SYNTHESIS AND STUDIES OF MONOAZO DISPERSE DYES BASED ON 2, 4-DIHYDROXY-6-CHLORO QUINOLINE

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ABSTRACT

2, 4 – dihydroxy – 6 – chloroquinoline has been coupled with various diazotized coupling components to prepare various disperse dyes. All the dyes were characterized by their percentage yield and elemental analysis. IR, H^1 NMR, CMR of some selected synthesized compounds have been carried out. Their dying performance were assessed on polyester fabric. The percentage dye bath exhaustion were found to be good and acceptable. The dyed fibres showed poor to fair good light fastness and good to excellent wash fastness.

Keywords: 2, 4 Dihydroxy – 6 – Chloro Quinolone, Dyeing, Exhaustion, Light Fastness, Wash Fastness.

I. INTRODUCTION

Disperse Dyes are relatively small molecules, with very low water solubility, which possess substantivity for hydrophobic fibres such as cellulose acetate and polyester. Most of the new disperse dyes introduced during the last decade have been intended for application to polyester and the majority represent advances in application and fastness properties over dyes previously available **[1,2]**. Useful reviews on structural factors affecting the fastness to light of dyed fibres**[3]** and on relations between the molecular structures of dyes and their technical properties have appeared **[4]**.

The development of disperse dyes is due to significant increase in the world production of polyester compared to other fibres. The disperse dyes have the most satisfactory results due to their simple application properties and abilities to cover regularities in yarn. Over 90% of disperse dyes usage is for the colouration of polyester and its blends.

Some of the dyes based on heterocyclic ring system are known to possess high tinctorial power and excellent fastness properties. The compactness extension of conjugation in the structures of heterocyclic compounds are important for the disperse dyes derived from them. Heterocyclic coupling components give heterocyclic azo disperse dyes with colour ranging from yellow to deep red. The synthesis and application of monoazo disperse dyes derived from 4-hydroxy-1-mehtyl-2-quinolone **[5,6]**, 4-hydroxy-1-phenyl-2-quinolone **[7]**, 5-hydroxyquinoline[2,1-b]-quinazolin-12[H]-one **[8]** have been earlier. Malankar and Desai **[9]** have prepared heterocyclic dyes using quinoline moiety. Desai and Desai **[10]** and Vashi and Mehta **[11,12]** have earlier reported quinoline based disperse dyes using quinoline as a coupling component. The synthesis and application of monoazo disperse dyes derived from 3-[(2,6-dimethyl-4-quinolinyl)amino] phenol **[13]** and 4-hydroxy-1-methylquinololin-2[1H]-one **[14]** and 4-hydroxy-2-phenyl-6/7 substituted quinolone **[15]**, 2,4-dihydroxy quinoline **[16]** and 2,4-dihydroxy-6-methyl quinolone **[17]** systems have also been reported to show excellent shades on polyester. These compounds when applied on polyester fabric gave brown, yellow and grey shades with excellent exhaustion and fastness properties.

In view of the encouraging reports about the technical applications of the heterocyclic dyes, it was thought interesting to undertake the synthesis and study of dyeing properties of the monoazo disperse dyes based on 2,4-dihydroxy-6-substituted quinoline system. Here, 2,4-dihydroxy-6-chloro quinoline was synthesized and series of monoazo disperse dyes were synthesized. The characterization of the dyes, evaluations of their technical properties were also performed. The aim of the present work was to find out the possibilities of increasing the shade range of these dyes.

II. EXPERIMENTAL

All the dyes synthesized were purified by crystallization. Melting points were determined by open capillary method and are uncorrected. IR spectra of the selected synthesized compounds were recorded in KBr pellets on a Perkin-Elmer Model – 377 spectrophotometer for structural elucidation, particularly for presence of functional groups. 1H NMR and CMR of some selected synthesized compounds has been carried out for the structural elucidation, particularly for the presence of protons and carbons. “High Temperature High Pressure” method has been employed for the application of disperse dyes on polyester fabrics**[18,19,20]**. Wash fastness was assessed with Grey Scale **[21]**. Light fastness was also assessed for synthesized dyes **[22]**. The exhaustion study of the synthetic dyes was also carried out.

2.1 Ethyl-3-[(4-Chloro Phenyl)Amino-3-Oxopropanoate

A mixture of p-chloroaniline (5.1 g , 0.04 mole) and diethylmalonate (6.5 g , 0.04 mole) was refluxed in boiling xylene (30 ml) with an air condenser for six hours on a sand bath. The solvent was evaporated leaving a residue.

2.2 2, 4 – Dihydroxy-6-Chloro Quinoline (DHCQ)

The residue obtained as above was mixed with freshly prepared poly phosphoric acid (P_2O_5 40 g , orthophosphoric acid 24 ml), stirred well for some time and the temperature was slowly raised to 120° ; it was kept in a desiccator overnight. Next day the temperature was slowly raised and lowered by 10°, until it reached 140° and the heating was continued at this temperature for two hours. This treatment helps in getting clean product in good yield. The reaction mass was poured slowly in to ice-cold water and neutralized with ammonium hydroxide on the acidic side. The product was filtered, washed with water, dried and crystallized from ethanol, Yield 60 %, mp>360° , [Found : N, 7.06 %; $C_9H_6O_2NCl$ required N, 7.20 %]; IR spectra (KBr) : 3200-2600 (-OH), 1251 (C-O), 1589,1502 (C=C), 817 (C-Cl) ; NMR spectra (DMSO-d_6) , δ 5.76 (1H,4-OH) , 11.36-11.56 (1H,2-OH); CMR Spectra (Chemical shift),163 (C_2,C-OH), 136 (C_3), 161 (C_4,C-OH), 122 (C_5), 117 (C_6), 89 (C_7), 116 (C_8), 125 (C_9), 131 (C_{10}).

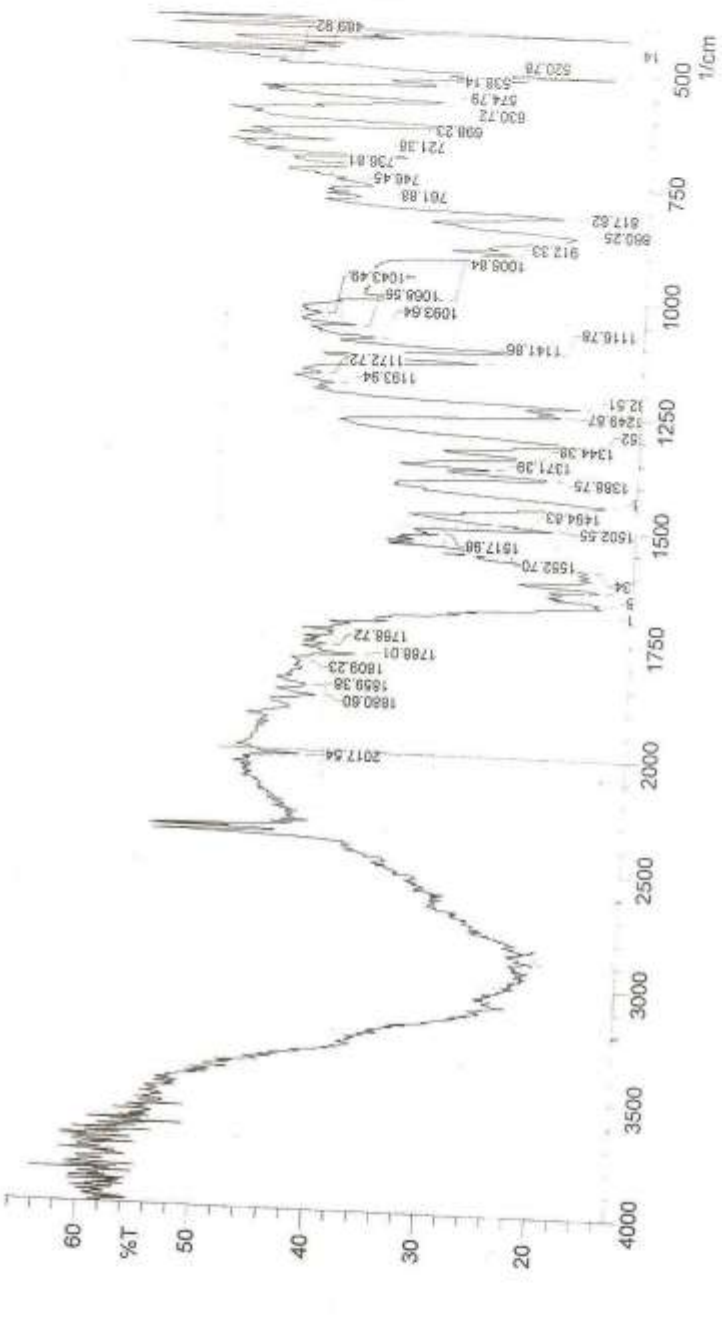
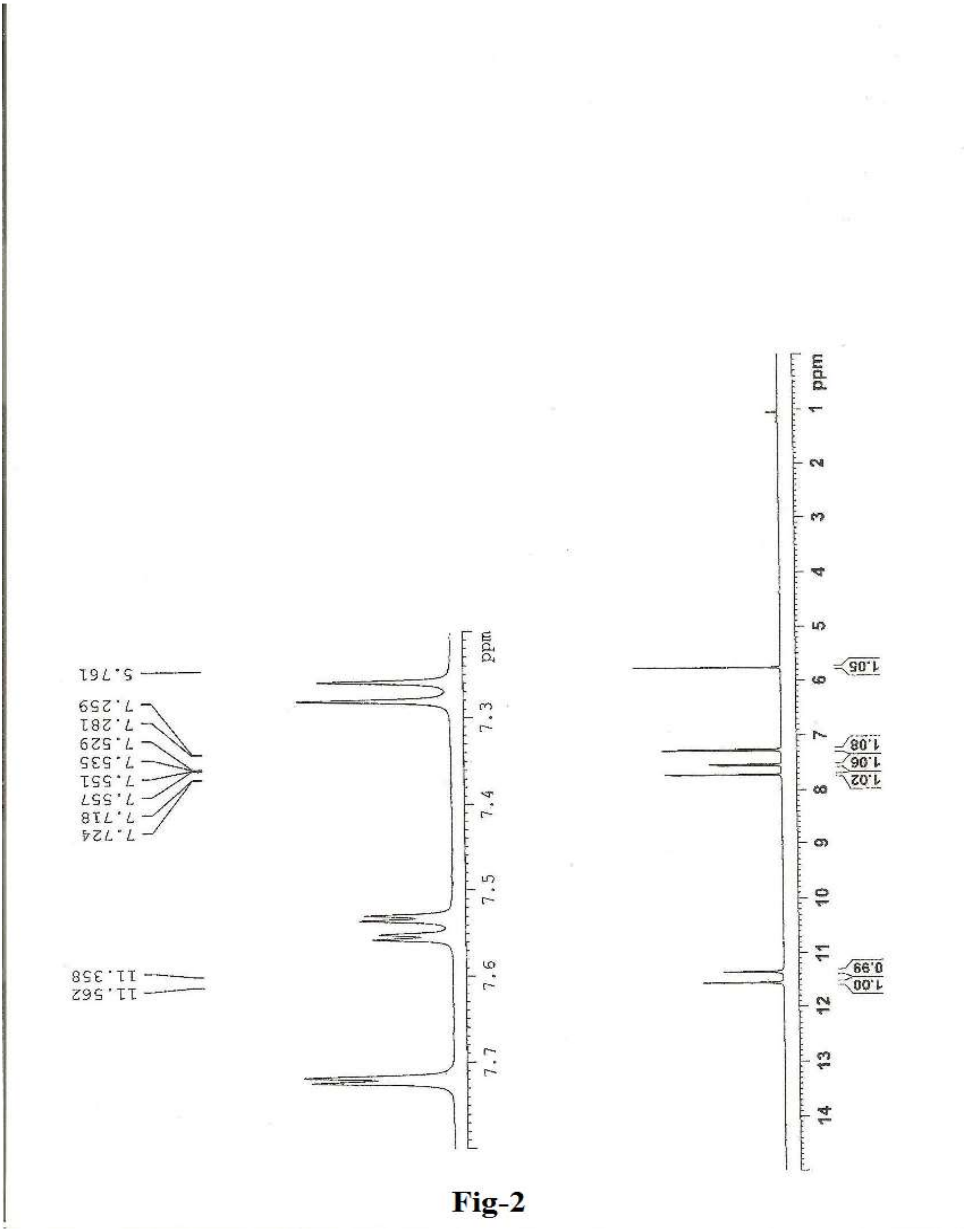


Fig-1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7.535
7.551
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ppm
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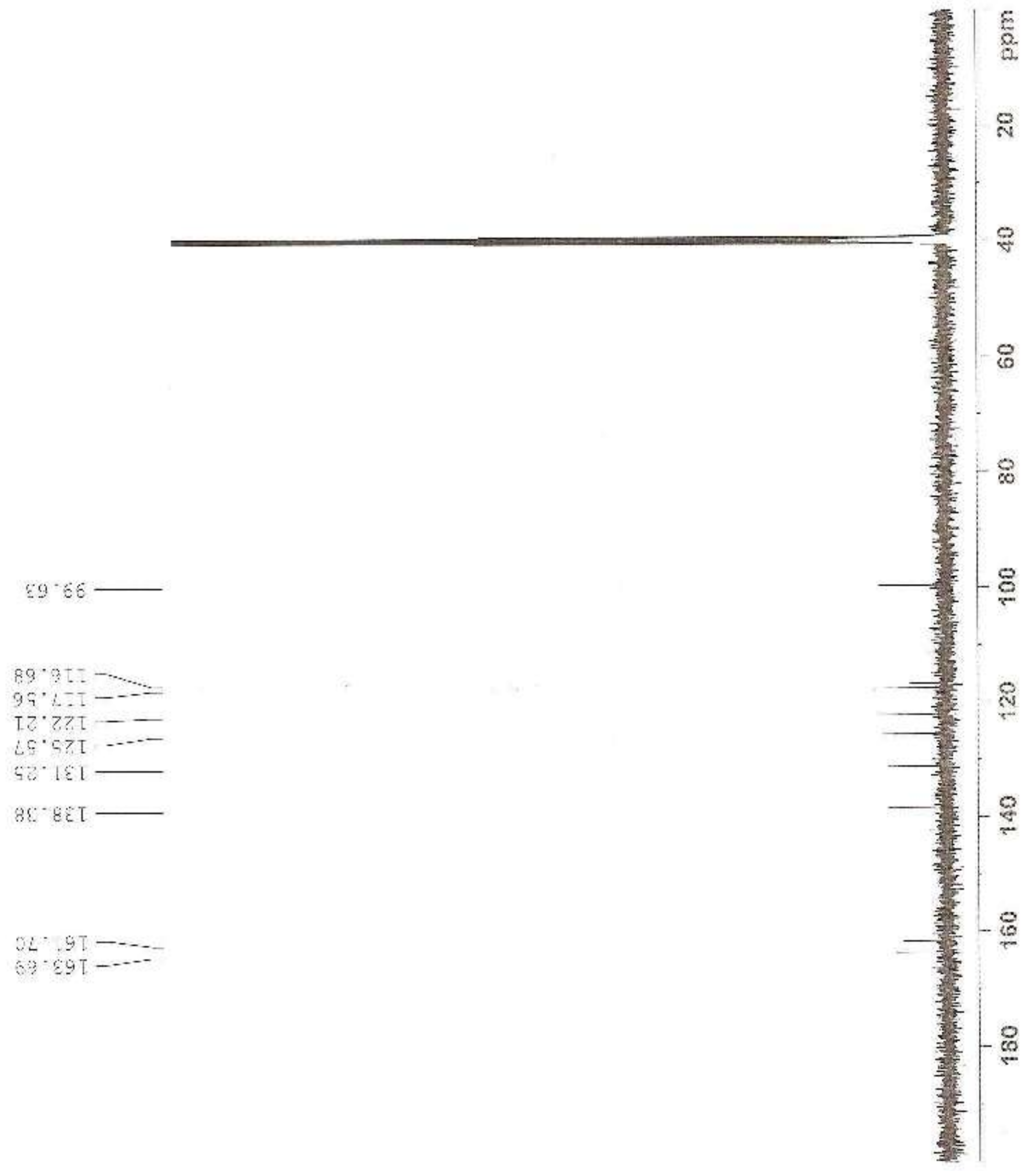
1.08
1.06
1.02
0.99
1.00

Fig-2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116.68
117.56
122.21
125.67
131.25
138.38
161.70
163.69
ppm
20
40
60
80
100
120
140
160
180

Fig. -3

Table-1 Results for IR of 2, 4-Dihydroxy-6-Chloro Quinolone (DHCQ)

O-H stretching vibrations (cm^{-1})	3200-2600
C-H stretching vibrations aromatic /aliphatic (cm^{-1})	-
C=C stretching vibrations (cm^{-1})	1589,1502
C-O stretching vibrations (cm^{-1})	1251
C-Cl stretching vibrations (cm^{-1})	817

Table-2 Results for NMR of 2, 4-Dihydroxy-6-Chloro Quinolone (DHCQ)

No	Chemical Shift (δ)	Number of Relative Protons	Assignment
1	5.76	1	4-OH
2	11.36-11.56	1	2-OH

Table-3 Results for CMR of 2, 4-Dihydroxy-6-Chloro Quinolone (DHCQ)

No.	Chemical Shift	Assignment
1	163	C_2 C-OH
2	136	C_3
3	161	C_4 C-OH
4	122	C_5
5	117	C_6
6	89	C_7
7	116	C_8
8	125	C_9
9	131	C_{10}

2.3 Diazotisation of Amino Compounds

Seventeen amino compounds were diazotized in the usual manner.

2.4 Coupling of Diazo Solution with DHCQ

A clear solution of DHCQ (0.976 g , 0.005 mole) in rectified spirit (15 ml) and sodium hydroxide (15 ml, 10%) was cooled below 5^0, stirred well and the diazo solution was added drop-wise over a period of 15 minutes maintaining the pH at 8-9. The stirring was continued for 2 hours at 0 – 5^0. The reaction mixture was diluted with water and the pH was adjusted at 7.0 with acetic acid. The product was washed with water and crystallized from DMF.

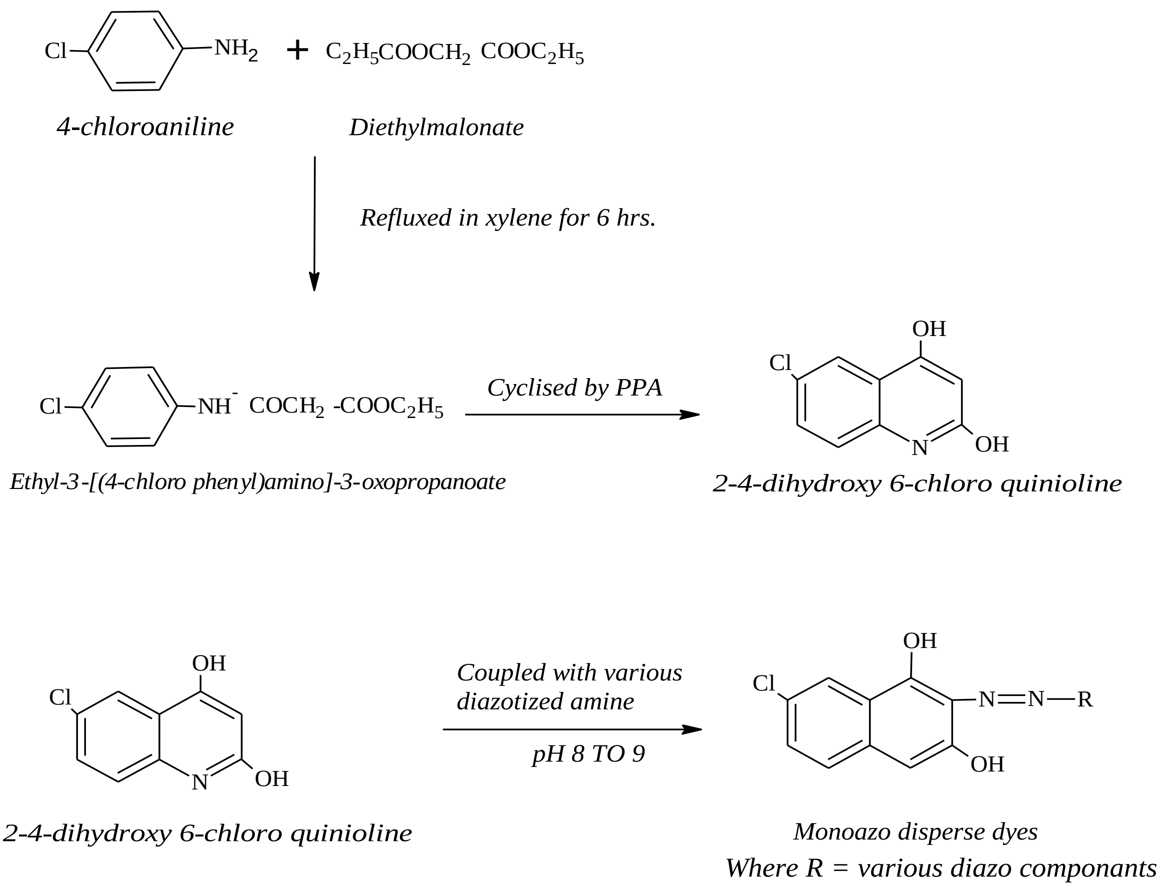

Table No. – 4 Characterisation Data of Diperse Dyes (D-1 to D-17)

Dye No.	Coupling Component	Molecular Formula	Mol. Wt. (g)	Yield (%)	M.P.^{0}C (d)	% Nitrogen	
						Found	Required
D -1	2-Amino-5,6-dichlorobenothiazole	$C_{16}H_4O_2N_4Cl_3S$	425.5	61	188	12.90	13.16
D -2	2-Amino-6-nitrobenzothiazole	$C_{16}H_8O_4N_5SCl$	401.5	61	210	17.18	17.43
D -3	3-Chloro-4-fluoroaniline	$C_{15}H_8O_2N_3Cl_2F$	352.0	64	165	11.72	11.93
D -4	4-Aminoacetanilide	$C_{17}H_{13}O_3N_4Cl$	356.5	64	218	15.47	15.71
D – 5	4-Nitroaniline	$C_{15}H_9O_4N_4Cl$	344.5	82	219	16.03	16.26
D -6	p-Toluidine	$C_{16}H_{12}O_2N_3Cl$	313.5	75	168	13.12	13.39
D -7	4-Chloroaniline	$C_{22}H_{16}O_2N_3Cl$	334.0	90	207	12.32	12.57

D -8	3-Aminoacetanilide	$C_{17}H_{13}O_3N_4Cl$	356.5	59	173	15.56	15.71
D -9	4-Chloro-2-nitroaniline	$C_{15}H_8O_4N_4Cl_2$	379.0	56	193	14.53	14.78
D -10	2,6-Dibromo-p-toluidine	$C_{16}H_{10}O_2N_3Cl\ Br_2$	471.5	65	197	8.62	8.91
D -11	6-Chloro-2,4-dinitroaniline	$C_{15}H_7O_6N_5Cl_2$	424.0	52	142	16.33	16.51
D -12	6-Bromo-2-cyano-4-nittroaniline	$C_{16}H_7O_4N_5ClBr$	448.5	55	175	15.42	15.61
D -13	4-Acetylamino-2-aminoanisole	$C_{18}H_{15}O_4N_4Cl$	386.5	75	225	14.26	14.49
D -14	2-Cyano-4-Nitroaniline	$C_{16}H_8O_4N_5Cl$	369.5	51	189	18.70	18.94
D -15	2,6-Dibromo-4-Nitroaniline	$C_{15}H_7O_4N_4ClBr_2$	502.5	60	178	10.93	11.14
D -16	3-Amino-O-sulphophenylphenol	$C_{21}H_{14}O_5N_3ClS$	455.5	68	146	9.02	9.22
D -17	5-Nitro-2-methoxyaniline(SCR base)	$C_{16}H_{11}O_5N_4Cl$	374.5	63	195	14.71	14.95

Table - 5 Percentage exhaustion, Light fastness and wash fastness on Polyester for Disperse dyes (D -1 to D-17)

Dye No.	Wavelength for absorbance measurement λ_{max}(nm)	% Exhaustion = (Y / 10) 100	Light Fastness	Wash Fastness
D – 1	287	47.5	2	4-5
D – 2	372	50.0	4	4-5
D – 3	399	42.5	3-4	4-5
D – 4	460	5.75	2	4-5
D – 5	424	71.0	2-3	4
D – 6	436	77.5	3	4-5
D – 7	424	77.5	3	4-5
D – 8	426	40.0	2	4-5

D – 9	427	70.0	2-3	4-5
D – 10	361	50.0	2	4-5
D – 11	346	72.5	4	4
D – 12	348	62.5	2-3	4-5
D – 13	475	57.5	3	4-5
D – 14	357	65.0	4	4-5
D – 15	364	67.5	3	4-5
D – 16	397	37.5	2-3	4-5
D – 17	428	62.5	2	4-5

III. RESULT AND DISCUSSION

Quinoline based monoazo disperse dyes have been prepared and characterized by elemental and spectral analysis. The % yields of the synthesized dyes were 51 to 90 %. Their dyeing performance on polyester fabric was assessed. All the synthesized dyes almost produce variety of different yellow shades with poor to fairly good light fastness, good to excellent wash fastness and the percentage dye bath exhaustion 77.5 % to 37.5 %.m In general, brilliance and beauty of the shade and excellent wash fastness reveal that some of the disperse dyes would prove to be useful dyes for dyeing polyester fabrics.

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