Study of Application of Mono azo Reactive Dyes on Cotton by Exhaust method and Printing Properties

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***Abstract*--** **This paper explores the printing properties and exhaust dyeing of four newly synthesized reactive dyes. Dyes were applied at different conditions of dyeing parameters such as pH, electrolyte concentration, time and temperature in order to get maximum fixation. After printing on fabric, color strength was determined with Spectraflash SF 600 spectrophotometer and fastness properties such as washing, crocking, light, perspiration, chlorinated water and dry cleaning were investigated by International organization of standardization (ISO) standard methods. Exhaustion and fixation values were evaluated by UV/Vis Spectrophotometer. All dyes showed remarkable color strength in the range of 70 to 80% for printing. Percentage dye bath exhaustion and fixation has been found to be in the range of 65 to 85% which is reasonably good and acceptable. Fastness properties were good to excellent.**

***Index Terms*—** **reactive dyes, exhaust method, fastness properties, printing property,**

I. INTRODUCTION

There are more than 1,00,000 types of dyes commercially available, with over 7,105 tones of dyestuff produced annually, which can be classified according to their structure as an- ionic and cationic [1].

In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate (SO_3) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups [2].

Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics [3]. Discharging dyes into the hydrosphere can cause environmental damages the dyes give water undesirable color [4].

In recent years, reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colors. Moreover, the use of reactive dyes is rapidly growing due to the increased use of cellulosic fibers. Generally reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazine as chromophore. Among the reactive dyes, approximately 66% is unmetallized azo dye [5].

The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali. One of the major factors determining the release of a dye into environment is its degree of fixation on the fiber. Reactive dye is hydrolyzed to some extent during application processes; some of reactive dyestuff is inactivated by a competing hydro- lysis reaction. Consequently, the release of reactive dyes into dyebath effluent is exacerbated by their relatively low fixation (50e90%) to cellulosic fibers, compared with other dyes such as acid, basic, disperse and direct dye [5,6].

Reactive dyes in dyeing wastewater have been identified as recalcitrant compounds since they contain high alkalinity, high concentration of organic materials and strong color in comparison with other dyes[7].

Reactive dyes are characterised by nitrogen-to-nitrogen dou- ble bonds, azo bonds (N N), and used mainly for dyeing cellu- lose fibres. The colour of the azo dyes is due to this azo bond and associated chromophores [8].

The dyes are first absorbed onto the cellulose and then react with the fibre. The reaction occurs by the formation of a covalent bond between the dye molecule and the fibre. The reactive systems of these dyes react with ionised hydroxyl groups on the cellulose substrate [9].

How-ever, hydroxyl ions present in the dye bath due to alkaline dyeing conditions compete with the cellulose substrate, resulting in a percentage of hydrolysed dyes which can no longer react with the fibre [10] and [9].

Reactive dyes are extensively used in dyeing processes in textile industry but about 20–40% of these dyes remain in the effluents [11,12]. Reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge [13].

Textile printing is the most versatile and important of the methods used for introducing color and design to textile fabrics. Considered analytically is a process of bringing together a design idea, one or more colorants and a textile substrate using a technique for applying the colorants with some precision [14].

Approximately 25% of the total print production in the world is performed by reactive printing [15]. The reactive dyes are one of themost commonly used dyes for textile printing because of their high wet fastness, brilliant colours and variety of hue [16]. In general, the reactive dyes used in printing often have a degree of fixation of only 60%, whereas in dyeing a degree of fixation of over 90% can be achieved [17].

The aim of this work is to examine the exhaustion and fixation efficiency on cotton fabric and printing properties of a series of synthesized reactive dyes. For determination of effect of different dyeing parameters such as time, temperature, pH and electrolyte on dyeing was carried out at different conditions. Fastness properties like washing, light, perspiration, crocking, dry cleaning and chlrorinated water were also evaluated after exhaust application and printing.

II. EXPERIMENTAL

A. Synthesis:

Four reactive dyes, two homofunctional and two bifunctional were synthesized at radiation chemistry Laboratory University of Agriculture, Faisalabad by following a general scheme of synthetic steps of diazotization and coupling.Structures of the dyes are given in the Table I.

Dyes 1 and 2:

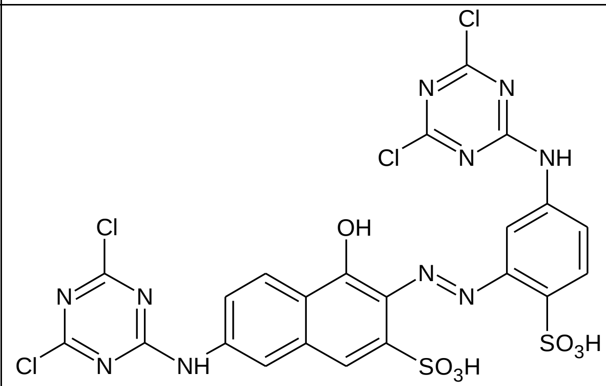
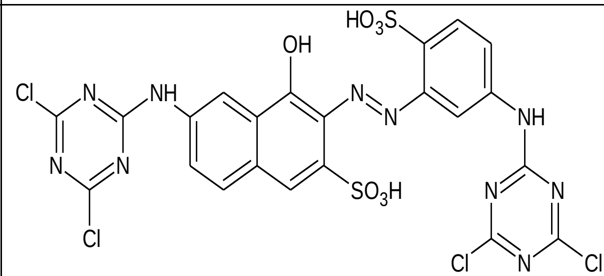
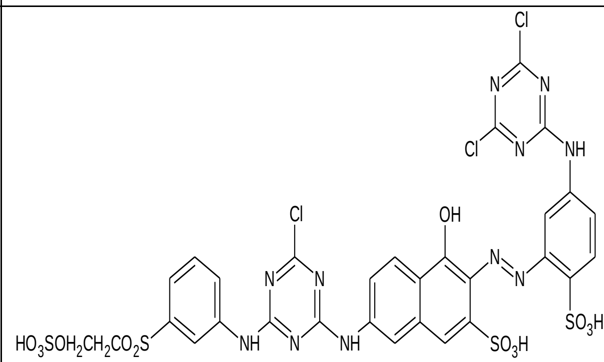
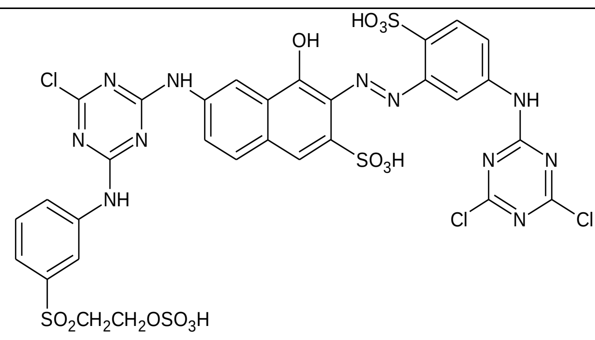
First dye was synthesized in different steps by following the scheme . 7-amino-4-hydroxynephthalene-2-sulfonic acid (J-acid) solution (0.01mole,) at pH 6 -7 was added to Cyanuric Chloride (0.01mole,1.9g) Suspension for condensation at temperature from 0-5°C with constant stirring.Completion of condensation was confirmed using paper chromatography. Another condensation was also carried out between m-phenylene diamine-4-sulfonic acid (0.01mole, 1.91g) mPDSA solution and Cyanuric chloride (0.01mole,1.9g) suspension as well. Condensation was carried out about for 2hrs and its completion was also confirmed by paper chromatography.

For diazotization to condensed solution of mPDSA and Cyanuric Chloride solution 25% sodium hydroxide solution was added to maintain pH 7. After it ice was added till 0-5°C temperature was obtained. Then 0.71g sodium nitrite and 10ml hydrochloric acid were added respectively, after it solution was tested with starch iodide and congo red filter paper. Starch paper was turned brown and congo red paper was turned blue. Then this solution was stirred for one hour. After one hour minute quantity of sulfamic acid was added until starch paper gives negative test. After diazotization, coupling was carried out by adding condensed cyanuric J acid solution to diazotized solution and then pH was maintained 7 with 20% sodium carbonate solution. After maintaining pH constant synthesized dye was dried in oven at 80-90°C.Dye D2 was prepared by the same same procedure except the coupling component used was6-amino-4-hydroxynephthalene-2-sulfonic acid (Gamma acid).

Dyes 3 and 4:

Dye D3 and D4 were prepared by repeating the procedure as in the case of Dye D1 and D2 respectively but one additional condensation was done before drying step. After coupling, meta ester of vinyl sulfone reactive group was added and temperature was raised up to 45°C for condensation, pH maintained at that step was 7 with 20% sodium carbonate solution.

TABLE I
Dye structures with IUPAC names

Dye No.	IUPAC name	Structure
D1	7-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-3-((*E*)-2-{5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-2-sulfophenyl}diazenyl)-4-hydroxy-2-naphthalenesulfonic acid	
D2	6-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-3-((*E*)-2-{5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-2-sulfophenyl}diazenyl)-4-hydroxy-2-naphthalenesulfonic acid	
D3	7-{[4-chloro-6-(3-{[2-(sulfooxy)ethyl]sulfonyl}anilino)-1,3,5-triazin-2-yl]amino}-3-((*E*)-2-{5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-2-sulfophenyl}diazenyl)-4-hydroxy-2-naphthalenesulfonic acid	
D4	6-{[4-chloro-6-(3-{[2-(sulfooxy)ethyl]sulfonyl}anilino)-1,3,5-triazin-2-yl]amino}-3-((*E*)-2-{5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-2-sulfophenyl}diazenyl)-4-hydroxy-2-naphthalenesulfonic acid	

B. Dyeing:

Dyes were applied to cotton fabric by exhaust method. Different parameters were taken into account and their different conditions were optimized. All dyeings (2% omf) were carried out in sealed stainless steel dyepots, housed in a

Roaches laboratory dyeing machine using a liquor ratio of 40:1.

C. Determination of exhaustion and fixation efficiency:

The extents of dye exhaustion (%E), dye fixation (%F) and overall fixation efficiency (%T) that occurred as a function of both dyeing temperature (60, 70, 80 and 90 °C) and pH (8, 9, 10, and 11), time (30,40,50 and 60 min.) and salt concentration of (40,60,80 and 100 g/1000ml) were determined.

D. Color fastness:

Light, washing, rubbing, dry cleaning, perspiration and chlorination to water were assessed according to standard methods [18].

E. Printing:

Preparation of the printing pastes:

The printing pastes of the reactive dyes were prepared with the following recipe: 3 g of reactive dye, 8 g of urea, 3 g sodium alginate, six percent of sodium bicarbonate was used to maintain pH 9 to 10.

Application:

Printing paste was applied to cotton by direct printing method at viscosity of 2300 cps at spindle No. 6 at 20 rpm. Steaming was carried out at 103°C for 15 minutes 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.

F. Color measurement:

Reflectance measurements on the dry dyed fabrics were carried out using a datacolor Spectraflash SF 600 spectrophotometer[8].The dyed fabric was folded twice so as to provide four layers to analysis.

G. Color fastness:

For assessment of quality of dyed fabric samples, color fastness to washing, light and crocking was carried out using AATCC standard methods. Rating of 1(poor) to 5(excellent) was given to the dyed samples by comparing with Grey scale. Washing tests were performed by following AATCC test method 107-1997, rubbing fastness were performed on crockmeter by AATCC 8-1996 method and light fastness were performed in by following AATCC 16-1998 standard method.

III. RESULTS AND DISCUSSION

A. Exhaustion and fixation study:

Effect of time:

Time is a very important dyeing parameter. When fabric is dipped into dye solution equilibrium is established between dye in the fiber and dye in the solution. If we give inappropriate time for dyeing then either dye will remain in solution or will start to shift from fabric to dye bath again. For this purpose different conditions of time were selected. It was seen that after attaining equilibrium dye started to shift from fabric to the dye bath. Effect of dyeing time on percentage exhaustion and fixation is shown in fig. 1 and 2 respectively. For most of the dyes 40 minutes dyeing time was found to be suitable after that hydrolysis decreased the exhaustion. Percentage exhaustion above 85 percent was found to be maximum and after washing fixation was up to 70 percent.

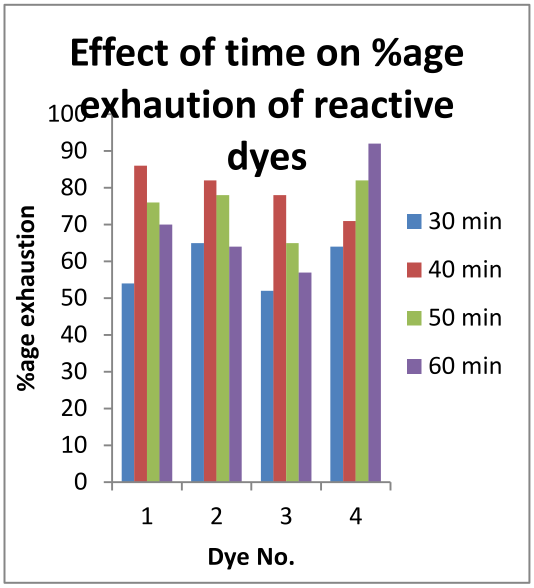


Fig. 1. Effect of dyeing time on %age exhaustion of reactive dyes

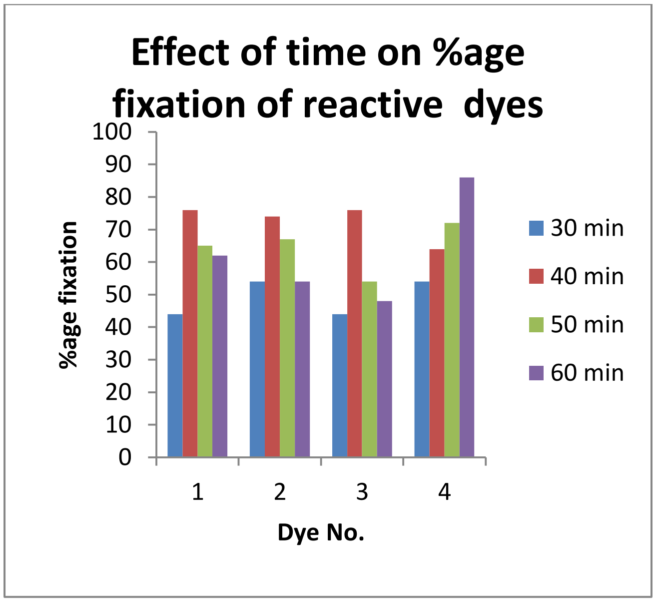


Fig 2. Effect of dyeing time on %age fixation of reactive dyes

Effect of temperature:

Dye exists in solution as an aggregate of various sizes. Small molecules are taken up by fabric and bigger aggregates break down slowly to diffuse. As the temperature is increased bigger molecules break down and amount of dye in solution form increases. Rise in temperature increases thermal oscillation of macromolecule chain which provoke an increase in the number of pores [19]. When equilibrium is reached dye starts to shift from fabric to the dye bath. Dyeing temperature effect on %age exhaustion and fixation is shown in fig. 3 and 4 respectively. Results show temperature up to 70-80°C was most suitable to attain maximum exhaustion and fixation.Exhaustion up to 80 percent was found in case of synthesized mono azo reactive dyes. Percentage fixation up to 70 percent was obtained after washings.

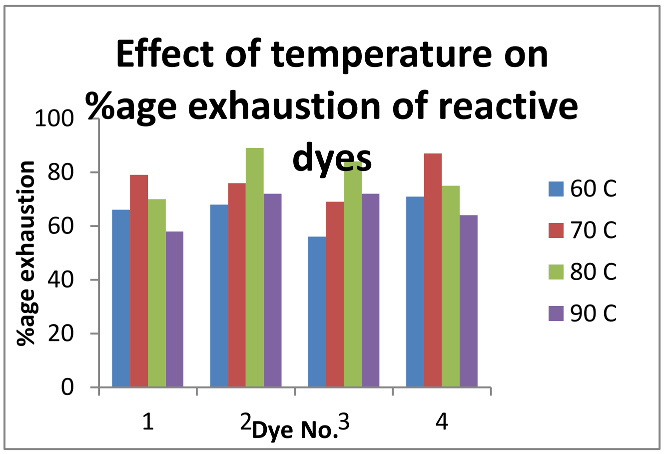


Fig. 3. Effect of dyeing temperature on %age exhaustion of reactive dyes

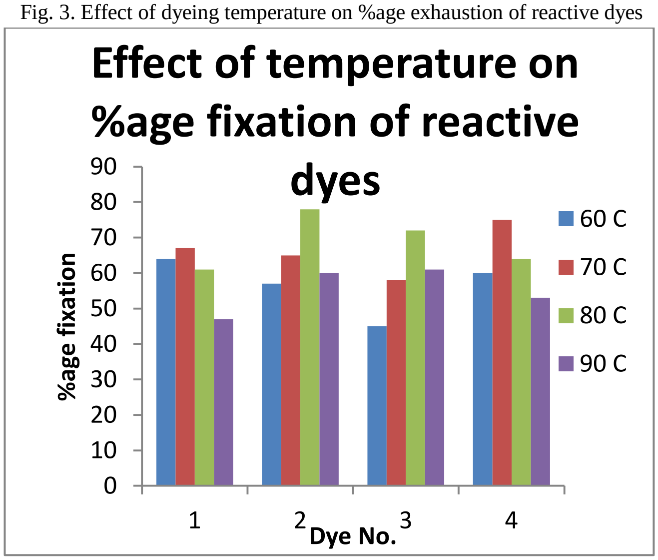


Fig. 4. Effect of dyeing temperature on %age fixation of reactive dyes

Effect of salt concentration:

The effect of salt concentration on the dye ability of cotton fabric was conducted at different salt concentrations. It was seen that exhaustion and fixation was increased with salt concentration and then decreased. It is considered that initial rise is due to response of dye to the lowering of electrical potential barrier to diffusion as the concentration of electrolyte increases [20].Results of effect of salt concentration on percentage exhaustion and fixation of reactive dyes dyed by exhaust method are shown in fig. 5 and 6 respectively. Results show salt concentration of 60-80g/L gave maximum percentage exhaustion and fixation in the range of 60 to 85 percent.

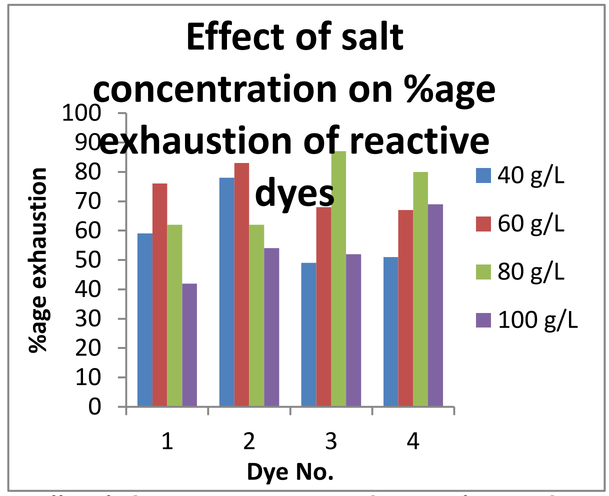


Fig. 5. Effect of salt concentration on %age exhaustion of reactive dyes

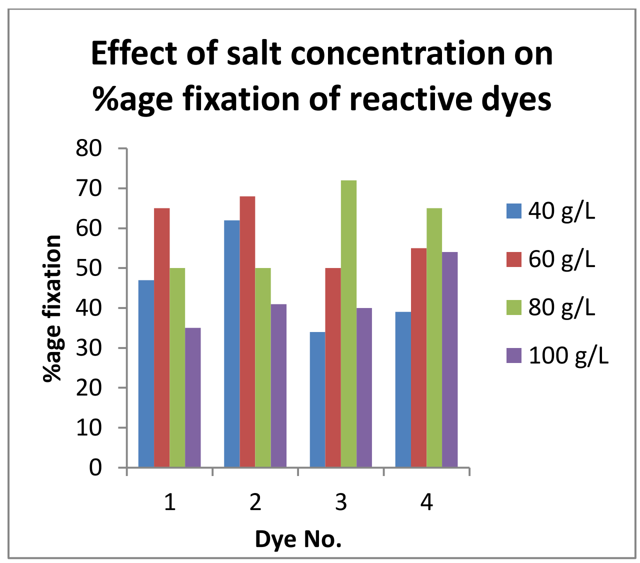


Fig. 6.Effect of salt concentration on %age fixation of reactive dyes

Effect of pH:

It is known that alkali is necessary for covalent bonding of reactive dye to cotton. For this purpose fabric was dyed at different pH values to show its effect. Exhaustion and fixation percentage was increased with increase in pH and then decreased in most of dye baths. Fig. 7 and 8 show effect of pH on percentage exhaustion and fixation of mono azo reactive dyes on cotton. Results show that pH 8 and 9 were most suitable for dyeing of reactive dyes. After that percentage exhaustion and fixation was decreased because high pH lead to hydrolysis at the cost of dye fiber reaction. Results show exhaustion and fixation in the range of 70 to 80 percent maximum.

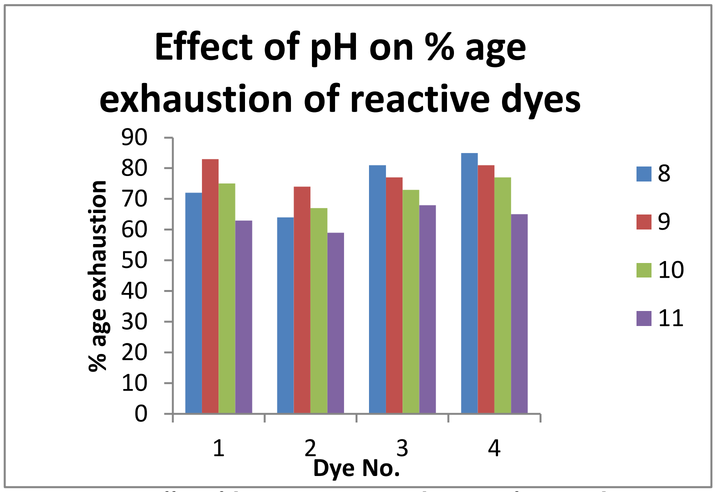


Fig. 7. Effect of dyeing pH on %age exhaustion of reactive dyes

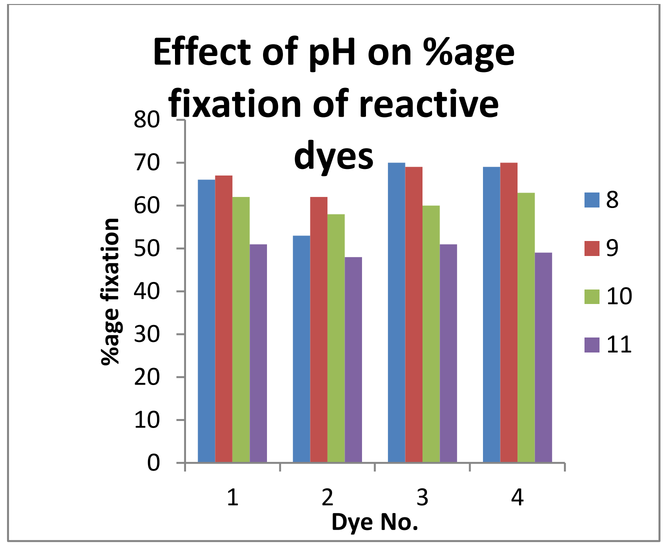


Fig. 8. Effect of dyeing pH on %age fixation of reactive dyes

B. Fastness Properties:

The gray scale rating for fastness properties such as washing, light, rubbing, dry cleaning and perspiration was performed and results were found to be very good. Results are presented in Table II.

TABLE II
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

C. Printing properties:

All dyes gave appreciable percentage absorption in case of printing so these dyes can be safely applied to cotton. Dyes showed absorbance above 65 percent as shown in Fig. 9.

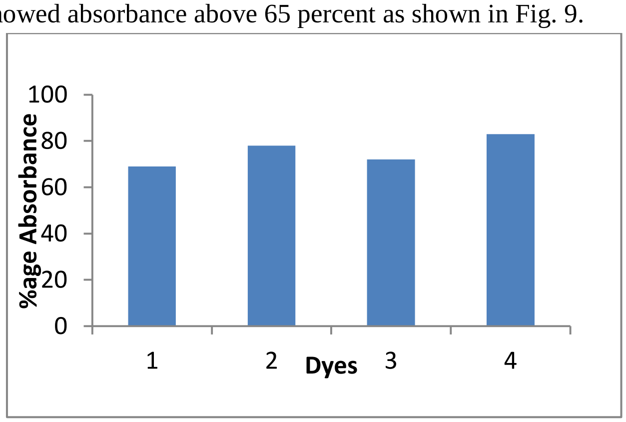


Fig. 9.Percentage absorbance of reactive dyes after printing

D. Color fastness after printing:

Fastness results as shown in Table III were appreciable ranging from moderate to good results in case of washing, rubbing and light fastness.

TABLE III
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

IV. CONCLUSION

Four mono azo reactive dyes were synthesized and applied successfully to cotton fabric. Dyes gave maximum exhaustion up to 85 % with very good fastness properties results. Synthesized dyes were also applied as printing paste on cotton and results were very appreciateable. Color strength up to 80% was found after printing and washing.After printing fabric was tested for fastness properties and gray scale rating was found to be good. So these dyes can be applied to cotton for dyeing and printing as well.

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