



Synthesis and antibacterial activity of some novel nucleus *N*-aminorhodanine based bis monofunctional and bifunctional reactive dyes and their application on wool and cotton fabrics

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Abstract

Herein, we aimed to synthesis two new reactive dyes based on derivatives of Aminorodanine as a chromoforic group, as well as to apply the dye and antibacterial activity to the dyed fabric. First, we synthesized 3-amino rhodanine with glutaraldehyde and terephthalaldehyde (2: 1 mole) to form compounds A & B respectively. After that we prepared monofunctional monochlorotriazine (MCT) and bifunctional monochlorotriazine sulphatoethyl sulphone (MCT/SES) by first condensation *m*-phenylene diamine sulphonic acid with Cyanuric chloride (1:1 mole) in ice bath then the second condensation takes place with sulfanilic acid or 1-Aminobenzene-4- β -sulphatoethylsulfone (PABSES) (1:1 mole) at room temperature; the pH was maintained at 5-6 by simultaneous addition 2 M sodium carbonate solution to form monofunctional reactive group C and bifunctional reactive group D respectively. Finally, we synthesized dyes by diazotized C and D by adding sodium nitrite (0.01 mol) to appropriate amines (0.01 mole) in concentrated HCl (6 ml) at (0-5 °C) under stirring then coupling with compounds A and B after dissolved them in ethanol with 2 M of sodium carbonate by 2 mol of the diazonium salt with 1 mole of coupler. The reactive dyes bis MCT **1**, **2** and Bis MCT/SES **3**, **4** are formed. We provided synthesized dyes structures by elemental analysis, IR, and ¹HNMR spectroscopy. These dyes are used in dyeing cotton and wool that show good light fastness, and are excellent for washing, rubbing, and sweating fastness. Also, we measure antibacterial activity for cotton and wool fabrics toward Gram-negative and Gram-positive

Keywords: Reactive dyes, bis monochlorotriazine, bis monochlorotriazine/ sulphatoethyl-sulphone, *N*-Aminorhodanine, cotton, and wool fabric, antibacterial.

1. Introduction

Reactive dyes were commercially the most popular dyes because they had an acceptable price, good colour, and good fastness properties. The authors worked on the optimization of jute fiber dyeing with reactive dyes and mordant dyestuffs under few external effects [1-6]. In some cases, the low exhaustion and low fixation were due to the decrease in reactivity of dyestuff with fabric [7-13]. Due to their wide shade range, application flexibility, and outstanding fastness properties on wool, silk, cotton, and regenerated cotton, reactive dyes are a highly successful class of modern synthetic dyes. [14-17]. Disazo reactive dyes were developed and used on silk, wool, and cotton fibers.[18-21]. reactive dyes have been synthesized applied on wool-acrylic fabrics

impart good light fastness [22-26]. some reactive dyes have been synthesized based on quinazoline and based on 4,4-methylene bis-(2-nitro aniline) [26-29].

We have synthesized some reactive dyes based on thiazolidinone as chromophoric moiety and applied them on cotton fabrics which have good fastness properties [30-32]. Also, We have synthesized some bifunctional dyes based on thiophene and applied them onto cotton fabric [33-36]. Two models of heterocyclic reactive dyes with a sulphatoethylsulphone reactive group, based on disazo pyrazolopyrimidine derivatives, were produced and characterized using elemental analysis, IR, and ¹HNMR. Cotton, wool, and silk fabrics were dyed with these dyes[37-40]. Thiazole derivatives were used to produce several reactive dyes. These dyes were used on cotton fabric, and the dyed fabrics had good colour

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strength and light fastness. In addition, the gram-negative and gram-positive bacteria were tested on the dyed cotton fabric [40-42]. To impart antibacterial properties, reactive dyes with varying degrees of molecular weight chitosan were applied to wool fabric. The influence of chitosan on the dyeing characteristics of wool fiber was investigated by evaluating the colour strength values of the treated substrate at different chitosan and dye concentrations [43]. We recently developed new bifunctional dyes based on the dimedone moiety that are bis (monochlorotriazine) and heterobifunctional (monochlorotriazine/sulphatoethylsulphone) to improve desirable properties such as colour strength and light fastness[42, 44]. The work aims to synthesize new reactive dyes based on N-aminorodanine derivatives as chromophoric moiety then we used them in dyeing cotton and wool fabrics. These dyes were investigated by elemental analysis. Also, we measure the antibacterial effect on cotton and wool fabrics[45, 46].

2. Materials and methods

2.1. Materials

2.1.1. Fabrics

Cotton fabric, 130 g/m² was obtained from El- Mahala Co., Egypt. Wool fabric, 310 g/m² supplied by Golden Tex. Co., Egypt. Wool fabrics were supplied from Golden TEX co., 10th of Ramadan, Egypt. Before dyeing, the fabric was treated with an aqueous solution containing 2 g/l non-ionic detergents for 1 h at 90 °C and at a liquor ratio of 50:1, then washed thoroughly in water and air-dried at room temperature.

2.1.2. Chemicals

Glutaraldehyde, terephthalaldehyde, 1-Aminobenzene-4-β-sulfatoethylsulfone (PABSES), and m- phenylene diamine sulphonic acid were obtained from Fluka Chemie AG. Cyanuric chloride (98 percent) was obtained from Merk-Schuchardt. All other chemicals used in the study were of laboratory reagent

2.2. Methods

2.2.1. Synthesis of intermediates

Synthesis of 3-amino rhodanine with dialdehyde derivatives (scheme 1)

Warm glutaraldehyde or terephthalaldehyde (1.00g, 1.34g, 0.01 mol) solutions were combined with warm 3-amino rhodanine (5.92, 0.02 mol) solutions in 50 mL of ethanol-water solution (1:2) and 5 drops of glacial acetic acid at 50°C. The resultant mixture was heated for 2 hours, after which the produced solid product was filtered, refined by ethanol crystallization, washed with diethyl ether, and dried in a vacuum desiccator over anhydrous calcium chloride. The yellow products A and B have yields of 82 percent and 92 percent, respectively.

pentane-1,5-diylidenebis(azanylylidene))bis(2-thioxothiazolidin-4-one) [A]:

Yellow powder; yield (gm, 82%); m.p (140-142°C); (C₁₁H₁₂N₄O₂S₄) [M⁺] = 360; C, 36.65; H, 3.36; N, 15.54 %; Found: C, 36.60, H,3.32; N, 15.50 %; FT-IR (cm⁻¹): 2924 (-CH₂-) 1690 (C=O), 1655 (C=N), 1205 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ 1.03-1.22 (m, 4H, 2CH₂), 1.90-1.97 (m, 2H, CH₂), 4.17 (s, 4H, 2CH₂), 6.55 (t, 2H, J = 8.2 Hz, 2CH=N)

(1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(2thioxothiazolidin-4-one) [B]:

Yellowish powder; yield (gm, 92%); m.p (180-182°C); (C₁₄H₁₀N₄O₂S₄) [M⁺] = 394 C, 42.62; H, 2.55; N, 14.20 %, Found: C, 42.60; H, 2.57; N, 14.05 %; FT-IR (cm⁻¹) 3050 (=CH), 2924 (-CH₂-), 1655 (C=O), 1588 (C=C), 1205 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ 4.69 (s, 4H, CH₂), 7.30 (d, 4H, J = 7.6 Hz, Ar-H), 8.50 (s, 2H, CH=N).

2.2.2. Synthesis of dyes

General synthetic method for Bis(monoazo) reactive dyes rhodanine derivatives [1, 2, 3,4], scheme 2

Solution of cyanuric chloride (1.88 g, 0.01 mole) stirred in acetone (50 mL) containing a few amounts of crushed ice at 0-5 °C in an ice/salt bath a solution of m-phenylene diamine sulphonic acid (2.0g, 0.01 mole) in water (30 mL) was adjusted at pH 6-7 by sodium carbonate solution was added, portion-wise. The sulfanilic acid (1.92 g, .01 mole) or 1-Aminobenzene-4-β-sulfatoethylsulfone (PABSES) (2.29 g, .01 mole) were dissolved in 50 ml H₂O with sodium carbonate then added dropwise to the solution and were adjusted pH until 4.5.

The solution cooled to 0-5 °C and was treated with concentrated hydrochloric acid (2.6ml, .01 mol) then a solution of sodium nitrite (.07 g, 0.01 mol in 20 ml H₂O) was added to obtain the diazonium salt. The produced diazonium salt was stirred for an extra 30 minutes at 0-5°C. In a separate glass beaker, cooled rhodanine analogs **A** (1.8 g, 0.005 mmol) and **B** (1.97 g, 0.005 mmol) were dissolved in 2 M of sodium carbonate. The produced mixture was vigorously stirred in the ice bath at 0-5°C, while the cold diazonium salt solution was added portion-wise. After stirring for an extra two hours, the crude product was filtered off under vacuum, washed with distilled water, recrystallized, and air-dried to afford the azo compounds in excellent yield

The reactive dyes bis MCT **1**, **2**, and Bis MCT/SES **3**, **4** are formed. We provided synthesized dyes structures by elemental analysis, IR, and ¹H-NMR spectroscopy.

pentane-1,5-diylidene bis2-((4-oxo-2-thioxothiazolidin-5-yl)diazenyl)-4-((4-chloro-6-((4-

sulfophenyl)amino)-1,3,5-triazin-2-yl)amino)benzenesulfonic acid) (1)

Dye 1 : yellow, m.p. >300°C, yield 80 %, λ_{\max} (H₂O) 380 nm. FT-IR (cm⁻¹) 3366.14 (NH), 2943.80 (C=N), 1717.30 (C=O), 1550.49 (N=N), 1231.33 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ = 1.29-1.39 (m, 2H, CH₂), 2.08 (t, 4H, *J* = 4.2 Hz, 2CH₂), 4.23 (s, 2H, CH rhodanine ring), 5.09 (s, NH), 6.76 (d, 2H, *J* = 4,3 Hz CHN), 6.88-6.98 (m, 4H, aromatic ring), 7.31 (d, *J* = 6 Hz , 2H,aromatic ring), 7.56-7.60 (m. 4H, aromatic ring), 7.73-7.79 (m, 4H, aromatic ring), 7.92 (s, NH). (C₄₁H₃₂Cl₂N₁₈O₁₄S₈), elemental analysis; C, 37.08; H, 2.43; N, 18.98 %, Found: C, 37.70; H, 2.01; N, 18.01 %.

(1,4-phenylenebis(methanylylidene)bis(azanylylidene) bis 2-((4-oxo-2-thioxothiazolidin-5-yl) diazenyl)-4-((4-chloro-6-((4-sulfophenyl)amino)-1,3,5-triazin-2-yl)amino)benzenesulfonic acid) (2)

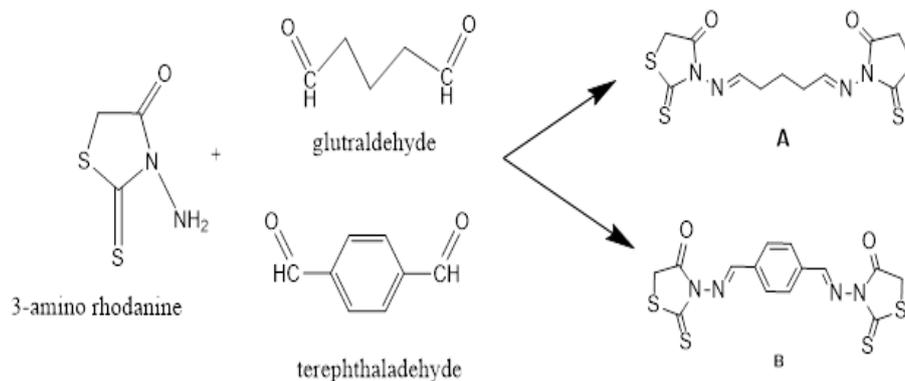
Dye 2: yellow, m.p. >300°C, yield 75 %, λ_{\max} (H₂O) 400 nm. FT-IR (cm⁻¹) 3394.10 (NH), 2772.98 (C=N), 1713.44 (C=O), 1563.99 (N=N), 1213.97 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ = 3.58 (s, 2H, CH rhodanine ring), 7.23 (t, 2H, *J* = 6 Hz, 2H, aromatic ring), 7.31-7.41 (m. 4H, aromatic ring) 7.45-7.51 (m. 4H, aromatic ring) 7.62 (t, 2H, *J* = 4,3 Hz, ,aromatic ring) 7.70 (d, 2H, *J* = 4.2 Hz, 2H, aromatic ring) 8.03 (s, 4H, aromatic ring ring) 8.90 (s, 2H, CHN), 9.51 (s, NH). (C₄₄H₃₀Cl₂N₁₈O₁₄S₈) elemental analysis; C, 38.80; H, 2.22; N, 18.51; Found: C, 38.11; H, 2.01; N, 18.14 %.

pentane-1,5-diylidene bis 2-((4-oxo-2-thioxothiazolidin-5-yl) diazenyl)-4-((4-chloro-6-((4-(2-(sulfooxy)ethyl)phenyl)amino))-1,3,5-triazin-2-yl)amino)benzenesulfonic acid) (3)

Dye 3: yellowish brown, m.p. >300°C, yield 70 %, λ_{\max} (H₂O) 419 nm. FT-IR (cm⁻¹) 3381.10 (NH), 2832.23 (C=N), 1712.48 (C=O), 1561.09 (N=N), 1184.08 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ = 1.80-1.88 (m, 2H, CH₂), 2.13 (t, 4H, *J* = 4.3 Hz, 2CH₂), 2.78 (t, 4H, *J* = 6,2 Hz, 2CH₂), 3.30 (t, 4H, *J* = 4,3 Hz, 2CH₂), 4.23 (s, 2H, CH rhodanine ring), 5.23 (s, NH), 6.76 (d, 2H, *J* = 4,2 Hz CHN), 7.12-7.18 (m, 4H, aromatic ring), 7.31 (d, *J* = 6 Hz , 2H,aromatic ring), 7.40-7.47 (m. 4H, aromatic ring), , 7.52-7.57 (m. 2H, aromatic ring), 7.80-7.85 (m, 2H, aromatic ring), 9.92 (s, NH). (C₄₅H₄₀Cl₂N₁₈O₁₆S₈) elemental analysis; C, 38.16; H, 2.85; N, 17.80 %, Found: C, 38.91; H, 2.51; N, 17.33 %.

(1,4-phenylenebis (methanylylidene) bis (azanylylidene) bis 2-((4-oxo-2-thioxothiazolidin-5-yl) diazenyl)-4-((4-chloro-6-((4-(2-(sulfooxy)ethyl)phenyl)amino)) - 1,3,5-triazin-2-yl)amino)benzenesulfonic acid) (4)

Dye 4: yellowish brown, m.p. >300°C, yield 72%, λ_{\max} (H₂O) 434 nm. FT-IR (cm⁻¹) 3391.10 (NH), 2725.17 (C=N), 1741.41 (C=O), 1560.13 (N=N), 1169.62 (C=S). ¹H-NMR (DMSO-d₆, ppm): δ = 2.54 (t, *J* = 2,1 Hz, 2CH₂), 2.80 (t, *J* = 4,2 Hz, 2CH₂), 3.16 (s, 2H, CH rhodanine ring), 7.11-7.21 (m, 4H, aromatic ring), 7.33 (d, *J* = 4.2 Hz, 2H, aromatic ring), 7.56 -7.62 (m. 4H, aromatic ring), 7.76 (d, *J* = 3.2 Hz, 2H, aromatic ring), 7.90 (d, *J* = 2.1 Hz 2H, aromatic ring), 8.15(s, 4H, aromatic ring), 8.96 (d, 2H, *J* = 4,3 Hz, CHN)11.16 (S, NH). (C₄₈H₃₈Cl₂N₁₈O₁₆S₈) elemental analysis; C, 39.75; H, 2.64; N, 17.38 %, Found: C, 39.14; H, 2.04; N, 17.98 %.



Scheme 1 Synthesis of 3-amino rhodanine with dialdehyde derivatives

2.2.3. Dye purification

Purification of the synthesised dyes 1-4 from impurities was required for convenient dyeing and chemical investigation [20, 21]. The dyes were dissolved in dimethylsulphoxide at 45 °C. Filtration was used to remove inorganic impurities, and the dye solutions were precipitated in n-butanol at room temperature. The dyes were filtered, washed with acetone, and dried at 40°C in a vacuum oven.

2.2.4. Dyeing procedures

2.2.4.1. Cotton

In an Ahiba dyeing machine, reactive dyes 1, 2, 3, and 4 were added in a 40:1 liquid ratio. The dyebath was started at 40°C for 30 minutes in the presence of 20, 40, and 60 g/l anhydrous sodium sulfate at a neutral pH with 2 % owf dye concentration. The temperature was then elevated to 50°C, 60°C, 70°C, and 80°C over 15 minutes while sodium carbonate (5-20 g/l) was added. The dyeing then proceeded for another 60 minutes at the required temperature of 80°C. The dye samples were washed with water before being extracted with 50% aqueous dimethylformamide (DMF) for 15 minutes at a boil.

2.2.4.2. Wool

Reactive dyes **1,2,3,4** were applied to the wool fabric at pH 3-7, ammonium sulfate 5% owf, and 1g/l Albigal A. Dyeing was started at 40 °C then the dye bath was raised to 100 °C over 30 min. The dyeing was continued for a further 60 min and the dyed samples were rinsed with water and dried.

2.2.5 Dye exhaustion

The uptake bis azo monofunctional and bifunctional reactive dyes **1,2,3,4** by cotton and wool fabric were measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath was measured on Shimadzu UV-2401 PC UV/V is spectrophotometer at λ_{max} . The percentage of dye bath exhaustion (%E) was calculated using equation(1) [47]

$$\%E = [1 - C_2/C_1] \times 100 \quad (1)$$

Where C_1 and C_2 are the dye concentrations in the dye bath before and after dyeing respectively.

2.2.6. Dye fixation

The dye fixation (%F), the percentage of the exhausted dye chemically bonded on the fabric, was measured by refluxing the dyed sample in 50 percent aqueous DMF(20:1 LR) for 15 min to extract the unfixed dye [48]. This procedure was repeated until the extract was clear. The concentration of the extract was then measured spectrophotometrically at the λ_{max}

value of each dye and the dye fixation ratio was calculated using equation(2) [49].

$$\%F = \frac{(C_1 - C_2 - C_3)}{C_1 - C_2} \times 100 \quad (2)$$

Where C_3 is the concentration of extracted dye. From the dye bath exhaustion (%E) and dye fixation (%F), The total dye fixation (%T), which is the percentage of dye chemically bound relative to the total amount of dye used, was calculated for cotton dyeing using equation (3)

$$\%T = \frac{(\%E \times \%F)}{100} \quad (3)$$

2.3. Characterization

IR spectra were recorded using Nexus 670 Fourier Transform-Infrared (FTIR) spectrophotometer on the KBr disc. ¹HNMR spectra were measured on a Varian 300 MHz Spectrometer in deuterated dimethylsulphoxide (DMSO-d₆) using tetramethylsilane (TMS) as the internal reference and chemical shifts(d) are given in ppm. Mass Spectra were performed on HP model MS-5988. UV/Visible spectra were measured on a Shimadzu UV-2401 PC UV/Vis spectrophotometer using distilled water. The visual colour strength (K/S) of dyed fabric was measured on Datacolor International SF 600 plus. Analytical data were performed on a Vario El III Elementar CHNS analyzer.

Colour measurements

The relative colour strength (K/S) and CIELAB coordinates (L* a* b*) of undyed and dyed cotton fabrics were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 108 standard observers [50].

Fastness testing

The dyed samples were washed-off using 2 g/l non-ionic detergents at 100 for 15 min and tested by standard methods (Methods of Tests for Colour Fastness of Textiles and leather, 1990). Wash fastness [ISO 105-C02 (19890), and fastness to perspiration [ISO 105-E0491989]] were evaluated using a visual ISO grey scale for colour change. Light fastness (Xenon arc) was evaluated using ISO 105-B02.

2.4. Evaluation of antibacterial activity in vitro

2.4.1. Materials

Two bacterial strains were *Staphylococcus aureus* (*S. aureus*, ATCC 6538) as Gram-positive bacteria and *Escherichia coli* (*E. coli*, ATCC 11229). These bacterial strains were selected as test cells because they are the most frequent microbes in wound infection. Fresh inoculants for antibacterial

assessment were prepared on nutrient broth at 37°C for 24 hours.

2.4.2. Test method

The antibacterial activity of dyes powders and dyed fabrics was evaluated by using the disk diffusion method [51].

3. Result and discussion

3.1. Synthesis of dye intermediates and reactive dyes

Synthetic techniques for preparing the intermediates A and B in Schemes 1 and 2. Scheme 2,3 shows the bis monofunctional and bifunctional reactive dyes 1, 2, 3, and 4. In the experimental section, the elemental analysis and spectrum data of produced reactive dyes are provided. The intermediates were synthesized by adding 3-amino rhodamine with glutaraldehyde or terephthalaldehyde in ethanol and drops of glacial acetic acid under heating for 2 hours. The yellow product A and B were formed respectively. (Scheme 1).

The reactive dyes were synthesized in two steps, first condensation *m*-phenylene diamine sulphonic acid with Cyanuric chloride (1:1 mole) in an ice bath then the second condensation takes place with sulfanilic acid or 1-Aminobenzene-4- β -sulfatoethylsulfone (PABSES) (1:1 mole) at room temperature; the pH was maintained at 5-6 by simultaneous addition 2 M sodium carbonate solution to form monofunctional reactive group C and bifunctional reactive group D respectively. Finally, we synthesized dyes by diazotized C and D by adding sodium nitrite to appropriate amines in concentrated HCl at (0-5 °C) under stirring then coupling with compounds A and B after dissolved them in ethanol with 2 M of sodium carbonate by 2mol of the diazonium salt with 1 mole of coupler. The reactive dyes bis MCT **1**, **2**, and Bis MCT/SES **3**, **4** are formed. We performed elemental analysis, IR, and ¹H-NMR spectroscopy to provide structures for synthesized dyes. These dyes' structures were confirmed using analytical and spectroscopic data. FT-IR, ¹H-NMR, and elemental analyses were used to describe compounds 1, 2, 3, and 4. FT-IR spectra of dyes 1, 2, 3, and 4 exhibited characteristic NH broad bands at 3366.14, 3381.10, 3394.10, and 3391.10 cm⁻¹, respectively. Furthermore, the absorption band for these dyes in the C=O group ranged from 1717 to 1741 cm⁻¹. However, for

compounds 1,2,3,4, the azo (-N=N-) group displayed a distinct band extending from 1550 to 1560 cm⁻¹.

¹H-NMR indicated multiplet at 1.29 and 1.80 ppm assigning to the aliphatic protons of (-CH₂) for dyes **1** and **3**. In addition, the triplet appeared at 2.08 ppm under the internal aliphatic proton (CH₂) for both dye **1** and 2.13 to 3.30 for dye **3**. Moreover, the methylene proton of rhodanine ring (-CH) of **1** singlet appeared at 4.33 ppm and 4.23 to dye **3**. On the other hand, a proton in aromatic rings appeared ranging from 6.88 to 7.73 in dye 1 and 7.12 to 7.80 in dye 3. In addition, two broad NH singlets appeared at 5.09 and 7.92 ppm for dye 1 and 9.92 for dye 3.

While the methylene proton of the rhodanine ring (-CH) singlet occurred at 3.16 and 3.58 ppm in azo compounds 2 and 4, the aliphatic protons of (-CH₂) appeared at 2.54 and 2.80 ppm in dye 4. At 9.51, 11.16 ppm, respectively, the azo compounds 2, 4 displayed a wide singlet corresponding to the NH group.

3.2. Colour assessment and dyeing properties

Data for λ_{\max} for bis monofunctional mono chlorotriazine reactive dyes **1**, **2** and bis bifunctional mono chlorotriazine sulphatoethylsulphone **3** and **4** are determined by the results of the experiments. UV data shows that compounds **2,4** have a bathochromic effect than compounds **1,3** so, λ_{\max} increases due to the conjugated system in the dye molecule. Also, the exhaustion dyes were showed higher on cotton with bis moochlorotriazine /sulphatoethylsulphone **3,4** than bis monochlorotriazine reactive dyes **1,2**.

Application of dyes

All reactive dyes 1,2,3, and 4 were dyed using the experimental dyes under specific exhaustion dyeing conditions.

3.3. Dyeing cotton

Effect of salt concentration(sodium sulfate)

At different concentrations of sodium sulfate (20-60 g/l) and sodium carbonate (20 g/l), the reactive dyes 1-4 were used. The dyeing was done using sodium sulfate at 40°C for 30 minutes, followed by 60 minutes of fixation in sodium carbonate at 80°C. By raising the salt content, the primary dye exhaustion was enhanced (**Fig. 1**). In addition, secondary exhalation and fixing (**Figs. 1,2**)

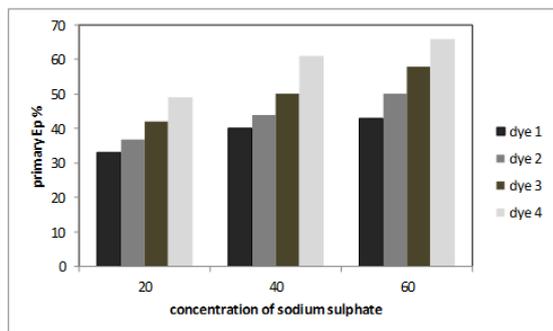


Fig. 1 Primary exhaustion (Ep) of dyes 1, 2, 3, 4 (2 percent owf) on cotton at 80°C with different sodium sulfate concentrations.

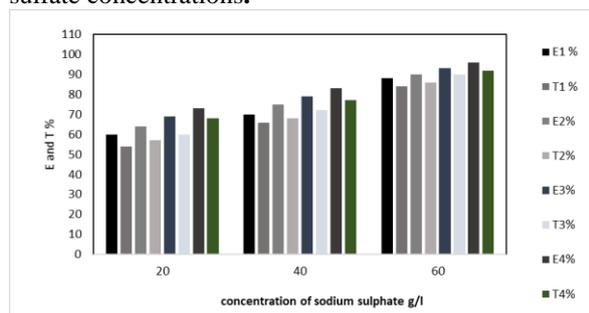


Fig. 2: Secondary exhaustion (E) and total fixation (T) of dyes 1, 2, 3, and 4 (2 % owf) on cotton after application of various salt concentrations at 80°C.

Effect sodium carbonate concentration

The reactive dyes 1-4 were applied at sodium sulfate 60g/l and different concentrations of sodium carbonate (5-10-15-20 g/l). The dyeing was done using sodium sulfate at 40°C for 30 minutes, followed by 60 minutes of fixation in sodium carbonate at 80°C. The coloured samples were removed with 50 percent aqueous DMF at the boil for 15 minutes after thorough rinsing. The results showed that when the sodium carbonate concentration increases, dye exhaustion, and total fixation values increase, with dye 4 having the highest exhaustion. (Fig. 3).

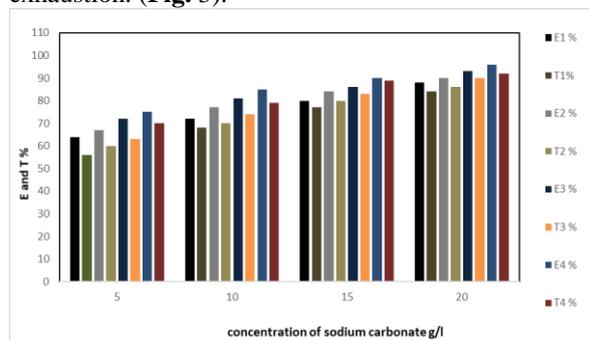


Fig. 3: Exhaustion (E) and total fixation (T) of dyes 1, 2, 3, and 4 (2 % owf) on cotton after application of various sodium carbonate concentrations at 80°C.

Effect of different dye concentrations

The reactive dyes (1-4) were mixed with 60g/l sodium sulfate and 20g/l sodium carbonate at varied dye concentrations (1-4 percent). The dyeing was done using sodium sulfate at 40°C for 30 minutes, followed by 60 minutes of fixation in sodium carbonate at 80°C. The coloured samples were extracted for 15 minutes with 50 percent aqueous DMF at a boil after thorough rinsing. The outcomes should be expected. (Fig. 4).

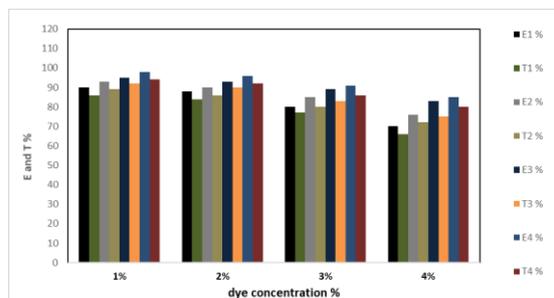


Fig. 4: Exhaustion (E) and total fixation (T) of dyes 1, 2, 3, and 4 applied to cotton at 40 g/l sodium sulfate and 20 g/l sodium carbonate at 80°C with varied concentrations of dyes 1, 2, 3, and 4.

3.4. Dyeing wool

Effect of pH

The reactive dyes (1-4) were used at different pH levels (3-7). Each dyeing was carried out at 40°C, with the temperature of the colour bath gradually rising to the boiling point over 30 minutes. The dyeing was kept at a boil for another 60 minutes. After the dyeing process, the samples were thoroughly rinsed and air-dried. The results show that at pH 4, there is a lot of weariness and fixation. Dye 4 also has a higher level of fatigue and fixation than the other colours. Fig. 5 shows that at pH 3, the exhaustion values on wool are quite high, whilst the fixation values appear to be quite low. At pH 4-5, the total fixation yields were quite high. The dyes' high substantivity at low dyebath pH can be attributed to a static contact between the anionic sites inside the dyes and the protonated amino teams on the fiber. At pH values, 4-5 end up in a rise in the total number of sites available for covalent bonding via both nucleophilic substitution and β -attack (MCT/SES dyes 3,4) mechanisms. (Fig. 5)

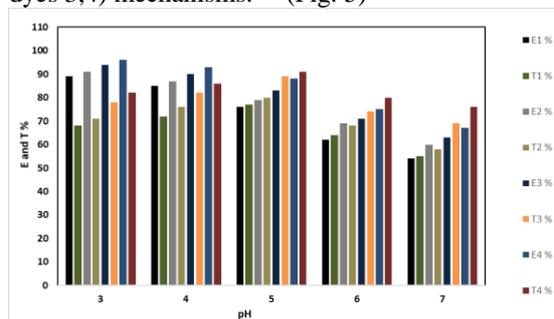


Fig. 5: Exhaustion (E) and complete fixation (T) at various pH were applied to wool (2%) at 100°C.

Effect of different dye concentrations

The reactive dyes (1-4) were added at varied dye concentrations (1-5 percent), pH 4, and dyeing was carried out at 40°C, with the dye bath temperature gradually rising to the boiling point over 30 minutes. For another 60 minutes, the colouring was kept at a boil. Fig. 6 indicates that the exhaustion and fixation values on wool are relatively high at 2%, after which the dyes clump on the substrate and do not penetrate to the fibers, causing the exhaustion and fixation values to diminish.. (Fig. 6)

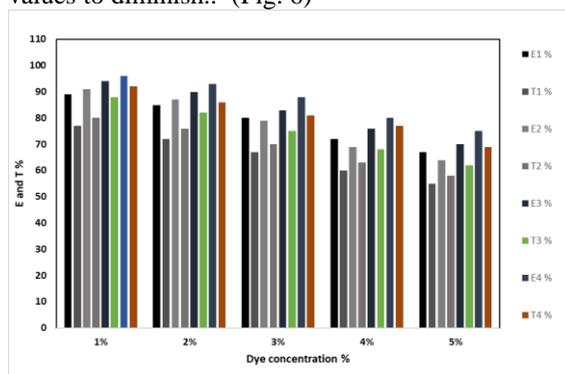


Fig. 6: Exhaustion (E) and total fixation (T) of dyes applied to wool (pH 4) at 100°C at different concentrations.

3.5. Colorimetric and fastness properties

The colour and fastness properties of the generated dyes 1, 2, 3, and 4 are evaluated on cotton and wool fabric. The colour fastness, washing, and perspiration properties of the dyes generated are shown in Table 1. The amount of dye applied to cotton fabrics, which ranges from good to exceptional, is fixed. In addition, Table II shows CIE L*a*b*C*h colorimetric data of coloured cotton and wool fabrics with 1, 2, 3, and 4. (Take in Table 1 and Table II).

Antibacterial Activity:

The dyes' antibacterial activity was tested in vitro using the disc diffusion method with two bacterial strains, *S. aureus* as a Gram-positive bacteria and *E. coli* as a Gram-negative bacteria, as well as tetracycline as a control. Table III demonstrates that dyes 1, 2, 3, and 4 had outstanding and very good activity against *S. aureus* and *E. coli*, respectively, when compared to the tetracycline antibiotic employed as a control.

Table I: Fastness properties of dyed wool (W) at pH 4 and cotton (C) fabrics using reactive dyes 1, 2, 3, and 4 (2% o.w.f)

Dyes	Fabrics	Fastness to Wash			Fastness to Perspiration						Fastness to Rubbing		Light	
		SC	SW	Alt	Acidic			Alkaline			Dry	Wet		
					SC	SW	Alt	SC	SW	Alt				
1	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	C	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
2	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	C	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
3	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	C	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
4	W	4	4	4	4	4	4	4	4	4	4	4	4	4
	C	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5

SC, staining on cotton; SW, staining on wool; Alt, color change of the dyed sample.

Table II: Colorimetric data of coloured wool (W) and cotton (C) fabrics dyed with reactive dyes 1, 2, 3, and 4 at pH 4 (2% o.w.f)

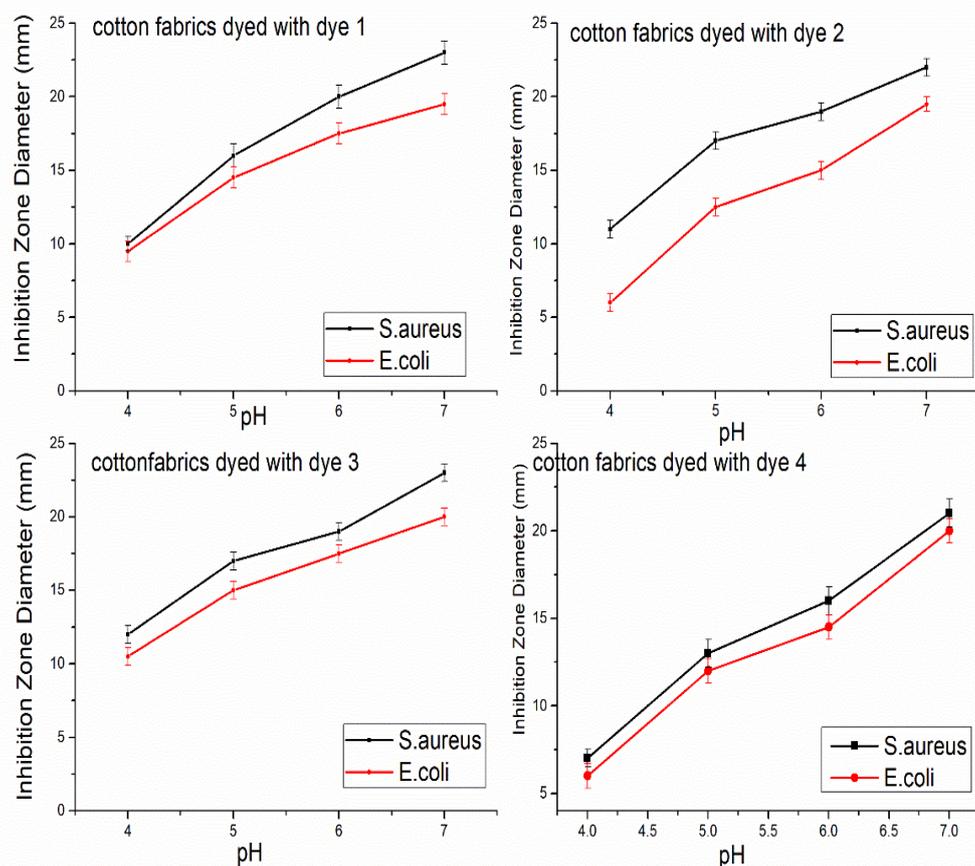
Dye	λ_{max}	Fabric	K/S	L*	a*	b*	C*	h ⁰	dE*
1	380	W	11.06	61.55	20.18	57.43	60.87	70.64	0.22
		C	10.93	57.61	18.34	54.64	57.64	71.45	5.27
2	400	W	34.71	42.93	37.28	52.07	64.04	54.40	25.94
		C	26.60	48.59	27.46	55.61	62.03	63.72	15.04
3	419	W	22.39	25.68	24.18	13.99	27.93	30.06	2.17
		C	18.91	27.47	25.34	13.65	28.79	28.30	0.45
4	434	W5	33.12	18.61	17.27	9.60	19.67	29.07	12.46
		C6	29.70	21.98	23.24	13.09	26.67	29.39	5.81

Table III: Results of antibacterial test for direct dyes solution

Dye No.	Zone of inhibition (diameter in mm)	
	<i>S. aureus</i>	<i>E. coli</i>
1	20	18
2	23	21
3	22	22
4	25	24
tetracycline	28	26

Cotton and wool fabrics dyed with the four colours were tested for antibacterial activity using the Disk

Diffusion susceptibility test method. The impact of pH on the antibacterial activity of these dyed materials with these four dyes was next investigated, with the results shown in **Fig. 7** and 8. In each example, the inhibitory zone (diameter) was measured. **Fig. 7** and 8 show the results. Undyed samples reveal clear bacterial growth under them with no inhibition zone, demonstrating that the undyed cloth does not suppress bacterial activity on its own. As evidenced by the absence of bacterial development under all treated samples, fabrics dyed with prepared colours inhibit bacterial growth. [25, 34, 52].

**Fig. 7:** The antibacterial activity of cotton fabrics dyed with dyes 1, 2, 3, and 4 is affected by pH values

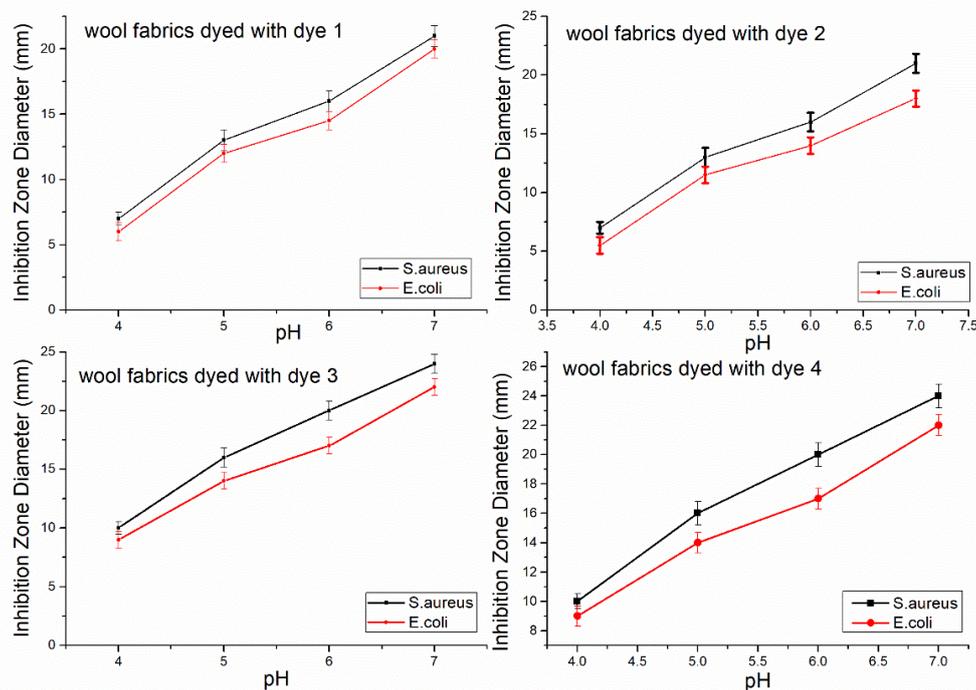


Fig. 8: The antibacterial activity of wool fabrics coloured with colours 1, 2, 3, and 4 is affected by pH values.

Higher inhibition was seen as a result of increased pH values, as evidenced by an increase in diameter. It is possible to deduce that the dyes are potent antibacterial agents. **Fig. 7** and **8** show that the zone of inhibition increases virtually linearly as the pH value of the dye increases. For the order $4 > 3 > 2 > 1$, the increase is much larger. The clear zone of inhibition obtained indicates that the dyes selected are bactericidal rather than bacteriostatic.

4. conclusion

Monofunctional monochlorotriazine containing one reactive group (MCT) and Bifunctional monochlorotriazine sulphatoethyl sulphone (MCT/SES) containing two reactive groups, has been synthesized by 3-amino rhodanine with glutaraldehyde and terephthalaldehyde (2: 1 mole) to form compound **A** and **B** respectively then we prepared monofunctional monochlorotriazine (MCT) and Bifunctional monochlorotriazine sulphatoethyl sulphone (MCT/SES) by first condensation m-phenylene diamine sulphonic acid with Cyanuric chloride (1:1 mole) in an ice bath then the second

condensation takes place with sulfanilic acid **C** or 1-Aminobenzene-4- β -sulphatoethylsulphone (PABSES) **D** (1:1 mole). Finally, we synthesized dyes by diazotized **C** and **D** then coupling with compounds **A** and **B** by (2:1 mole) respectively. The reactive dyes bis MCT **1**, **2**, and Bis MCT/SES **3**, **4** are formed. The primary purpose of developing these dyes was to demonstrate improved exhaustion, fixation, and colour fastness on cotton and wool materials. These dyes also show antibacterial activity against Gram-negative bacteria like *E. coli* and Gram-positive bacteria like *S. aureus* in cotton and wool fibers.

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