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RESEARCH ARTICLE

Synthesis of Several Newly Acid Dyes and their Application in Textile Dyeing

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Abstract

Synthesis of new acid dyes, mono azo and diazo derived from 3-[2-(cyanomethyl)-thiazol-4-yl]coumarin and 3-(2-amino-thiazol-4-yl)coumarin using various derivatives amine, and their utilization in dyeing of textile fabrics is attempted in this article. The prepared dyestuffs were established using melting point, elemental analysis, infrared, ultraviolet-visible spectroscopy (UV/VIS) and nuclear magnetic resonance (^{1}H-NMR) data. The suitability of the prepared dyestuffs for dyeing of wool and silk fabrics has been investigated. The dyed fabric show good light fastness, very good rubbing, perspiration, washing and excellent sublimation fastness. These dyes have been color shade from blue to violet with very good depth and levelness on fabrics. The dye bath exhaustion and fixation on fabric has been found to be very good.

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INTRODUCTION

Coumarins are attractive and versatile molecules that find applications in various fields like medicine, perfumery, dyes, pigments, optical brighteners, lasers, optical data storage devices, solar cells, etc. [1]. The coumarin is not fluorescent, but the introduction of an electron-withdrawing group such as a diazotized aromatic amine or an acetyl group makes it highly fluorescent. The coumarins are generally very convenient compounds for chemical modification due to the ease of synthesis [2]. Coumarin (chromen-2-one) establishes a family of dyes [3–5] that are applicable in different fields of science and technology. Coumarin and their derivatives has been a subject of considerable interest in numerous fields [6–8]. They exhibit strong fluorescence in the UV– VIS region that makes them suitable to use as colorants, dye laser media and nonlinear optical chromophore**.** Acid or anionic dyes are dyes with water solubilizing ionic substituents. These dyes are completely ionized in the acidic condition used in the dyeing process [9]. Mostly acid dyes are applied to nitrogenous fibers like wool, silk and nylon [10, 11]. Acid dyes are attached to the wool not only by electrostatic attraction but also by its affinity toward the fiber.

The bond between dye anions and amino groups in the fiber are easily broken and reformed and in consequence many of the dyes migrate in hot wet conditions. Ease of migration is advantage and it gives good leveling properties but it leads to poor fastness to wet treatment [12, 13].

Acid dyes are classified based on affinity, dyeing properties and chemical constitution of the dyes. There are many acid dyes reported in literature such as anthraquinone based acid dyes [14,15], acid nitro dyes [16], triphenylmethane acid dyes [17] and acid azo dyes [18-20]. Out of these, acid nitro dyes have good light fastness but low color strength [16]. Triphenylmethane acid dyes are suffering from poor light fastness properties [21] and replacement of anthraquinone dyes with equivalent azo dyes has great importance [22]. The class of azo dyes plays an important role due to their wide range of color, brightness, simplicity and ease of manufacturing and dyeing performance [23-26]. They are used in dyeing textiles, leather, paper, food, cosmetic products [27]. They are also used in high tech applications such as lasers and non-linear optical systems [28], photodynamic therapy [29], dye sensitized solar cells [30], metallochromic indicators [31], thermal transfer printing and fuel cells [32]. Acid azo dyes containing aromatic heterocyclic moiety have been investigated due to their wide applications. Heterocyclic azo dyes have been periodically reviewed [33-35]. The use of heterocyclic diazo or coupling component has made the production of colorants having brilliant color and chromophoric strength [36]. Fastness properties of acid azo dyes can be enhanced by the presence of hydroxyl, amino or acetamido groups at ortho position relative to the azo bridge [13], which is responsible for hydrogen bonding between hydroxyl and azo groups. The anionic azo dyes which are discussed here constitute the most widely used group of this class of dyes.

Most often sulfonic acid groups serve as hydrophilic substituents, because they are readily introduced and, as strong electrolytes, are completely dissociated in the acidity range used in the dyeing process. Almost invariably the products manufactured and employed are water-soluble sodium salts of the sulfonic acids.

The present work was carried out with the following objectives, synthesis and identification of some newly acid dyes based on coumarin derivatives, and the possibility of its use in dyeing of wool and silk fibers fabrics.

1. Experimental

1.1. Materials

Wool fabric

Wool fabric of 310 g/m2, supplied by Golden Tex Co., Tenth of Ramadan-Egypt, was initially treated in an aqueous solution with a liquor ratio 50:1 containing 0.5 g/l sodium carbonate and 2 g/l nonionic detergent at 60°C for 30 min, then thoroughly washed, and air dried at room temperature.

Silk fabric

Degummed and bleached silk fabric (El-Khateib Co., Egypt) weighing 90 g/m2 was used throughout this work. Before dyeing, the fabric was treated in an aqueous solution containing 2 g/l non-ionic detergent for 1 h at 90 °C and at a liquor ratio 50:1, then washed thoroughly in water and air dried at room temperature.

Chemicals

H-acid, γ-acid and 4-aminoazobenzene-3, 4’-disulphonic acid, 1-amino-3-bromo-5,10dioxoanthracene-2-sulphonic acid were obtained from Fluka Chemie AG. All other chemicals used in the study were of reagent grade and applied without further purification.

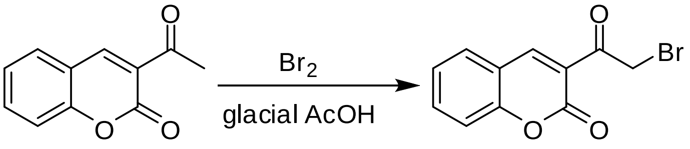
2.2. Dyestuff synthesis

2.2.1. Synthesis of 3-acetylcoumarin (1)

A mixture of salicylaldehyde (0.01 mol), ethyl acetoacetate (0.01 mol), piperidine (0.5 mL), glacial acetic acid (2 drops) was refluxed in absolute ethanol (50 mL) for 5h. The reaction mixture was poured into beaker, filtered, washed and dried to yield 3-acetylcoumarin, yellow precipitate [37]. Yield: 80 %, m.p. 112-114 ^{o}C; IR (KBr) ν_{max} 2930 (CH-aliphatic), 1742 (O-C=O), 1677 (C=O); ^{1}H-NMR (DMSO-d$_6$), δ = 2.55 (3H, s, CH_3), 7.38-7.89 (4H, m, Ar-H), 8.58 (1H, s, coumarin H-4).

2.2.2. Synthesis of 3-(2-bromoacetyl)coumarin (2)

To a solution of compound **1** (0.01 mol) in acetic acid glacial, bromine (0.01 mol) was added with stirring. The mixture was warmed to decompose an addition product. The mixture was heated for 15 min, cooled and filtered to get a solid mass which on washing with diethyl ether gave the desired product. It was recrystallized from acetic acid to give colorless needles [38]**.** Yield: 75%, m.p. 160-163 ^{0}C; IR (KBr) ν_{max} 2930 (CH-aliphatic), 1731 (O-C=O), 1686 (C=O); ^{1}H-NMR ($CDCl_3$) δ = 4.45 (2H, s, CH_2), 7.69-7.75 (4H, m, Ar-H), 8.66 (1H, s, coumarin H-4).

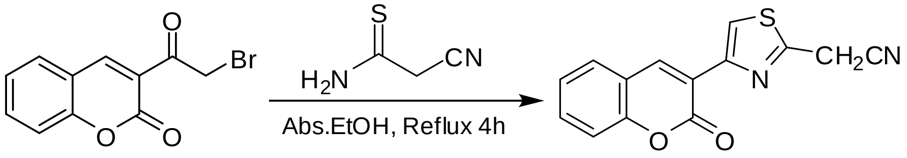


1 **2**

(equation 1)

2.2.3. Synthesis of 3-[2-(cyanomethyl)-thiazol-4-yl]coumarin (3)

A mixture of 3-(2-bromoacetyl)coumarin (**2**; 0.01 mol) and cyanothioacetamide (0.01 mol) in ethanol (50 mL) was heated under reflux for 4h. During the reflux period, a brown crystalline solid was separated. The separated solid was filtered off, washed with ethanol and recrystallized from ethanol-benzene to give the compound (**3**). Yield: 80%, m.p. 174-176 ^{0}C. MS m/z (%): $C_{14}H_8N_2O_2S$; 271 [M^++3], 268 [M^+] (100), IR (KBr) ν_{max} = 2220 (C≡N), 1720 (O-C=O), 1600 (C=S); ^{1}H-NMR: δ = 2.52 (2H, s, CH_2), 7.14-7.84 (4H, m, ArH), 8.12 (1H, s, CH-thiazole), 8.56 (1H, s, coumarin H-4).



2 **3**

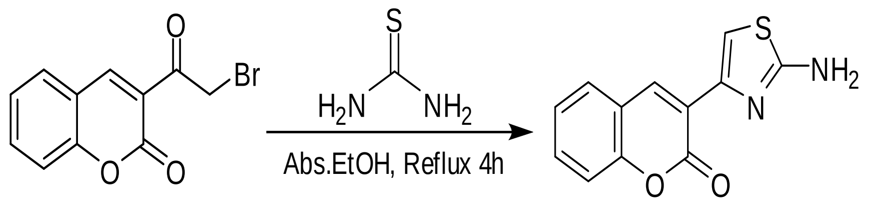
(equation 2)

General procedure for preparation of (D1-D4)

To a stirred solution of (**3**; 0.01 mol) in ethanol (50 ml) containing, sodium acetate (3gm) diazonium salt (prepared by adding sodium nitrite (0.01 mol) to appropriate amines (0.01 mol) in conc. HCl (6 ml) at (0-5 ^{o}C) under stirring) was added drop wise while cooling to (0-5 ^{o}C) and stirring. The reaction mixture was then left at room temperature for 2h. and the solid product formed was collected by filtration and recrystallized from the appropriate solvent to give (**D1-D4)**.

2.2.4. Synthesis of 3-(2-amino-thiazol-4-yl)coumarin (4)

A suspension of compound **2** (0.01 mol) in ethanol was heated with thiourea (0.01 mol), giving a clear solution that soon deposited crystals. They were filtered, washed with ethanol and then boiled with water containing sodium acetate yielding the target compound. The product obtained was recrystallized from ethanol [39]. Yield: 68%, m.p. 223-225 ^{o}C; IR: 3300, 3210 (NH_2), 1720 (O-C=O), 1630 (C=N), 1600(C=C); ^{1}H NMR: δ = 4.88 (2H, br, NH_2), 7.14-8.12 (6H, m, ArH, coumarin-H-4, CH-thiazole),.



2 **4**

(equation 3)

2.2.5. Procedure for preparation of (D5)

Compound (**4;** 0.01 mol) was suspended with stirring in Conc. H_2SO_4 (3 mL) and cooled to 0-5 ^{o}C. The amine was diazotized by adding $NaNO_2$ (0.013 mol) drop wise at 0-5 ^{o}C. After stirring at 0 ^{o}C for 1 h, the diazonium salt solution was checked with starch paper for the presence of HNO_2. There was a color change from white to brown; sulfamic acid was added to destroy excess HNO_2. Coupler compound H-acid (0.01mol) was dissolved in NaOH solution (3mL, 20%) at 0 ^{o}C. The cold solution of diazo compound prepared above was added to this solution, keeping the temperature at 0-5 ^{0}C and maintaining pH 4 by adding sodium acetate. After stirring for 1h at 0 ^{o}C, the dissert **D5**.

2.3. Dyeing procedures

Wool and silk fabrics were dyed using dyes **D1-5** at 1- 5% o.w.f in an Ahiba dyeing machine with 3 g samples at a LR.1:50. The dye bath was prepared at pH 4 at which the exhaustion of these acid dyes takes place well. The pH was obtained by weak acid, 1-3% acetic acid (80%). Dyeing was started at 40°C and then the temperature was raised to 100°C over 45 minutes. To study the effect of dyeing time, dyeing was examined at intervals up to total dyeing time of 90 minutes. After dyeing process, all dyed samples were rinsed with water and dried with air. Dye exhaustion on wool and silk fabrics were evaluated spectrophotometric ally.

2.4. Measurements and Testing

2.4.1. Melting point

Melting points of synthesized dyes were determined in open glass capillaries on Gallenkamp melting point apparatus.

2.4.2. IR spectra

The infra-red spectrum of synthesized dyes was measured using Infra-red spectrometer, Perkin Elmer/1650 FT-IR.

2.4.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectra for the synthesized dyes was measured in a Varian 400 MHz spectrometer.

2.4.4. Mass spectra

Mass spectra for the synthesized dyes were recorded in a Varian MAT112 spectrometer. Analytical data were obtained from the micro analytical data center at Cairo University.

2.4.5. Spectrophotometer measurements

The absorbance of the dyes was measured in the ultraviolet visible region between 300 and 700 nm by a UNICAM UV spectrophotometer using 1 cm quartz cell. The dyes were dissolved in absolute ethanol in Concentration of 1024 mole/l.

2.4.6. Dye Exhaustion

Uptake of the dye by the wool and silk fabrics was measured by sampling the dye bath before and after dyeing on a Shimadzu UV-2401PC UV/V is spectrophotometer at the λ_{max} value using a calibration curve previously obtained using known dye concentrations (g/L). The percentage of dye bath exhaustion (%E) was calculated using Eq. 1.

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

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

2.4.7. Colour measurements

The colour parameters of the un-dyed and dyed wool, and silk fabrics were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 10° standard observer [40, 41].

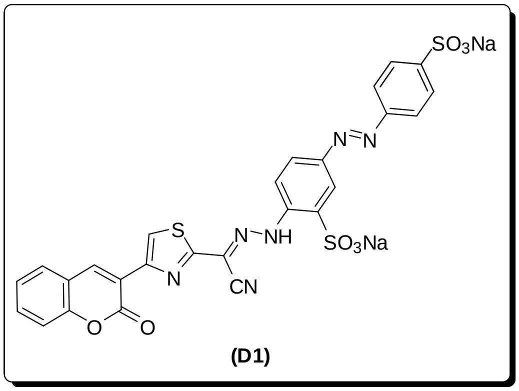
2.4.8. Fastness Testing

Dyed wool and silk samples, after washing-off using 2 g/L nonionic detergent at 80°C for 15 min, were tested by standard ISO methods. Wash fastness (ISO 105-C02 (1989), crock fastness (ISO 105-X12 (1987), and fastness to perspiration (ISO 105-E04 (1989) were evaluated using the visual ISO Gray Scale for both color change (AATCC Evaluation Procedure (EP) 1-similar to ISO 105-A02) and color staining (AATCC EP 2—same as ISO 105-A03). Light fastness (carbon arc) was evaluated using ISO 105-B02.

3. Results and Discussion

3.1. Synthesis of various Acid dyes.

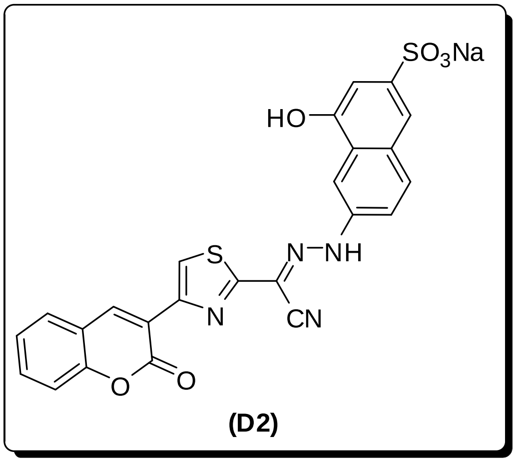
Disodium 2-[2-(cyano(4-(coumarin-3-yl)thiazol-2-yl)methylene)hydr-azinyl)-5-((4-sulfonatophenyl)diazenyl)-benzenesulfonate (D1)



(D1)

Yield: 90 %, m.p. >300 °C, Brownish, λ_{max} 400 nm; $C_{26}H_{14}N_6O_8S_3$ Na_2 $[M^+]$ = 680, Calcd.: C, 45.88; H, 2.07; N, 12.35; S, 14.13 %, Found: C, 46.05; H, 2.17; N, 12.05; S, 14.34 %; IR (ν, cm^{-1}): 3455 (NH), 2225 (C≡N) 1710 (O-C=O), 1475 (N=N). ^{1}H-NMR; δ = 7.2-8.8 (13H, m, 3ArH, coumarin-H-4, CH-thiazole), 13.8 (s,1H, NH).

Sodium 2-(-2-(cyano(4-(coumarin-3-yl)thiazol-2 yl)methylene)-hydrazinyl)-5-(-(4-sulfophenyl)diazenyl)benzenesulphonate (D2)

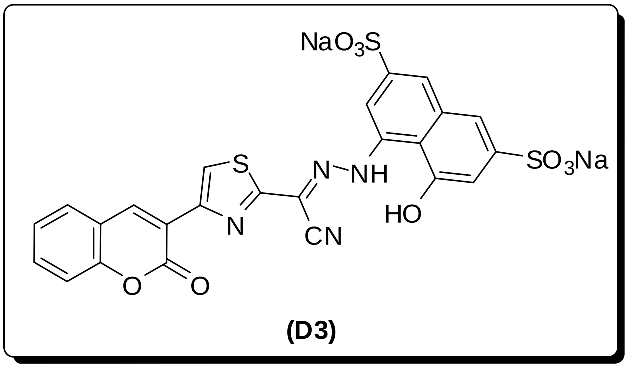


(D2)

Yield: 80%, m.p. > 300 °C, Violet, λ_{max} 515; $C_{24}H_{13}N_4O_6S_2Na$ $[M^+]$ = 540, Calcd.: C, 53.33; H, 2.42; N, 10.37; S, 11.86%, Found: C, 53.53; H, 2.02; N, 10.87; S, 12.02%; IR (ν, cm^{-1}): 3498 (OH), 3428 (NH), 2220 (C≡N)

1712 (C=O), 1489 (N=N). ^{1}H-NMR: δ = 7.0-8.8 (11H, m, ArH, naphthyl-H, coumarin-H-4, CH-thiazole), 12.5, 13.0 (2H, s, NH, OH).

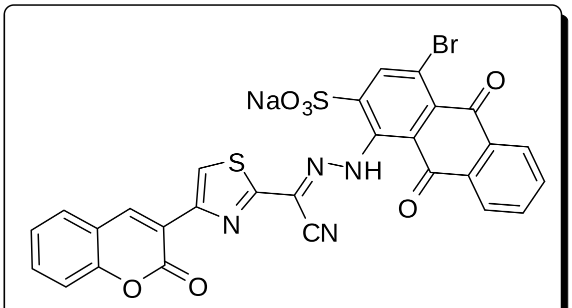
Sodium 4-(2-(cyano(4-(coumarin-3-yl)thiazol-2-yl)methylene)-hydr-azinyl)-5-hydroxynaphthalene-2,7-disulphonate (D3)



(D3)

Yield: 85%, m.p. >300 °C, Violet, λ_{max} 528; $C_{24}H_{12}N_4O_9S_3$ Na_2 [M$^+$] = 642, Calcd.: C, 44.86; H, 1.88; N, 8.72; S, 14.97 %, Found: C, 45.04; H, 2.06; N, 8.32; S, 15.07 %, IR (ν, cm^{-1}): 3500 (OH), 3428 (NH), 2250 (C≡N) 1713 (C=O), 1432 (N=N). ^{1}H-NMR: δ = 7.2-8.21 (10H, m, ArH, naphthyl-H, coumarin-H-4, CH-thiazole), 13.0, 13.3 (2H, s, NH, OH).

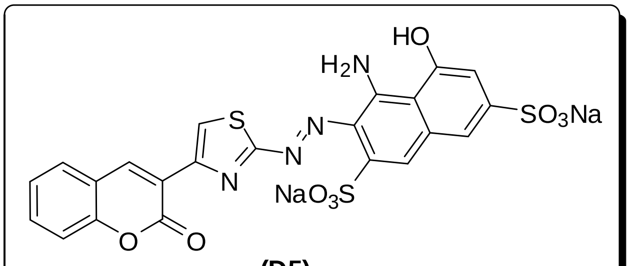
Sodium 4-bromo-1-(2-(cyano(4-(coumarin-3-yl)thiazol-2-yl)meth-ylene)hydrazinyl)-9,10-dioxo-9,10-dihydroanthracene-2-sulfonate (D4)



(D4)

Yield: 82%, m.p. > 300 °C, Brownish, λ_{max} 464; $C_{28}H_{12}BrN_4O_7S_2Na$ [M$^+$] = 682 Calcd.: C, 49.21; H, 1.77; N, 8.20; S, 9.38%, Found: C, 49.58; H, 2.03; N, 8.02; S, 9.16 %, IR (ν, cm^{-1}): 3425 (OH), 2258 (C≡N), 1713 (C=O), 1600 (C=O), 1421 (N=N). ^{1}H-NMR: δ = 7.1-8.9 (11H, m, ArH, anthracen-H, coumarin-H-4, CH-thiazole), 13.3 (1H, s, OH).

Sodium 4-amino-5-hydroxy-3-((4-(coumarin-3-yl)thiazol-2-yl)diazen-yl)naphthalene-2,7-disulfonate (D5)



(D5)

Yield: 85%, m.p. >300 °C, Violet, λ_{max} 540; $C_{22}H_{12}N_4O_9S_3$ Na_2 $[M^+]$ = 618, C, 42.72; H, 1.96; N, 9.06; S, 15.55 %, Found: C, 43.01; H, 2.06; N, 9.56; S, 15.45 %, IR (ν, cm^{-1}): 3502 (OH), 3434 (NH), 1632 (C=O), 1468 (N=N). ^{1}H-NMR: δ = 4.5 (2H, s, NH_2), 7.0-9.11 (9H, m, ArH, naphthyl-H, coumarin-H-4, CH-thiazole), 13.0 (1H, s, OH).

3.2. Dyeing of coumarine containing thiazole derivatives on wool D1-5

3.2.1. Effect of pH on percent of exhaustion dyeing

Dyeing was carried out using 2% o.w.f dye concentration at 100 ˚C by varying the dye bath pH from 3 to 7 to examine dye exhaustion. It is observed that the best results obtained when dyeing in acid medium, the dyes D1-5 recorded maximum values in pH 3, 4 intervals for wool. Figure 1 show the effect of pH on the exhaustion of acid dyes on wool fabric. The data revealed that at lower dyeing pH values (pH 3), the substantivity of the acid dyes on wool is virtually high. The wool fiber produce cationic sites in water under acidic conditions, as the acidity of the solution is increased more cationic sites are produced under these strongly acidic conditions.

These cationic sites are thus available for the acid dye anions to combine with through ionic bonding. These linkages are strong enough to break, and thus dyeing produced is fast. In the case of dyeing in acid medium, the results revealed an average affinity of the dyes for wool fabrics. In the case of dyeing in neutral medium, the affinity of dyes is lower.

From these results we can deduce the dye **D2** is the most exhaustion value because this dye has low molecular weight and less steric hindrance than dye **D4**. The low substantively of acid dye **D1** is due to high molecular weight which decreases substantivety.

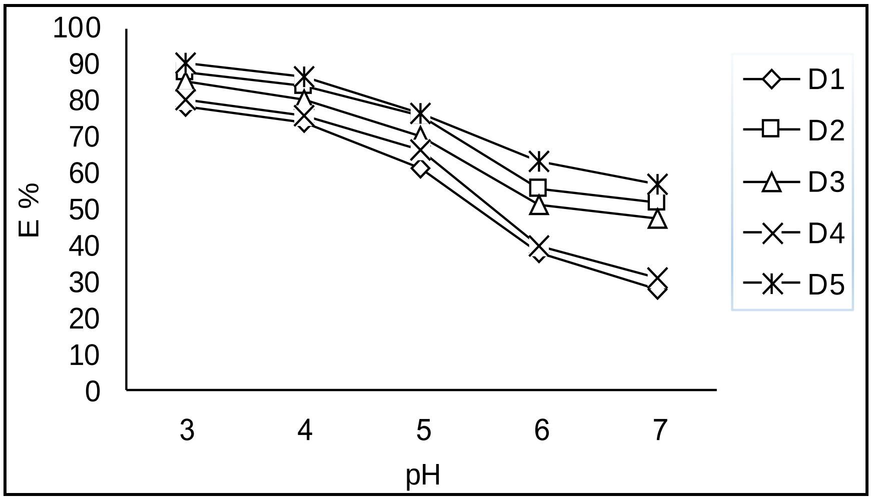


Figure 1: Exhaustion of acid dyes 1-5 on wool at various pH values using (2% o.w.f.)

3.2.2.. Effect of dye concentration on percent of exhaustion dyeing

The exhaustion of the dyes on wool was examined using different depth of shades (1-5% owf) at pH 4 (i.e. which is the optimum pH) and 100 ˚C. There are a large number of amino groups present in the wool fibre. As a guide, there are approximately twenty times as many amino groups on wool as on nylon and five times as many amino groups on wool as on silk. Dark shades can be readily obtained on wool because of the highly amorphous nature of the fibre, which results in relatively easy penetration of the fibre polymer by the dye molecule and because of the presence of amino groups, as shown in Figure 2. Increasing the dye concentration reduces the exhaustion on wool.

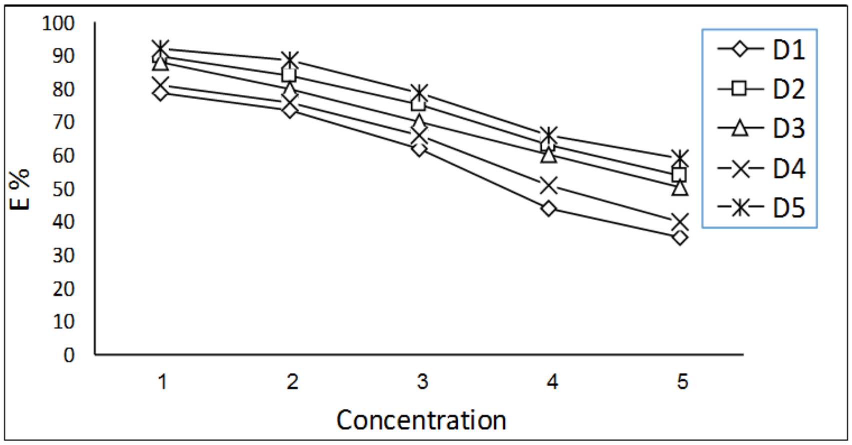


Figure 2: Exhaustion of acid dyes 1-5 on wool using various concentrations at pH 4

3.2.3. Effect of time dyeing on percent of exhaustion dyeing

Figure 3 shows that, the effect of time on dying of wool fabric on the percentage of exhaustion of dyes D1-5 at pH 4 using 2% o.w.f. dye concentration. From the results given in figure 3, it is apparent that the dye-fibre reaction is characterized by fast initial rate followed by slower rate which levels off within the last 30 min of dyeing process, also we noticed that increasing the time of dyeing lead to increasing the exhaustion of dyes i.e. higher color strength values.

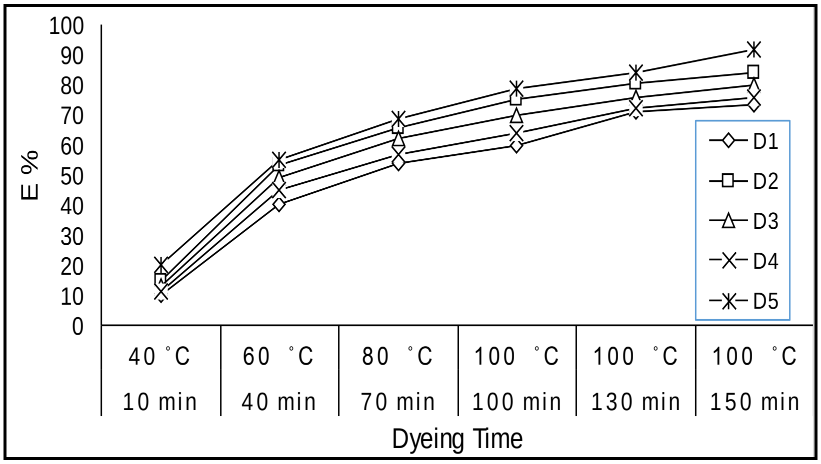


Figure 3: Exhaustion of acid dyes 1-5 on wool at pH 4 (2 %o.w.f.) with varying of dyeing time.

3.3. Dyeing of coumarin containing thiazole derivatives on silk D1-5

3.3.1. Effect of pH on percent of exhaustion dyeing

Silk is a natural protein, like wool fibre, due to this, mechanism of dyeing silk is dependent not only on free amino and carboxyl groups but also on phenolic with accessible –OH group. Because of slightly cationic character of silk with isoelectric point at above pH 5.0, it can be dyed with anionic acid dye.

Dyeing was carried out using 2% owf dye concentration at 100 ˚C by varying the dye bath pH from 3 to 7 to examine dye exhaustion. It is clear from Table 4, that the substantivity of dyes increases by increasing the dyeing pH up to 5 then it is relatively decrease. Also Figure 4 show the effect of pH on the exhaustion of Acid dyes D1-5 on silk fibre. From these results we can deduce the dye D2 is the most exhaustion value because this dye has low molecular weight than others. The low substantively of acid dye D1 is due to high molecular weight which decrease substantivety.

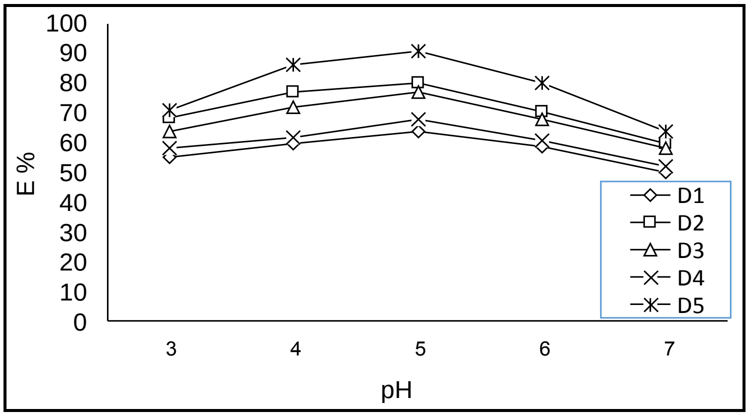


Figure 4: Exhaustion of acid dyes D1-5 on silk at various pH at (2% o.w.f.)

3.3.2. Effect of dye concentration on percent of exhaustion dyeing

Increasing the dye concentration reduces the exhaustion on silk fabric so the optimum conditions for dyeing silk at 2% shade.

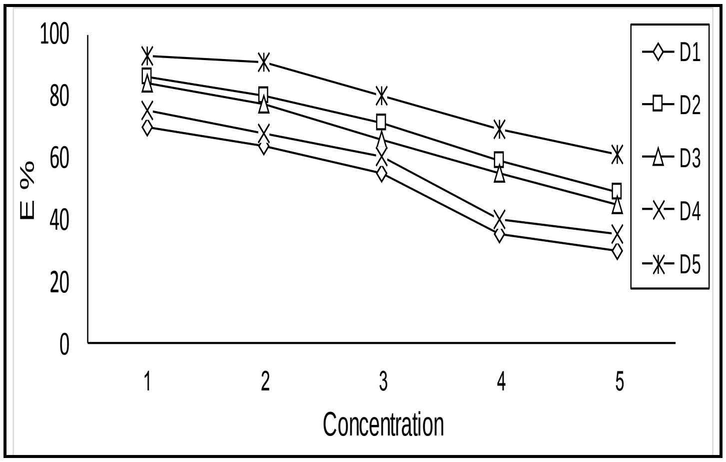


Figure 5: **Exhaustion of acid dyes** D1-5 **on silk at various concentrations at pH 5** and 100 ˚C

3.3.3. Effect of dyeing time on percent of exhaustion dyeing

Having established that the optimum dyeing pH was 5 for dyes the extent of exhaustion was investigated on silk at different dyeing time using 2% owf dye concentration. From the results given in figure 6, it is apparent that the dye-fibre reaction is characterized by fast initial rate followed by slower rate which levels off within the last 30 min of dyeing process

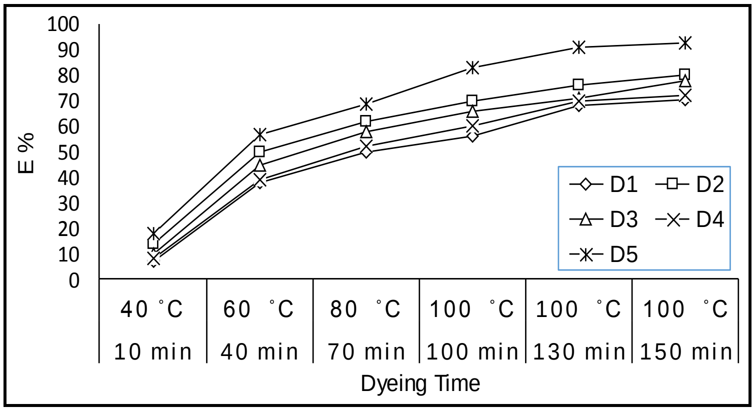


Figure 6**: Exhaustion of acid dyes** D1-5 **silk at pH 5 (2 %o.w.f.) with varying of dyeing time**

3.3. Colorimetric and Fastness properties

The colorimetric CIE L*a*b*C*ho data of the dyed wool and silk using the dye are shown in Table 1. The colour parameters were evaluated by means of the CIE lab system and the modified CIE L* C * ho (D65/10o) system. The following colour parameters for the dyed samples were obtained by the digital CIE lab system: L* – lightness, a* – redness if positive coordinates, or greenness if negative coordinates, b* – yellowness if positive coordinates, or blueness if negative coordinates, [42]. As shown in Table 2, the fastness to washing, rubbing and perspiration of all samples dyed with the dye were excellent to very good irrespective to the fabric used. Chromatic parameters were determined in comparison for samples dyed with all dyes.

The light fastness of the dyes was found to depend on the mobility of electrons through conjugated system from conjugated system from thiazole ring with coupler compounds afforded a good value of light fastness. The visible absorption spectra of some dyes showed that colours of dyes in the range of blue-purple. and others in range of yellow-brown. The fastness of dyed fabrics to water, washing, alkaline and acid perspirations and rubbing were found to be very high irrespective of degree of sulphonation in the coupling component.

Table 1 Colorimetric data of the dyed wool and silk fabrics using dyes D1-5 (2% owf) at 100°C and at pH 4.

Dye	Fabric	K/S	L*	a*	b*
D1	W	18.99	45.75	16.48	36.49
	S	5.03	58.22	14.86	33.07
D2	W	23.12	17.36	10.2	-3.01
	S	7.09	32.10	6.47	-9.64
D3	W	18.19	20.91	11.20	-3.79
	S	5.96	33.28	6.27	-9.69
D4	W	20.1	43.21	15.42	34.21
	S	6	52.21	13.81	30.21
D5	W	27.24	16.10	8.98	-2.29
	S	8.93	30.13	13.81	-8.15

Table 2 Fastness properties of dyed wool and silk fabrics using dyes D1-5 (2% owf) at 100°C and at pH 4.

Dye	Fabric	Fastness to rubbing		washfastness			Fastness to Perspiration						Light
							Alkaline			Acidic			
		Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
D1	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	S	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
D2	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	S	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
D3	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	S	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
D4	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	S	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
D5	W	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	S	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4

Alt. colour change of dyed sample; SC, staining on cotton; SW staining on wool**.**

4. Conclusion

The main purpose of this paper is to synthesise, characterise and find out properties of some new acid dyes, mono azo and diazo derived from 3-[2-(cyanomethyl)-thiazol-4-yl]coumarin and 3-(2-amino-thiazol-4-yl)coumarin using various derivatives amine. The suitability of the prepared dyestuffs for dyeing of wool and silk fabrics has been investigated. The results assessed for dyeing indicate that showed higher exhaustion and fixation values, colour yield and fastness properties than common acid dyes. The dyeing properties of the dye were initially investigated on wool fabric by varying the pH from 3 to 7. It is observed that the best results obtained when dyeing in acid medium, the dyes recorded maximum values in pH 3, 4 intervals for wool. The data revealed that at lower dyeing pH values (pH 3), the substantivity of the acid dyes on wool is virtually high. The wool fiber produce cationic sites in water under acidic conditions, as the acidity of the solution is increased more cationic sites are produced under these strongly acidic conditions.

The results indicate that dyeing silk show the substantivity of dyes increases by increasing the dyeing pH up to 5 then it is relatively decrease. Also, we can deduce the dye D2 is the most exhaustion value because this dye has low molecular weight than others. The low substantively of acid dye D1 is due to high molecular weight which decreases substantivety. The fastness to washing, rubbing and perspiration of all samples dyed with the dye were excellent to very good irrespective to the fabric used. The light fastness of the dyes was found to depend on the mobility of electrons through conjugated system from thiazole ring with coupler compounds afforded a good value of light fastness. The visible absorption spectra of all dyes showed that colours of dyes in the range of violet and brown. The structure of these dyes are characterized and confirmed by melting point, elemental analysis, infrared, ultraviolet-visible spectroscopy (UV/VIS) and nuclear magnetic resonance (^{1}H-NMR) data.

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