

Divyesh R. Patel · Keshav C. Patel

# Synthesis, Antimicrobial Activity and Colorimetric Studies of Some New Bromo-quinazolinone Derivative as Potential Reactive Dyes

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**Abstract** The objective of the current study was to introduce the quinazolinone molecule into a conventional reactive dye system. On this basis ten novel quinazolinone-based monochloro-*s*-triazine reactive dyes (**7a–j**) were rapidly and efficiently synthesized by coupling route of diazotized 3-{4'-[4''-amino-2'',5''-dichlorobenzyl]-2', 5'-dichlorophenyl}-6-bromo-2-phenylquinazolin-4(3*H*)-one (**3**) with a variety of *m*-nitro anilino cyanurated coupling components (**6a–j**). Their characterization was done using elemental analysis, UV–Vis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The solvatochromism was evaluated with respect to spectroscopic properties in organic solvents, viz., DMSO, DMF, methanol, acetic acid and chloroform. A detailed study of pharmacological screening (in vitro), solvatochromic effect, fastness properties, colorimetric data ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $H^*$ ,  $K/S$ ) and thermogravimetric analysis was also investigated. These dyes showed generally moderate to very good light fastness and good to excellent washing and rubbing fastness properties and also showed good antimicrobial activity.

**Keywords** Quinazolinone · Solvatochromism · Pharmacological screening · Colorimetric data · Thermogravimetric analysis.

## الخلاصة

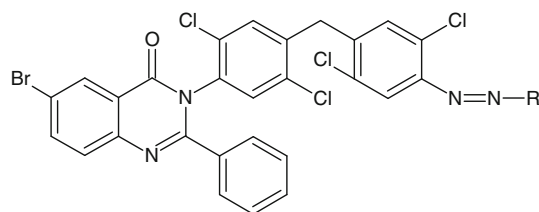
يتمثل هدف الدراسة في إدخال بناء كوينازولينون في نظام صبغة فعالة تقليدي. وقد تم - على هذا الأساس- بسرعة وكفاءة توليف عشر مركبات كوينازولينون قيمة اعتمادا على أصباغ سترائيزين أحادية الكلور الفعالة (**7a–j**) باستخدام مسار الربط لدايزوتازيد 3-{4'-[4''-أمينو-2'',5''-دايكلوروبينزل]-2', 5'-دايكلوروفينيل}-6-برومو-2-فينيلكوينازولينون-4(3*H*)-أون (**3**) مع تشكيلة من مكونات الربط سيانيترويد ميثا-نيترو أنيلين (**6a–j**), حيث تم وصف المركبات المولفة باستخدام تحليل العناصر ومطيافية الأشعة فوق البنفسجية-المرئية ومطيافية الأشعة تحت الحمراء والرنين المغناطيسي لأنوية الهيدروجين والكربون. وقد تم تقييم امتصاص اللون بالنسبة للخواص الطيفية في المذيبات العضوية: داي ميثيل سلفوكساييد وداي ميثيل فورم أميد والميثانول وحمض الخليك والكلوروفورم. تم أيضا بحث دراسة تفصيلية للخواص الدوائية (في المختبر) وتأثير المذيب اللوني وخصائص الثبات والبيانات اللونية ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $H^*$ ,  $K/S$ ) والتحليل الوزنية الحرارية (TGA). وقد أظهرت هذه الأصباغ بعامة ثباتا ضوئيا من متوسط إلى جيد جدا ومن جيد إلى ممتاز بالنسبة إلى خواص الغسيل وثبات الفرق مع فعالية ضد المايكروبات.

## 1 Introduction

It was observed that dyes based on heterocyclic moiety are highly interesting as they possess high degree of brightness and tinctorial strength as compared to the azo dyes derived from simple aniline [1–6]. Such dyes also used as antibacterial and chemotherapeutic agents to stain and paralyze specific microorganism [7]. Azo dyes derived from thiophene, pyrazolone and quinazolinone moieties are reported earlier by various researchers

D. R. Patel (✉) · K. C. Patel  
Department of Chemistry, Veer Narmad South Gujarat University, Surat 395007, Gujarat, India  
E-mail: divyeshpatel905@gmail.com





**Reactive Dyes 7a-j**

**Fig. 1** General structure of the reactive dyes **7a–j**, where R = different *m*-nitro anilino cyanurated coupling components **6a–j** (Table 1)

which showed advanced dyeing as well as excellent pharmacological properties [8–11]. The quinazolinone molecule possesses significant pharmacological activity and was found to be a key component in a variety of colored products [12–15]. These dyes showed visible absorption maxima ( $\lambda_{\text{max}}$ ) in the yellow to orange region due to weakly delocalized electron in the quinazolinone ring. Many researchers proved that quinazolinone-based monoazo dyes showed excellent fastness properties including good depth and levelness on various fibres [14, 16–18].

We have previously reported the synthesis and dyeing properties of some sulfo- and chloro-substituted quinazolinone-based reactive dyes on various fibres [19, 20]. The comparison of bromo-substituted quinazolinone dyes with respect to previously reported sulfo and chloro-substituted dyes, the present dyes showed higher color strength (K/S) than sulfo and lower color strength (K/S) than chloro-substituted dyes in terms of H-acid-based reactive dyes derivative. Bromo- and chloro-substituted quinazolinone derivative showed higher absorption maxima than sulfo-substituted quinazolinone dyes. Chloro-substituted dyes showed higher antimicrobial activity against selected microorganism with respect to standard drugs and also showed higher fixation value on different fibres than bromo-substituted quinazolinone dyes.

Our aim is to synthesize a series of some new bromo-substituted quinazolinone-based monoazo reactive dyes and to investigate their dyeing properties along with thermal stability behavior. Solvatochromic effect, in vitro antimicrobial screening (antibacterial and antifungal), colorimetric analysis and fastness properties are studied in detail. General structure of the newly synthesized monochloro-*s*-triazine reactive dyes (**7a–j**) is given in Fig. 1.

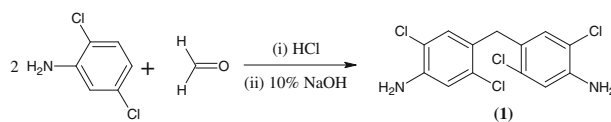
## 2 Experimental

### 2.1 Materials and Methods

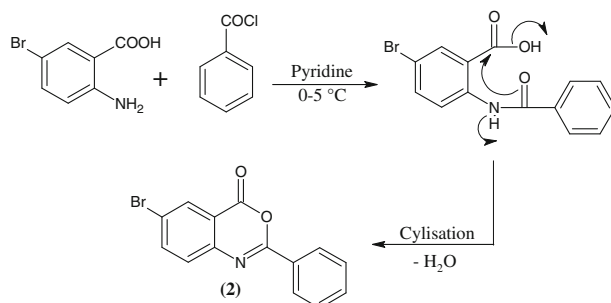
The entire reactions were monitored by employing TLC technique [21] using Silica gel-G F<sub>254</sub> plates and the spots were rendered visible by exposing to UV light and iodine. Melting points of dyes intermediates were determined in open capillaries and are uncorrected. The solvents used were of spectroscopic grade and used without further purification. The coupling components used in the dyes synthesis were received from Atul Ltd. Cyanuric chloride was purified by crystallization from pure benzene (146 °C). Silk, wool and cotton fibres were purchased from Kiran Threads, Vapi.

IR spectra were recorded on a Perkin Elmer Model 377 spectrophotometer in KBr pellet. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance II (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) NMR spectrometer in DMSO-*d*<sub>6</sub> solvent with TMS as internal standard. Absorption spectra were recorded in 1 cm quartz cells on a Thermo Scientific Evolution 300 spectrophotometer in a range of solvents, i.e. DMSO, DMF, methanol, acetic acid and chloroform at the various concentrations (10<sup>-6</sup> to 10<sup>-8</sup> M). Elemental analyses were performed on Carlo Erba 1108 elemental analyzer. Colorimetric data (*L*\*, *a*\*, *b*\*, *C*\*, *H*\* and *K/S*) were recorded on Reflectance spectrophotometer Gretag Macbeth CE: 7000A (D65 illumination, 10° observer). Thermogravimetric analysis (TGA) was carried out on Pyris 6 PerkinElmer Thermal Analyzer instrument. pH measurement of reaction mass was done using Equiptronics EQ-614 A digital pH meter.





**Scheme 1** Synthetic route of dye intermediate (1)



**Scheme 2** Synthetic route of dye intermediate (2)

## 2.2 Synthesis of 4,4'-Methylene Bis(2,5-Dichloro Aniline) [22, 23] (1)

2,5-Dichloro aniline (16.2 g, 0.1 mol) was first mixed with sufficient HCl to reach pH 4 of the medium. Then, the pale yellow colored solution was put into a three-necked flask fitted with a stirrer and was mixed at 50 °C temperature. Formaldehyde (35 mL, 3 % v/v) was added at interval of 10 min over a period of 1 h and the stirring was continued for further 10 h maintaining temperature at 60 °C. The stirring was then stopped and the product was washed with NaOH (2 % w/v) first and then with water till the reaction mixture became neutral. Finally, the yellowish colored product (1) was dried and recrystallized from acetic acid. Yield: 12.65 g (75.3 %). Pale yellow powder. M.p., 118 °C. TLC:  $R_f = 0.72$  (PhMe:EtOAc, 3:1 v/v). IR (KBr):  $\nu \text{ cm}^{-1} = 3,395, 3,315$  (N–H), 2,995 (C–H), 1,595 (N–H bend.), 785 (C–Cl).  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  ppm = 2.22 (s, 2H, CH<sub>2</sub>), 6.25 (s, 4H, NH<sub>2</sub>), 6.63–7.12 (m, 4H, Ar–H).  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  ppm = 36.24, 36.52, 36.76 (CH<sub>2</sub>), 123.6, 132.2, 144.2 (Ar). Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub> (336.04 g/mol): C, 46.46 %; H, 3.00 %; N, 8.34 %. Found: C, 46.41 %; H, 2.96 %; N, 8.28 % (Scheme 1).

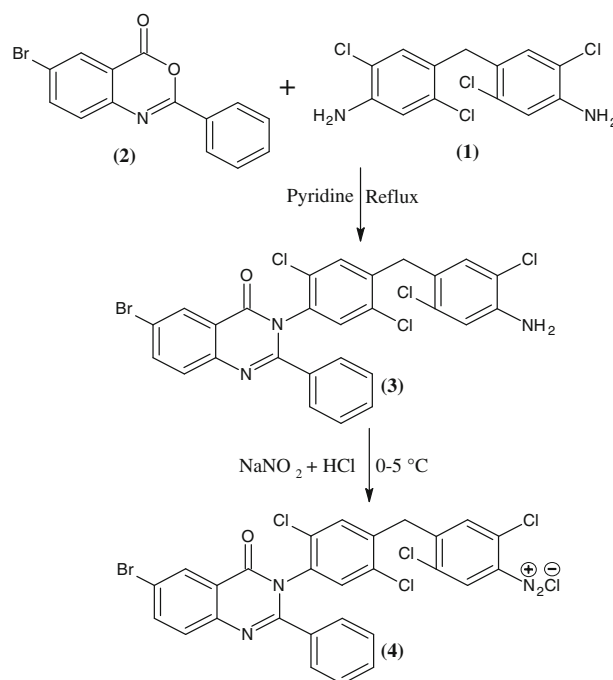
## 2.3 Synthesis of 6-Bromo-2-Phenyl-4H-Benzo[1,3]Oxazine-4-One [24] (2)

To a stirred solution of 5-bromo anthranilic acid (2.16 g, 0.01 mol) in pyridine (60 mL), benzoyl chloride (1.16 mL, 0.01 mol) was added dropwise, maintaining the temperature 0–5 °C for 1 h. The reaction mixture was then stirred for another 2 h at room temperature until a solid product was formed. The reaction mixture was neutralized with saturated Na<sub>2</sub>CO<sub>3</sub> solution. Yellow color solid (2) separated was filtered, washed with water and recrystallized from ethanol. Yield: 2.37 g (78.6 %). Pale yellow powder. M.p., 175 °C. TLC:  $R_f = 0.70$  (PhMe:EtOAc, 3:1 v/v). IR (KBr):  $\nu \text{ cm}^{-1} = 3,066$  (C–H), 1,615 (C–N), 1,755 (C=O), 1,058 (C–O–C), 536 (C–Br).  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  ppm = 7.55–8.14 (m, 8H, Ar–H).  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  ppm = 159.6 (CO), 118.6, 122.2, 124.5, 128.6, 129.5, 131.4, 135.5, 139.6, 146.4, 157.6 (Ar). Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>NBr (302.12 g/mol): C, 55.66 %; H, 2.67 %; N, 4.64 %. Found: C, 55.60 %; H, 2.62 %; N, 4.58 % (Scheme 2).

## 2.4 Synthesis of 3-{4'-[4''-Amino-2'',5''-Dichlorobenzyl]-2',5'-Dichlorophenyl}-6-Bromo-2-Phenyl quinazolin-4(3H)-One [25] (3)

4,4'-Methylene bis(2,5-dichloro aniline) (1.68 g, 0.005 mol) (1) and 6-bromo-2-phenyl-4H-benzo[1,3]oxazine-4-one (1.51 g, 0.005 mol) (2) were dissolved in pyridine (40 mL) and then reflux the reaction mass for 6 h under anhydrous reaction condition and then adjust the reaction mass temperature to 28–30 °C. The reaction mixture was then treated with ice cooled dilute hydrochloric acid. A solid separated out which was filtered off and washed with water to remove any adhered pyridine. The crude quinazolinone (3) thus obtained was dried





**Scheme 3** Synthetic route of dye intermediate (3) and its diazonium salt (4)

under vacuum and recrystallized from ethanol. Yield: 2.19 g (70.5 %). Dark yellow powder. M.p., 128 °C. TLC:  $R_f = 0.62$  (PhMe:EtOAc, 3:1 v/v). IR (KBr):  $\nu$  cm<sup>-1</sup> = 3,404, 3,365 (N–H) 3,028 (C–H), 1,596 (C–N), 1,666 (C=O), 786 (C–Cl), 550 (C–Br). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta_H$  ppm = 2.55 (s, 2H, CH<sub>2</sub>), 6.18 (s, 2H, NH<sub>2</sub>), 7.45–8.05 (m, 12H, Ar–H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta_C$  ppm = 38.42, 38.56, 38.75 (CH<sub>2</sub>), 160.4 (CO), 118.6, 121.7, 123.5, 123.9, 124.8, 128.5, 129.6, 130.7, 132.5, 134.7, 135.7, 136.9, 144.6, 147.8, 156.9 (Ar). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>ON<sub>3</sub>Cl<sub>4</sub>Br (620.15 g/mol): C, 52.29 %; H, 2.60 %; N, 6.78 %. Found: C, 52.22 %; H, 2.57 %; N, 6.73 % (Scheme 3).

### 2.5 General Method for Preparation of Diazonium Salt Solution (4)

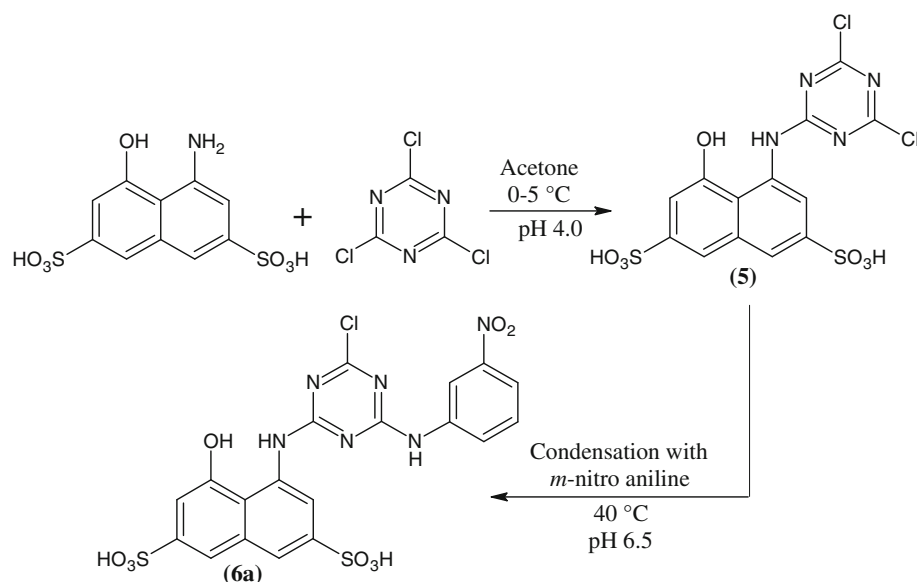
3-{{4'-[4''-amino-2'',5''-dichlorobenzyl]-2',5'-dichlorophenyl}-6-bromo-2-phenylquinazolin-4(3H)-one (3.10 g, 0.005 mol) (3) was added in a mixture of water (25 mL), conc. HCl (1.88 mL, 0.015 mol) and ice (10 g). The reaction mixture was cooled to 0–5 °C using an ice bath. NaNO<sub>2</sub> (0.35 g, 0.005 mol) dissolved in water (10 mL) was then added dropwise. The solution was stirred for 30 min and excess HNO<sub>2</sub> was decomposed by adding sulphamic acid. Activated carbon was added with stirring and the reaction mixture was filtered at 0–5 °C to give the clear yellow color solution (4) (Scheme 3).

### 2.6 General Method for the Preparation of Coupling Component (6a)

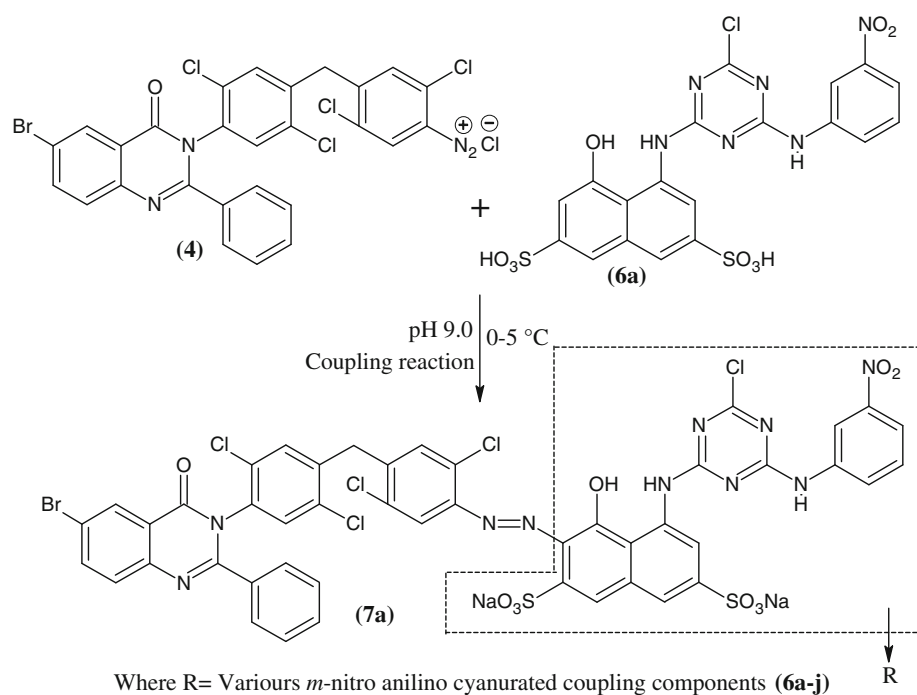
H-acid (3.19 g, 0.01 mol) was dissolved in water (15 mL) at pH 7.5, using 20 % (w/v) Na<sub>2</sub>CO<sub>3</sub>. A solution of cyanuric chloride (1.85 g, 0.01 mol) in acetone (20 mL) was cooled to 0–5 °C and then added dropwise to the stirred H-acid solution at 0–5 °C. After 10 min, the solution was adjusted to pH 4 by adding 20 % (w/v) Na<sub>2</sub>CO<sub>3</sub>, and the reaction stirring was continued for 1 h at 0–5 °C. The reaction progress was followed by TLC using *n*-PrOH:*n*-BuOH:EtOAc:H<sub>2</sub>O (2:4:1:3 v/v) in which the product 5 had  $R_f = 0.75$  (Scheme 4).

*m*-Nitro aniline (1.38 g, 0.01 mol) was added to a well-stirred solution of 5 (0.01 mol) and after adjusting to pH 6.5 using Na<sub>2</sub>CO<sub>3</sub> solution (20 % w/v), 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<sub>2</sub>O, 2:4:1:3 v/v), where the 6a had  $R_f = 0.38$  (Scheme 4).





**Scheme 4** Synthetic route of *m*-nitro anilino cyanurated H-acid (6a)



**Scheme 5** Synthetic route of reactive dye 7a

## 2.7 General Method for the Synthesis of Reactive Dyes (7a)

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 Na<sub>2</sub>CO<sub>3</sub> solution (20 % w/v) and the coupling step was continued for 4 h at 0–5 °C. Then, urea (10 % w/v) was added [26] and the dye (7a) was isolated from the reaction mixture by adding the appropriate amount of NaCl (12 g) and filtering the resulting purple color solid dye (Scheme 5).

The eluent system for TLC was 2-BuOH:EtOH:NH<sub>4</sub>OH:pyridine (4:1:3:2 v/v). Dye 7a had  $R_f = 0.42$ , with minor impurities at  $R_f = 0.22$ .



Salt was removed by the following purification process:

The crude dye (**7a**) was dissolved in dimethyl-formamide (50 mL). Next, the temperature was raised to 90 °C for half an hour. The dye solution was filtered through Whatman filter paper to remove insoluble impurities, such as electrolytes and other inorganic salts. Chloroform (100 mL) was slowly added to the filtrate with continuous stirring. The solution was cooled for 24 h, when the violet dye (**7a**) was precipitated. The precipitated dye was then filtered, washed with chloroform and dried at 60 °C.

Same coupling procedure and controlled condition were followed for the synthesis of other reactive dyes (**7b–j**) using a range of *m*-nitro anilino cyanurated coupling components such as J-acid (**6b**), *N*-methyl-J-acid (**6c**), *N*-phenyl-J-acid (**6d**), Gamma acid (**6e**), *N*-methyl-Gamma acid (**6f**), *N*-phenyl-Gamma acid (**6g**), *N*-(3-sulfophenyl)-Gamma acid (**6h**) K-acid (**6i**) and Chicago acid (**6j**).

Various *m*-nitro anilino cyanurated coupling components are summarized in Table 1 and characterizations data of reactive dyes **7a–j** are as follows.

### 2.7.1

Dye **7a** was synthesized using *m*-nitro anilino cyanurated H-acid as coupling component. Yield 5.31 g (85.2 %). Dark purple powder. M.p. >300 °C.  $R_f = 0.42$ . UV/Vis (DMF)  $\lambda_{\max}(\epsilon_{\max}) = 530$  nm (25,165.68 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,469 (O–H), 3,295 (N–H), 2,930, 2,850 (C–H), 1,675 (C=O), 1,595 (C=N), 1,620 (N=N), 1,570, 1,360 (N=O), 1,385, 1,179 (S=O), 756 (C–Cl), 692 (C–Br); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta_H$  ppm: 2.57 (2H, s, CH<sub>2</sub>), 4.32 (1H, s, OH), 8.31 (2H, s, NH), 6.89–7.81 (19H, m, Ar–H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_C$  ppm: 39.19, 39.40, 39.61 (CH<sub>2</sub>), 161.94 (C=O), 109.38, 113.90, 114.50, 115.18, 118.34, 119.28, 121.11, 123.16, 125.95, 128.34, 130.71, 132.28, 134.94, 136.60, 139.62, 142.34, 144.50, 147.54, 148.44, 152.34, 155.94, 165.05, 169.62 (Ar). Anal. Calcd for C<sub>46</sub>H<sub>24</sub>O<sub>10</sub>N<sub>10</sub>S<sub>2</sub>Na<sub>2</sub>Cl<sub>5</sub>Br (1,244.02): C, 44.41 %; H, 1.94 %; N, 11.26 %. Found C, 44.28 %, H, 1.82 %, N, 11.14 %.

### 2.7.2

Dye **7b** was synthesized using *m*-nitro anilino cyanurated J-acid as coupling component. Yield 4.61 g (80.6 %). Light yellow powder. M.p. >300 °C.  $R_f = 0.40$ . UV/Vis (DMF)  $\lambda_{\max}(\epsilon_{\max}) = 480$  nm (20,617.12 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,412 (O–H), 3,298 (N–H), 2,935, 2,845 (C–H), 1,672 (C=O), 1,596 (C=N), 1,616 (N=N), 1,536, 1,359 (N=O), 1,385, 1,175 (S=O), 770 (C–Cl), 695 (C–Br); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta_H$  ppm: 2.39 (2H, s, CH<sub>2</sub>), 4.35 (1H, s, OH), 8.30 (2H, s, NH), 7.17–7.68 (20H, m, Ar–H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_C$  ppm: 39.18, 39.39, 39.60 (CH<sub>2</sub>), 162.38 (C=O), 108.52, 112.76, 114.61, 115.80, 120.26, 121.67, 123.85, 126.41, 128.83, 131.54, 133.18, 134.62, 135.54, 136.27, 139.86, 142.97, 144.61, 147.95, 150.23, 152.67, 156.78, 165.81, 170.29 (Ar). Anal. Calcd for C<sub>46</sub>H<sub>25</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,141.98): C, 48.38 %; H, 2.21 %; N, 12.27 %. Found C, 48.22 %, H, 2.10 %, N, 12.15 %.

### 2.7.3

Dye **7c** was synthesized using *m*-nitro anilino cyanurated *N*-methyl-J-acid as coupling component. Yield 4.38 g (75.7 %). Dark orange powder. M.p. >300 °C.  $R_f = 0.38$ . UV/Vis (DMF)  $\lambda_{\max}(\epsilon_{\max}) = 498$  nm (18,519.54 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,410 (O–H), 3,288 (N–H), 2,945, 2,860 (C–H), 1,675 (C=O), 1,594 (C=N), 1,610 (N=N), 1,542, 1,338 (N=O), 1,370, 1,165 (S=O), 772 (C–Cl), 690 (C–Br); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta_H$  ppm: 2.48 (2H, s, CH<sub>2</sub>), 2.73 (3H, s, CH<sub>3</sub>), 4.40 (1H, s, OH), 8.28 (1H, s, NH), 7.10–7.85 (20H, m, Ar–H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_C$  ppm: 39.12, 39.35, 39.56 (CH<sub>2</sub>), 21.40, 21.55, 21.72, 21.86 (CH<sub>3</sub>), 161.62 (C=O), 109.24, 112.66, 114.80, 115.25, 118.42, 120.64, 121.48, 123.63, 125.94, 126.88, 128.41, 132.25, 133.58, 134.72, 135.93, 137.46, 139.18, 143.35, 144.42, 147.55, 150.36, 153.22, 155.27, 166.79, 170.52 (Ar). Anal. Calcd for C<sub>47</sub>H<sub>27</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,156.00): C, 48.83 %; H, 2.35 %; N, 12.12 %. Found C, 48.66 %, H, 2.16 %, N, 12.02 %.

### 2.7.4

Dye **7d** was synthesized using *m*-nitro anilino cyanurated *N*-phenyl-J-acid as coupling component. Yield 4.78 g (78.3 %). Dark red powder. M.p. >300 °C.  $R_f = 0.37$ . UV/Vis (DMF)  $\lambda_{\max}(\epsilon_{\max}) = 510$  nm (20,623.18 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,422 (O–H), 3,245 (N–H), 2,952, 2,855 (C–H), 1,670 (C=O),



**Table 1** Structures of *m*-nitro anilino cyanurated coupling components (6a–j)

<p>(6a)</p>	<p>(6f)</p>
4-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)amino-5-hydroxy naphthalene-2,7-disulfonic acid	6-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)(methyl)amino-4-hydroxynaphthalene-2-sulfonic acid
<p>(6b)</p>	<p>(6g)</p>
7-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)amino-4-hydroxy naphthalene-2-sulfonic acid	6-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)(phenyl)amino-4-hydroxynaphthalene-2-sulfonic acid
<p>(6c)</p>	<p>(6h)</p>
7-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)(methyl)amino-4-hydroxynaphthalene-2-sulfonic acid	6-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)(3-sulfonylphenyl)amino-4-hydroxynaphthalene-2-sulfonic acid
<p>(6d)</p>	<p>(6i)</p>
7-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)(phenyl)amino-4-hydroxynaphthalene-2-sulfonic acid	4-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)amino-5-hydroxynaphthalene-1,7-disulfonic acid
<p>(6e)</p>	<p>(6j)</p>
6-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)amino-4-hydroxynaphthalene-2-sulfonic acid	4-([4-chloro-6-(3-nitrophenyl)amino]-1,3,5-triazin-2-yl)amino-5-hydroxynaphthalene-1,3-disulfonic acid

Arrow indicate the coupling position



1,600 (C=N), 1,612 (N=N), 1,542, 1,350 (N=O), 1,382, 1,162 (S=O), 775 (C–Cl), 692 (C–Br);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.50 (2H, s, CH<sub>2</sub>), 4.34 (1H, s, OH), 8.32 (1H, s, NH), 7.15–7.86 (25H, m, Ar–H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.15, 39.42, 39.65 (CH<sub>2</sub>), 162.25 (C=O), 109.24, 112.26, 114.61, 115.59, 118.64, 119.54, 121.65, 122.58, 123.42, 125.74, 126.96, 128.72, 130.26, 133.66, 134.40, 136.24, 139.52, 143.63, 144.24, 146.65, 148.53, 154.13, 156.44, 166.21, 169.25 (Ar). Anal. Calcd for C<sub>52</sub>H<sub>29</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,218.07): C, 51.27 %; H, 2.40 %; N, 11.50 %. Found C, 51.11 %, H, 2.24 %, N, 11.34 %.

### 2.7.5

Dye **7e** was synthesized using *m*-nitro anilino cyanurated Gamma acid as coupling component. Yield 4.60 g (80.4 %). Dark yellow powder. M.p. >300 °C.  $R_f = 0.36$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) = 485 nm (16,128.56 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,482 (O–H), 3,255 (N–H), 2,932, 2,840 (C–H), 1,678 (C=O), 1,602 (C=N), 1,622 (N=N), 1,529, 1,350 (N=O), 1,384, 1,203 (S=O), 735 (C–Cl), 695 (C–Br);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.66 (2H, s, CH<sub>2</sub>), 4.32 (1H, s, OH), 8.24 (2H, s, NH), 7.19–7.78 (20H, m, Ar–H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.18, 39.39, 39.80 (CH<sub>2</sub>), 161.94 (C=O), 108.28, 111.20, 113.89, 114.93, 119.29, 122.16, 126.41, 126.85, 127.87, 128.33, 129.33, 131.10, 132.28, 133.58, 134.94, 139.64, 141.92, 142.34, 147.48, 157.66, 158.01, 165.04, 169.63 (Ar). Anal. Calcd for C<sub>46</sub>H<sub>25</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,141.98): C, 48.38 %; H, 2.21 %; N, 12.27 %. Found C, 48.23 %, H, 2.09 %, N, 12.12 %.

### 2.7.6

Dye **7f** was synthesized using *m*-nitro anilino cyanurated *N*-methyl-Gamma acid as coupling component. Yield 4.76 g (82.2 %). Light orange powder. M.p. >300 °C.  $R_f = 0.37$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) = 495 nm (20,517.21 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,456 (O–H), 3,266 (N–H), 2,950, 2,865 (C–H), 1,665 (C=O), 1,595 (C=N), 1,625 (N=N), 1,562, 1,355 (N=O), 1,375, 1,185 (S=O), 765 (C–Cl), 692 (C–Br);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.43 (2H, s, CH<sub>2</sub>), 2.78 (3H, s, CH<sub>3</sub>), 4.38 (1H, s, OH), 8.22 (1H, s, NH), 6.95–7.74 (20H, m, Ar–H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.15, 39.42, 39.65 (CH<sub>2</sub>), 21.35, 21.46, 21.60, 21.77 (CH<sub>3</sub>), 161.75 (C=O), 108.65, 111.68, 115.82, 116.20, 118.23, 120.77, 121.60, 123.20, 125.12, 126.34, 128.34, 131.45, 133.12, 134.26, 135.45, 137.76, 138.11, 142.43, 144.46, 147.51, 150.32, 153.12, 155.17, 166.54, 170.13 (Ar). Anal. Calcd for C<sub>47</sub>H<sub>27</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,156.00): C, 48.83 %; H, 2.35 %; N, 12.12 %. Found C, 48.70 %, H, 2.22 %, N, 12.05 %.

### 2.7.7

Dye **7g** was synthesized using *m*-nitro anilino cyanurated *N*-phenyl-Gamma acid as coupling component. Yield 5.22 g (85.5 %). Dark red powder. M.p. >300 °C.  $R_f = 0.38$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) = 508 nm (22,613.96 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,475 (O–H), 3,273 (N–H), 2,944, 2,852 (C–H), 1,668 (C=O), 1,596 (C=N), 1,620 (N=N), 1,572, 1,358 (N=O), 1,380, 1,178 (S=O), 770 (C–Cl), 695 (C–Br);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.52 (2H, s, CH<sub>2</sub>), 4.54 (1H, s, OH), 8.35 (1H, s, NH), 7.02–7.69 (25H, m, Ar–H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.12, 39.34, 39.60 (CH<sub>2</sub>), 161.88 (C=O), 109.11, 112.20, 113.33, 115.56, 118.72, 119.23, 121.22, 122.53, 123.12, 125.65, 127.16, 128.18, 130.78, 132.60, 135.12, 136.68, 139.92, 143.58, 144.06, 146.43, 148.35, 154.47, 157.41, 166.26, 169.17 (Ar). Anal. Calcd for C<sub>52</sub>H<sub>29</sub>O<sub>7</sub>N<sub>10</sub>SNaCl<sub>5</sub>Br (1,218.07): C, 51.27 %; H, 2.40 %; N, 11.50 %. Found C, 51.16 %, H, 2.28 %, N, 11.39 %.

### 2.7.8

Dye **7h** was synthesized using *m*-nitro anilino cyanurated *N*-(3-sulfophenyl)-Gamma acid as coupling component. Yield 5.76 g (87.1 %). Light purple powder. M.p. >300 °C.  $R_f = 0.40$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) = 518 nm (23,877.34 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (KBr)  $\nu$  cm<sup>-1</sup>: 3,436 (O–H), 3,270 (N–H), 2,942, 2,857 (C–H), 1,672 (C=O), 1,598 (C=N), 1,622 (N=N), 1,560, 1,340 (N=O), 1,384, 1,185 (S=O), 772 (C–Cl), 692 (C–Br);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.45 (2H, s, CH<sub>2</sub>), 4.37 (1H, s, OH), 8.26 (1H, s, NH), 7.05–7.73 (24H, m, Ar–H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.23, 39.45, 39.65 (CH<sub>2</sub>), 161.78 (C=O), 108.94, 110.82, 112.11, 114.22, 116.26, 118.33, 120.22, 123.76, 124.78, 126.23, 127.52, 129.61, 131.53, 133.55, 134.45, 135.23, 137.88, 139.76, 142.80, 145.12, 147.74, 150.12, 152.35, 156.67, 166.19, 169.40 (Ar). Anal.





Calcd for  $C_{52}H_{28}O_{10}N_{10}S_2Na_2Cl_5Br$  (1,320.12): C, 47.31 %; H, 2.14 %; N, 10.61 %. Found C, 47.18 %, H, 2.02 %, N, 10.48 %.

### 2.7.9

Dye **7i** was synthesized using *m*-nitro anilino cyanurated K acid as coupling component. Yield 4.91 g (78.9 %). Light yellow powder. M.p.  $>300^\circ\text{C}$ ;  $R_f = 0.38$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}} = 475 \text{ nm}$ ) ( $19,743.56 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). IR (KBr)  $\nu \text{ cm}^{-1}$ : 3,460 (O–H), 3,250 (N–H), 2,940, 2,856 (C–H), 1,670 (C=O), 1,597 (C=N), 1,618 (N=N), 1,564, 1,355 (N=O), 1,371, 1,165 (S=O), 755 (C–Cl), 690 (C–Br);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.51 (2H, s,  $\text{CH}_2$ ), 4.34 (1H, s, OH), 8.33 (2H, s, NH), 6.98–7.71 (19H, m, Ar–H).  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.17, 39.32, 39.50 ( $\text{CH}_2$ ), 161.70 (C=O), 109.19, 112.20, 114.24, 115.11, 118.16, 119.66, 121.17, 123.52, 125.45, 128.41, 130.65, 133.35, 134.67, 136.56, 139.75, 142.24, 144.76, 147.30, 148.27, 152.66, 155.25, 165.57, 169.82 (Ar). Anal. Calcd for  $C_{46}H_{24}O_{10}N_{10}S_2Na_2Cl_5Br$  (1,244.02): C, 44.41 %; H, 1.94 %; N, 11.26 %. Found C, 44.25 %, H, 1.86 %, N, 11.16 %.

### 2.7.10

Dye **7j** was synthesized using *m*-nitro anilino cyanurated Chicago acid as coupling component. Yield 5.15 g (82.7 %). Light yellow powder. M.p.  $>300^\circ\text{C}$ ;  $R_f = 0.36$ . UV/Vis (DMF)  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}} = 465 \text{ nm}$ ) ( $19,555.67 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). IR (KBr)  $\nu \text{ cm}^{-1}$ : 3,474 (O–H), 3,248 (N–H), 2,955, 2,852 (C–H), 1,671 (C=O), 1,600 (C=N), 1,615 (N=N), 1,555, 1,347 (N=O), 1,382, 1,180 (S=O), 762 (C–Cl), 694 (C–Br);  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  ppm: 2.42 (2H, s,  $\text{CH}_2$ ), 4.44 (1H, s, OH), 8.26 (2H, s, NH), 7.03–7.76 (19H, m, Ar–H).  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$  ppm: 39.26, 39.46, 39.71 ( $\text{CH}_2$ ), 161.81 (C=O), 108.68, 111.96, 113.47, 115.11, 118.68, 119.91, 121.28, 123.13, 125.56, 128.57, 130.62, 132.76, 134.87, 136.69, 139.27, 142.54, 144.64, 147.75, 148.38, 152.56, 155.52, 165.45, 169.78 (Ar). Anal. Calcd for  $C_{46}H_{24}O_{10}N_{10}S_2Na_2Cl_5Br$  (1,244.02): C, 44.41 %; H, 1.94 %; N, 11.26 %, found C, 44.29 %, H, 1.85 %, N, 11.15 %.

## 2.8 Pharmacological Screening

The entire reactive dyes (**7a–j**) were tested for their antibacterial as well as antifungal screening (in vitro) by broth dilution method [27] with two Gram-positive bacteria (*Staphylococcus aureus* MTCC 96, *Staphylococcus pyogenes* MTCC 442) and two Gram-negative bacteria (*Escherichia coli* MTCC 443, *Pseudomonas aeruginosa* MTCC 1688) and fungi *Candida albicans* MTCC 227, *Aspergillus niger* MTCC 282 and *Aspergillus clavatus* MTCC 1323 organism taking gentamycin, ampicillin, chloramphenicol, nystatin and greseofulvin as standard drugs. The activity was presented as minimal inhibitory concentration (MIC) and compared with the activity of 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. The MIC values were determined after incubation at  $37^\circ\text{C}$  for 18–24 h.

## 2.9 Dyeing of Fibres

The reactive dye samples were applied on silk, wool and cotton fibres at 2 % (owf) depth according to following batchwise exhaust dyeing procedure which gives yellow to purple hues with good depth and levelness. The variety in hues depends on the coupling components used, i.e. when using H-acid as coupling component, it gives purple hue, J-acid and Gamma acid gives yellow hue, *N*-methyl-J-acid and *N*-methyl-Gamma acid gives orange hue, while *N*-phenyl-J-acid and *N*-phenyl-Gamma acid gives red hue.

### 2.9.1 Pretreatment of Fibres

The fibres (silk, wool and cotton) were soaped with a solution of 2 g/L Lissapol detergent at  $100^\circ\text{C}$  for 15 min and then washed thoroughly with cold water to completely remove the adhered detergent and unwanted impurities such as wax, oil, starch, resin and coloring matter.



### 2.9.2 Dyeing of Silk Fibres

The dye (40 mg) was dissolved by pasting up in cold water and then addition of hot water and stirred well to give a clear solution. The pH of the dye bath was adjusted to 3.0 by adding acetic acid solution (2.0 mL, 10 % v/v) and the silk fabric (2 g) was introduced into the dye liquor with stirring and the total volume was adjusted to 80 mL by adding required amount of distilled water. The temperature of the dyebath was gradually increased to 85 °C over a period of 10 min. At this temperature formic acid (1.5 mL, 40 % v/v) was added to the dye bath to achieve good exhaustion. The dyeing was continued for 60 min more. The dyed fibres were then removed from the dyebath and washed with cold water (500 mL) for several times.

### 2.9.3 Dyeing of Wool Fibres

The dye (40 mg) was dissolved by pasting up in cold water and then addition of hot water. Anhydrous Glauber's salt solution (1.5 mL, 10 % w/v) was added to it. The pH of the dye bath was adjusted to 5.5 by adding acetic acid solution (1.5 mL, 10 % v/v) and 1 g/L Albigal B was added as amphoteric surfactant. The total volume was adjusted to 80 mL by adding required amount of distilled water. The temperature of the dyebath was raised to 50 °C and the wool fabric (2 g) was introduced into the dye liquor with stirring. The temperature of the dyebath was gradually increased to 80 °C over a period of 30 min and this temperature was maintained for another 60 min. The dyed fibres were then removed and washed with cold water (500 mL) for several times.

### 2.9.4 Dyeing of Cotton Fibres

The dye (40 mg) was dissolved by pasting up in cold water and then addition of hot water. Anhydrous Glauber's salt solution (1.0 mL, 10 % w/v) and sodium chloride (0.5 g) were added. Cotton fibres (2 g) were then introduced in to the dyebath. The total volume of the dyebath was adjusted to 80 mL by adding required amount of distilled water. The temperature of the dyebath was gradually increased to 80 °C over a period of 30 min and at this temperature the pH of the dyebath was adjusted to 11.0 by adding soda ash solution (1.0 mL, 2 % w/v) to bring about fixation. Dyeing was continued for further 60 min at 80 °C temperature. After that the dyed fibres were removed from the dyebath.

### 2.9.5 Wash-Off Process

The dyed fabrics (silk, wool and cotton) were first rinsed in warm water, scoured with 2 g/L Lissapol detergent at 100 °C for 15 min and rinsed again in warm water. After washing the dyed fibres were rinsed with cold water and then dried in dryer. The dyed fabrics afforded color in the first warm water rinse, less color in the scouring bath and practically no color in the second water rinse. This indicated that the unfixed dyes were easily removed from the fibres' surface. The amount of the hydrolyzed dye having low substantivity released easily from the substrate after two or three washes.

## 3 Results and Discussion

### 3.1 Spectral Characteristics

IR spectra [28] of reactive dyes **7a–j** showed broad band within the range 3,410–3,482  $\text{cm}^{-1}$  confirming the presence of corresponding hydroxyl group. The spectra also showed medium band located at 3,245–3,298  $\text{cm}^{-1}$  which predicted N–H stretching vibration of imino group. The carbonyl stretching vibration of intermediate **2** predicted sharp peak at 1,755  $\text{cm}^{-1}$  while the intermediate **3** and the entire dyes (**7a–j**) showed carbonyl stretching vibration in the range 1,665–1,678  $\text{cm}^{-1}$  which confirmed the conversion of  $\delta$ -lactone to  $\delta$ -lactam ring and also prove the presence of amide linkage. The quinazolinone moiety was confirmed by the stretching vibration of C=N band at 1,594–1,602  $\text{cm}^{-1}$ . The azo group showed absorption band in the region 1,610–1,625  $\text{cm}^{-1}$ . Two strong bands at 1,529–1,572  $\text{cm}^{-1}$  and 1,338–1,360  $\text{cm}^{-1}$  showed asymmetric and symmetric stretching vibrations of nitro group. The sulfonic acid group (sodium salt) was confirmed by the presence of asymmetric and symmetric bands at 1,370–1,385  $\text{cm}^{-1}$  and 1,162–1,203  $\text{cm}^{-1}$ , respectively. Chloro and bromo groups were confirmed by the presence of strong bands at 735–770  $\text{cm}^{-1}$  and 690–695  $\text{cm}^{-1}$ .



**Table 2** Solvent effect, acid and base effect on absorption maxima of reactive dyes **7a–j**

Dye no.	DMSO <sup>a</sup> (46.7) <sup>b</sup> (nm)	DMF <sup>a</sup> (36.7) <sup>b</sup> (nm)	Methanol <sup>a</sup> (32.7) <sup>b</sup> (nm)	Acetic acid <sup>a</sup> (06.2) <sup>b</sup> (nm)	Chloroform <sup>a</sup> (04.8) <sup>b</sup> (nm)	DMSO + piperidine (nm)	DMF + piperidine (nm)	Methanol + 0.1 M KOH (nm)	Methanol + 0.1 M HCl (nm)
<b>7a</b>	540	530	480	495	500	560	554	520	485
<b>7b</b>	485	480	452	465	472	492	498	498	460
<b>7c</b>	505	498	458	468	478	520	510	478	464
<b>7d</b>	522	515	475	486	495	534	530	495	480
<b>7e</b>	492	485	440	458	468	495	487	472	442
<b>7f</b>	505	495	443	452	469	515	501	480	450
<b>7g</b>	516	508	468	481	495	522	512	495	475
<b>7h</b>	530	518	470	484	498	538	525	498	478
<b>7i</b>	488	475	448	456	465	498	486	482	455
<b>7j</b>	476	465	432	442	457	480	470	465	446

<sup>a</sup> Solvent used as received (dilution of the solvents were  $10^{-6}$  to  $10^{-8}$  M for solvatochromism)

<sup>b</sup> Dielectric constant

The  $^1\text{H}$  NMR [29] spectra of dyes **7a–j** showed signal at 2.39–2.66 $\delta$  ppm confirmed the presence of methylene proton. Hydroxyl proton showed signal at 4.32–4.54 $\delta$  ppm for all dyes. Dyes **7c** and **7f** showed signals at 2.73 $\delta$  ppm and 2.78 $\delta$  ppm, respectively, due to the methyl proton. The imino group showed signal at 8.22–8.35 $\delta$  ppm for all dyes. The aromatic proton showed signals at 6.89–7.86 $\delta$  ppm as multiplet.

The  $^{13}\text{C}$  NMR [29] spectra of dyes **7a–j** showed signal at 39.12–39.80 $\delta$  ppm due to the presence of methylene carbon. The carbonyl carbon showed signal in the region 161.62–162.38 $\delta$  ppm for all dyes. Dyes **7c** and **7f** showed signal at 21.35–21.86 $\delta$  ppm due to the N–CH<sub>3</sub> carbon. The aromatic carbon of dyes **7a–j** showed signal at 108.28–170.52 $\delta$  ppm.

### 3.2 Solvatochromic Effect

Solvatochromism is observed in many dyes due to the different solvation of the ground state and the first excited state of the light absorbing molecule. On increasing solvent polarity, the ground state molecule stabilizes better by solvation than the excited state molecule, this effect is called blue shift or negative solvatochromism or hypsochromic shift, while on increasing solvent polarity, dye molecule stability increases in excited state rather than ground state, this effect is called red shift or positive solvatochromism or bathochromic shift.

To study the solvent effect on the dyes, absorption spectra of synthesized dyes (**7a–j**) were recorded in various solvents such as DMSO, DMF, methanol, acetic acid and chloroform and the results are summarized in Table 2. The absorption spectra of all the dyes did not correlate with the solvent polarity. The choice of solvents was based on their polarity.

From the data summarized in Table 2, it is apparent that the entire dyes showed bathochromic shift in  $\lambda_{\text{max}}$  for the dye solution in DMSO and DMF with respect to dye solution in chloroform (Figs. 2, 3). This is due to the interaction of H-atom of the imino group with the basic solvent such as DMSO and DMF where the solvent polarity increases in the excited state. Hypsochromic shift was observed in the  $\lambda_{\text{max}}$  for the dye solution in acetic acid and methanol with respect to dye solution in chloroform (Figs. 2, 3).

A positive solvatochromism is observed between chloroform–DMF–DMSO, while negative solvatochromism is observed between chloroform–acetic acid–methanol solvent systems.

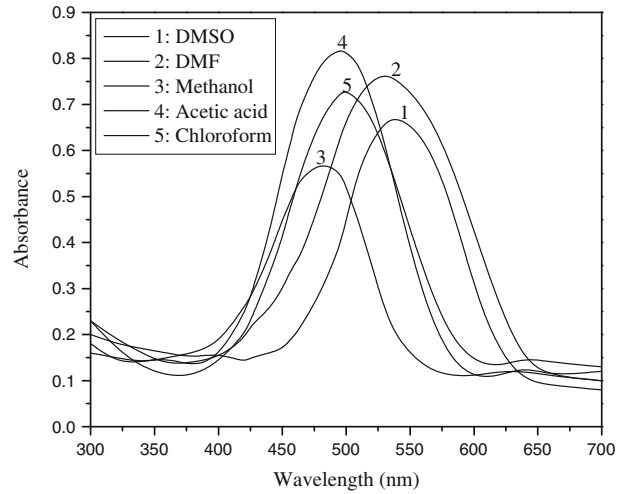
### 3.3 Acid and Base Effect on UV–Vis Spectra

The acid or base effect on the absorption spectra was also examined and the results are shown in Table 2.

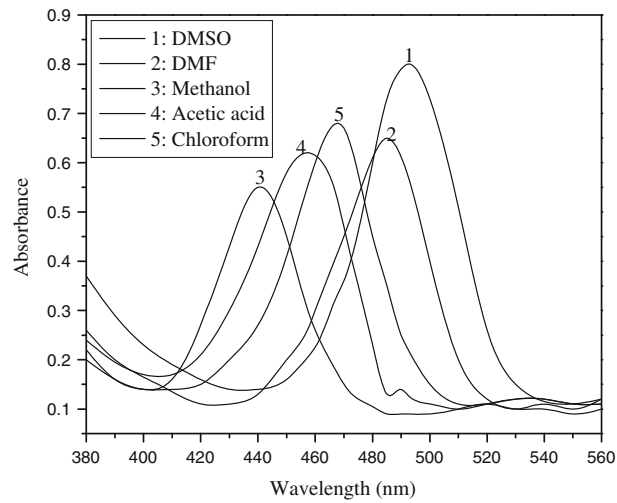
It was observed that, when piperidine was added to the dye solution in DMSO, the entire dyes showed bathochromic shift. Dyes **7a**, **7c**, **7d**, **7f** and **7i** showed large bathochromic shift, while the rest showed minor bathochromic shift. Similarly, bathochromic shift was observed for all these dyes in DMF solvent by the addition of piperidine (Fig. 4).

When KOH solution was added to the dye solution in methanol, a large bathochromic shift was observed. These results showed good sensitivity of all dyes towards the addition of KOH to the dye solution in methanol. Similarly, when HCl solution was added to dyes solution in methanol, slight bathochromic shift was observed (Fig. 5).

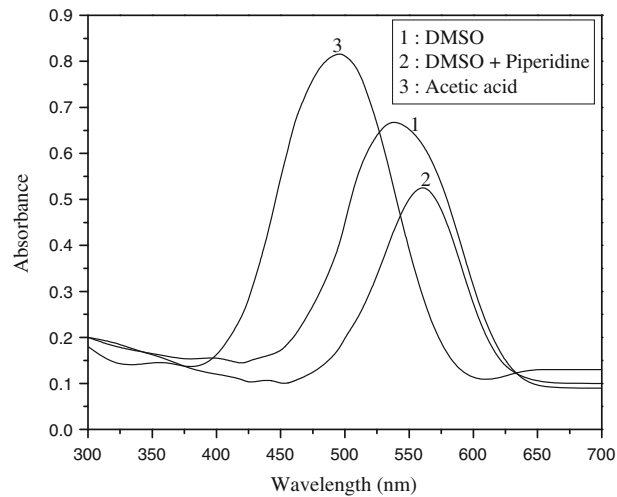




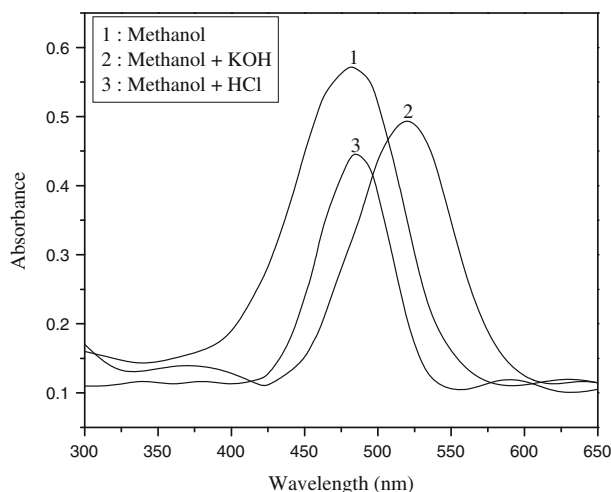
**Fig. 2** Absorption spectra of dye **7a** in various solvents



**Fig. 3** Absorption spectra of dye **7e** in various solvents



**Fig. 4** Absorption spectra of dye **7a** in acidic and basic solution



**Fig. 5** Absorption spectra of dye **7a** in acidic and basic solution

### 3.4 Substituent Effect

Absorption maxima ( $\lambda_{\max}$ ) of all these dyes **7a–j** were recorded in DMF solution ( $10^{-6}$  M). The introduction of electron donating and attracting groups at suitable positions in the coupler ring affects the absorption characteristic of the synthesized dyes. The maximum value of molar extinction coefficient ( $\epsilon_{\max}$ ) was calculated by Lambert–Beer's law (Eq. 1). Dye **7a** showed maximum value of  $\epsilon_{\max}$ .

$$A = \epsilon cl, \quad (1)$$

where  $A$  is the absorbance or optical density,  $\epsilon$  the molar absorptivity,  $c$  the concentration of the solution and  $l$  is the thickness of the absorbing layer.

The introduction of methyl group in dye **7c** ( $\lambda_{\max} = 498$  nm) resulted in bathochromic effect (red shift) and shifts the absorption maxima to longer wavelength relative to dye **7b** ( $\lambda_{\max} = 480$  nm). Similar effect was observed in the case of dye **7d** ( $\lambda_{\max} = 510$  nm). The introduction of phenyl ring in dye **7d** produced bathochromic effect and shifting of  $\lambda_{\max}$  to higher wavelength ( $\lambda_{\max} = 515$  nm) relative to dye **7b** ( $\lambda_{\max} = 480$  nm) and **7c** ( $\lambda_{\max} = 498$  nm). Similar results were observed in the case of dye **7e** ( $\lambda_{\max} = 485$  nm), **7f** ( $\lambda_{\max} = 495$  nm) and **7g** ( $\lambda_{\max} = 508$  nm) by the introduction of methyl group and phenyl group in gamma acid. The introduction of 3-sulfophenyl group to the gamma acid showed large bathochromic shift in dye **7h** ( $\lambda_{\max} = 518$  nm) as compared to dye **7e** ( $\lambda_{\max} = 485$  nm). Dye **7a** ( $\lambda_{\max} = 530$  nm) showed higher value of  $\lambda_{\max}$  as compared with dyes **7i** ( $\lambda_{\max} = 475$  nm) and **7j** ( $\lambda_{\max} = 465$  nm) due to the planar structure of dye, which accelerate the oscillation of electron in dye **7a**.

### 3.5 Pharmacological Screening

#### 3.5.1 Antibacterial Assay

Dyes **7d**, **7g** and **7h** showed equipotential activity against *E. coli*, dyes **7c** and **7g** showed equipotential activity against *P. aeruginosa*, dyes **7e** and **7h** showed fairly good activity against *S. aureus*, while dyes **7a** and **7b** showed equipotential activity against *S. aureus* with respect to standard drug Ampicillin. The remaining dyes displayed weak activity against all microbes under investigation. The antibacterial activity data are summarized in Table 3.

#### 3.5.2 Antifungal Assay

Dyes **7c** and **7h** showed equipotential activity against *C. albicans* with respect to standard drug Nystain and dyes **7a**, **7d**, **7e** and **7g** showed very good activity against *C. albicans*, while dye **7b** showed equipotential activity against *C. albicans* with respect to standard drug Griseofulvin. The antifungal activity data are summarized in Table 3.



**Table 3** Antimicrobial screening of reactive dyes **7a–j**

Dye no.	Minimal bactericidal concentration ( $\mu\text{g/mL}$ )				Minimal fungicidal concentration ( $\mu\text{g/mL}$ )		
	Gram-negative		Gram-positive		<i>C. albicans</i> MTCC 227	<i>A. niger</i> MTCC 282	<i>A. clavatus</i> MTCC 1323
	<i>E. coli</i> MTCC443	<i>P. aeruginosa</i> MTCC 1688	<i>S. aureus</i> MTCC 96	<i>S. pyogenes</i> MTCC 442			
<b>7a</b>	200	500	<b>250</b>	200	<b>200</b>	500	500
<b>7b</b>	500	500	<b>250</b>	500	<b>500</b>	1,000	1,000
<b>7c</b>	250	<b>100</b>	500	1,000	<b>100</b>	250	250
<b>7d</b>	<b>100</b>	500	500	1,000	<b>200</b>	500	500
<b>7e</b>	500	500	<b>200</b>	200	<b>200</b>	500	500
<b>7f</b>	200	500	500	500	1,000	>1,000	>1,000
<b>7g</b>	<b>100</b>	<b>100</b>	500	1,000	<b>200</b>	500	500
<b>7h</b>	<b>100</b>	200	<b>200</b>	200	<b>100</b>	250	250
<b>7i</b>	500	200	1,000	1,000	1,000	>1,000	>1,000
<b>7j</b>	500	1,000	500	1,000	1,000	>1,000	500
Gentamycin	0.05	1	0.25	0.5	–	–	–
Ampicillin	100	100	250	100	–	–	–
Chloramphenicol	50	50	50	50	–	–	–
Nystatin	–	–	–	–	100	100	100
Greseofulvin	–	–	–	–	500	100	100

Values in bold show significant activity

*E. coli* *Escherichia coli*, *P. aeruginosa* *Pseudomonas aeruginosa*, *S. aureus* *Streptococcus aureus*, *S. pyogenes* *Streptococcus pyogenes*, *C. albicans* *Candida albicans*, *A. niger* *Aspergillus niger*, *A. clavatus* *Aspergillus clavatus*, MTCC microbial type cultural collection

The results demonstrated that certain dyes are able to reduce the growth of microorganism very effectively in the case of *E. Coli* and *C. Albicans* against standard drug Ampicillin and Nystatin. Selected dyes would therefore be important for the dyeing of sheets and gowns for hospital use.

### 3.6 Color Measurement (CIELab)

The color on silk, wool and cotton fibres are expressed in terms of CIELab ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $H^*$ ,  $K/S$ ) values and the following CIELab coordinates were measured to determined the color properties of the dyed fabrics.

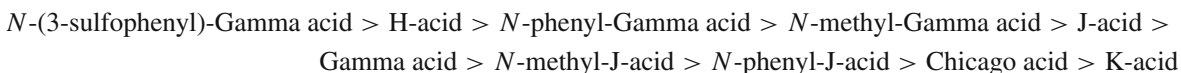
$L^*$  represents the degree of lightness (positive) and darkness (negative), chroma  $C^*$  represents the degree of brightness (positive) and dullness (negative),  $a^*$  represents the degree of redness (positive) and greenness (negative),  $b^*$  represents the degree of yellowness (positive) and blueness (negative) and H represents the hue angle from  $0^\circ$  to  $360^\circ$ . A reflectance spectrophotometer was used for the colorimetric measurements of the dyed fibres.  $K/S$  value (color strength) given by the reflectance spectrophotometer is calculated at  $\lambda_{\text{max}}$  and is directly correlated with the dye concentration on the substrate according to the Kubelka–Munk equation [30,31] (Eq. 2):

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

where  $K$  is the absorbance coefficient,  $S$  the scattering coefficient and  $R$  is the reflectance ratio.

The color coordinates (Table 4) indicate that these dyes have good affinity towards all fibres. The data summarized for silk fibres in Table 4 showed that on going from compound **7b** to **7d**, the compound became more lighter, greener, bluer, duller and decreasing value of color strength while on going from compound **7e** to **7g** the opposite results were obtained, i.e. the compound became darker, greener, yellower, duller and increasing value of  $K/S$ . On comparing compounds **7e** and **7h**, compound **7h** becomes lighter, greener, yellower, brighter and increasing value of  $K/S$  than dye **7e** and on comparing compounds **7a**, **7i** and **7j**, compounds **7i** and **7j** became more darker, greener, bluer, duller and decreasing value of  $K/S$  than dye **7a**.

The decreasing order of  $K/S$  value for silk fibres in terms of coupling component was found to be:



For wool fibres, on going from compound **7b** to **7d**, the compound became more darker, redder, bluer, duller and increasing value of color strength ( $K/S$ ), while on going from compound **7e** to **7g** the compound became

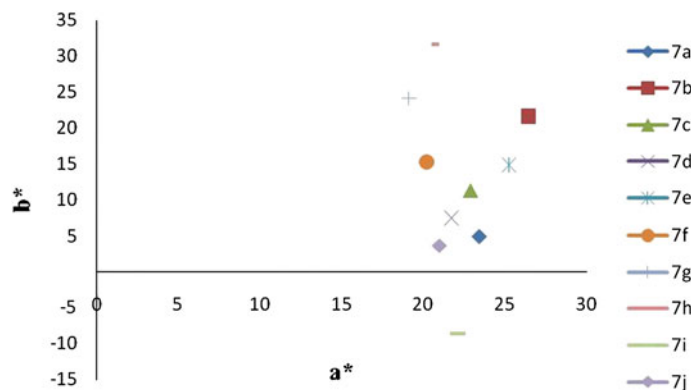


**Table 4** Color measurement (CIELab) of reactive dyes **7a–j** on silk, wool and cotton fibres

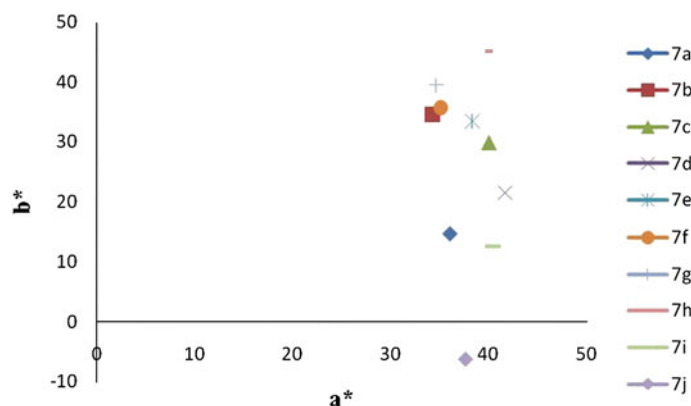
Dye no.	$L^*$			$a^*$			$b^*$			$C^*$			$H^*$			$K/S$		
	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C
<b>7a</b>	66.85	42.88	42.93	23.45	36.05	42.56	04.96	14.76	10.14	23.97	38.96	43.75	11.94	22.26	13.40	03.97	06.99	08.07
<b>7b</b>	68.50	58.26	67.59	26.44	34.31	30.24	21.58	34.58	24.62	34.13	48.72	38.99	39.22	45.22	39.15	01.45	04.48	01.66
<b>7c</b>	70.87	52.72	62.71	22.89	40.07	35.01	11.26	29.84	22.62	25.51	47.96	41.68	26.20	36.68	32.87	00.77	06.23	02.42
<b>7d</b>	71.83	33.01	42.06	21.74	41.71	45.59	07.54	21.48	20.28	23.01	46.91	49.90	19.13	27.25	23.98	00.71	21.14	11.16
<b>7e</b>	68.73	51.53	62.71	25.26	38.34	31.36	14.82	33.46	32.28	25.22	50.89	45.01	30.40	41.11	45.83	01.07	06.62	03.06
<b>7f</b>	64.15	55.15	65.14	20.22	35.12	29.85	15.22	35.67	30.46	22.74	51.34	39.39	34.24	45.78	47.15	01.55	07.22	01.58
<b>7g</b>	60.85	60.34	66.64	19.15	34.67	28.58	24.10	39.46	28.87	18.47	54.32	37.41	41.22	46.82	48.60	01.75	07.45	02.56
<b>7h</b>	72.15	62.26	68.16	20.55	39.68	33.48	31.62	45.15	34.76	31.36	55.16	45.58	40.59	48.47	51.10	05.35	10.24	04.95
<b>7i</b>	55.92	42.30	50.15	22.14	40.45	39.11	-8.66	12.55	25.70	22.12	39.18	37.50	352.55	34.40	36.40	00.56	03.46	01.09
<b>7j</b>	56.38	41.82	52.09	20.98	37.65	36.33	3.65	-6.25	26.44	20.21	41.55	33.54	32.48	328.67	31.65	00.69	02.27	01.18

S silk, W wool, C cotton





**Fig. 6** Chromaticity graph of  $b^*$  versus  $a^*$  for silk fibre



**Fig. 7** Chromaticity graph of  $b^*$  versus  $a^*$  for wool fibre

more lighter, greener, yellower, brighter and increasing value of  $K/S$ . On comparing compounds **7e** and **7h**, compound **7h** becomes more lighter, redder, yellower, brighter and increasing value of  $K/S$  than dye **7e** and on comparing compounds **7a**, **7i** and **7j**, compounds **7i** and **7j** became more darker, redder, bluer, brighter and decreasing value of  $K/S$  than dye **7a**.

The decreasing order of  $K/S$  value for wool fibres in terms of coupling component was found to be:

*N*-phenyl-J-acid > *N*-(3-sulfophenyl)-Gamma acid > *N*-phenyl-Gamma acid > *N*-methyl-Gamma acid > H-acid > Gamma acid > *N*-methyl-J-acid > *N*-phenyl-J-acid > K-acid > @ Chicago acid

And for cotton fibres, on going from compound **7b** to **7d**, the compound became more darker, redder, bluer, brighter and increasing value of color strength ( $K/S$ ), while on going from compound **7e** to **7g**, the compound became more lighter, greener, bluer, duller and increasing value of  $K/S$ . On comparing compounds **7e** and **7h**, compound **7h** becomes more lighter, redder, yellower, brighter and increasing value of  $K/S$  than dye **7e** and on comparing compounds **7a**, **7i** and **7j**, compounds **7i** and **7j** became more lighter, greener, yellower, duller and decreasing value of  $K/S$  than dye **7a**.

The decreasing order of  $K/S$  value for cotton fibres in terms of coupling component was found to be:

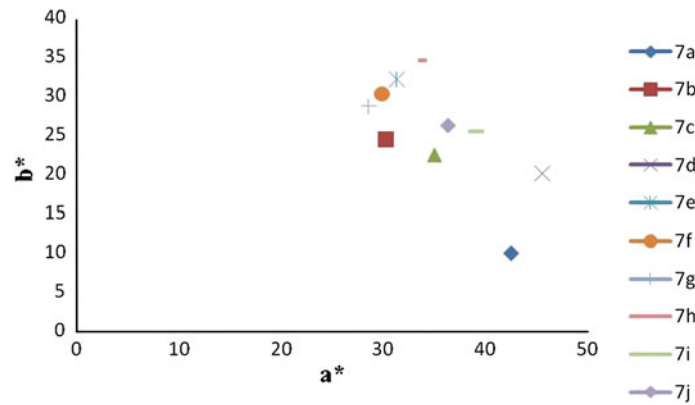
*N*-phenyl-J-acid > H-acid > *N*-(3-sulfophenyl)-Gamma acid > Gamma acid > *N*-phenyl-Gamma acid > *N*-methyl-J-acid > J-acid > *N*-methyl-Gamma acid > Chicago acid > K-acid

The color strength values ( $K/S$ ) seem to be higher on wool in comparison to silk and cotton fibres. This is probably due to the high substantivity of these dyes on wool fibres.

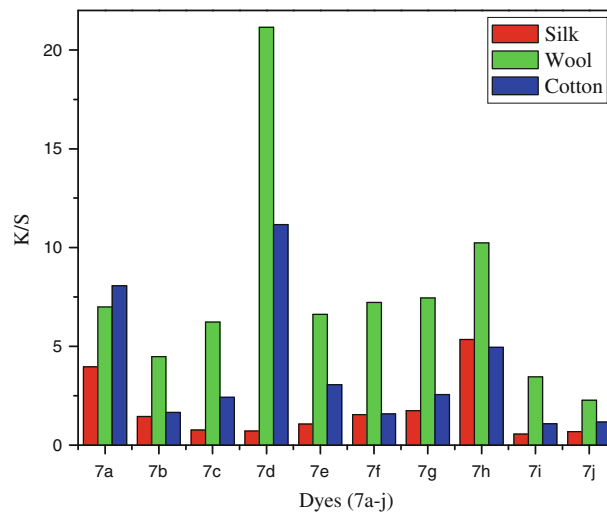
Chromaticity graph of  $b^*$  versus  $a^*$  for silk, wool and cotton fibres is shown in Figs. 6, 7 and 8, respectively, and  $K/S$  graph of dyes **7a–j** for silk, wool and cotton fibres is shown in Fig. 9.







**Fig. 8** Chromaticity graph of  $b^*$  versus  $a^*$  for cotton fibre



**Fig. 9**  $K/S$  value of reactive dyes **7a–j** on silk, wool and cotton fibres

### 3.7 Exhaustion and Fixation Study

The percentage dyebath exhaustion ( $\%E$ ) and fixation ( $\%F$ ) of the dyed fabric were determined according to known method [32] and are shown in Table 5.

Exhaustion means proportion of dye taken up by the fibres at any stage of the process relative to the amount originally available. The percentage dyebath exhaustion of 2 % (owf) dyeing on silk fabric ranges from 85.75 to 90.28 %, in which dye **7a** shows maximum exhaustion (90.28 %) while dye **7e** shows minimum exhaustion (85.75 %). For wool fabric the percentage dyebath exhaustion ranges from 86.15 to 91.28 %, in which dye **7d** shows maximum exhaustion (91.28 %), while dye **7a** shows minimum exhaustion (86.15 %). And finally the percentage dyebath exhaustion for cotton fabric ranges from 85.95 to 90.12 %, in which dye **7h** shows maximum exhaustion (90.12 %), while dye **7i** shows minimum exhaustion (85.95 %).

Fixation means proportion of dye remaining on the fibres at the end of the process relative to the amount originally available. The percentage dyebath fixation of 2 % (owf) dyeing on silk fabric ranges from 74.14 to 78.65 %, in which dye **7h** shows maximum fixation value (78.65 %), while dye **7j** shows minimum fixation value (74.14 %). For wool fabric percentage fixation ranges from 76.35 to 80.95 %, in which dye **7e** shows maximum fixation value (80.95 %), while dye **7i** shows minimum fixation value (76.35 %). And for cotton fabric, the percentage fixation ranges from 74.03 to 79.90 %, in which dye **7a** shows maximum fixation value (79.90 %), while dye **7e** shows minimum fixation value (74.03 %).

The data summarized in Table 5 showed that the dyebath exhaustion and fixation value on different fabrics were very good which indicate that these dyes have good compatibility with the fabric. The exhaustion value depends on the structure of fibres. Here, exhaustion is very good which is due to the fact that the diffusion rate

**Table 5** %Exhaustion, %fixation and fastness properties data of reactive dyes 7a-j

Dye no.	Exhaustion <sup>a</sup> (%)			Fixation <sup>b</sup> (%)			Relative fixation <sup>c</sup> (%)			Light fastness			Wash fastness			Dry			Wet			
	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	
7a	90.28	86.15	89.75	75.47	77.95	79.90	83.60	90.48	89.03	4-5	6	5	5	5	4-5	5	4-5	5	4-5	5	4-5	5
7b	88.83	88.60	87.00	76.56	80.70	79.31	86.19	91.08	91.16	5	5-6	4-5	4-5	4	4-5	3-4	4	4-5	4	4	4-5	4
7c	87.93	87.25	89.62	75.63	79.66	78.00	86.01	91.30	87.03	4-5	5	5	4	4	4	4	3-4	4	3-4	4	3-4	4
7d	86.13	91.28	88.37	78.60	78.35	74.98	91.26	85.83	84.85	4	4-5	5-6	3-4	3-4	4	3	4	4	3	4	3	3-4
7e	85.75	86.80	87.13	75.80	80.95	74.03	88.40	93.26	84.96	3-4	3-4	3-4	4-5	3	3	4	3	3-4	4	3	3-4	3-4
7f	86.12	88.10	86.11	74.85	79.12	75.68	86.91	89.80	87.89	4	5-6	5-6	4-5	5	4	3-4	4-5	5	4	4	4	4-5
7g	88.65	87.26	88.78	76.67	79.85	76.35	86.49	91.51	86.00	4-5	5	4-5	4-5	4	4-5	4	4-5	4	4-5	4	4-5	5
7h	89.62	89.27	90.12	78.65	78.13	78.98	87.76	87.52	87.64	6	5	4-5	3-4	4	3-4	5	3-4	5	3	3-4	5	4-5
7i	86.68	86.59	85.95	75.15	76.35	76.12	86.70	88.17	88.56	4-5	4-5	5-6	3	3-4	3-4	3-4	4	3-4	3-4	4	3-4	3-4
7j	86.79	87.55	86.10	74.14	77.95	74.36	85.42	89.03	86.36	3-4	3	3-4	4-5	3	3	3	3-4	4	3-4	3	3-4	3-4

S silk, W wool, C cotton; light fastness 1 poor, 2 slight, 3 moderate, 4 fair, 5 good, 6-very good; Wash and rubbing fastness: 1 poor, 2 fair, 3 good, 4 very good, 5 excellent

<sup>a</sup> Exhaustion: portion of the dye absorbed on fibres during dyeing process

<sup>b</sup> Fixation: portion of the dye forming covalent bond with fibres;

<sup>c</sup> Relative fixation value: fixation value/exhaustion value



of the dye molecule within the fabric is higher, which accelerates the absorption rate of the dye molecule to the fabric. The introduction of *s*-triazine group to the dye molecule increases the substantivity which improves the exhaustion and fixation value. Higher substantivity means a greater proportion of the reactive dye absorbs on the fibres, making it more likely that the dye will react with the fibres rather than with the water, so that the process of fixation will become more efficient.

### 3.8 Relationship Between Coupling Component and Dyeing Properties

On the basis of dyeing procedure for silk, wool and cotton fibres, the relationship between coupling components and dyeing properties were determined by the relative fixation value (Table 5).

For silk fibres, dye **7d** having *N*-phenyl-J-acid as coupling component possesses higher relative fixation value (91.26) than other dyes. For wool fibres, dye **7e** having Gamma acid as coupling component possesses higher relative fixation value (93.26) than other dyes and for cotton fibres, dye **7b** having J-acid as coupling component possesses higher relative fixation value (91.16) than other dyes.

### 3.9 Fastness Properties

These are the properties which indicate the tolerance of the dyes on silk, wool and cotton fibres towards the action of light, washing and rubbing. The fastness to light was assessed in accordance with BS: 1006-1978 [33]. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961 [34] and the wash fastness test in accordance with IS: 765-1979 [35]. Fastness properties data of dyes **7a–j** are summarized in Table 5.

The entire dyes showed generally moderate to very good (rating 3–6 on gray scale) light fastness property and good to excellent (rating 3–5 on gray scale) washing and rubbing fastness properties on silk, wool and cotton fibres. This is attributed to good penetration and affinity of these dyes to the fibres. The good light fastness may be due to the conversion of these dyes into the fibres from a disperse state to a crystalline state.

### 3.10 Thermogravimetric Analysis

Thermal decomposition is carried out under inert atmosphere in order to investigate their thermal stability and the measurement of change in weight as a function of the temperature. Thermogravimetric curves obtained at a heating rate of 10 °C/min in nitrogen (30 mL/min) atmosphere. Thermogravimetric analysis curve of dyes **7a** and **7f** is shown in Figs. 10 and 11, respectively, and the data are given in Table 6.

On the basis of initial decomposition temperature 150 °C, thermal stabilities of the reactive dyes are as follows



All reactive dyes (**7a–j**) start their initial degradation at around 150 °C and weight loss of about 1.60–4.04 % was observed and at 450 °C temperature, the weight loss was observed in the range 7.89–11.25 %. The degradation rate increased rapidly between 750 and 900 °C and the weight loss of about 20.01–33.89 % was observed hence 66–70 % weight of material left undecomposed after analysis at the maximum temperature of 900 °C. These results demonstrate that the dyes (**7a–j**) showed good thermal stability and particularly dye **7h** showed highest thermal stability at initial (150 °C) temperature. Dyes having 3-sulfophenyl group at the imino nitrogen atom of coupler ring are responsible for its highest thermal stability at initial temperature.

## 4 Conclusion

In this study, ten new bromo-quinazolinone-based monochloro-*s*-triazine reactive dyes were synthesized by classical method of diazotization-coupling. The synthesized dyes were confirmed by spectral and elemental analyses. The synthesized dyes showed generally moderate to very good light fastness property and good to



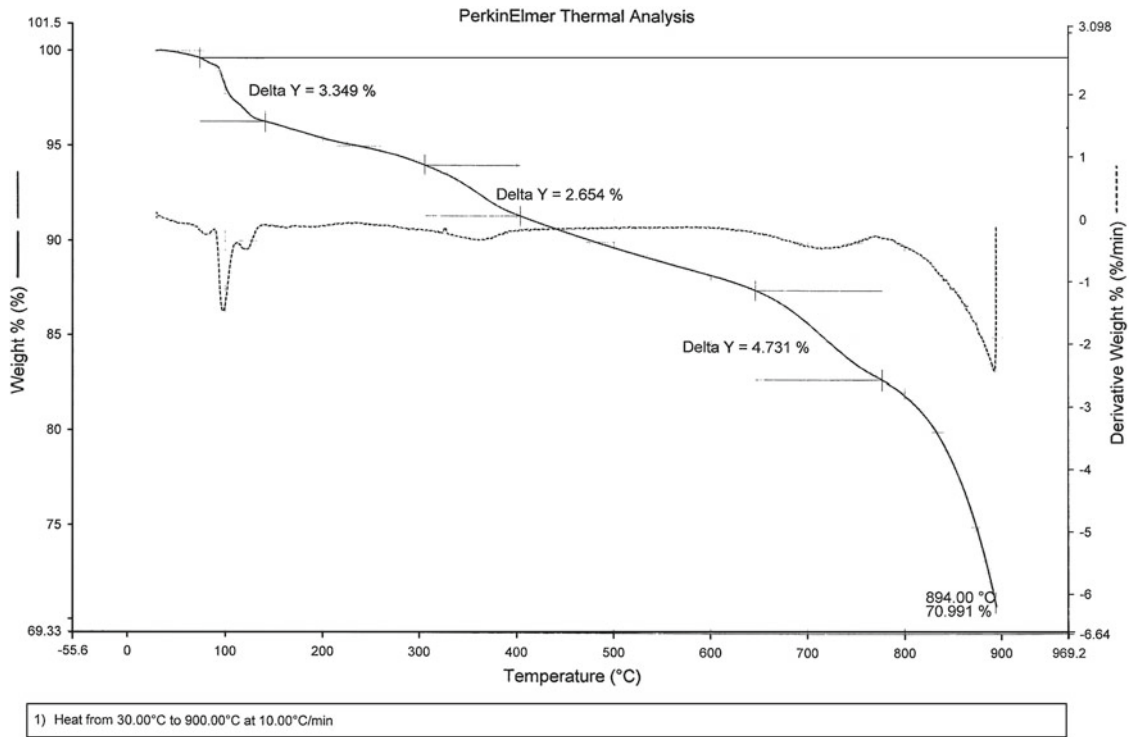


Fig. 10 Thermogravimetric analysis curve of dye 7a

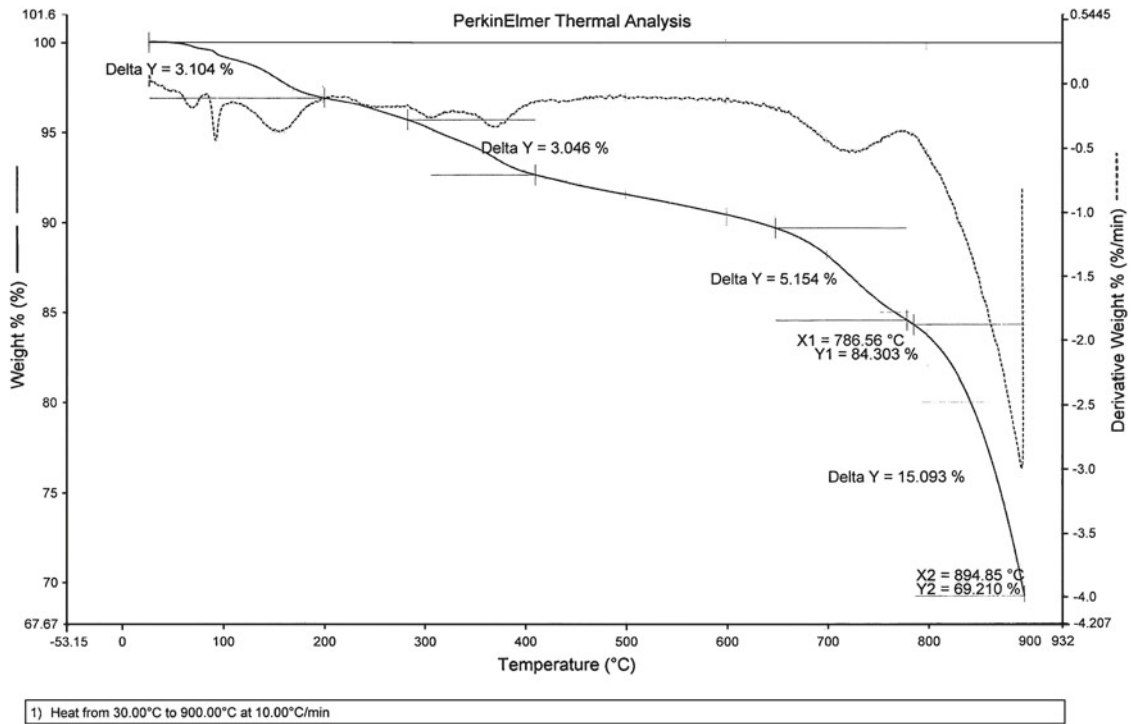


Fig. 11 Thermogravimetric analysis curve of dye 7f

**Table 6** Thermogravimetric analysis (TGA) data of reactive dyes **7a–j**

Dye no.	Weight loss at various temperature (°C) from TGA (%)					
	150	300	450	600	750	900
<b>7a</b>	03.85	05.89	09.49	11.75	16.45	30.01
<b>7b</b>	03.22	06.92	10.18	12.52	22.50	29.54
<b>7c</b>	04.04	06.94	09.55	14.46	22.12	30.39
<b>7d</b>	03.12	05.10	08.75	11.75	18.90	33.89
<b>7e</b>	03.25	07.61	11.25	15.78	25.95	33.83
<b>7f</b>	01.84	04.64	07.89	09.56	14.27	30.88
<b>7g</b>	02.78	06.34	09.50	15.43	24.53	32.90
<b>7h</b>	01.60	05.52	08.02	10.77	18.97	30.66
<b>7i</b>	03.78	05.65	09.26	12.67	19.88	31.03
<b>7j</b>	03.16	05.22	08.24	15.60	23.78	32.57

excellent washing and rubbing fastness properties with good depth and levelness. The solvent and substituent effects were determined. The absorption maxima were found in the range of 465–530 nm with respect to DMF solvent and showed larger bathochromic shift in DMSO than in other solvent. The CIELab data were evaluated and  $K/S$  value seems to be higher on wool fibres as compared to silk and cotton. Antimicrobial screening of the synthesized compound showed remarkable antimicrobial activity against selected bacteria and fungi. Thermogravimetric analysis data showed good thermal and storage stability and they can be used for high technology polymeric applications.

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