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Synthesis, antimicrobial activity and application of some novel quinazolinone based monoazo reactive dyes on various fibres

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ABSTRACT

The main target of this paper was to synthesize novel reactive dyes that not only give good dyeing property but also show pharmacological activity i.e. antimicrobial activity (antibacterial and antifungal). In this regard ten novel monoazo quinazolinone based reactive dyes **(7a–j)** were made by coupling of diazotised 3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2-phenylquinazolin-4(3*H*)-one **(4)** with various *p*-chloro anilino cyanurated coupling components **(6a–j)**. The structures of all these synthesized dyes were confirmed by elemental analysis and spectral methods. The antimicrobial activity, colorimetric data, solvent effect and fastness properties of these dyes were also investigated.

1. Introduction

The compound having fused heterocyclic system like 4(3*H*)-quinazolinone and its derivatives are known to possess good pharmacological activities and are also used as intermediates in the dyestuff industry [1–5]. The dyes containing heterocyclic moiety like quinazolinone have been found to give a wide range of color shades (yellow to red) with very good depth and levelness on fabrics and also showed excellent brightness and good fastness properties like sublimation, washing and light and also show high thermal stability [6,7].

In continuation of our interest in the direction of synthesis of reactive dyes based on quinazolinone moiety [8,9], the present paper deals with the facile and convenient synthesis of novel quinazolinone reactive dyes and study of their dyeing properties, fastness properties, antimicrobial activity, colorimetric data and solvent effect are reported.

2. Experimental

2.1. Materials and methods

The coupling components used for the synthesis of dyes were received from Atul Ltd., Gujarat, India. The solvents used were of spectroscopic grade.

All melting points are uncorrected and are expressed in °C. TLC analysis was carried out on silica gel G F_{254}-precoated aluminum sheets [10]. IR spectra were recorded on a Perkin–Elmer Model 377 system using the potassium bromide wafer technique. Both ^{1}H and ^{13}C NMR spectra were determined on Bruker Avance II 400 MHz in DMSO-d_6 solvent using TMS as internal standard, UV–vis absorption spectra were recorded on a Thermo Scientific Evolution 300 Spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. water, DMF, methanol, DCM and chloroform at the various concentrations (1×10^{-6}–10^{-8}).

Elemental analysis (C, H and N) was carried out using C, H and N analyzer, Carlo Erba, Italy. The dyeing was done by using Laboratory Rota Dyer instrument.

Colorimetric data (L*, a*, b*, C*, H* and K/S) were recorded on Reflectance Spectrophotometer Gretag Macbeth CE: 7000. Antimicrobial activity (antibacterial and antifungal) was performed using broth dilution method [11].

2.2. Synthesis of 4,4′-methylene bis(m-nitro aniline) (1)

m-Nitro aniline (13.8 g, 0.1 mol) was dissolved in water (125 ml) and 36.5% hydrochloric acid (25 ml) at 50 °C. The reaction mixture was then reacted with 3% aqueous formaldehyde (35 ml) solution at 60 °C with stirring for 1 h and neutralized with 10% sodium hydroxide solution. The reddish precipitates obtained were filtered, washed with hot water, dried and recrystallized from acetic acid. Yield 78%, m.p. 65–68 °C. TLC: $R_f = 0.75$ (PhMe:EtOAc, 3:1 v/v). IR (KBr) cm^{-1}: 3430, 3385 (N–H), 3097 (C–H), 1625 (N–H bend.),

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1523, 1349 (N=O). ^{1}H NMR (DMSO-d_6) δ ppm: 2.38 (2H, s, CH_2), 6.28 (4H, s, NH_2), 6.95–7.42 (6H, m, Ar–H). Anal. Calcd. for $C_{13}H_{12}O_4N_4$ (288.26): C, 54.17%; H, 4.20%; N, 19.44%, found, C, 54.11%; H, 4.14%; N, 19.38%. (Scheme 1).

2.3. Synthesis of 7-chloro-2-phenyl-4H-benzo[1,3] oxazine-4-one **(2)**

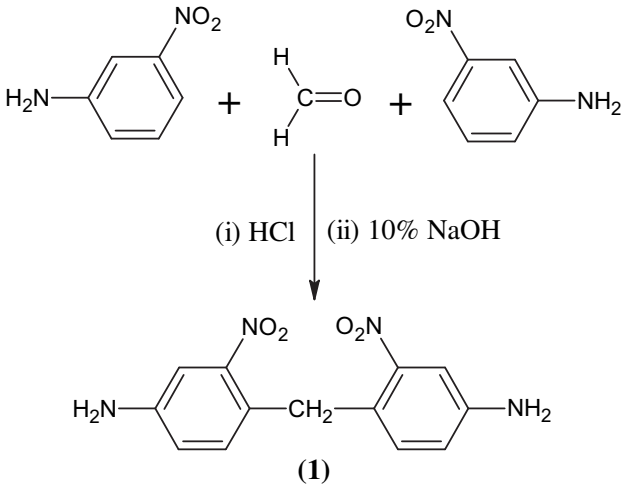
To a stirred solution of 4-chloro anthranilic acid (1.72 g, 0.01 mol) in pyridine (60 ml), Benzoyl chloride (1.16 ml, 0.01 mol) was added dropwise, maintaining the temperature near 0–5 °C for 1 h. The reaction mixture was stirred for another 2 h at room temperature until a solid product was formed. The reaction mixture was neutralized with saturated sodium bicarbonate solution. A white solid which separated was filtered, washed with water and recrystallized from ethanol. Yield 70%, m.p. 192–195 °C. TLC: R_f = 0.68 (PhMe:EtOAc, 3:1 v/v). IR (KBr) cm^{-1}: 3075 (C–H), 1613 (C=N), 1756 (C=O), 1062 (C–O–C), 1177 (C–O), 779 (C–Cl). ^{1}H NMR (DMSO-d_6) δ ppm: 7.58–8.03 (8H, m, Ar–H). Anal. Calcd. for $C_{14}H_8O_2NCl$ (257.67): C, 65.26%; H, 3.13%; N, 5.44%, found, C, 65.22%; H, 3.08%; N, 5.38%. (Scheme 2).

2.4. Synthesis of 3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2-phenylquinazolin-4(3H)-one **(3)**

4,4′-Methylene bis(*m*-nitro aniline) (1.44 g, 0.005 mol) and 7-chloro-2-phenyl-4*H*-benzo[1,3]oxazine-4-one (1.29 g, 0.005 mol) were dissolved in pyridine (40 ml) and heated under reflux for 6 h under anhydrous reaction conditions and then allowed to cool at room temperature. The reaction mixture was then treated with ice cooled dilute hydrochloric acid and stirred. A solid separated out which was filtered off and washed with water to remove any adhered pyridine. The crude quinazolinone thus obtained was dried under vacuum and recrystallized from ethanol. Yield 72%, m.p. 157–160 °C. TLC: R_f = 0.64 (PhMe:EtOAc, 3:1 v/v). IR (KBr) cm^{-1}: 3425, 3380 (N–H) 3045 (C–H), 1613 (C=N), 1674 (C=O), 1494 (C–N), 1525, 1350 (N=O), 778 (C–Cl). ^{1}H NMR (DMSO-d_6) δ ppm: 2.28 (2H, s, CH_2), 6.22 (2H, s, NH_2), 7.52–8.06 (14H, m, Ar–H). Anal. Calcd. for $C_{27}H_{18}O_5N_5Cl$ (527.92): C, 61.43%; H, 3.44%; N, 13.27%, found, C, 61.38%; H, 3.40%; N, 13.22%. (Scheme 2).

2.5. Preparation of diazonium salt solution **(4)**

3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2-phenylquinazolin-4(3*H*)-one (2.64 g, 0.005 mol) **(3)** was stirred in a mixture of water (25 ml), conc. HCl (1.88 ml, 0.015 mol) and ice (10 g). The reaction mixture was cooled to 0–5 °C using an ice bath. $NaNO_2$ (0.35 g, 0.005 mol) dissolved in water (10 ml) was then added dropwise. The solution was stirred for 30 min and excess HNO_2 was decomposed by adding sulphamic acid. Activated carbon was added with stirring and the mixture was filtered at 0–5 °C to give the clear yellow solution **(4)**. (Scheme 2).



Scheme 1. Preparation of dye intermediate (**1**).

2.6. Preparation of coupling components **(5)** and **(6a)**

H-acid (3.19 g, 0.01 mol) was dissolved in water (15 ml) at pH 7.5, using 20% (w/v) Na_2CO_3. A solution of cyanuric chloride (1.85 g, 0.01 mol) in acetone (20 ml) was cooled to 0–5 °C and added dropwise to the stirred H-acid solution at 0–5 °C (Scheme 1). After 10 min, the solution was adjusted to pH 4 by adding 20% (w/v) Na_2CO_3, and the reaction was continued for 1 h at 0–5 °C. The progress of the reaction was followed by TLC using *n*-PrOH:*n*-BuOH:EtOAc:H_2O, 2:4:1:3, in which the product **5** had R_f = 0.72. (Scheme 3).

p-Chloro aniline (1.28 g, 0.01 mol) was added to a well-stirred solution of **5** (0.01 mol) and after adjusting to pH 6.5 using 20% (w/v) Na_2CO_3, the solution was stirred for 1 h at 40 °C. The progress of the reaction was followed by TLC (*n*-PrOH:*n*-BuOH:EtOAc:H_2O, 2:4:1:3), where the **6a** had R_f = 0.36. (Scheme 3).

2.7. Synthesis of reactive dyes **(7a–j)**

Freshly prepared diazonium salt solution (0.005 mol) **(4)** was added dropwise to well-stirred solution of **6a** (0.005 mol). The solutions were maintained at pH 9 by adding 20% (w/v) Na_2CO_3 and the coupling step was continued for 4 h at 0–5 °C. Then, 10% (w/v) urea was added [12] and the dyes were isolated by salting out of solution using NaCl (12 g). The pH was adjusted to 7 using HCl (6% w/v) and stirring was continued for 2 h. The dye was collected by filtration and washed with 5% (w/v) NaCl. Salt was removed by stirring the crude dyes with dimethylformamide (DMF), followed by the dye precipitation by adding EtOAc to the filtrate. The dye **7a** was collected, washed with EtOAc and air dried. The eluent system for TLC was 2-BuOH:EtOH:NH_4OH:pyridine, 4:1:3:2. Dye **7a** had R_f = 0.38, with minor impurities at R_f = 0.20. (Scheme 4).

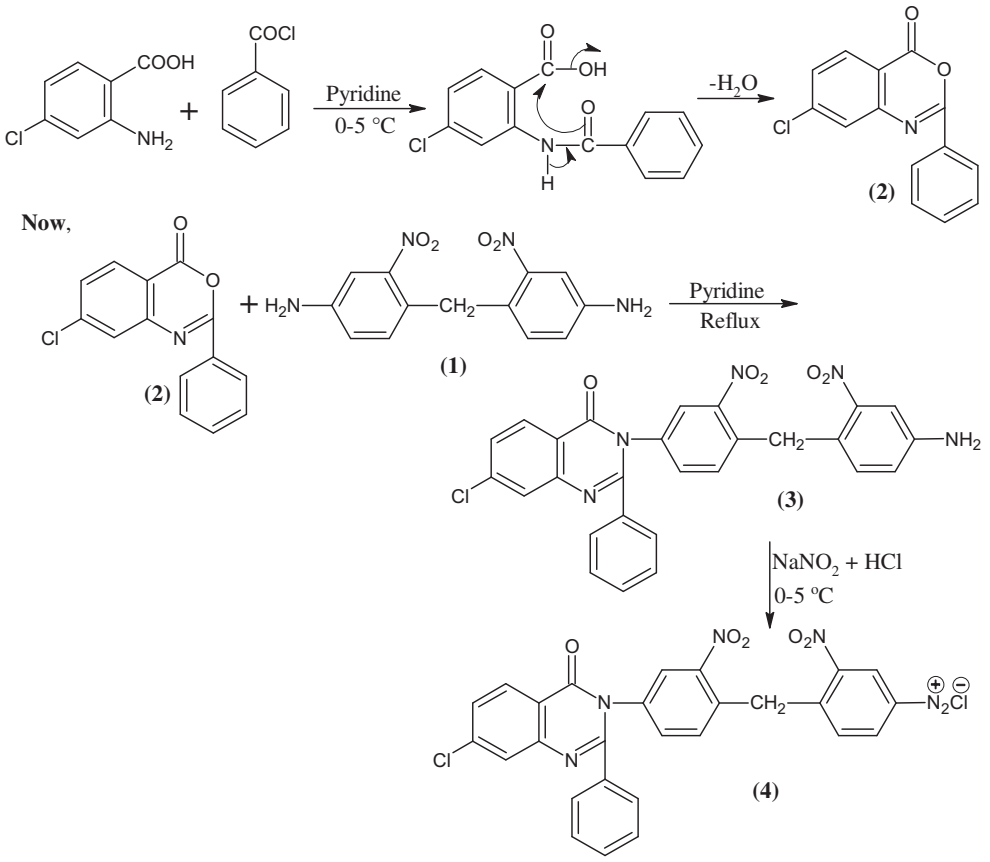
Same coupling procedure and condition was followed for other reactive dyes **7b–j** were synthesized using *p*-chloro anilino cyanurated coupling components such as J-acid **(6b)**, N-methyl-J-acid **(6c)**, N-phenyl-J-acid **(6d)**, Bronner acid **(6e)**, Gamma acid **(6f)**, Tobias acid **(6g)**, Sulpho Tobias acid **(6h)**, Peri acid **(6i)** and Koch acid **(6j)**. All the *p*-chloro anilino cyanurated coupling components are summarized in Chart 1.

Characterizations of all the dyes **7a-j** are given below:

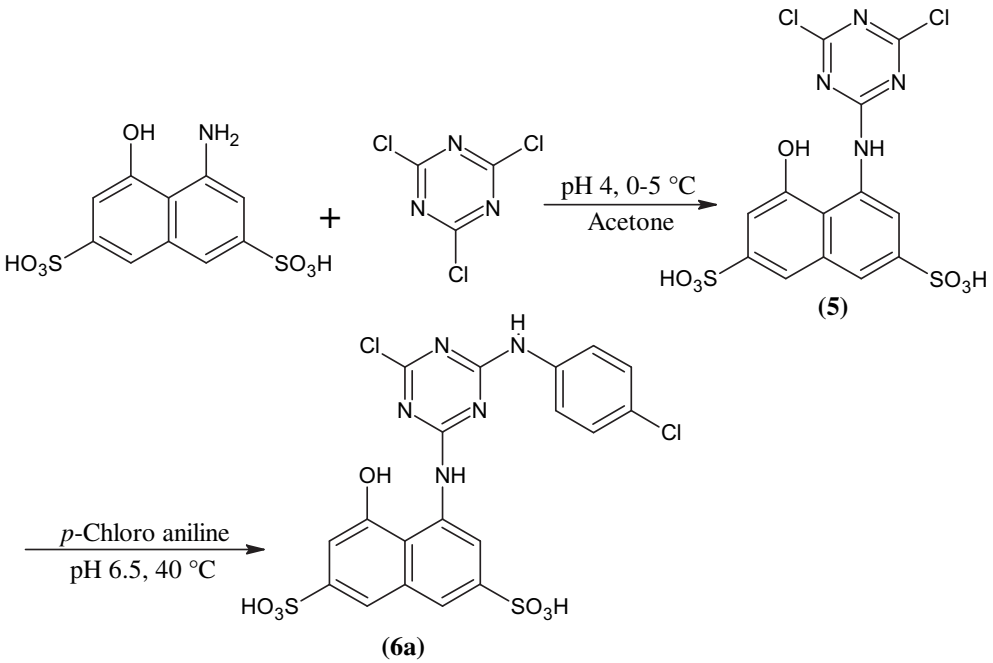
(1) Dye **7a** (*p*-chloro anilino cyanurated H-acid):

Dye **7a** was obtained in 80% yield (Dark purple); **Mp** > 300 °C; **R_f** = 0.38; **IR (KBr) ν cm^{-1}**: 3456 (O–H), 3326 (N–H), 3094 (C–H), 1664 (C=O), 1595 (C=N), 1613 (N=N), 1530, 1346 (N=O), 1382, 1155 (S=O), 779 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.60 (2H, s, CH_2), 4.42 (1H, s, OH), 8.73 (2H, s, NH), 6.64–7.58 (21H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.12, 39.44, 39.71 (CH_2), 162.12 (C=O), 108.22, 112.75, 113.52, 116.28, 118.32, 119.20, 121.15, 124.12, 125.90, 128.30, 131.75, 132.20, 134.90, 136.65, 139.55, 141.30, 144.10, 146.52, 148.12, 152.22, 155.35, 164.90, 169.22 (Ar); $C_{46}H_{26}O_{12}N_{11}S_2Cl_3Na_2$ (1141.23): **calc**. C, 48.41%; H, 2.30%; N, 13.50%, **found** C, 48.33%, H, 2.22%, N, 13.44%.

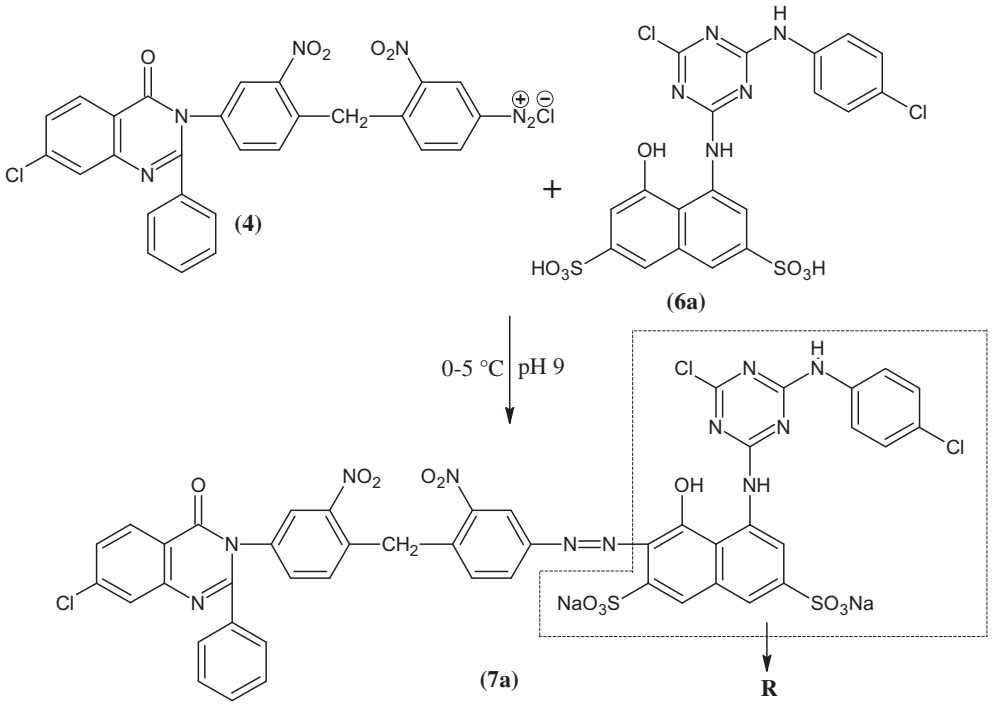
(2) Dye **7b** (*p*-chloro anilino cyanurated J-acid):



Scheme 2. Preparation of dye intermediates **(2), (3)** and **(4)**.



Scheme 3. Preparation of *p*-chlro anilino cyanurated H-acid **(6a)**.



Where R=Various *p*-chloro anilino cyanurated coupling components **(6a-j)**

Scheme 4. Synthesis of dye **7a**.

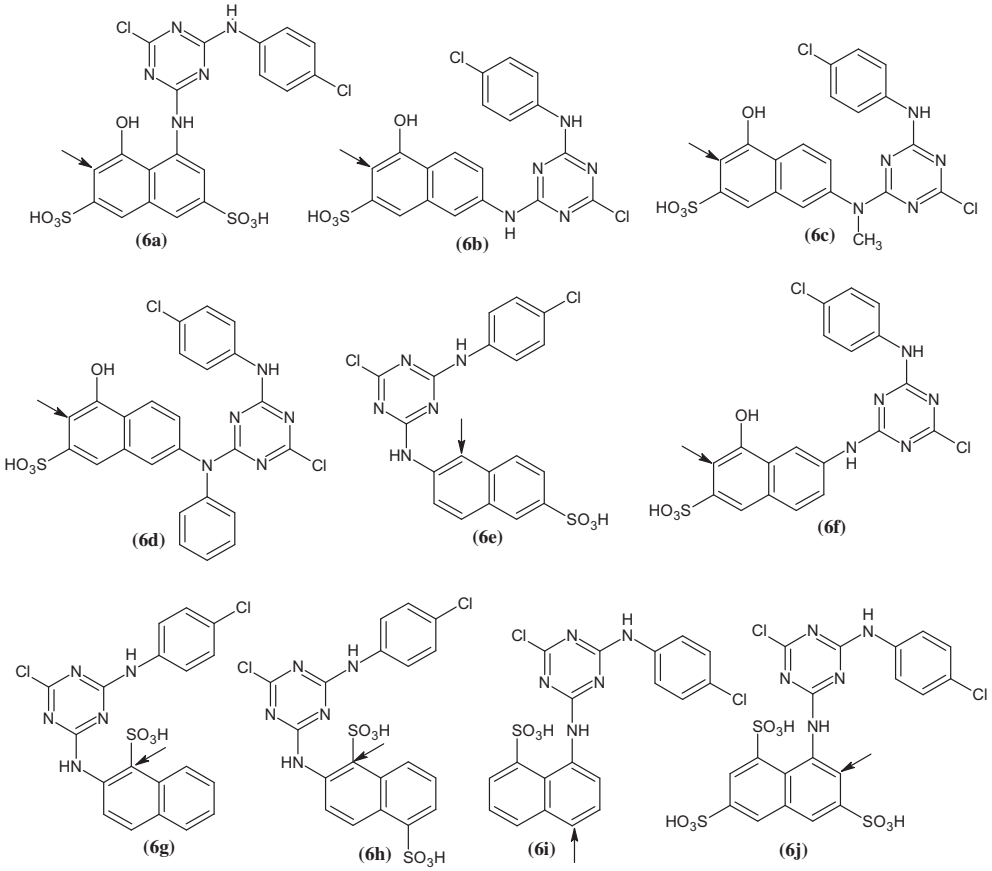


Chart 1. Various *p*-chloro anilino cyanurated coupling components **(6a–j)**. (Arrow indicates the coupling position).

Dye **7b** was obtained in 78% yield (Reddish yellow); **Mp** > 300 °C; **R_f** = 0.42; **IR (KBr) ν cm^{-1}**: 3571 (O–H), 3318 (N–H), 3121 (C–H), 1683 (C=O), 1598 (C=N), 1622 (N=N), 1574, 1353 (N=O), 1382, 1158 (S=O), 779 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.58 (2H, s, CH_2), 4.63 (1H, s, OH), 8.23 (2H, s, NH), 7.46–7.69 (22H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.10, 39.22, 39.52 (CH_2), 162.25 (C=O), 109.12, 112.22, 113.60, 115.12, 120.22, 121.55, 122.95, 125.40, 128.15, 131.50, 133.10, 134.22, 135.50, 136.12, 139.44, 142.10, 144.45, 146.15, 150.25, 152.68, 156.50, 165.80, 170.06 (Ar); $C_{46}H_{27}O_9N_{11}SCl_3Na$ (1039.19): calc. C, 53.17%, H, 2.62%, N, 14.83%, found C, 53.11%, H, 2.55%, N, 14.78%.

(3) Dye **7c** (*p*-chloro anilino cyanurated N-methyl-J-acid):

Dye **7c** was obtained in 77% yield (Reddish orange); **Mp** > 300 °C; **R_f** = 0.36; **IR (KBr) ν cm^{-1}**: 3485 (O–H), 3285 (N–H), 3035 (C–H), 1670 (C=O), 1596 (C=N), 1618 (N=N), 1540, 1322 (N=O), 1375, 1160 (S=O), 775 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.42 (2H, s, CH_2), 2.65 (3H, s, N–CH_3), 4.45 (1H, s, OH), 8.38 (1H, s, NH), 7.12–7.60 (22H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 21.25, 21.38, 21.60, 21.72 (N–CH_3), 39.25, 39.48, 39.60 (CH_2), 162.68 (C=O), 109.12, 112.22, 114.10, 115.20, 117.22, 120.10, 121.40, 123.22, 125.75, 126.22, 128.35, 132.20, 133.38, 134.70, 135.12, 136.16, 138.58, 143.30, 144.25, 147.50, 150.25, 154.20, 155.16, 166.40, 169.80 (Ar); $C_{47}H_{29}O_9N_{11}SCl_3Na$ (1053.22): calc. C, 53.60%, H, 2.78%, N, 14.63%, found C, 53.54%, H, 2.72%, N, 14.58%.

(4) Dye **7d** (*p*-chloro anilino cyanurated N-phenyl-J-acid):

Dye **7d** was obtained in 82% yield (Dark red); **Mp** > 300 °C; **R_f** = 0.40; **IR (KBr)p ν cm^{-1}**: 3428 (O–H), 3258 (N–H), 3008 (C–H), 1672 (C=O), 1605 (C=N), 1610 (N=N), 1553, 1330 (N=O), 1380, 1145 (S=O), 780 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.38 (2H, s, CH_2), 4.50 (1H, s, OH), 8.30 (1H, s, NH), 7.10–7.68 (27H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.10, 39.32, 39.55 (CH_2), 161.80 (C=O), 108.44, 112.20, 114.15, 115.22, 118.09, 119.28, 121.30, 122.50, 123.34, 125.49, 126.60, 128.70, 130.21, 132.64, 134.30, 135.20, 139.67, 143.55, 144.20, 146.62, 148.14, 154.10, 156.22, 166.56, 169.03 (Ar); $C_{52}H_{31}O_9N_{11}SCl_3Na$ (1115.28): calc C, 56.00%, H, 2.80%, N, 13.81%, found, C, 55.96%, H, 2.76%, 13.75%.

(5) Dye **7e** (*p*-chloro anilino cyanurated Bronner acid):

Dye **7e** was obtained in 75% yield (Reddish yellow); **Mp** > 300 °C; **R_f** = 0.42; **IR (KBr) ν cm^{-1}**: 3283 (N–H), 3031 (C–H), 1683 (C=O), 1595 (C=N), 1614 (N=N), 1523, 1340 (N=O), 1384, 1160 (S=O), 758 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.59 (2H, s, CH_2), 8.28 (2H, s, NH), 7.46–7.60 (23H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.22, 39.42, 39.60 (CH2), 161.98 (C=O), 109.15, 111.25, 113.82, 114.35, 118.56, 120.18, 125.45, 126.12, 127.66, 128.34, 129.78, 131.88, 132.22, 133.40, 134.56, 139.12, 140.95, 142.08, 146.44, 157.62, 158.10, 165.23, 169.12 (Ar); $C_{46}H_{27}O_8N_{11}SCl_3Na$ (1023.19): calc C, 54.00%, H, 2.66%, N, 15.06%, found, C, 53.95%, H, 2.60%, N, 15.01%.

(6) Dye **7f** (*p*-chloro anilino cyanurated Gamma acid):

Dye **7f** was obtained in 77% yield (Dark yellow); **Mp** > 300 °C; **R_f** = 0.38; **IR (KBr) ν cm^{-1}**: 3456 (O–H), 3292 (N–H), 3023 (C–H), 1672 (C=O), 1598 (C=N), 1612 (N=N), 1523, 1349 (N=O), 1385, 1169 (S=O), 775 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.49 (2H, s, CH_2), 4.52 (1H, s, OH), 8.41 (2H, s, NH), 7.21–7.78 (22H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.09, 39.25, 39.50 (CH_2), 162.22 (C=O), 109.12, 111.25, 112.56, 114.25, 118.70, 120.22, 123.68, 126.40, 128.75, 130.85, 132.55, 134.50, 135.20, 137.22, 139.10, 142.55, 144.05, 146.18, 150.44, 152.35, 155.60, 165.55, 169.32 (Ar); $C_{46}H_{27}O_9N_{11}SCl_3Na$ (1039.19): calc. C, 53.17%, H, 2.62%, N, 14.83%, found, C, 53.10%, H, 2.57%, N, 14.75%.

(7) Dye **7g** (*p*-chloro anilino cyanurated Tobias acid):

Dye **7g** was obtained in 80% yield (Light yellow); **Mp** > 300 °C; **R_f** = 0.38; **IR (KBr) ν cm^{-1}**: 3312 (N–H), 3015 (C–H), 1668 (C=O), 1598 (C=N), 1620 (N=N), 1520, 1355 (N=O), 765 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.50 (2H, s, CH_2), 8.35 (2H, s, NH), 6.98–7.70 (24H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.06, 39.26, 39.48 (CH_2), 162.08 (C=O), 108.15, 110.24, 111.60, 114.20, 115.55, 119.12, 120.20, 123.24, 125.76, 129.52, 132.60, 133.40, 134.10, 135.34, 137.24, 138.58, 140.12, 144.65, 147.14, 150.10, 155.35, 166.08, 169.25 (Ar); $C_{46}H_{28}O_5N_{11}Cl_3$ (921.14): calc. C, 59.98%, H, 3.06%, N, 16.73%, found, 59.92%, H, 3.01, N, 16.68%.

(8) Dye **7h** (*p*-chloro anilino cyanurated Sulpho tobias acid):

Dye **7h** was obtained in 75% yield (Reddish yellow); **Mp** > 300 °C; **R_f** = 0.40; **IR (KBr) ν cm^{-1}**: 3350 (N–H), 3012 (C–H), 1672 (C=O), 1602 (C=N), 1610 (N=N), 1544, 1360 (N=O), 1372, 1145 (S=O), 770 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.45 (2H, s, CH_2), 8.42 (2H, s, NH), 7.06–7.42 (23H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.20, 39.35, 39.58 (CH_2), 162.20 (C=O), 109.20, 109.35, 111.60, 113.35, 115.22, 118.45, 121.55, 123.75, 125.55, 129.12, 131.78, 133.56, 135.80, 136.76, 138.55, 140.12, 143.54, 144.65, 146.07, 150.13, 154.15, 165.22, 169.42 (Ar); $C_{46}H_{27}O_8N_{11}SCl_3Na$ (1023.19): calc. C, 54.00%, H, 2.66%, N, 15.06%, found, C, 53.92%, H, 2.58%, N, 15.00%.

(9) Dye **7i** (*p*-chloro anilino cyanurated Peri acid):

Dye **7i** was obtained in 77% yield (Light yellow); **Mp** > 300 °C; **R_f** = 0.36; **IR (KBr) ν cm^{-1}**: 3345 (N–H), 3020 (C–H), 1670 (C=O), 1608 (C=N), 1612 (N=N), 1540, 1338 (N=O), 1370, 1138 (S=O), 765 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.62 (2H, s, CH_2), 8.55 (2H, s, NH), 7.10–7.62 (23H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.15, 39.32, 39.56 (CH_2), 161.90 (C=O), 108.90, 110.12, 111.07, 113.15, 115.20, 119.22, 122.66, 123.43, 125.44, 128.78, 129.70, 130.25, 132.60, 133.50, 134.21, 136.83, 139.14, 140.66, 144.10, 145.03, 150.32, 154.45, 166.39, 169.11 (Ar); $C_{46}H_{27}O_8N_{11}SCl_3Na$ (1023.19): calc. C, 54.00%, H, 2.66%, N, 15.06%, found, C, 53.94%, H, 2.59%, N, 15.02%.

(10) Dye **7j** (*p*-chloro anilino cyanurated Peri acid):

Dye **7j** was obtained in 80% yield (Greenish yellow); **Mp** > 300 °C; **R_f** = 0.38; **IR (KBr) ν cm^{-1}**: 3325 (N–H), 3010 (C–H), 1675 (C=O), 1603 (C=N), 1615 (N=N), 1565, 1362 (N=O), 1365, 1175 (S=O), 770 (C–Cl); **^{1}H NMR (400 MHz, DMSO-d_6) δ ppm**: 2.45 (2H, s, CH_2), 8.45 (2H, s, NH), 7.22–7.85 (21H, m, Ar–H); **^{13}C NMR (400 MHz, DMSO-d_6) δ ppm**: 39.14, 39.35, 39.62 (CH_2), 161.85 (C=O), 109.55, 110.32, 111.34, 113.68, 114.12, 115.44, 116.80, 118.04, 120.60, 122.78, 123.65, 124.55, 125.80, 126.14, 129.77, 130.54, 134.12, 136.40, 140.43, 144.45, 151.20, 154.29, 165.22, 168.96 (Ar); $C_{46}H_{25}O_{14}N_{11}S_3Cl_3Na_3$ (1227.28): calc. C, 45.02%, H, 2.05%, N, 12.55%, found, C, 44.95%, H, 2.00%, N, 12.48%.

Abbreviation: s-singlet, m-multiplet.

3. Results and discussion

3.1. Spectral characteristics

The structures of all the dyes **7a**–**j** were confirmed by various spectroscopic techniques, including IR, ^{1}H NMR and ^{13}C NMR.

The IR spectra [13] of dyes **7a**–**d** and **7f** showed characteristic broad absorption band at 3428–3571 cm^{-1} region corresponding to the O–H stretching vibration of hydroxyl group. The band at 3258–3350 cm^{-1} region corresponding to the N–H stretching vibration of secondary amino group and another band at 1610–1622 cm^{-1} region is due to the N=N stretching vibration of azo group. Intermediate **2** showed carbonyl (C=O) stretching vibration at 1756 cm^{-1} while intermediate **3** and all the dyes **7a**–**j** showed carbonyl stretching at 1664–1683 cm^{-1}, which confirmed the formation of amide linkage via conversion of δ-lactone to δ-lactum ring. The band at 1595–1608 cm^{-1} showed the confirmation of C=N group of quinazolinone ring. Other characteristic band of all the dyes **7a**–**j** appearing at 1520–1574, 1322–1362 cm^{-1} are due to the asymmetric and symmetric N=O stretching of nitro group, 1365–1385, 1138–1175 cm^{-1} are due to the asymmetric and symmetric S=O stretching of sulfonic acid group and 765–780 cm^{-1} is due to the C–Cl stretching of chloro group.

The ^{1}H NMR spectra [14] of all the dyes **7a**–**j** were recorded in DMSO. All the dyes **7a**–**j** showed singlet at δ = 2.38–2.62 ppm, which can be attributed to the methylene proton. The dyes showed singlet at δ = 4.42–4.63 ppm which can be attributed to the phenolic proton except for dyes **7e** and **7g**–**j**. All the dyes **7a**–**j** showed singlet in the downfield at δ = 8.23–8.73 ppm which can be attributed to amino proton, this downfield shift is probably due to the intermolecular hydrogen bonding between amino group and solvent (DMSO). The aromatic protons were observed from 6.64 to 7.85 ppm in the ^{1}H NMR spectra.

The ^{13}C NMR spectrum [14] of all the dyes **7a**–**j** showed triplet at δ = 39.06–39.71 ppm, which can be attributed to methylene carbons. Dye **7c** showed quartet at δ = 21.25–21.72 ppm which can be attributed to methyl carbon of N-methyl group of coupler moiety. Carbonyl carbon showed singlet at δ = 161.85–162.68 ppm. All the dyes **7a**–**j** showed characteristic band of aromatic carbon at δ = 108.15–170.06 ppm.

3.2. Solvent effect on UV–vis spectra

The visible absorption spectra of all the dyes **(7a**–**j)** in pure solvents of different dielectric constant via water (78.39), DMF (36.71), ethanol (24.55), dichloro methane (8.93) and chloroform (4.81) were recorded and shown in Table 1, which showed that the bands were observed in the region 430–530 nm in water, 422–522 nm in DMF, 415–515 nm in ethanol, 435–502 nm in dichloro methane and 450–495 nm in chloroform. (Absorption spectra of dyes **7a** and **7f** in different solvent are summarized in Figs. 1and 2 respectively).

The bathochromic shift (positive solvatochromism) was observed in water relative to DMF, ethanol, DCM and chloroform, is a result of the increase in the solvent polarity because of the increase in the dielectric constant of water relative to DMF, ethanol, DCM and chloroform. This positive solvatochromism is observed in dyes **7a**, **7c**, **7d** and **7f**. These results suggest that the excited state in these dyes were more polar than the ground state.

The hypsochromic shift (negative solvatochromism) occurring in water related to DMF, ethanol, DCM and chloroform. This effect is observed in dyes **7b**, **7e**, **7g**, **7h**, **7i** and **7j**. The negative solvatochromism observed is due to the solute solvent interaction through intermolecular hydrogen bond formation between water and lone pair of electron of secondary amino nitrogen atom.

3.3. Acid and base effect on UV–vis spectra

The effect of acid and base on the absorption of dye solution was investigated and the results are shown in Table 1.

The absorption spectra of the dyes in methanol were quite sensitive to the addition of 0.1 M KOH. The λ_{max} of all the dyes **(7a**–**j)** showed bathochromic shift by addition of 0.1 M KOH, this suggests that these dyes were present in different tautomeric form as in methanol. And when 0.1 M HCl was added to the dye solution in methanol, all the dyes **(7a**–**j)** showed large bathochromic shift except dyes **7g** and **7j**. This showed that all the dyes except **7g** and **7j** exist in the cationic form in acidic methanolic solution.

When piperidine was added to the dye solution in chloroform λ_{max} of all the dyes **(7a**–**j)** did not change significantly except dyes **7d** and **7f**. Dyes **7d** and **7f** shows large bathochromic shift when piperidine was added to the solution of chloroform. (Absorption spectra of dyes **7f** in acidic and basic solution are shown in Figs. 3 and 4).

3.4. Substituent effect

Absorption maxima of all the dyes **(7a**–**j)** were recorded in water and are shown in Table 1. The introduction of electron donating or electron attracting groups at the suitable position in the coupler ring affected the absorption characteristic of dyes. As can be seen from the data in Table 1, the bathochromic shift can be obtained by introducing methyl group in dye **7c**, this gave considerable shift of 5 nm relative to dye **7b**. An additional bathochromic shift of 15 nm can be obtained by introducing phenyl ring in dye **7d** relative to dye **7b**. The introduction of auxochromic group like sulfonic acid group which cause bathochromic shift by increase polarisability in the dye molecule. Here bathochromic shift of 30 nm, 45 nm, 20 nm and 12 nm was observed by introducing sulfonic acid group in dye **7e**, **7f**, **7h** and **7i** relative to dye **7g**. The lower absorption maxima value of dye **7j** (435 nm) is due to the moderating effect of three sulfonic acid group.

3.5. Dyeing of fibres

All the dyes **7a**–**j** were applied on silk, wool and cotton fibres in 2% (owf) shade according to following procedure. The variation in the hues of the dyed fibres results from changing the coupling

Table 1
Influence of solvent and effect of acid & base on λ_{max} (nm) of dyes **7a**–**j.**

Dye no.	Water	DMF	Methanol	DCM	Chloroform	Methanol + KOH	Methanol + HCl	Chloroform + Piperidine
7a	530	525	515	505	490	530	542	492
7b	480	472	465	460	475	475	495	478
7c	485	480	472	465	456	482	492	456
7d	495	488	485	470	462	498	505	495
7e	460	455	450	468	478	462	472	480
7f	475	465	460	455	445	470	490	470
7g	430	426	424	440	462	435	426	465
7h	450	444	438	452	465	445	460	468
7i	442	436	428	435	450	432	450	452
7j	435	422	415	440	468	428	418	466

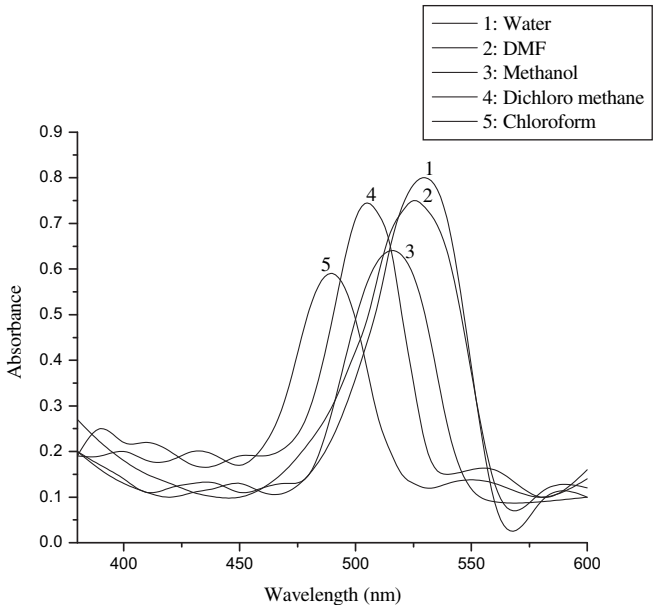


Fig. 1. Absorption spectra of dye **7a** in various solvents.

components used, i.e. When H-acid used as coupling component, it gives pink hues, J-acid gives yellow color hue and N-phenyl-j-acid gives red color hue. A remarkable degree of levelness after washing indicates good penetration and excellent affinity of these dyes with silk, wool and cotton fibres.

3.5.1. Dyeing of silk

The dye (0.2 g) was pasted with a drop of cold water and then about 80 ml of cold water was added and stirred well to give a clear solution. The resulting dye solution was made up to 100 ml with the dye solution (20 ml), acetic acid (2 ml of 10% v/v) and water 18 ml. The dyebath temperature was maintained at 30 °C and silk fabric (2 g) was entered, and the temperature was raised to 40 °C over 20 min. At this temperature formic acid (1.5 ml of 40% v/v) was added to the dyebath to achieve good exhaustion. The dyeing was continued for 40 min more and then the dyed material was washed with cold water, soaping and dried.

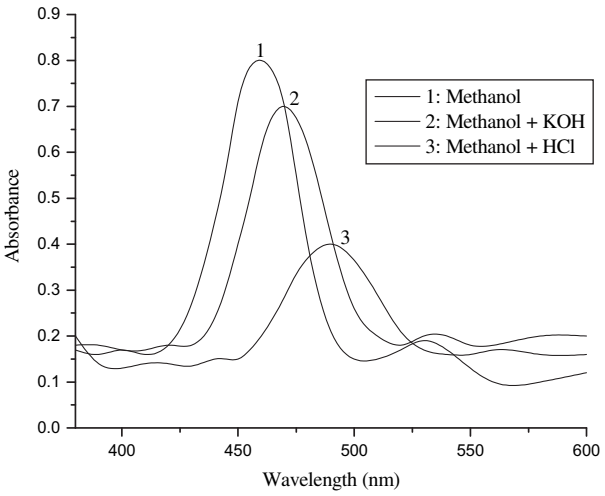


Fig. 3. Absorption spectra of dye **7f** in acidic and basic solutions.

3.5.2. Dyeing of wool

Dye (0.2 g) was pasted with a few drops of cold water, then about 80 ml cold water was added, and the mixture was stirred and made up to 100 ml with dye solution (20 ml), acetic acid (1.5 ml of 10% v/v), glaubers's salt solution (4 ml of 10% w/v) and water (14.4 ml). A wool fabric (2 g) was introduced in to the dyebath at 30 °C and the temperature was raised up to 40 °C over 20 min. Sulphuric acid (0.4 ml of 10% v/v) was then added and the dyeing was continued for 40 min more at the same temperature. The material was then removed, rinsed with cold water, soaping and dried.

3.5.3. Dyeing of cotton

Dye (0.2 g) was pasted with a few drops of cold water, then about 80 ml cold water was added, and the mixture was stirred and made up to 100 ml with dye solution (20 ml), glaubers's salt solution (4 ml of 10% w/v) and water (14.4 ml). A cotton fabric (2 g) was introduced in to the dyebath at 30 °C and the temperature was raised up to 40 °C over 20 min. Soda ash (Na_2CO_3) solution (0.4 ml of 10% v/v) was then added to bring about fixation and the dyeing was continued for 40 min more at the same temperature. The material was then removed, rinsed with cold water, soaping and dried.

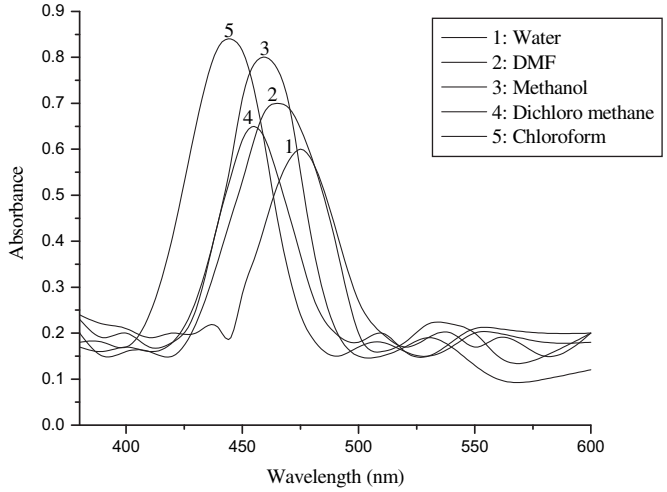


Fig. 2. Absorption spectra of dye **7f** in various solvents.

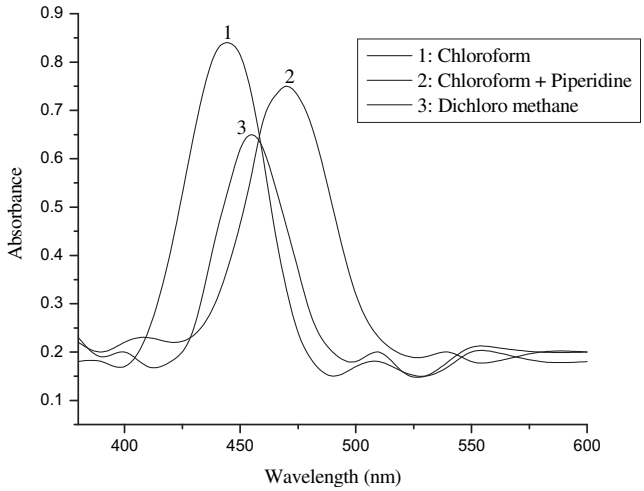


Fig. 4. Absorption spectra of dye **7f** in acidic and basic solutions.

3.6. Exhaustion and fixation study

The percentage dyebath exhaustion (%E) and percentage dyebath fixation (%F) of the dyed fabric were determined according to known method [15].

The percentage dyebath exhaustion of 2% dyeing ranges from 84 to 91% for silk, 84–90% for wool and 83–91% for cotton fibre. The percentage dyebath fixation of 2% dyeing ranges from 74 to 81% for silk, 75–83% for wool and 74–80% for cotton fibres. The exhaustion is good for all the dyes **7a**–**j**, which shows good attachment of the dye to the fibre. The presence of reactive group like *s*-triazine group also improves the exhaustion and fixation value. The percentage exhaustion and fixation data were summarized in Table 2.

3.7. Fastness properties

The light fastness, wash fastness and rubbing fastness properties were assessed according to the standard method [16].

All the dyes **7a**–**j** show generally moderate to very good (3–6 value on grayscale) light fastness property and good to excellent (3–5 value on grayscale) washing and rubbing fastness properties. The results are given in Table 2 and they reveal that these dyes have good fastness properties.

The higher values of rubbing fastness (Table 2) are associated with higher molecular weights of the dyes, here dyes **7a**, **7d** and **7j** gave higher rubbing fastness properties than the other dyes investigated.

3.8. Color measurement

The color of a dyeing on silk, wool and cotton fibres are expressed in terms of CIELAB values (Table 3) and the following CIELAB coordinates were measured, Lightness (L*), chroma (C*), hue angle form 0° to 360° (H), a* value represent the degree of redness (positive) and greenness (negative) and b* represents the degree of yellowness (positive) and blueness (negative). A reflectance spectrophotometer was used for the colorimetric measurements on the dyed samples. K/S values given by the reflectance spectrophotometer are calculated at λ_{max} and are directly correlated with the dye concentration on the substrate according to the Kubelka–Munk equation [17]:

$$K/S = (1-R)^2/2R,$$

Where K – Absorbance coefficient, S – scattering coefficient and R – reflectance ratio.

The color coordinates (Table 3) indicates that the dyes have good affinity to silk, wool and cotton fibres.

The data summarized in Table 3 showed that, for silk fabric the dyeing obtained using dye **7c** was greener (as evidenced by the lower a* value), duller (as shown by the lower C* value) and lighter (as shown by the higher L* value) than the dye **7b**. Similar result was obtained by comparison of dye **7c** with dye **7b**. The dyeing obtained by using dye **7h** was greener, duller and darker than the dye **7g**, while the dye **7i** was redder, duller and darker than the dye **7g**. The color strength (K/S) values of all the dyes **7a**–**j** for silk fabric followed the following order:

7a > **7b** > **7c** > **7d** > **7f** > **7e** > **7g** > **7h** > **7i** > **7j**

Dye **7a** having maximum value of color strength (K/S) while dye **7j** having minimum value of color strength (K/S).

From the data summarized in Table 3 showed that, for wool fabric the dyeing obtained using dye **7c** was greener, duller and darker than dye **7b**, while dye **7d** was redder, duller and darker than dye **7b**. The K/S value of dyes **7a**–**j** for wool fabric followed the following order:

7a > **7b** > **7d** > **7c** > **7e** > **7f** > **7h** > **7j** > **7i** > **7g**

Here dye **7a** having maximum value of K/S while dye **7g** having minimum value of K/S.

And finally for cotton fabric the data summarized in Table 3 showed that, the dye **7c** was greener, duller and lighter than dye **7b** while dye **7d** was redder, duller and darker than dye **7b**. Further dye **7h** was redder, brighter and darker than dye **7g**. Similar results can be obtained by comparing dyes **7i** and **7g**. The K/S value of dyes **7a**–**j** for cotton fabric followed the following order:

7a > **7b** > **7d** > **7c** > **7i** > **7f** > **7h** > **7e** > **7j** > **7g**

Dye **7a** having highest K/S value while dye **7g** having minimum K/S value.

From the above data it is apparent that dye **7a** having highest K/S value on silk, wool and cotton fibres, showed that the dye **7a** having highest affinity for all these fabric.

3.9. Antimicrobial activity

All the synthesized dyes **(7a–j)** were tested for their antibacterial and antifungal activity (MIC) *in vitro* by broth dilution method with

Table 2
%Exhaustion, %Fixation and fastness properties data of dyes **7a-j.**

Dye No.	%Exhaustion			%Fixation			Light fastness			Wash fastness			Rubbing fastness					
	S	W	C	S	W	C	S	W	C	S	W	C	Dry			Wet		
													S	W	C	S	W	C
7a	89.15	89.58	90.25	80.20	82.61	79.78	4	6	6	5	4–5	4	5	5	4–5	5	5	4–5
7b	90.13	88.06	88.35	78.78	80.07	78.01	5	5–6	5	4–5	5	4–5	4	4–5	4	4–5	4	3–4
7c	90.60	85.53	85.15	78.92	77.76	76.34	4–5	5	4–5	4	4–5	4	3–4	4	3–4	4	4	3–4
7d	88.15	87.23	84.13	76.00	76.81	74.29	4–5	4	4	3–4	4	4	5	5	4–5	4–5	5	5
7e	87.63	87.55	86.25	75.89	75.39	76.52	5	4–5	6	3	3	3–4	3–4	3	3	3	3–4	4
7f	86.75	88.13	87.65	76.10	77.73	77.58	3–4	3–4	3–4	3	4	3	4	3–4	3	3–4	3	3–4
7g	85.10	85.55	84.48	76.38	77.15	74.58	4	6	3–4	4	4–5	4	3	4	3–4	3–4	3	3
7h	86.08	84.13	83.76	74.93	76.08	74.63	6	3–4	6	3–4	3	3–4	3–4	4	3	4	3–4	4
7i	85.35	86.20	84.16	74.98	78.88	75.46	4–5	4–5	3–4	4	4	4	4	3	3–4	3–4	4	4–5
7j	84.92	87.10	86.63	74.18	79.22	79.08	6	5	4–5	4–5	5	3–4	5	4–5	5	5	4–5	4–5

Abbreviations: S-Silk, W-Wool, C-Cotton.
Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good.
Wash & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

Table 3
Colorimetric (CIELAB) data of dyes **7a**–**j** on silk, wool and cotton fibres.

Dye No.	L*			a*			b*			C*			H*			K/S		
	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C
7a	45.41	32.36	42.05	54.18	49.00	54.00	06.36	17.38	11.48	54.55	51.99	55.21	06.70	19.53	12.00	10.76	26.18	13.30
7b	60.86	53.40	64.17	39.06	38.02	36.56	49.14	51.80	50.52	62.78	64.26	62.36	51.52	53.72	54.11	07.65	14.35	06.20
7c	68.41	51.36	64.30	29.46	35.65	34.05	33.98	45.64	38.06	44.98	57.91	51.07	49.07	52.01	48.19	02.52	13.26	03.74
7d	71.21	43.45	51.39	22.51	39.93	38.83	14.56	32.38	31.06	26.81	51.41	49.72	32.90	39.04	38.66	00.91	14.12	07.02
7e	78.23	55.38	67.14	13.63	34.92	26.11	14.94	45.42	25.24	20.22	57.29	36.31	47.63	52.44	44.03	00.47	08.75	01.60
7f	72.32	50.73	63.97	22.62	35.27	29.60	15.34	29.64	24.38	27.33	46.07	38.35	34.15	40.04	39.48	00.84	06.34	01.97
7g	83.64	69.92	79.22	05.71	13.67	13.83	21.36	27.70	27.32	22.11	30.89	30.62	75.04	63.73	63.15	00.43	02.05	00.89
7h	83.21	64.20	73.65	05.01	23.17	16.04	18.38	44.98	35.04	19.05	50.60	38.54	74.77	62.75	65.41	00.41	04.33	01.86
7i	79.54	67.97	69.89	14.48	16.54	17.45	12.34	30.90	29.22	19.02	35.05	34.03	40.44	61.85	59.16	00.40	02.83	02.51
7j	85.37	57.70	73.23	02.13	31.55	12.80	14.02	24.46	20.62	14.18	39.92	24.27	81.34	37.78	58.18	00.33	03.44	01.31

Abbreviations: S-Silk, W-Wool, C-Cotton

Table 4
Antibacterial and antifungal activity data of dyes **7a**–**j.**

Dye No.	Minimal bactericidal concentration (μg/ml)				Minimal fungicidal concentration (μg/ml)		
	Gram-negative		Gram-positive				
	E. coli MTCC443	*P. aeruginosa* MTCC 1688	*S. aureus* MTCC 96	*S. pyogenes* MTCC 442	*C. albicans* MTCC 227	*A. niger* MTCC 282	*A. clavatus* MTCC 1323
7a	62.5	200	200	200	500	>1000	>1000
7b	500	500	500	1000	500	500	500
7c	100	200	200	200	1000	1000	>1000
7d	500	1000	500	500	100	250	250
7e	250	250	500	500	1000	1000	>1000
7f	62.5	200	250	500	100	250	250
7g	500	200	500	1000	1000	1000	1000
7h	1000	1000	1000	1000	100	250	250
7i	1000	1000	1000	500	500	>1000	>1000
7j	500	500	100	1000	1000	500	500
Ampicillin	100	100	250	100	–	–	–
Chloramphenicol	50	50	50	50	–	–	–
Nystatin	–	–	–	–	100	100	100
Greseofulvin	–	–	–	–	500	100	100

two Gram-positive bacteria *S. aureus* **MTCC 96**, *Streptococcus pyogenes* **MTCC 442** and two Gram-negative bacteria *Escherichia coli* **MTCC443**, *Pseudomonas aeruginosa* **MTCC 1688** and fungi *Candida albicans* **MTCC 227**, *Aspergillus niger* **MTCC 282** and *Aspergillus clavatus* **MTCC 1323** organism taking gentamycin, ampicillin, chloramphenicol, ciprofloxacin, norfloxacin, nystatin and greseofulvin as standard drug. All MTCC cultures were collected from Institute of Microbial Technology, Chandigarh and tested against known drugs ampicillin and greseofulvin. Mueller–Hinton broth was used as nutrient medium to grow and dilute the drug suspension for the test.

3.9.1. Antibacterial activity

Dye **7a** showed excellent activity against *E. coli* and very good activity against *S. aureus* with respect to standard drug Ampicillin. Dye **7j** showed excellent activity against *S. aureus* with respect to standard drug Ampicillin. Dye **7f** showed excellent activity against *E. coli* and equipotential activity against *S. aureus* with respect to standard drug Ampicillin and dye **7c** showed equipotential activity against *E. coli* and very good activity against *S. aureus* with respect to standard drug Ampicillin. Antibacterial activity data were summarized in Table 4.

3.9.2. Antifungal activity

Dyes **7d**, **7f** and **7h** showed equipotential activity against *C. albicans* with respect to standard drug Nystatin while dyes **7a**, **7b** and **7i** showed equipotential activity against *C. albicans* with respect to standard drug Greseofulvin. Antifungal activity data were summarized in Table 4.

4. Conclusions

A series of monoazo reactive dyes based on 3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2-phenylquinazolin-4(3*H*)-one **(3)** have been prepared by conventional method in good yield. The spectral properties, solvatochromic behavior, antimicrobial activity, colorimetric data and their fastness properties have been evaluated.

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