



Synthesis and Application of Novel Reactive Dyes Based on Dimedone Moiety



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Abstract

The aim of this study is synthesising, characterizing and finding out properties of some new bifunctional dye Bis (monochlorotriazine) (MCT) and heterobifunctional (monochlorotriazine / sulphatoethylsulphone) (MCT/SES) reactive dyes using Dimedone moiety (5,5-Dimethylcyclohexane-1,3-dione) to enhance favorable properties such as, color strength and light fastness. The first dye A was prepared then coupled with diazonium salts having the reactive groups. But the second dye B was synthesiezed of Dimedone moiety (2-amino4,4-dimethy,3-cyano,6-oxo-beno[b] thiophene) after that we diazotized and coupled it with 1-amino-8-naphthol-3,6-disulphonic acid (H-acid) to produce mono azo intermediate. This product was reacted with 2,4,6-trichloro-1,3,5-triazine in 1:1 molar ratio via The aim of this study is synthesising, characterizing and finding out properties of some new bifunctional dye Bis (monochlorotriazine) (MCT) and heterobifunctional (monochlorotriazine / sulphatoethylsulphone) (MCT/SES) reactive dyes using Dimedone moiety (5,5-Dimethylcyclohexane-1,3-dione) to enhance favorable properties such as, color strength and light fastness. The first dye A was prepared then coupled with diazonium salts having the reactive groups. But the second dye B was synthesiezed of Dimedone moiety (2-amino4,4-dimethy,3-cyano,6-oxo-beno[b] thiophene) after that we diazotized and coupled it with 1-amino-8-naphthol-3,6-disulphonic acid (H-acid) to produce mono azo intermediate. By reacting this product with 2,4,6-trichloro-1,3,5-triazine with 1:1 molar ratio via nucleophilic displacement with 1,4-phenylenediamine in 2:1 molar ratio to produce bis monochlorotriazine reactive dyes thus yielding the new reactive dye. These two dyes were applied onto fabrics of silk, cotton and wool under the optimum conditions of the dyeing exhaust, then the dyeing properties were examined. The results indicate quality of the highest dyeing properties. However, the homobifunctional (bis MCT) dyes showed higher values of exhaustion and fixation, fastness properties and color yield than heterobifunctional (MCT/SES).

Keywords: Cotton, Wool; Silk, Fabric; Bifunctional reactive dyes; Dimedone; Bis monochlorotriazine dyes; Dyeing

1. Introduction

Dimedone (5,5-dimethylcyclohexane-1,3-dione) is considered as an alicyclic diketone, it is building blocks in synthesis and design of a wide variety of heterocycles [1]. It is one of the most studied β -diketone because its derivatives have been found to be fungicides and herbicides. Dimedone, gamma pyrone and barbituric acid, they were treated with dimethyl sulphoxide and acetic anhydride reagent, a

very versatile reagent was formed which can be evaluated for medicinal uses [2]. besides having other applications. 4-hydroxy-6-methyl-2H-pyran-one (triacetic acid lactone or gamma pyrone) is an aliphatic analogue of hydroxycoumarin with which it shares similar chemical properties [3, 4].

Dimedone is used as the basis for synthesis of a novel group of compounds that derivative 1,3-cyclohexadione, a dimedone analogue because it traps sulfenic acids that reporter tags such as biotin for affinity capture and fluorescent labels for visual detection. These reagents have ability to indicate the

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sensitive to oxidation as cysteine sites and proteins and also it gives the cellular cases that the oxidations occur [5]. Dimedone is versatile in most organic transformations. The crystals white and yellow Dimedone is used in many series of organic reaction including multi-component transformations [6]

Dimedone and its derivatives are used in many biological activities such as antihistaminic, antioxidant, anticarcinogenic, and anticoagulant [7]. Dimedone react by The Gewald's reaction which using sulfur and any active methylene group such as malononitrile or ethyl cyanoacetate to give thiophene derivatives are used in heterocyclization reactions then it react with any diazonium salts to give the arylhydrazone derivatives have potentially anticancer agents [8].

In the past, pyrazolo[1,2-a] pyrazole 3-carboxylic acid fused systems are used as moiety to prepare new bifunction reactive azo dyes which give good strength, lightfastness, colour and other desirable properties. These dyes were used to dye wool and cotton fabrics [9, 10]. Also, we have synthesised new bifunctional dyes bis (monochlorotriazine) based on tetrahydrobenzo[b]thiophene systems [11].

Cotton and viscose fibers are used to be dyed by reactive dyes and also wool and polyamide. A large number of dyeing techniques are available to be used for reactive dyes [12, 13]. In dyeing cellulose fibers with reactive dyes, Alkali, Salt, Urea are added to the padding liquor in continuous processes. While in the cold pad-batch method, Sodium silicate may be added. Moreover, the development of meterable products has been encouraged by automated dye works. Reactive dyes should also display good cold water solubility [14-19].

The incorporation of two reactive groups into a single dye molecule is a well-established route to increased fixation efficiency. Procion H-E is of the earliest examples to be exploited commercially were the dyes, which possess two similar monochlorotriazine groups [20-25].

The present work aims to synthesizing heterobifunctional monochlorotriazine/sulphatoethylsulphone (MCT/SES) and bifunctional Bis (monochlorotriazine) reactive dyes based on Dimedone as chromophoric moiety and applied these dyes on cotton, wool and silk fabrics with studying all dyeing and fastness properties .

2. Experimental

2.1. Materials

2.1.1. Fabrics

Mill-scoured and bleached cotton fabric (130 g/m²; Misr El- Mahalla Co., Egypt), wool fabric (310 g/m²; Golden Tex Co., Egypt) were used throughout this work. Degummed and bleached silk fabric, 80 g/m² was obtained from El-Khateib Co. Before application, the fabric was treated in an aqueous solution containing 2 g/L (Hostapal CV, Clariant, Egypt) for 1 h at 80 °C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature.

2.1.2. Chemicals

Hostapal CV (Clariant, Egypt) was used as a nonionic detergent. Albegal A (amphoteric levelling agent; Ciba) was used as an auxiliary for dyeing wool. 2,4-Diaminobenzenesulphonic acid (98 per cent) and 1-aminobenzene-4-β-sulphatoethyl sulphone (PABSES) (96 per cent) were obtained from Amar Impex, Mumbai, India. 4-Amino-2-diphenylamine-sulphonic acid (96 per cent), 4-aminoazobenzene-3,4-disulphonic acid (96 per cent) were obtained from Isma Dyestuff and Chemical Co., Egypt. Cyanuric chloride (98 per cent), Dimedone and maleic acid (98 per cent) were purchased from Merck Co., USA. All other chemicals used in this study were of laboratory reagent grade and applied without further purification.

2.2. Synthesis

2.2.1. Synthesis of disazo heterobifunctional monochlorotriazine/ sulphatoethylsulphone (MCT/SES) reactive dye

3,3 dimethyl-1,5-dioxo -6-[5-[4-chloro-6-(β-sodiumsulphonatoethylsulphonyl-4-phenylamino) -1,3,5-triazine-2-ylamino]-2-sodiumsulphonato1-phenylazo] cyclohexane

The method was carried out by initial preparation of the MCT/SES diazonium salt a suspension of cyanuric chloride (1.88 g, 0.01mol) in acetone (20 mL) and crushed ice (10-20 g) was stirred at 0-5 °C. A solution of 2,4-diaminobenzenesulphonic acid (1.91g, 0.01mol) in water (30ml) at 5 °C and pH 4.5-5 was slowly added to this suspension. The mixture was stirred for 2 h at 0-5 °C and pH 4.5. The reaction product was then treated with 1-aminobenzene-4-β-sulphatoethylsulphone PABSES (2.86 g, 0.01mol) in water (50ml) at pH 5.5-6, allowing the temperature to rise gradually to 30 °C and the pH to 6.5-7. The reaction was completed within 4-5 h (stable pH). The solution was filtered, cooled to 0-5 °C and then treated with 10ml HCl/0.69 g NaNO₂ to produce the diazonium salt.

The resulting solution of the diazonium salt was then added slowly to a stirred solution of dimedone. The desired reactive dye 1 was precipitated by slow addition of sodium chloride (15 per cent w/v), filtered and dried under vacuum at 40 °C

Dye 1: yellow, m.p. 300 °C, yield 80 per cent, λ_{\max} (H₂O) 365 nm

C₂₅H₂₃N₇O₁₁ClNa₂ (678.5), calcd.: C, 44.22; H, 3.39; N, 14.44 % found: C, 44.20; H, 3.29; N, 14.41 %. IR (ν, cm⁻¹): 3424 (2 NH, acid), 1623-1616 (2C=O), 1488 (N=N). ¹HNMR (δ, ppm), 1.32 (s, 6H, 2CH₃), 2.32 (s, 4H, CH₂), 3.45 (t, 2H, CH₂(SES)), 4.09 (t, 2H, CH₂(SES)), 7.30-7.79 (m, 7H, C₆H₄, C₆H₃), 9.43, 9.40 (2s, 2H, 2NH).

2.2.2. Synthesis of intermediate monoazodye-2-azo(1-amino-8-hydroxynaphthalene-7-yl-3,6-disulphonic acid)-4,4 dimethyl 5-hydro-6Oxo benzo[b]thiophene-3-carbonitrile

2-Amino-4,4 dimethyl 5-hydro-6Oxo-benzo[b]thiophene 3- Carbonitrile was prepared by Adding Dimedone (0.1 mol, 14.00 g) in absolute ethanol (30 mL) containing a catalytic amount of triethylamine (0.50 mL) to malononitrile (0.1 mol, 6.60 g) and elemental sulfur metal (0.1 mol, 3.2 g). The whole reaction mixture was heated under reflux for 1 h and the formed solid product, upon pouring onto ice/water containing few drops of hydrochloric acid, was collected by filtration. Compound 1 (2.20 g, 0.01 mol) was treated with concentrated hydrochloric acid (5ml) then was added sodium nitrite solution (0.70 g, mol in 10 mL H₂O) to give the corresponding diazonium salt. After complete diazotization, the diazonium salt solution was coupled with H-acid (3.19 g, 0.01mol) 1-amino-8-naphthol-3,6-disulphonic acid at pH 2-3 and 0°C-5°C. The resultant monoazo dye 2 intermediates was filtrated off and dried under vacuum at 50°C.

Dye 2: yellow, m.p>300°C, yield 90 per cent. C₂₁H₁₈N₄O₈S₃ (550) [M+1]= 549, calcd.: C, 45.90; H, 3.28; N, 10.20; S, 17.49 %, found: C, 45.23; H, 3.63; N, 10.50; S, 17.12 %. IR (ν, cm⁻¹): 3576-3415 (3OH, NH₂), 2210 (CN), 1610 (C=O) 1488 (N=N). ¹HNMR (δ, ppm): 1.32 (s, 6H, 2CH₃), 2.39 (s, 4H, CH₂), 7.051 (s, 2H, NH₂) 7.27-7.77(s, 3H, naphthyl) 13.15 (s, 3H, 3OH).

2.2.3. Synthesis of bisazo bifunctional bismonochlorotriazine reactive dye

N, N'-Bis[2-azo(1-amino-8-hydroxy-nathalene-7-yl-3,5-disulphonic acid)4,4 dimethyl- 5 hydro-6Oxo benzo[b]thiophene-3-carbonitrile -(N-4-chlorotriazino-6-yl)]-1, 4-phenylenediamine

Solution of cyanuric chloride (1.88 g, 0.01 mol) stirred in acetone (50 mL) containing a few amount of crushed ice at 0-5 °C in an ice/salt bath a solution

of each of the monoazo dye intermediate 2 (5.50 g, 0.01 mol) in water (30 mL) was adjusted at pH 6-7 by sodium carbonate solution was added, portion wise. The reaction mixture was stirred at 0-5 °C for 4 h then a neutral solution of 1,4-phenylenediamine (0.58 g, 0.005 mol) in ethanol (40 mL) added dropwise to the whole solution. The respective bisazo bifunctional bismonochlorotriazine reactive dye (bis MCT) 3 was precipitated by adding sodium chloride solution (10% w/v), the dye was filtered off and dried at 40 °C under vacuum.

Dye 3: yellow, m.p. >300 oC, yield 89 %, λ_{\max} (H₂O) 405 nm. C₅₄H₃₆N₁₆O₁₆S₆Na₄Cl₂ (1520.20), calcd.: C, 42.66; H, 2.37; N, 14.75; S, 12.64 %, found: C, 42.06; H, 2.41; N, 14.82; S, 12.60 %. IR (ν, cm⁻¹): 3520 (2 OH), 3468- 3338 (4NH), 3055 (CH aromatic), 2210 (2bis CN), 1640 (2 bis C=O), 1500 (2 bis N=N). ¹HNMR (δ, ppm): 1.30 (s, 12H, 4CH₃), 2.41 (s, 8H, 4CH₂), 7.80-7.91 (s, 3H, 2 X naphthyl H), 7.15(d, 4H, C₆H₄), 10.01 (s, 2H, 2NH), 10.31 (s, 2H, 2 NH), 13.11 (s, 2H, 2 X OH).

3. Dyeing Procedures, Color Measurements and Fastness Testing of the Dyed fabrics

3.1. Exhaust dyeing and application properties of the synthesized dyes

All dyeing were carried out in distilled water using 2% (o.w.f.) dye concentration. The dyeing procedures of all dyes used were applied at 40:1 liquor ratio with cotton and at 50:1 liquor ratio with wool and silk fabrics.

3.2. Exhaustion and fixation measurements

The dyeing application on wool and silk fabrics for studying the exhaustion and fixation yield was done at pH 4 for wool and pH 5 for silk using liquor ratio 50:1 and 2% dye concentration. The dyeing process was started at 40°C, allowing the temperature of the dyebath to raise to the boil over 30 min. The dyeing was continued for a further 60 minutes and the dyed samples were thoroughly rinsed with water and dried.

Dye exhaustion

The dye exhaustion was measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath was measured spectrophotometrically at λ_{\max} of each dye. The percentage of dye exhaustion (% E) was calculated using equation (1):

$$(1)$$

where C₁ and C₂ are the concentrations of dye in the dye bath before and after dyeing, respectively.

Dye fixation

Dye fixation (%F) (percentage of the exhausted dye that chemically bound on the fiber) was measured by

refluxing the dyed samples in 50% aqueous DMF (liquor ratio 20:1) for 15 min to extract the unfixed dye [11, 26-29]. This procedure was repeated until the extract was colorless. The concentration of the extract was then measured spectrophotometrically at λ_{max} of each dye and the dye fixation ratio calculated using equation 2:

$$(2)$$

Where, C3 is the concentration of extracted dye.

From the dyebath 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 the prepared dyes using equation 3:

Primary exhaustion

The percentage of the dye absorbed onto the cotton fiber before the addition of sodium carbonate, relative to the amount of the dye used for experiment.

Secondary exhaustion (or exhaustion) (E%)

The percentage of the dye adsorbed or chemically bound to the fiber at the end of the dyeing process but before extraction with 50% DMF solution, relative to the amount of the dye used for experiment.

Fixation ratio (F%)

The percentage of the dye chemically bound to cellulose at the end of the dyeing process, relative to secondary exhaustion on cotton (or exhaustion on other fibres).

Total dye Fixation yield (T%) exhaustion (or exhaustion) (E%)

The percentage of dye chemically bound to the fibre at the end of the dyeing process, relative to the amount of dye used for the experiment.

3.3. Fastness testing

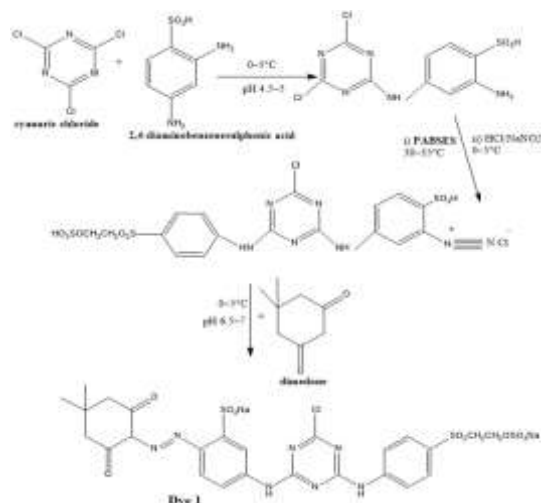
The dyed samples were tested, after washing-off using 2g/l non-ionic detergent at 80°C for 30 min, were tested for their wash fastness, light fastness, rub fastness and perspiration fastness according to ISO standard methods [30].

3.4. Colour measurements

The colour parameters of the un-dyed and dyed cotton fabrics were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 108 standard observer [31, 32].

4. Results and discussion

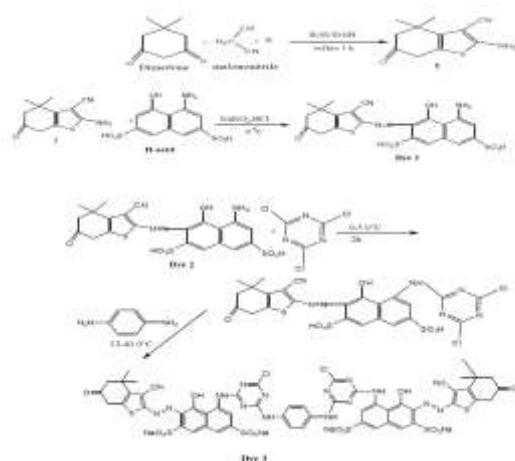
4.1. Synthesis of heterobifunctional monochlorotriazine/sulphatoethyl-sulphone (MCT/SES) reactive dye 1 (system I)



The structure elucidation and spectral data of dye 1 is revealed accordance to its molecular structure. The **System I : Synthesis of reactive dye 1 disazo heterobifunctional monochloro-triazine/sulphatoethylsulphone (MCT)**

mass spectra, molecular ion peaks at m/z 678.5. The data showed are in correspondence to its expected molecular formulae $C_{25}H_{23}N_7O_{11}ClNa_2$. The IR spectra obtained, a characteristic two C=O stretching modes of Dimedone in 1623 - 1616 cm^{-1} regions and stretching modes of N=N at 1488. The 1H -NMR spectrum characterized by two triplets (t, 2H, CH₂) (SES) at δ 3.45 and 4.09 ppm of sulphatoethylsulphone moiety 3.45 (t, 2H, CH₂) (SES), 4.09 (t, 2H, CH₂) (SES).

4.2. Synthesis of bisazo bifunctional



bismonochlorotriazine reactive dye 3 (system II)

System II: Synthesis of bisazo bifunctional bismonochlorotriazine reactive dyes

The experimental part illustrates the spectral data and the elemental analyses of the synthesized dye. 2-Amino-4,4-dimethyl-5-hydroxy-6-oxo-benzo[b]thiophene 3-Carbonitrile was prepared by adding Dimedone to malononitrile. This reaction is taken place through two steps, firstly, Dimedone, malononitrile and sulfur were condensed with triethyl amine to obtain the 2-Amino-4,4-dimethyl-5-hydroxy-6-oxo-benzo[b]thiophene 3-Carbonitrile. After washed and dried this compound it coupled with H-acid at C-2 to form monoazo dye intermediate 2. Secondly, this dye was reacted with 2,4,6-trichloro-1,3,5-triazine in 1:1 molar ratio via nucleophilic displacement, After that it was subjected to condensation reaction with the 1,4-phenylenediamine in 2:1 molar ratio to give bisazo bifunctional bismonochlorotriazine reactive dyes. The bisazo dye is revealed by analytical and spectral data in accordance to its molecular structure. Dye 3 displayed, its mass spectra, molecular ion peaks at m/z 1519 $[M^+]$. The data shown correspond to the expected molecular formula $C_{54}H_{36}N_{16}O_{16}S_6Na_4Cl_{12}$. The IR spectra on dye 3 revealed the presence of 4NH stretching bands around 3468- 3338 cm^{-1} , also the two bis C=O absorption bands appear at 1640. Absorption bands of bis N=N appear at 1500 cm^{-1} . The 1H -NMR spectrum was revealed two NH groups of the bismonochlorotriazine moiety by two singlet (2H each) at δ 10.01 and 10.31 ppm which indicating this compounds.

4.3. Color evaluation

Data for λ_{max} of disazo heterobifunctional monochlorotriazine/sulphatoethylsulphone (MCT/SES) dye 1 and bisazo bifunctional bismonochlorotriazine dye 3 are included in the experimental part. The data showed a bathochromic shift is taken in dye 1 due to presence of sulphonic acid which increase the mobility of the resonating electrons throughout the conjugated systems and thus increase λ_{max} and also solubility of dyes increase. But in dye 3 presence aryl group (H-acid) of the arylazo moiety and sulphonilic acid together showed more bathochromic effect than dye 1 which increase the solubility of dye and thus increase λ_{max} .

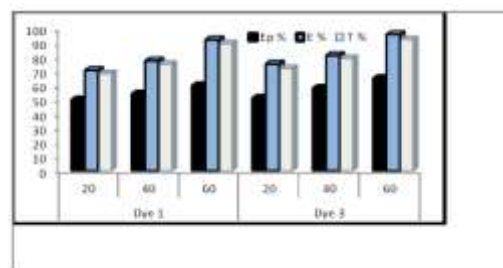
4.4. Application of dyes

4.4.1. Dyeing of cotton

4.4.1.1. The effect of sodium sulphate concentration

The reactive dyes (1,3), were applied at various concentration of sodium sulphate (20-40-60g/l) and 20g/l sodium carbonate at 80°C figure 1. The sodium sulphate was used for dyeing for 30 min., at 40°C and then sodium carbonate was used for fixation for 60 min. The dyed samples, after a thorough rinsing,

were boiled with 50% aqueous DM at for 15 min. By increasing salt concentration, The primary exhaustion of dyes initially increases. After adding 20 g/l sodium carbonate at 80 °C so, the secondary exhaustion and fixation yield of both dyes 1 and 3 increased. Figure 1 indicates that, at any level of salt concentration, the exhaustion (E) and total fixation (T) of dye 3 are

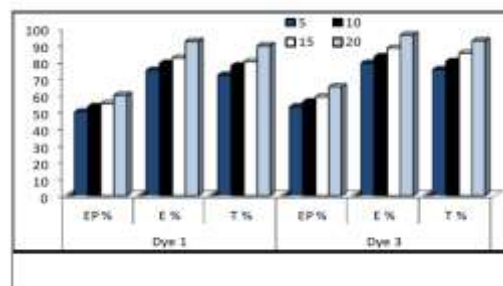


higher than that of dye 1. This can be attributed to bismonochlorotriazine has planarity, high molecular weight and has more reactive group than bifunctional groups of monochlorotriazine sulphatoethylsulphone

Figure 1: fixation and Exhaustion yield of dye 1 and dye 3 on cotton at different salt concentration (20-60g/l).

4.1.1.2. The effect of sodium carbonate concentration

The reactive dyes (1,3), were applied at sodium sulphate 60g/l and at various concentration of sodium carbonate (5, 10, 15, 20 g/L) at 80 °C. After a thorough rinsing, the dyed samples was boiled with 50% aqueous DMF for 15 min. The results indicate at figure 2 that the total fixation and exhaustion values of dye 3 are higher than that of dye 1 at these dyeing

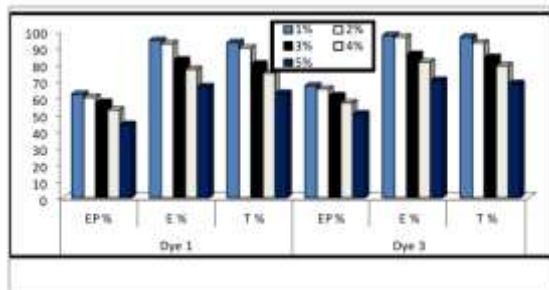


conditions. Also, the total fixation and exhaustion values of dyes 3 and 1 increase with increasing concentration of sodium carbonate (5-20 g/L).

Figure 2. Exhaustion and fixation values of dye 1 and dye 3 at different alkali concentration (5-20g/l) on cotton

4.1.1.3 The Effect of different dye concentrations

The reactive dyes (1,3) were applied at various concentration of dye (1-5 %), with 20 g/L sodium carbonate and 60g/L sodium sulphate. The results showed that at lower concentration of dyes the exhaustion and total fixation on cotton fabric was higher than using higher concentration of dyes. These results refer to the increasing of dye concentration lead to the dye aggregation increase and thus lead to reduction in the penetration of the



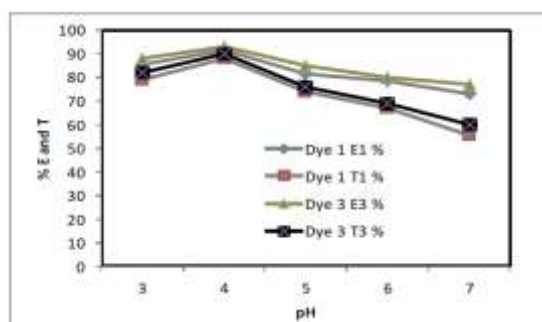
dye through the fibre. Figure 3 indicates that the fixation and exhaustion of dye 3 is higher than that of dye 1 at 2% shade of dyes.

Figure 3: Exhaustion and fixation yield of dye 1 and dye 3 on cotton at different dye concentration (1-5%) on cotton

4.1.2. Dyeing of wool

4.1.2.1. The Effect of pH

The reactive dyes (1,3), were applied at various pH (3-7). The total fixation and exhaustion of dyeing wool were applied at pH values from 3-7. Figure 4 indicate that the fixation and exhaustion values of dyes 1, 3 were high at pH 4-5. But at pH 3 the exhaustion values are very high due to electrostatic interaction between the anionic sites in the dyes and the protonated amino groups on the fiber while the fixation values are apparently low. Also the results refer to that the exhaustion and total fixation of dye 3 on wool were higher values than dye 1 because dye 3 has planarity and has more covalent bonds with

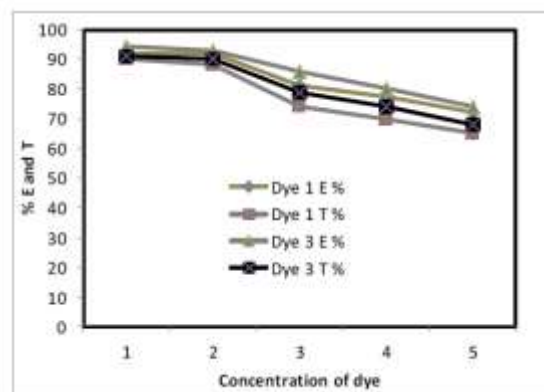


fibers. Each dyeing was performed at 40 °C, allowing the temperature of the dye bath to raise to the boil over 30 min. This conditions of dyeing was continued at 100°C for more 60 min. Then the samples were rinsed and air -dried.

Figure 4: Exhaustion and fixation values of dye 1 and dye 3 on wool at pH(3-7)

4.1.2.2. The Effect of different dye concentrations

The reactive dyes (1,3), were applied at various concentration of dye (1-5 %) and pH 4 and dyeing was performed at 40°C, allowing the temperature of the dye bath to raise to the boil over 30 min. The dyeing process was applied at 100°C for another 60



min. Finally, the dyed samples were rinsed and air-dried. Figure 5 illustrates that, dye 3 has higher fixation and exhaustion values than that of dye 1. Moreover, the results revealed that, at 2% shade of dye (i.e lower dye concentration) give higher total fixation and exhaustion values than the shade of higher depth.

Figure 5: total fixation and Exhaustion values of dye 1 and dye 2 at different dye concentrations (1-5%owf) on wool

4.1.3. Dyeing of silk

3.1.3.1. The Effect of pH

The dyeing process of the reactive dyes (1,3) starts at 40 °C and at various pH values (4, 6, 8 and 10) . After 10 min., the dye bath was heated to 90°C through 30 min. Dyeing was applied at different pH value for another 60 min. Then, all samples were washed and air- dried. Figure 6 illustrate that the higher exhaustion and fixation at pH 5. Also, the data revealed that exhaustion and fixation values of dye 3 on the silk is higher than the dye 1.

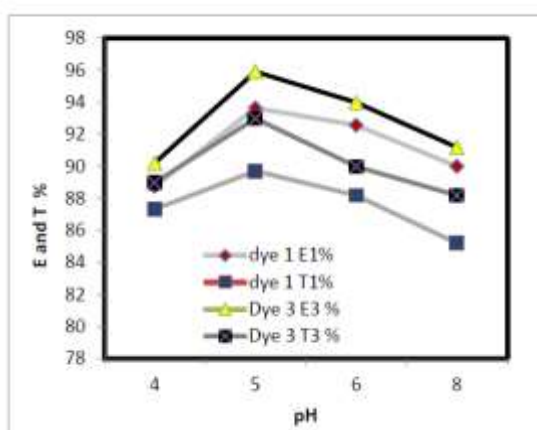


Figure 6: fixation and Exhaustion yield of dye 1 and 3 on silk at pH (4-8)

4.1.3.2. The Effect of different dye concentrations

Reactive dyes (1,3) were applied at various concentration of dye (1-5 %), pH 5 and dyeing was performed at 40°C, allowing the temperature of the dye bath to raise to the boil over 30 min. The dyeing was performed at 100 °C for 60 min. After that, the samples were washed and air-dried. Figure 7 indicate that The results showed the best exhaustion and fixation values at concentration 2%. The data

Table I: The fastness properties of the dye 1 and 3 on the fabric.

Dye	Sample dyed	K/S	Fastness to rubbing		Wash fastness	Fastness to perspiration						light
			Dry	Wet		Alkaline			Acidic			
						Alt	Sc	Sw	Alt	Sc	Sw	
1	C	4.02	4-5	4-5	4-5	4-5	5	4-5	4-5	5	4-5	5-6
	W	8.56	4-5	5	4-5	4-5	4-5	4-5	4-5	4-5	5	6
	S	7.15	4	4-5	4-5	4	4-5	4-5	5	4-5	4-5	6
3	C	5.01	4-5	5	4-5	4-5	5	4-5	4-5	5	5	6
	W	9.24	4-5	4-5	4-5	4-5	5	4-5	4-5	5	5	6
	S	8.1	4-5	4-5	4-5	4-5	5	4-5	4-5	5	5	6

5. . Conclusion

The aim of this work is designing and synthesising new reactive azo dyes based on a Dimedone moiety. We reported the synthesis of bifunctional dye Bis (monochlorotriazine) (MCT) N, N' -Bis[2-azo(1-amino-8-hydroxy-nathalene-7-yl-3,5- disulphonic acid) 4,4 dimethyl- 5 hydro-6Oxo benzo[b]thiophene-3- carbonitrile -(N-4-chlorotriazino -6-yl)]-1, 4-phenylenediamine and heterobifunctional (MCT/SES) reactive dyes (3,3 dimethyl-1,5-dioxo -6-[5-[4-chloro -6- (β-sodiumsulphonato ethylsulphony -1-4-phenylamino) -1,3,5-triazine -2-ylamino] -2-

revealed that exhaustion and fixation values of dye 3 is higher than the dye 1 due to increase the covalent bond between fibers and reactive groups in dye 3

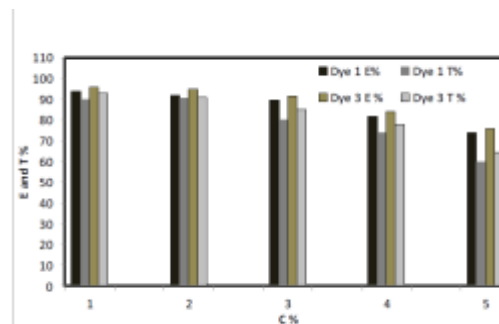


Figure 7: fixation and Exhaustion yield of dye 1 and 3 on silk at different concentration

4.5. Color strength and studying the fastness

The reactive dyes 1 and 3 were evaluated on cotton, wool and silk fabrics according to the color yield and fastness properties. Table (I) illustrates that color fastness against rubbing, washing and perspiration and all data of dyed fabrics were from excellent to good. These data indicate that the dyes were fixed very well on fabrics. Also, table 1 were showing the colorimetric K/S data of dyed fabrics ;cotton, silk and wool; with reactive dyes 1 and 3.

sodiumsulphonato1 -phenylazo] cyclohexane). All reactive dyes 1 and 3 were applied on cotton, wool and silk fabrics. Data indicate that these dyes have higher exhaustion and fixation values on all dyed fabrics. Also the results of colour yield and fastness properties were proved that all excellent and the dye 3 that heterobifunctional MCT/SES has more higher exhaustion and fixation values than dye 1. The newly manufactured reactive dyes have high quality dyeing properties and good fabric accumulation, and these accomplishments are very important for use in commercial and industrial applications in the field of dyes.

6. Conflicts of interest

There are no conflicts to declare.

7. References

- [1] M. M Heravi, V. Zadsirjan, B. Fattahi, N. Nazari, Applications of Dimedone in the Synthesis of Heterocycles: An Update, *Current Organic Chemistry* 20(16) (2016) 1676-1735.
- [2] T. Ara, K.Z. Khan, Synthesis of some derivatives of dimedone, γ -pyrone and barbituric acid, *J. Pharm. Res. (Mohali, India)* 8 (2014) 786-790.
- [3] N.I. Abdel Sayed, K. El Badry, H.M. Abdel Mohsen, Conductimetric studies of charge transfer complexes of p-Chloranil with some alicyclic amines in polar media, *Journal of the Chinese Chemical Society* 50(2) (2003) 193-199.
- [4] H.M. Ibrahim, O.A. Farid, A. Samir, R.M. Mosaad, Preparation of chitosan antioxidant nanoparticles as drug delivery system for enhancing of anti-cancer drug, *Key Engineering Materials*, 2018, pp. 92-97.
- [5] C. Klomsiri, K.J. Nelson, E. Bechtold, L. Soito, L.C. Johnson, W.T. Lowther, S.-E. Ryu, S.B. King, C.M. Furdui, L.B. Poole, Use of dimedone-based chemical probes for sulfenic acid detection: evaluation of conditions affecting probe incorporation into redox-sensitive proteins, *Methods in enzymology*, Elsevier 2010, pp. 77-94.
- [6] K. Nikoofar, F.M. Yielzoleh, A concise study on dimedone: A versatile molecule in multi-component reactions, an outlook to the green reaction media, *Journal of Saudi Chemical Society* 22(6) (2018) 715-741.
- [7] L.M.G. Antunes, M.C.P. Araújo, J.D.A.C. Darin, P.B. Maria de Lourdes, Effects of the antioxidants curcumin and vitamin C on cisplatin-induced clastogenesis in Wistar rat bone marrow cells, *Mutation Research/Genetic Toxicology and Environmental Mutagenesis* 465(1-2) (2000) 131-137.
- [8] R.M. Mohareb, F.O. Al Farouk, W.W. Wardakhan, Uses of dimedone for the synthesis of new heterocyclic derivatives with anti-tumor, c-Met, tyrosine, and Pim-1 kinases inhibitions, *Medicinal Chemistry Research* 27(8) (2018) 1984-2003.
- [9] F. Mohamed, Y. Youssef, Synthesis and application of bifunctional reactive dyes pyrazolo [1, 2- a] pyrazole 3- carboxylic acid, *Pigment & Resin Technology* (2012).
- [10] R.M. Mosaad, A. Samir, H.M. Ibrahim, Median lethal dose (LD50) and cytotoxicity of Adriamycin in female albino mice, *Journal of Applied Pharmaceutical Science* 7(3) (2017) 77-80.
- [11] F.A. Mohamed, R.M. Mohareb, Synthesis and applications of new bifunctional dyes bis (monochlorotriazine) based on tetrahydrobenzo [b] thiophene moiety, *Pigment & Resin Technology* (2013).
- [12] N.A. Ibrahim, G.A. Kadry, B.M. Eid, H.M. Ibrahim, Enhanced antibacterial properties of polyester and polyacrylonitrile fabrics using Ag-Np dispersion/microwave treatment, *AATCC Journal of Research* 1(2) (2014) 13-19.
- [13] S. Farag, M.M.S. Asker, M.G. Mahmoud, H. Ibrahim, A. Amr, Comparative study for bacterial cellulose production Using Egyptian *Achromobacter* sp, *Research Journal of Pharmaceutical, Biological and Chemical Sciences* 7(6) (2016) 954-969.
- [14] R. Chavan, Environmentally friendly dyes, *Handbook of textile and industrial dyeing*, Elsevier 2011, pp. 515-561.
- [15] F.A. Mohamed, H.M. Ibrahim, E.A. El-Kharadly, E.A. El-Alfy, Improving dye ability and antimicrobial properties of cotton fabric, *Journal of Applied Pharmaceutical Science* 6(2) (2016) 119-123.
- [16] T. Aysha, M. El-Sedik, S.A. El Megied, H. Ibrahim, Y. Youssef, R. Hrdina, Synthesis, spectral study and application of solid state fluorescent reactive disperse dyes and their antibacterial activity, *Arabian Journal of Chemistry* 12(2) (2019) 225-235.
- [17] S. Farag, H.M. Ibrahim, A. Amr, M.S. Asker, A. El-Shafai, Preparation and characterization of ion exchanger based on bacterial cellulose for heavy metal cation removal, *Egyptian Journal of Chemistry* 62 (2019) 457-466.
- [18] B.M. Eid, G.M. El-Sayed, H.M. Ibrahim, N.H. Habib, Durable Antibacterial Functionality of Cotton/Polyester Blended Fabrics Using Antibiotic/MONPs Composite, *Fibers and Polymers* 20(11) (2019) 2297-2309.
- [19] H. Ibrahim, E.M.R. El- Zairy, E.A.M. Emam, E. Adel, Combined antimicrobial finishing dyeing properties of cotton, polyester fabrics and their blends with acid and disperse dyes, *Egyptian Journal of Chemistry* 62(5) (2019) 965-976.
- [20] F.A. Mohamed, S.A. Abd El-Megied, M.S. Bashandy, H.M. Ibrahim, Synthesis, application and antibacterial activity of new reactive dyes based on thiazole moiety, *Pigment and Resin Technology* 47(3) (2018) 246-254.
- [21] F.A. Mohamed, H.M. Ibrahim, M.M. Reda, Eco friendly dyeing of wool and cotton fabrics with reactive dyes (bifunctional) and its antibacterial activity, *Der Pharma Chemica* 8(16) (2016) 159-167.
- [22] F.A. Mohamed, H.M. Ibrahim, A.A. Aly, E.A. El-Alfy, Improvement of dyeability and antibacterial properties of gelatin treated cotton fabrics with synthesized reactive dye, *Bioscience Research* 15(4) (2018) 4403-4408.
- [23] H.M. Ibrahim, A. Dakrory, A. Klingner, A.M.A. El-Masry, Carboxymethyl chitosan electrospun nanofibers: Preparation and its antibacterial activity, *Journal of Textile and Apparel, Technology and Management* 9(2) (2015).
- [24] H. Ibrahim, E.A.M. Emam, T.M. Tawfik, A.T. El-Aref, Preparation of cotton gauze coated with carboxymethyl chitosan and its utilization for

-
- water filtration, *Journal of Textile and Apparel, Technology and Management* 11(1) (2019).
- [25] H.M. Ibrahim, M.M. Saad, N.M. Aly, Preparation of single layer nonwoven fabric treated with chitosan nanoparticles and its utilization in gas filtration, *International Journal of ChemTech Research* 9(6) (2016) 1-16.
- [26] K. Bredereck, C. Schumacher, Structure reactivity correlations of azo reactive dyes based on H-acid: I. NMR chemical shift values, pKa values, dyestuff aggregation and dyeing behaviour, *Dyes and Pigments* 21(1) (1993) 23-43.
- [27] S. Burkinshaw, Y.-A. Son, M. Bide, The application of heterobifunctional reactive dyes to nylon 6, 6: process modifications to achieve high efficiencies, *Dyes and pigments* 48(3) (2001) 245-251.
- [28] Y. Youssef, A. Mousa, Structure—reactivity studies of a new polyfunctional disulphide bis (ES- MCT/SES) reactive dye applied to silk, *Coloration technology* 118(6) (2002) 325-329.
- [29] Y. Youssef, A. Mousa, Synthesis and application of a hetero- bifunctional disulphidebis (ethylsulphone/monochlorotriazine) reactive dye, *Coloration technology* 118(1) (2002) 20-25.
- [30] I.O.f. Standardization, ISO 105 X12—Textiles—tests for colour fastness: Part X12: Colour fastness to rubbing, Author Geneva, Switzerland, 2016.
- [31] J.-z. Hu, P. Skrabal, H. Zollinger, A comparison of the absorption spectra of a series of blue disperse dyes with the colorimetric evaluation of their dyeings, *Dyes and Pigments* 8(3) (1987) 189-209.
- [32] P. Savarino, G. Viscardi, R. Carpignano, E. Barni, G. Ferrero, Disperse and cationic dyes from aminophenyl-X-azolo-pyridines, *Dyes and pigments* 11(3) (1989) 163-172.