they react with the cellulose in aqueous alkali medium and form covalent bonds with the fibre. The ease of application, brilliance of shades and high washing fastness are three important properties of reactive dyes and are responsible for their successful use[1-3].

A schematic illustration of the structure of a reactive dye is shown Fig. 1. There are four important structural features of reactive dye molecules which may be identified: the chromophore, the water solubilizing group, the bridging group and the reactive group. The covalent bond, between the fibre and dye molecule reveals dyeing performance on reactive dyeing. During reactive dyeing are expected to be obtained dyeing yield and fastness properties[4].

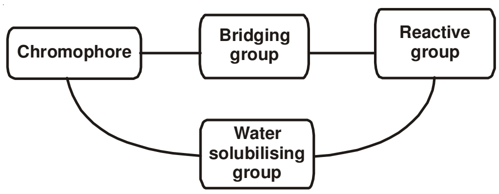


Fig. 1. Schematic representation of reactive dyes

Two principal covalent bond formation reactions, nucleophilic addition and nucleophilic substitution are employed in reactive dyeing, in this way the vinyl sulphonyl and chlorotriazinyl groups are incorporated into the dye molecules for use on cellulosic fibres. Although the chlorotriazinyl reactive group is widely used in reactive dye, tetrazine is not used as a reactive group[5,6]. The chlorotriazine and chlorotetrazine groups are shown in Fig. 2.

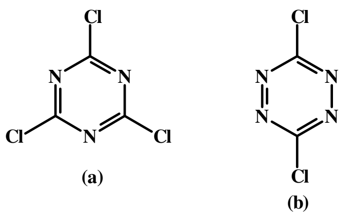


Fig. 2. Chlorotriazine (a) and chlorotetrazine (b) reactive groups

Dye hydrolysis, reacting with water molecule, a major disadvantage in reactive dyeing. Hydrolyzed dyes lose the ability to react with fibre and reactive dyed fabric needs to be thoroughly washed until any excess reactive dye is removed. Many studies have been done on reactive dyeing systems and different reactive groups have been tested to increase dyeing yield and fastness properties[7-9]. In this study, three novel reactive dyes from the tetrazinyl reactive group and traditional triazinyl reactive dyes were applied and compared for dyeing yield and fastness properties.

EXPERIMENTAL

In this study the following materials were used throughout.

Fabric: The knitted cotton fabrics, scoured, bleached and free of fluorescent whitening agents, were supplied by Balgünes Textile Company, Kayseri (Turkey). The weight of the fabric was 150 g/m^2.

Dyes and chemicals: We examined previously synthesized azo and antraquinone chromophore[10], as well as the dichlorotriazine and monochlorotetrazine reactive system. The structure of the dyes used is shown Table-1. The dyes and all chemicals used were of general pupose grade.

Dyeing and fastness tests: All dyeing processes were carried out in a laboratory dyeing machine (Termal, Turkey) at a liquor ratio of 20:1 according to the exhaustion technique, in the presence of 1 g/L of wetting agent and 50 g/L of salt. Dyeings were carried out at four different concentrations (0.25, 0.5, 1.0 and 2.0 % owf, on weight of fibre) in the presence of 30 g/L of soda. After dyeing, the washing of the dyed cotton fabrics was carried out in cold, boiled and boiled water with non-ionic detergents followed by cold rinsing. The washing and rubbing fastnesses of the dyed samples were determined according to ISO 105-C06 and ISO-105-X12 standards, respectively. The dyeing diagram is given in Fig. 3.

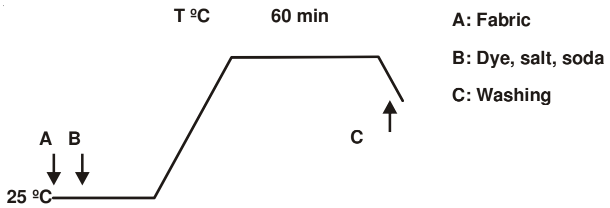


Fig. 3. Dyeing diagram (50 ºC for triazine, 40 ºC for tetrazine)

Measurement dye exhaustion and fixation: First of all, dye solutions prepared at different concentrations and their absorbance values were noted using UV/VIS spectrophotometer. The results were then graphed to make a calibration curve from which the unknown concentrations could be determined by their absorbance values. The uptake of the reactive dyes by cotton was measured before and after the dyeing. The absorbance of the unknown dye solution was measured on an PG T80 spectrophotometer on the basis of λ_{max} of the dyes. From the spectrophometrical values, the individual dye exhaustion (E %) and fixation (F %) values were calculated[11] using eqns. 1 and 2:

$$E\,(\%) = \frac{D_1 - D_2}{D_1} \times 100 \quad (1)$$

$$F\,(\%) = \frac{D_1 - D_2 - D_3}{D_1} \times 100 \quad (2)$$

where D_2 is the amount of dye in the dyebath after dyeing in t min, D_1 is the initial dye amount in the dyebath before dyeing and D_3 is the amount of dye in the soaped bath at 10 min.

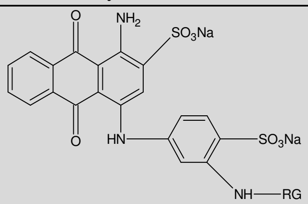
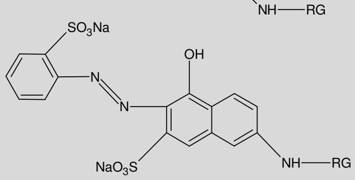
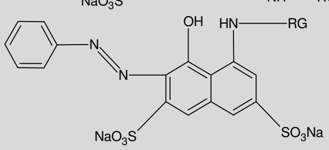
RESULTS AND DISCUSSION

Dyeing yield: The exhaustion and fixation rates of the model reactive dyes are given in Fig. 4. The exhaustion (%) results were obtained from examining the washing water containing waste dye. According to the dyeing yield results (Fig. 4) blue reactive dye fixation rates are between 52.5-62.6 %, orange reactive dye fixation rates are between 49.8-61.8 % and red dye fixation rates are between 36.7-52.3 %. The cause of such low fixation rates was probably due to impurities in the synthesized dyes. The exhaustion and fixation rates of the tetrazinyl dyes are lower than the triazinyl dyes for all dyeings. The difference of dyeing yield between the tetrazinyl and triazinyl groups on red dye is higher than on the orange and blue dyes. In general, the dyeing performance of the tetrazinyl group is lower than the triazinyl group with respect to fixation rates.

Relative fixation yield: The ratio of fixation value to exhaustion value is called the relative fixation rate. A high ralative fixation rate means higly a high proportion of dyes connected to the fibres. In comparison with the results of other experimental studies, the relative fixation rate of red reactive dyes were higher than those of blue and orange dyes.

Fig. 5 shows the relative fixation percentages for each of the reactive dyes: triazinyl blue (71.7-75.6 %), tetrazinyl blue (70.2-73.3 %), triazinyl orange (70.3-77.5 %), tetrazinyl orange

TABLE-1
MODEL DYE STRUCTURE AND MAX ABSORBANCE WAVELENGTH OF DYES USED

Dye structure	RG (Reactive group)	Model dye	λ_{max} (nm)
	Chlorotriazine	**1a**	584
	Chlorotetrazine	**1b**	589
	Chlorotriazine	**2a**	433
	Chlorotetrazine	**2b**	475
	Chlorotriazine	**3a**	498
	Chlorotetrazine	**3b**	514

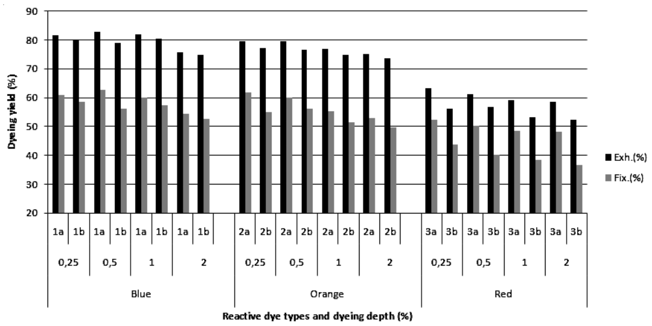


Fig. 4. Dyeing yield of reactive dyes

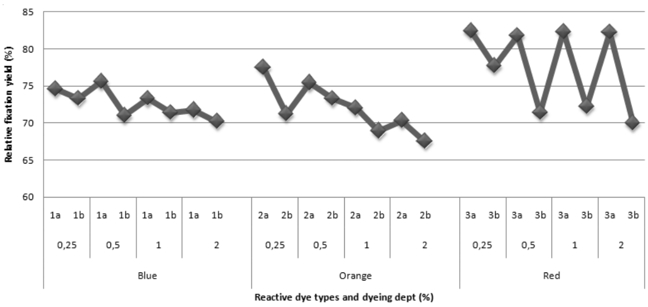


Fig. 5. Relative fixation rates of model reactive dyes

(67.5-73.3 %), triazinyl red (81.8-82.4 %) and tetrazinyl red (70.0-77.7 %) respectively. In this case, the best relative fixation results were obtained by triazinyl red reactive dyes. Relative dyeing yield decreased with increasing dyeing depth in all dyes.

Fastness to rubbing and washing: The fastness properties of the cotton fabrics dyed with the model reactive dyes were evaluated and are given in Tables 2 and 3. The results show that the colour fastness to rubbing and washing for triazinyl and tetrazinyl reactive dyes are more or less the same, depending on the dye fixation rate. The dry and wet rubbing fastness of all dyeings seem to be with in normal range. The high fastness performance is probably due to the fact that dyes are reactive and penetrated well into the cotton fibre.

TABLE-2
RUBBING FASTNESS OF DYED FABRICS

Dye	Dyeing depth (%)	Dyes from the triazine reactive group		Dyes from the tetrazine reactive group	
		Dry	Wet	Dry	Wet
Blue	0.25	5	4	5	4
	0.50	5	4	5	4
	1	4/5	3/4	4/5	3/4
	2	4/5	3/4	4	3
Orange	0.25	5	4/5	5	4/5
	0.50	5	4/5	5	4/5
	1	5	4	5	4
	2	4/5	3/4	4	3
Red	0.25	5	4	5	4
	0.50	4/5	4	4	3/4
	1	4/5	3/4	4	3/4
	2	4/5	3/4	3/4	3

Washing fastness was examined in terms of colour change. We found that the washing fastness of triazine reactive dye was slightly better than that of tetrazine reactive dye. However,

TABLE-3
WASHING FASTNESS OF DYED FABRICS

Dye	Dyeing depth (%)	Dyes from the triazine reactive group		Dyes from the tetrazine reactive group	
		Changing	Staining	Changing	Staining
Blue	0.25	3/4	4/5	3	4
	0.50	3/4	4/5	3	4
	1	3	4	2/3	3/4
	2	3	4	2/3	3/4
Orange	0.25	4	3/4	4/5	4
	0.50	3/4	3	4/5	4
	1	3/4	3	4/5	4
	2	3	2/3	4	4
Red	0.25	3/4	4	3	4
	0.50	3/4	4	3	4
	1	3	3/4	2/3	3/4
	2	3	3/4	2/3	3/4

the best washing fastness value was obtained by the blue dye. Washing fastness was also examined in terms of staining. We found that the washing fastness of the triazinyl reactive dye and tetrazinyl reactive dye were aproximately the same.

Conclusion

Reactive dyes from the dichlorotriazinyl and monochlorotetrazinyl groups were compared as reactive groups. The synthesized reactive dyes were applied to knitted cotton fabrics by the exhaustion method. It was observed that reactive dyes from the tetrazinyl group could be dyed at low temperatures. The dyeing performance of tetrazinyl reactive dyes was lower than triazinyl reactive dyes. However, the difference in dyeing yields was close to each other.

Considering the evaluation of experimental results on rubbing and washing fastnesses, for dry, wet, colour change and staining the triazinyl and tetrazinyl reactive dyes showed a similar performance. However, the rubbing and washing fastnesses of triazinyl dyes were slightly better than those of tetrazinyl dyes. In addition, the difficult synthesis of the tetrazinyl reactive group route was a disadvantage.

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