



PERFORMANCE AND MICROBIAL STUDIES OF ACID ANTHRAQUINONE DYES CONTAINING TRIAZOLE ON VARIOUS FIBRES

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ABSTRACT

A series of anthraquinone acid dyes were synthesized by condensation of bromamine acid with 1, 2, 4-triazole. This condensed product is diazotized and coupled with various naphthalene based acid coupling components to get novel series of acid anthraquinone dyes. The dyeing performance on wool, silk and nylon fibres has been assessed. All the synthesized dyes gave orange to violet shades. The purity of the synthesized dyes was checked by thin layer chromatography. The IR spectra showed all characteristic bands and representative dye ¹H NMR spectra showed all the signals. The percentage dye-bath exhaustion on different fibres was good and acceptable. The dyed fibres showed moderate to very good fastness to light, washing and rubbing. All the synthesized dyes have been screened for their antimicrobial activity.

Key words : Anthraquinone, Acid dyes, Dyeing, Wool, Silk, Nylon.

INTRODUCTION

Acid anthraquinone dyes are one of the most important classes of acid dyes being principally used for green, blue or violet shades having excellent light and wet fastness. One important group of such dyes are those obtained by condensation of bromamine acid with 1, 2, 4-triazole by an Ullmann reaction catalyzed by copper salt. This condensed amine is diazotized and coupled with various coupling components. This group of the acid dyes has important usage value¹.

Acid dyes have found wide applications in dyeing wool, polyamide fibres and blends of both fibres^{2,3} but they meet very high requirements as regards to their application and fastness. The characteristics chromophore of the anthraquinone series consists of one or more carbonyl groups in association with a conjugated system. The more

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important are acid, direct moderant, vat, solvent and reactive dyes even as pigments⁴⁻⁹. As a class, anthraquinone acid dyes are known for their specific colour and high light fastness characteristics. Anthraquinone acid dyes provide a number of bright fast to light blue and green colours, which are neither available among the azo dyes nor in fact equaled by any other class of dyes. The colour of anthraquinone dyes depends upon substitution among definite lines^{10,11}.

EXPERIMENTAL

The purity of all the dyes has been checked by TLC¹². IR spectra were recorded in KBr on a Perkin Elmer Model 881 spectrophotometer and ¹H NMR spectra on Bruker AVANCE II 400 NMR spectrometer (SAIF, Punjab University, Chandigarh) using TMS as an internal standard and DMSO as solvent. Absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analysis of C, H and N was carried out on Carlo Erba 1108 instruments. The light fastness was assessed in accordance with BS: 1006-1978¹³. The rubbing fastness test was carried out with corkmeter (Atlas) in accordance with AATCC-1961¹⁴ and the wash fastness test in accordance with IS : 765-1979¹⁵.

1-Amino-4-(1,2,4-triazolyl) anthraquinone-2-sulfonic acid (B)

Bromamine acid (A) 0.1 mol was dissolved in 400 mL hot water (70-80°C), 1, 2, 4-triazolyl (0.1 mol), acid binding agent solium bicarbonate (0.2 mol), copper sulfate (0.5 g) and ferrous sulfate (0.5 g) catalysts were then added to it. The reaction mixture was stirred and heated to 90°C. Temperature was maintained at 90°C for 6 hour under stirring. Charcoal (1 g) was added and stirred for 15 min and the solution was filtered by slowly adding diluted hydrochloride acid (1 : 1) under stirring. The product was salted out by adding sodium chloride and cooled. It was then stirred for 30 min at room temperature, filtered and washed with 10% w/v brine solution and dried (85 % yield) –

IR (KBr) cm⁻¹ : 3570, 3400 (-NH₂), 1285 (C-N), 1680 (C=O), 1150, 1055 (-SO₃H)

Diazotization of 1-amino-4-(1, 2, 4-triazolyl) anthraquinone-2-sulfonic acid (C)

The solution of 1-amino-4-(1, 2, 4-triazolyl)anthraquinone-2-sulfonicacid (B) (0.01 mol) was prepared in water. Hydrochloric acid (0.015 mol) was added to this and well stirred. The solution was cooled to 0-5 °C in an ice bath. A solution of sodium nitrite (NaNO₂ 0.015 mol) in water (8 mL) previously cooled to 0-5°C, was then added over a period of five minutes with stirring. The stirring was continued for an hour, temperature

was maintained till it gave positive test for nitrous acid on starch iodide paper. After stirring for one hour, the excess of nitrous acid was just destroyed with required amount of a solution of sulfamic acid. The resulting diazo solution obtained at 0-5 °C was used for subsequent coupling reaction.

Coupling of diazo solution with G-acid

G-acid (2.39 g, 0.01 mol) was suspended in water (20 mL) and dissolved at neutral pH with sodium carbonate (10 % w/v) to obtain a clear solution. The solution was cooled to below 0-5°C in an ice bath. To this well stirred solution, diazo chloride solution (C) was added dropwise over a period of 10-15 min maintaining the pH 7.5-8.0 by simultaneous addition of sodium carbonate solution (10% w/v). The stirring was continued for three hrs keeping the temperature at 0-5 °C. The temperature of reaction mixture was then raised to 60°C and sodium chloride was added to precipitate the coloring material. The stirring was continued for 1 hour. It was filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90 °C and extracted with DMF. The DMF extract was coupled with excess of chloroform. The dye thus obtained; was filtered, washed with chloroform and dried at 60 °C (81% yield).

Other acid dyes; D₂ to D₂₀ were synthesized by same procedure using various naphthalene base acid coupling components such, m-amino benzoyl K-acid, N-methyl – acid, epsilon acid, Schaeffer acid, acetyl H-acid, N-(3-sulfophenyl)-gamma acid, acetyl gamma acid, m-aminobenzoyl H-acetyl J-acid, H-acid and N-benzoyl H-acid. Characterization data, IR spectral data and ¹H NMR data of all the synthesized dyes are given in Tables 1, 2 and 3, respectively.

Table 1 : Characterization data of D₁-D₂₀

Dye No.	Coupling component	Molecular formula	Yield (%)	Found (Calcd) %			R _f Value
				C	H	N	
D ₁	J-acid	C ₂₈ H ₁₄ O ₉ N ₆ S ₂ Na ₂	81	48.72 (48.79)	2.03 (2.11)	10.49 (10.54)	0.47
D ₂	Gamma acid	C ₂₈ H ₁₄ O ₉ N ₆ S ₂ Na ₂	79	48.73 (48.79)	2.04 (2.11)	10.48 (10.54)	0.4
D ₃	m-Amino benzoyl K-acid	C ₃₃ H ₁₈ O ₁₃ N ₇ S ₃ Na ₃	84	44.68 (44.74)	1.97 (2.03)	11.00 (11.07)	0.44

Dye No.	Coupling component	Molecular formula	Yield (%)	Found (Calcd) %			R _f Value
				C	H	N	
D ₁₇	m-Amino benzoyl H-acid	C ₃₅ H ₂₅ O ₁₃ N ₆ S ₃ Na ₃	81	44.69 (44.74)	1.99 (2.03)	11.02 (11.07)	0.44
D ₁₈	Acety J-acid	C ₃₀ H ₂₃ O ₁₀ N ₅ S ₂ Na ₂	79	47.54 (47.59)	2.22 (2.27)	11.84 (11.89)	0.43
D ₁₉	H-acid	C ₂₈ H ₂₀ O ₁₂ N ₅ S ₃ Na ₃	80	41.68 (40.73)	1.64 (1.70)	10.93 (10.97)	0.4
D ₂₀	N-benzoyl H-acid	C ₃₅ H ₂₄ O ₁₃ N ₅ S ₃ Na ₃	74	45.47 (45.52)	1.88 (1.95)	9.59 (9.65)	0.42

Table 2 : IR Spectral data of D₁ - D₂₀

Comp.	IR spectra
D ₁	-NH ₂ asym & sym (3542, 3426), -OH (3393), -C = O str. (1682), -N = N- (1452), -C-N (1272), -S = O asym & sym (1197, 1048)
D ₂	-NH ₂ asym & sym (3544, 3436), -OH (3380), -C = O str. (1684), -N = N- (1462), -C-N (1274), -S = O asym & sym (1207, 1056)
D ₃	-NH ₂ asym & sym (3535, 3420), -OH (3410), -C = O str. (1685), -CONH- (1660), -N = N- (1455), -C-N (1269), -S = O asym & sym (1192, 1044)
D ₄	-NH- (3390), -OH (3375), -C = O str. (1674), -N = N- (1468), -C-N (1283), -S = O asym & sym (1185, 1054)
D ₅	-NH ₂ asym & sym (3525, 3430), -OH (3380), -C = O str. (1689), -N = N- (1463), -C-N (1268), -S = O asym & sym (1190, 1039)
D ₆	-OH (3382), -C = O str. (1672), -N = N- (1453), -S = O asym & sym (1200, 1055)
D ₇	-OH (3389), -C = O str. (1685), -N = N- (1440), -S = O asym & sym (1210, 1060)
D ₈	-NH- (3500), -OH (3375), -C = O str. (1682), -N = N- (1470), -S = O asym & sym (1199, 1055)

Cont...

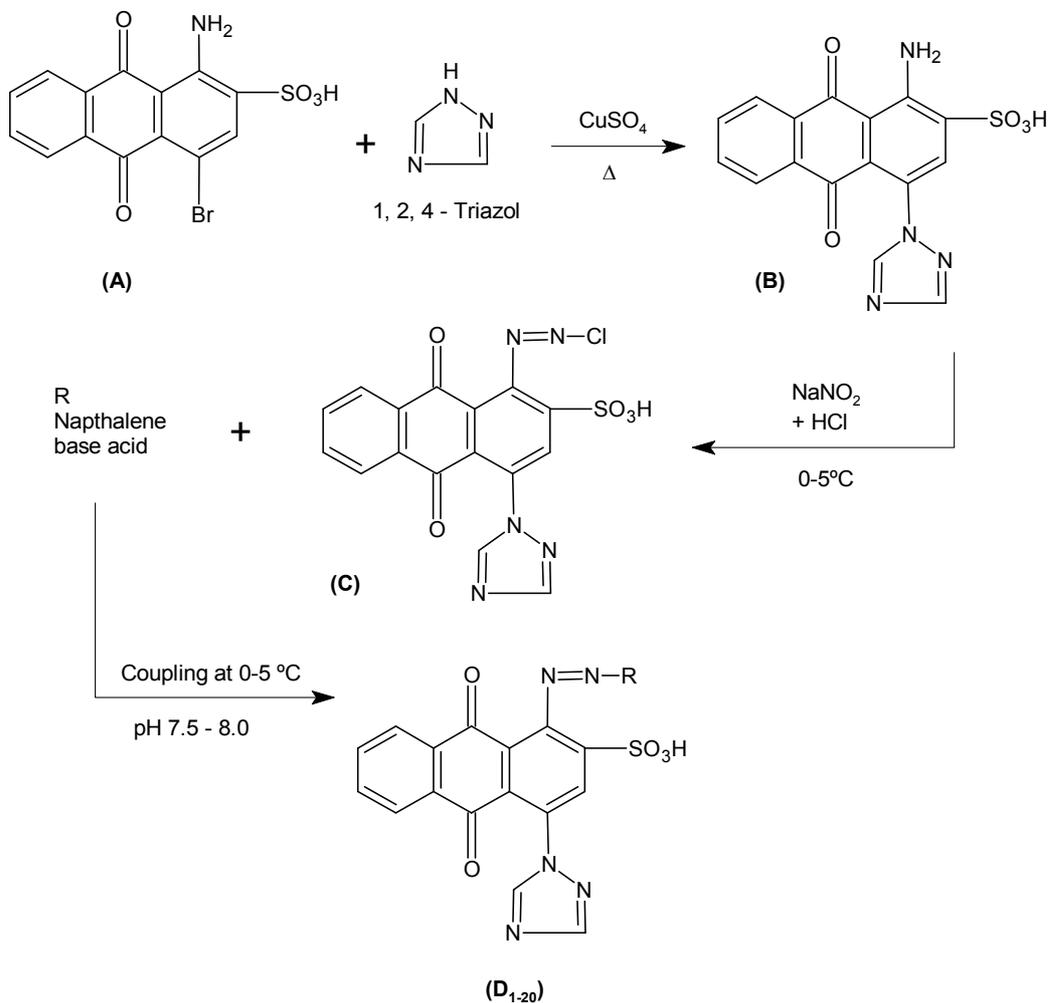
Comp.	IR spectra
D ₉	-OH (3393), -C = O str. (1696), -N = N- (1459), -C-N (1287), -S = O asym & sym (1189, 1064)
D ₁₀	-OH (3402), -C = O str. (1665), -N = N- (1460), -S = O asym & sym (1179, 1068)
D ₁₁	-OH (3384), -C = O str. (1675), -CONH- (1668), -N = N- (1473), -S = O asym & sym (1189, 1064)
D ₁₂	-OH (3377), -C = O str. (1680), -N = N- (1454), -S = O asym & sym (1193, 1049)
D ₁₃	-OH (3375), -C = O str. (1670), -N = N- (1456), -S = O asym & sym (1200, 1050)
D ₁₄	-OH (3376), -C = O str. (1674), -CONH- (1654), -N = N- (1459), -S = O asym & sym (1196, 1040)
D ₁₅	-NH- (3392), -OH (3384), -C = O str. (1674), -N = N- (1453), -S = O asym & sym (1190, 1043)
D ₁₆	-OH (3364), -C = O str. (1675), -N = N- (1464), -S = O asym & sym (1205, 1061)
D ₁₇	-NH ₂ asym & sym (3550, 3447), -OH (3360), -C = O str. (1671), -CONH- (1642), -N = N- (1453), -C-N (1296), -S = O asym & sym (1199, 1057)
D ₁₈	-OH (3365), -C = O str. (1687), -CONH- (1661), -N = N- (1463), -S = O asym & sym (1204, 1053)
D ₁₉	-NH ₂ asym & sym (3550, 3440), -OH (3388), -C = O str. (1675), -N = N- (1456), -C-N (1290), -S = O asym & sym (1205, 1050)
D ₂₀	-OH (3370), -C = O str. (1672), -CONH- (1657), -N = N- (1464), -S = O asym & sym (1210, 1054)

Table 3 : ¹H NMR Spectral data of D₁ - D₂₀

Comp.	NMR spectra
D ₁	-CH ₂ - (2H, t, 2.40), -NH ₂ (2H, s, 3.79) -OH (1H, s, 5.28), Ar-H (9H, m, 7.22 - 8.41)
D ₂	-CH ₂ - (2H, t, 2.50), -NH ₂ (2H, s, 3.73) -OH (1H, s, 5.23), Ar-H (9H, m, 7.25 - 8.44)

Cont...

Comp.	NMR spectra
D ₃	-CH ₂ - (2H, t, 2.54), -NH ₂ (2H, s, 3.69) -OH (1H, s, 5.15), Ar-H (12H, m, 7.20 - 8.35), -NHCO- (1H, s, 9.63)
D ₄	-NH- (1H, t, 1.69), -CH ₂ - (2H, t, 2.41), -OH (1H, s, 5.10), Ar-H (9H, m, 7.30 - 8.43)
D ₅	-CH ₂ - (2H, t, 2.46), -NH ₂ (2H, s, 3.75) -OH (1H, s, 5.20), Ar-H (8H, m, 7.28 - 8.30)
D ₆	-CH ₂ - (2H, t, 2.36), -OH (1H, s, 5.13), Ar-H (8H, m, 7.32 - 8.40)
D ₇	-CH ₂ - (2H, t, 2.33), -OH (1H, s, 5.15), Ar-H (9H, m, 7.13 - 8.25)
D ₈	-NH- (1H, t, 1.74), -CH ₂ - (2H, t, 2.43), -OH (1H, s, 5.20), Ar-H (13H, m, 7.29 - 8.45)
D ₉	-CH ₂ - (2H, t, 2.42), -OH (1H, s, 5.07), Ar-H (9H, m, 7.18 - 8.42)
D ₁₀	-CH ₂ - (2H, t, 2.47), -OH (1H, s, 5.19), Ar-H (9H, m, 7.24 - 8.42)
D ₁₁	-CH ₂ - (2H, t, 2.43), -OH (1H, s, 5.16), Ar-H (13H, m, 7.27 - 8.43), -NHCO- (1H, s, 9.70)
D ₁₂	-CH ₂ - (2H, t, 2.43), -OH (1H, s, 5.19), Ar-H (9H, m, 7.35- 8.37)
D ₁₃	-CH ₂ - (2H, t, 2.45), -OH (1H, s, 5.21), Ar-H (10H, m, 7.25- 8.36)
D ₁₄	-CH ₂ - (2H, t, 2.41), -OH (1H, s, 5.12), Ar-H (8H, m, 7.24 - 8.35)
D ₁₅	-NH- (1H, t, 1.74), -CH ₂ - (2H, t, 2.44), -OH (1H, s, 5.17), Ar-H (13H, m, 7.12 - 8.32)
D ₁₆	-CH ₂ - (2H, t, 2.53), -OH (1H, s, 5.15), Ar-H (7.15 - 8.33), -NHCO- (1H, s, 9.75)
D ₁₇	-CH ₂ - (2H, t, 2.47), -OH (1H, s, 5.19), Ar-H (12H, m, 7.20 - 8.42), -NHCO- (1H, s, 9.66)
D ₁₈	-CH ₂ - (2H, t, 2.45), -OH (1H, s, 5.12), Ar-H (9H, m, 7.25 - 8.36), -NHCO- (1H, s, 9.60)
D ₁₉	-CH ₂ - (2H, t, 2.49), -NH ₂ (2H, s, 3.65) -OH (1H, s, 5.12), Ar-H (8H, m, 7.24 - 8.39), -NHCO- (1H, s, 9.68)
D ₂₀	-CH ₂ - (2H, t, 2.50), -OH (1H, s, 5.17), Ar-H (13H, m, 7.30 - 8.44), -NHCO- (1H, s, 9.63)



R = Naphthalene base acid coupling component

Scheme

RESULTS AND DISCUSSION

A new series of acid anthraquinone dyes containing 1, 2, 4-triazole was obtained on diazotization and coupling with various naphthalene based acid coupling components. This series of dyes have found wide applications in dyeing wool, polyamide fiber and blend. In this series, chromophoric group such as carbonyl group is condensed with conjugated system like anthraquinone to produce violet shades and high light fastness characteristics.

Dyeing of fibres

All the dyes D₁-D₂₀ were applied on wool, silk and nylon by using different procedures having dye bath material as given below.

Dye-bath materials

Materials	For wool	For silk	For nylon
Fibre (g)	2.0 g	2.0 g	2.0 g
Amount of dye (mg)	40.0 mg	40.0 mg	40.0mg
Glauber salt (20%)	1.5 mL	1.0 mL	1.0 mL
Formic acid soln. (10%)	1.5 mL	1.0 mL	1.5 mL
pH	3.0	3.0	3.0
MLR	1.40	1.40	1.40
Dyeing time (min)	60 min	40 min	90 min
Dyeing temp. (°C)	100°C	85°C	100°C
Total volume	80 mL	80 mL	80 mL

Exhaustion and fixation study

The percentage exhaustion of 2% dyeing on wool fabric shows exhaustion 69.12% to 77.18 %, on silk fabric shows exhaustion 63.33% to 77.10% and on nylon fabric shows exhaustion 67.92% to 79.02%. The percentage fixation of 2% dyeing on wool fabric shows fixation 78.27% to 92.64%, for silk fabric shows fixation 82.38% 92.32% and for nylon fabric shows fixation fixation 82.22 to 88.87. Exhaustion and fixation data of D₁-D₂₀ on wool, silk and nylon are given in Table 4.

Table 4 : Exhaustion and fixation study of D₁-D₂₀ on wool, silk and nylon

Dye No.	Wool		Silk		Nylon	
	% Exhaustion	% Fixation	% Exhaustion	% Fixation	% Exhaustion	% Fixation
D ₁	71.05	83.04	73.25	86.68	74.05	85.08
D ₂	71.95	81.03	66.90	90.43	72.45	82.82

Cont...

Dye No.	Wool		Silk		Nylon	
	% Exhaustion	% Fixation	% Exhaustion	% Fixation	% Exhaustion	% Fixation
D ₃	75.93	90.40	71.80	89.13	75.60	85.32
D ₄	76.20	87.27	74.00	89.18	76.20	80.05
D ₅	76.03	91.42	71.85	86.29	74.93	86.75
D ₆	69.50	85.61	74.25	85.52	77.10	88.20
D ₇	71.05	81.63	69.90	88.53	75.30	88.31
D ₈	67.80	78.90	66.90	91.18	71.73	86.44
D ₉	68.25	78.38	72.60	87.47	73.80	84.68
D ₁₀	76.35	84.48	76.35	84.48	75.55	84.71
D ₁₁	68.08	79.32	69.50	85.61	74.07	83.71
D ₁₂	72.90	82.99	71.40	90.34	70.72	82.72
D ₁₃	68.90	80.55	79.00	85.44	76.15	88.64
D ₁₄	81.28	83.64	69.25	87.36	70.77	86.19
D ₁₅	71.05	81.63	70.15	89.81	76.30	83.22
D ₁₆	71.40	90.34	80.05	88.69	74.25	80.80
D ₁₇	74.28	85.49	76.20	87.27	75.45	80.80
D ₁₈	74.30	82.77	77.15	86.84	72.37	80.10
D ₁₉	70.35	90.97	78.32	90.00	70.60	84.98
D ₂₀	69.25	87.36	72.06	87.47	70.52	85.07

Fastness properties

All the dyes give good to very light fastness on wool, silk and nylon. All the dyes give moderate to very fastness to washing and rubbing on each fiber. Fastness properties data of D₁-D₂₀ are given in Table 5.

Microbial studies

All the acid anthraquinone dyes are inactive against both Gram positive (*Pseudomonas Sp.* & *B. Subtilis*) and Gram negative (*Ceretium* & *E. coli*) bacteria at 100

$\mu\text{g/mL}$ and $200 \mu\text{g/mL}$ concentration compared to penicillin, ampicillin and amoxicillin.

All the acid anthraquinone dyes are inactive against *C. albicans* at $100 \mu\text{g/mL}$ and $200 \mu\text{g/mL}$ concentration compared to amphotericine-B.

Table 5 : Fastness properties of D₁-D₂₀ on wool, silk and nylon

Dye No.	Wool				Silk				Nylon			
	Light	Wash	Rubbing		Light	Wash	Rubbing		Light	Wash	Rubbing	
			Dry	Wet			Dry	Wet			Dry	Wet
D ₁	4-5	4	3-4	3	4	2-3	2	2-3	4	4	4	4-5
D ₂	3-4	3	3-4	3-4	4	3-4	3-4	3	3	5	3-4	4
D ₃	4	3	3-4	3-4	3-4	3	2-3	2-3	4	3	3	4
D ₄	4-5	4	4	3-4	4-5	4	4	3	4.5	4-5	3	4
D ₅	5-6	4	4	3-4	4-5	3	3	4-5	3	3	3-4	3
D ₆	4	4	4	3-4	3	2-3	3	3	5	3-4	4	4-5
D ₇	3	3	3-4	3	4	3	3-4	3	4-5	5	3	4
D ₈	3-4	4	4	3-4	5	4	4	3-4	4	3	3-4	5
D ₉	3-4	4	3-4	3	3-4	3	3	3	3	4	4-5	4-5
D ₁₀	4-5	3-4	3-4	3	3-4	3-4	4	3-4	4-5	5	3	4
D ₁₁	4	3-4	3-4	3	4	3-4	3-4	3	5	3	5	4
D ₁₂	4	3	3-4	3	5	4	4	3-4	4-5	3-4	4	3
D ₁₃	4-5	4	3-4	3	5-6	4	4	3-4	4	4	3	3-45
D ₁₄	4	3	3-4	3-4	6	4	4	3-4	5-6	5	4-5	4-5

Cont...

Dye No.	Wool				Silk				Nylon			
	Light	Wash	Rubbing		Light	Wash	Rubbing		Light	Wash	Rubbing	
			Dry	Wet			Dry	Wet			Dry	Wet
D ₁₅	4	3	3	4	3	4	4	3-4	5	4	3-4	4
D ₁₆	3	3	3	4	4-5	4	4	3-4	3-4	4	4	4-5
D ₁₇	4	3	4	3-4	3-4	3-4	3	3	4	5	5	3-4
D ₁₈	4-5	4	4	3	5	4	3-4	3	4	3-4	3-4	3-4
D ₁₉	4-5	4	3-4	3	4-5	3-4	3	4	4-5	3-4	4	4
D ₂₀	4-5	4-5	3-4	3-4	3	3-4	3	3-4	3-4	5	3-4	4

Light: Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7
Wash and Rubbing: Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7

Table 6 : Calibration data for exhaustion study of acid dyes

Substrate for dyeing: Wool (2.0 g), Silk (2.0 g) and Nylon (2.0 g)

Medium of spectral study: Aqueous

Dye No.	Wave length (nm)	Absorbance of dye solution at specified wavelength				Slope of linear plot K*
		Conc. x 10 ⁻³ mg.mL ⁻¹				
		4.0	8.0	12.0	16.0	
D ₃	435	0.055	0.110	0.164	0.220	13.75
D ₉	495	0.064	0.129	0.192	0.256	16.12
D ₁₇	480	0.093	0.185	0.279	0.371	23.25

Absorbance = K* (Conc. x 10⁻³ mg.mL⁻¹)

Table 7 : Calibration data for fixation study of acid dyes

Substrate for dyeing : Wool (2.0 g), Silk (2.0 g) and Nylon (2.0 g)
 Medium of spectral Study : Conc. Sulfuric acid

Dye No.	Wave length (nm)	Absorbance of dye solution at specified Wavelength				Slope of linear plot K*
		Conc. x 10 ⁻³ mg.mL ⁻¹				
		4.0	8.0	12.0	16.0	
D ₃	470	0.056	0.112	0.169	0.224	14.00
D ₁₁	475	0.062	0.120	0.180	0.240	15.50
D ₁₉	484	0.086	0.171	0.258	0.344	21.50

Absorbance = K* (Conc. x 10⁻³ mg.mL⁻¹)

CONCLUSION

All the synthesized dyes gave excellent uniformity of coloration on wool, silk, and nylon. A remarkable degree of levelness indicates good penetration and affinity of these dyes to the fabrics. The difference in the colour of newly synthesized dyes depends upon the substituents present and/or the position of substituents on the ring. The dyes D₁, D₄, D₅, D₁₀, D₁₃, D₁₈, D₁₉ and D₂₀ gave fair to very good light fastness on wool, while D₄, D₅, D₁₃ and D₁₉ gave fair to very good light fastness on silk. The dyes D₉, D₁₄, D₁₇ and D₂₀ gave good to very good wash and rubbing fastness on nylon.

ACKNOWLEDGEMENT

The authors express their gratitude to the Head, Department of Chemistry, Veer Narmad South Gujarat University, Surat for providing necessary research facilities, Sophisticated Analytical Instrumental Facilities, Chandigarh for spectral studies and Atul Ltd., Atul for providing dyeing and analytical facilities.

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Accepted : 06.10.2008