Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2473-2476

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17929

Printing and Dyeing Physiognomies of Synthesized Azo-Multifunctional Reactive Dyes Using Exhaust Technique

Q. SAEED[1,*], I.A. BHATTI[1], M. ZUBER[2], H.N. BHATTI[1] and M.A. ZIA[1]

[1]Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad, Pakistan
[2]Department of Applied Chemistry and Biochemistry, Government College University, Faisalabad, Pakistan

*Corresponding author: E-mail: qura_phd@yahoo.com

Received: 1 May 2014; *Accepted*: 14 August 2014; *Published online*: 30 March 2015; AJC-17059

Four poly-functional reactive dyes keeping mono or *bis* reactive group have been synthesized and applied successfully to cotton fabric. The main target of study was to synthesize novel reactive dyes having multiple reactive cites to show maximum colour strength. In order to explore the best dyeing conditions, dyeing parameters such as dyeing time, temperature and pH of dyeing bath as well as salt concentration were optimized. Textile printing is the most versatile method used for introducing varieties of design to textile fabrics. These synthesized dyes were applied to fabric for evaluating their printing potential. Fastness properties such as washing, light, rubbing, dry cleaning and perspiration were also investigated after application by exhaust method and printing techniques at Noor Fatima Textile Industry (Pvt.), Faisalabad, Pakistan. The percentage dye exhaustion and fixation was found to be reasonably good and acceptable. All the dyes, after fixation onto the fabrics, showed moderate to excellent fastness properties and colour strengths. The prints of these reactive dyes also demonstrated equitably good colour fixation and fastness characteristics.

Keywords: Azo reactive dyes, Synthesis, Exhaustion, Fabrics, Fixation, Fastness, Printing.

INTRODUCTION

Dyeing is commonly a textile wet process that gives colour to textile materials. Finishing processes in textile industry are of high rates energy consumption particularly exhaustion because frequent washing is necessary after dyeing[1]. The main challenge that textile industry faces these days is to modify production at a competitive price by using safe dyes and chemicals as well as reducing cost of treatment. Fiber reactive dyes are anionic water soluble colour imparting organic compounds that are capable of forming a covalent bond between reactive groups of the dye molecule and nucleophilic groups within the fiber. Consequently, the dyes become chemically part of the fiber by producing dye-polymer linkages *e.g.* with the hydroxyl groups of cellulose, the amino, hydroxyl and mercapto groups of proteins and the amino groups of polyamides[2].

Dyeing of cotton fabrics with reactive dyes generally proceeds in the presence of high concentrations of potentially toxic non-biodegradable salts at elevated pH of dye solution. In the presence of alkali, reactive dyes react with hydroxyl groups of cellulose, mostly *via* neucleophilic substitution or addition reaction, to form covalent bonds. The strength of this bonding between cellulose fabric and dye molecules ensures excellent wash fastness properties. However, the dyes can also react with hydroxyl groups of water present in the dye bath instead of reacting with cellulose. Thus, low fixation of reactive dye due to hydrolysis and the use of high concentration of electrolyte would lead to environmental problems[3].

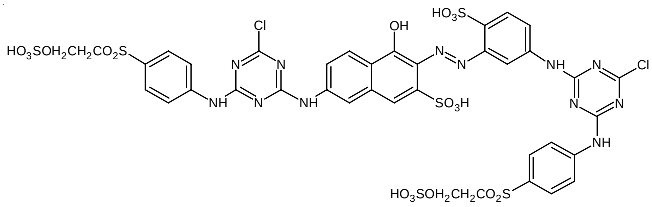
Generally, reactive dyeing can be divided into two segments, namely exhaustion and fixation. The process is extensive, because much time is consumed on the controlled heating of dye bath and portion wise addition of salt and alkali in order to avoid uneven dyeing and maximizing the exhaustion and fixation[4].

Textile printing is the most important and multipurpose method used for introducing colour and design to textile fabrics. Printing involve bringing together a design idea, colourants and textile substrate on which one or more colourants are applied using specific techniques[5]. Reactive textile printing is not only the oldest but also more than 45 % of the printed goods are based on pigment printing by virtue of its obvious advantages such as versatility of processing, ease of getting final print at the printing stage[6]. This paper describes the different steps involved in the synthesis of mono and *bis* azo reactive dyes and the influence of dyeing parameters such as dyeing time, temperature, salt and pH on exhaustion and fixation of newly synthesized dyes. After application colour fastness properties like washing, rubbing, light, dry cleaning, perspiration and chlorination were also determined.

After printing the fastness properties of the printed fabrics were also evaluated.

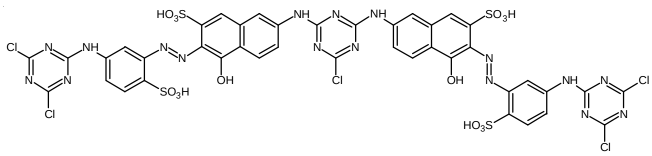
EXPERIMENTAL

Synthesis of mono azo reactive dye (D1): The dye (D1) was synthesized by following the condensation, diazotization and coupling steps. Condensation was carried out by dissolving, 7-amino-4-hydroxynaphthalene-2-sulfonic acid (J acid) solution to cyanuric chloride suspension and *m*-phenylene diamine-4-sulfonic acid to cyanuric chloride. After diazotization, coupling was carried out and in the last step para ester of vinyl sulfone reactive group was condensed with the product at 45 °C by keeping pH 7.



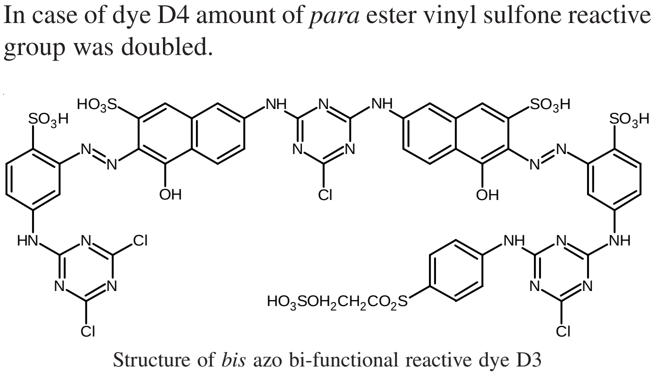
Structure of monoazo reactive dye D1

Synthesis of *bis* azo monofunctional reactive dye (D2): Reactive dye was synthesized which contains two azo groups. This experiment was also carried out in different steps. First condensation was carried out by dissolving, 7-amino-4-hydroxynaphthalene-2-sulfonic acid (J acid) solution in water to cyanuric chloride suspension and second condensation was carried out by adding J acid to first condensed product. And diazotization of condensed product of *m*-phenylene diamine-4-sulfonic acid and cyanuric chloride suspension was carried out. In last step coupling was carried out by adding second condensed solution of cyanuric J acid along with stirring to diazotized solution and product was dried in oven.

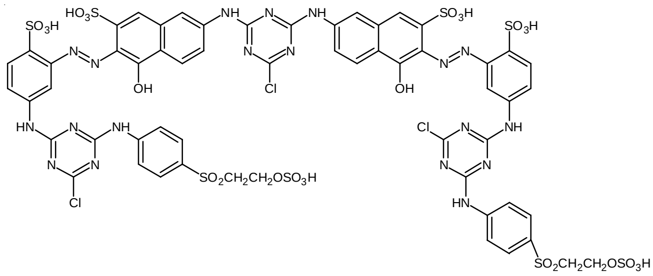


Structure of *bis*azo mono-functional reactive dye D2

Synthesis of *bis*azo multifunctional reactive dyes (D3) and (D4): For the synthesis of dye D3 procedure was repeated as in the case of dye D2 but *para* ester vinyl sulfone reactive group was added at temperature 45 °C for condensation. Then pH was maintained at 7 with sodium carbonate (20 % w/v). In case of dye D4 amount of *para* ester vinyl sulfone reactive group was doubled.



Structure of *bis* azo bi-functional reactive dye D3



Structure of *bis* azo hetero-bi-functional reactive dye D4

Optimization of dyeing conditions: All dyeing were performed in sealed stainless steel dye pots in Roaches laboratory dyeing machine using liquor ratio of 40:1. The extent of exhaustion and fixation was determined as a function of dyeing parameters such as time (30, 40, 50, 60 min), temperature (60, 70, 80 and 90 °C), pH (8, 9, 10, and 11) and salt concentration (40, 60, 80 and 100 g/1000 mL)[7]. Percentage exhaustion and fixation was calculated using eqn. 1 and 2 where C_1 is the concentration of dye solution prior to dyeing, C_2 is the concentration of dye solution at time *t* minutes and C_3 is concentration of dye after rinsing and washing of dyed fabric[8]. The concentration of the extract was measured spectrophotometerically at λ_{max} absorption maxima for each dye.

$$E\,(\%) = \frac{(C_1 - C_2)}{C_1} \times 100 \quad (1)$$

$$F\,(\%) = \frac{(C_1 - C_2 - C_3)}{(C_1 - C_2)} \times 100 \quad (2)$$

Printing: Printing paste consisting of dye, urea and sodium alginate was applied to cotton by direct printing method at viscosity of 2300 cps using spindle No. 6 at 20 rpm. Steaming was carried out at 103 °C for 15 min. and then washing of the goods printed with synthesized reactive dyes was carried out first by rinsing with cold water and then heating at 60 °C. Reflectance measurements on the dry dyed fabrics were performed using a Datacolour Spectraflash SF-600 spectrophotometer[9]. The dyed fabric was folded twice so as to provide four layers for analysis.

Fastness properties: Fastness to light, washing, crocking, perspiration, chlorinated water and dry cleaning was assessed in accordance with American Association of Textile Chemists and Colorists (AATCC) standard methods[10].

RESULTS AND DISCUSSION

Synthesis: Azo reactive dyes were synthesized by means of utilizing the multiple reactive groups following the general procedure of condensation; diazotization and coupling[11].

Effect of dyeing temperature: Figs. 1 and 2 show the effect of dyeing temperature on percentage exhaustion and fixation of dyes. The dye reacts with the hydroxyl (-OH) groups on the cotton fabrics, as the temperature increases the dyestuff completes its reaction with the cotton in the presence of alkali.Since both cotton fabrics and water have -OH groups; there can also be a reaction with the (-OH) of the water which is called dye hydrolysis. Attachment of dye on to the fabric increased with temperature because bigger molecules break down and amount of dye in solution increased[12]. Results show that the dyeing temperature up to 80 °C was the most suitable to attain

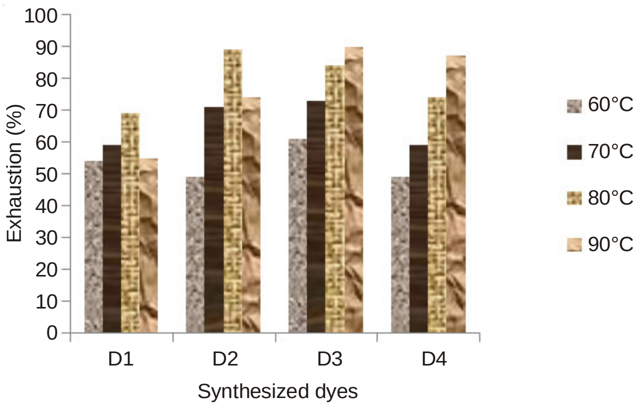


Fig. 1. Effect of dyeing temperature on percentage exhaustion of reactive dyes

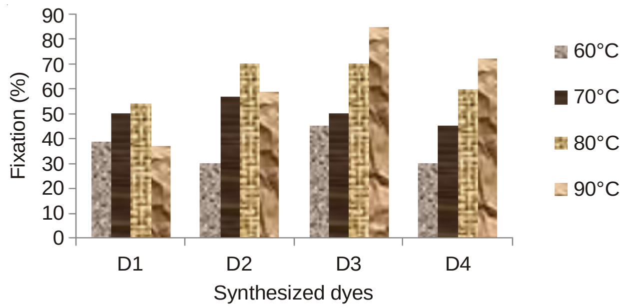


Fig. 2. Effect of dyeing temperature on percentage fixation of reactive dyes

maximum exhaustion and fixation. Exhaustion up to 80 % and percentage fixation up to 70 % have been obtained after washing in case of synthesized *bis* azo reactive dyes.

Effect of dyeing time: Dyeing time is a very important dyeing parameter since its optimization gives excellent dyeing characteristics. When fabric is dipped into dye solution equilibrium is established between dye in the fiber and dye in the solution and after reaching at equilibrium no further exchange occurs[13]. If we give inappropriate time for dyeing then either dye will remain in solution or will start shifting from fabric to dye bath again. For this purpose different dyeing intervals are selected. It was seen that after attaining equilibrium dye molecules migrate rapidly from fabric to the dye bath which might cause weakening the shade and colour strength of the dyed fabrics. Effect of dyeing time on percentage exhaustion and fixation is shown in Figs. 3 and 4 respectively. For the reactive dyes used in this study, 40 min. dyeing time was found to be suitable after that hydrolysis starts which can decrease the exhaustion. After washing, fixation and exhaustion characteristics of the synthesized dyes were observed to 70 and 80 %, respectively.

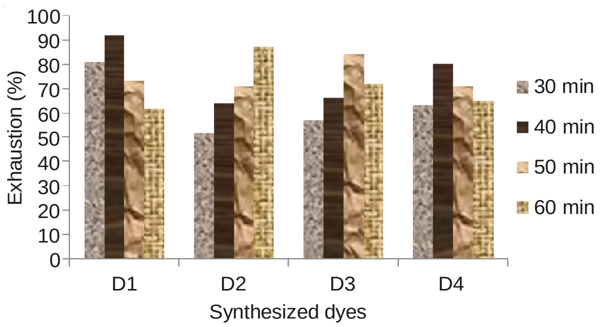


Fig. 3. Effect of dyeing time on percentage exhaustion of reactive dyes

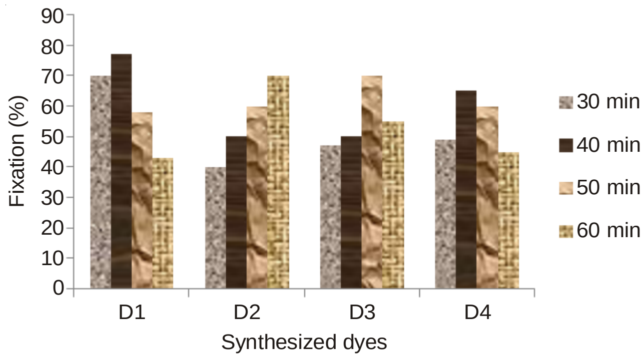


Fig. 4. Effect of dyeing time on percentage fixation of reactive dyes

Effect of salt concentration: Addition of electrolyte in dye bath is necessary because cellulose and dye both have negative charges which create electrostatic barrier and reduces interaction between fiber and the dye. Salt helps to suppress this potential barrier allowing better contact between dye moiety and the fiber[14]. Effect of electrolyte concentration on exhaustion and fixation was studied and the results are shown in Figs. 5 and 6. It is found that the dye fixation increased with the salt concentration, maximum colour strength was obtained using 60 g/L of salt concentration in dye bath for the dyes. Percentage exhaustion up to 80 % and fixation up to 70 % was obtained using optimum salt concentration.

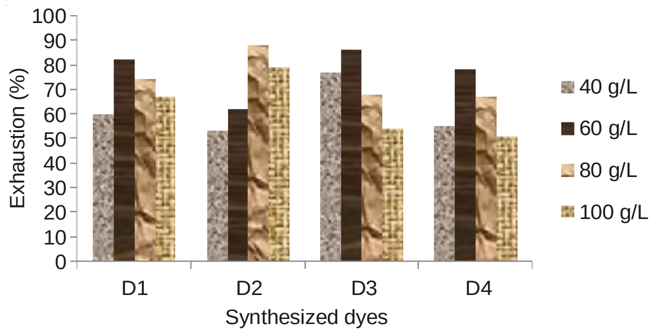


Fig. 5. Effect of salt concentration on percentage exhaustion of reactive dyes

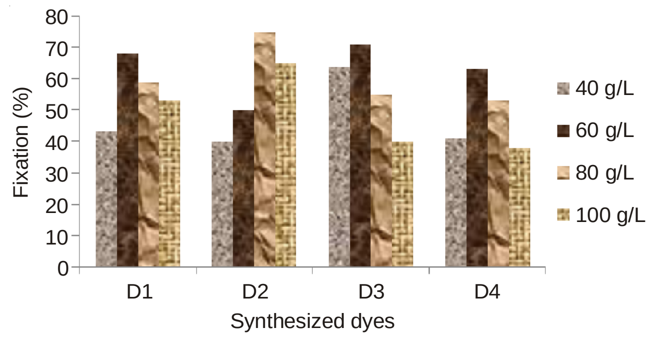


Fig. 6. Effect of salt concentration on percentage fixation of reactive dyes

Effect of pH: It is essential during dyeing to maintain the pH of the dye solution to an optimum level. Alkali is added to generate hydroxyl ions on cellulose fiber and to form vinyl sulfone group from sulfato ethylsulone reactive group because both these steps are necessary for bonding of dye with the fabrics. Figs. 7 and 8 show the effect of pH during application of dyes. Results show maximum exhaustion and fixation at pH 8 and 9 because this was most suitable for the dyes to form linkages with the fiber and further increase in pH caused the

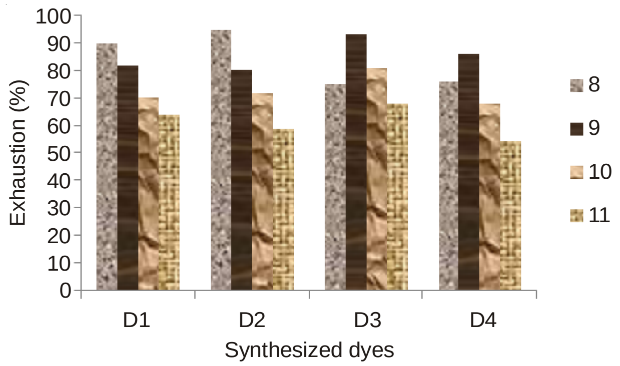


Fig. 7. Effect of dyeing pH on percentage exhaustion of reactive dyes

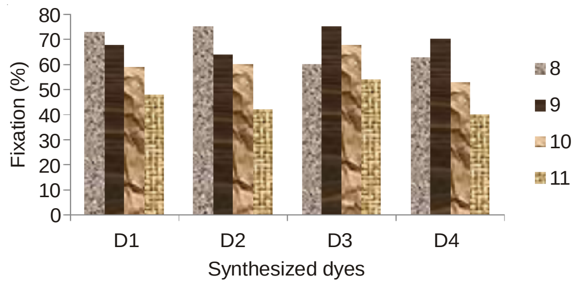


Fig. 8. Effect of dyeing pH on percentage fixation of reactive dyes

dye hydrolysis at the cost of dye fiber reaction that reduced the ultimate exhaustion and fixation. At higher alkaline pH hydroxyl groups might attach to dye instead of fiber linkage. However, exhaustion up to 90 % and fixation up to 70 % were obtained at pH 8 and 9, respectively.

Printing: Fibre reactive dyes are one of the most commonly used dyes for cellulose fibres (cotton, linen, viscose). These dyes are great for dip dyeing, screen printing, batik, mono printing and painting onto fabric. Unlike a pigment which just 'binds' to the surface of the fibre. Fibre reactive dyes create a permanent bond between the dye molecule and the fibre. The colours are fast under normal washing and light conditions. All the dyes under investigation gave appreciable percentage absorption in case of printing therefore these dyes can be safely applied to cotton. Dyes showed absorbance in the range of 60 to 70 % as shown in Fig. 9.

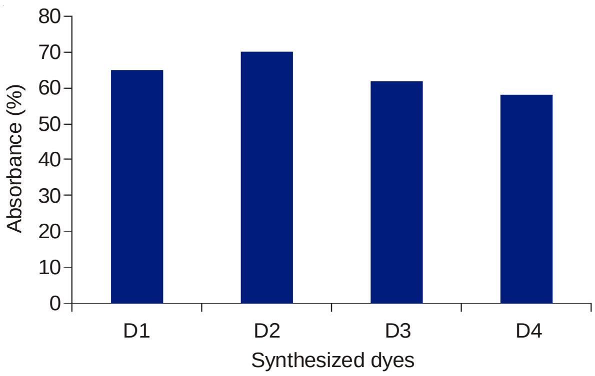


Fig. 9. Percentage absorbance of dyes after printing

Fastness properties: The gray scale rating for fastness properties such as washing, light, rubbing, dry cleaning and perspiration was performed. Results after dyeing and printing are shown in Tables 1 and 2, respectively. Results for colour fastness tests were appreciable ranging from moderate to good.

TABEL-1
FASTNESS RESULTS OF REACTIVE DYES APPLIED BY EXHAUST METHOD

Dye no.	Wash fastness	Light fastness	Dry cleaning fastness	Perspiration Fastness	Rubbing fastness	
					Wet	Dry
1	5	4	5	5	4	5
2	5	4	5	5	4	5
3	5	4	5	5	4	5
4	5	4	5	5	4	5

TABEL-2
FASTNESS RESULTS OF REACTIVE DYES AFTER PRINTING

Dye No.	Light fastness	Wash fastness	Rubbing fastness	
			Dry	Wet
1	3	4	4	3
2	3	4	4	3
3	4	4	4	3
4	4	4	4	3

Conclusion

Dyes were applied on the fabrics for dyeing and printing at optimum conditions. During dyeing exhaustion of dyes was more than 90 %, colour yields after printing on fabric was also appreciable and absorption up to 70 % was obtained in case of *bis* azo reactive dye (D2) which has same kind of reactive group. Chlorotriazine with five reactive sites gave very nice colour fastness results both for dyeing and printing when applied to cotton. These newly synthesized dyes seems a good addition in textile dyeing since they have shown better exhaustion and fixation characteristics as compared to most of the dyes used today.

ACKNOWLEDGEMENTS

The authors thank Higher Education Commission, Pakistan for financial support in carrying out this project and Noor Fatima Textile (Pvt) Ltd. Faisalabad, for providing the facility of fastness tester.

REFERENCES

1. A. Cay, I. Tarakçioglu and A. Hepbasli, *Appl. Therm. Eng.*, **29**, 2554 (2009).
2. M.K. Uddin and S.S. Hossain, *Int. J. Eng. Technol.*, **10**, 6 (2010).
3. N.S.E. Ahmed, *Dyes Pigments*, **65**, 221 (2005).
4. M. Iftikhar, N.A. Jamil and B. Shahbaz, *Int. J. Agr. Bio.*, **3**, 1 (2001).
5. S. Chiou and P.E.J. Schoen, *Appl. Poly. Sci.*, 4958 (2006).
6. R. Adhikari, C. Damm, G.H. Michler, H. Münstedt and F.J. Baltá-Calleja, *Compos. Interfaces*, **15**, 453 (2008).
7. M.S. Alam, G.M.A. Khan, S.M.A. Razzaque, M.J. Hossain and M.M. Haq, *Indian J. Fib. Text. Res.*, **33**, (2008).
8. S.A. Abo Farha, A.M. Gamal, H.B. Sallam, G.E.A. Mahmoud and L.F.M. Ismail, *J. Am. Sci.*, **6**, 109 (2010).
9. S.M. Burkinshaw and M. Paraskevas, *Dyes Pigments*, **88**, 212 (2011).
10. AATCC, Technical Manual, American Association of Textile Chemists and Colorists, North Carolina, USA (1999).
11. R. Patel and K.C. Patel, *Dyes Pigments*, **90**, 1 (2011).
12. F. Sadov, M. Korchagain and M. Matesky, Chemical Technology of Fibrous Materials, Mir Publishers, Moscow, p. 139, 315, 340 (1973).
13. S.R. Cocket and K.A. Hilton, Dyeing of Cellulosic Fibre and Related Processes, Leonard Hill Books Ltd. London, p. 212, (1961).
14. A. Johnson, The Theory of Colouration of Textiles, Bradford: SDC, edn 2, p. 121 (1989).