European Journal of Molecular & Clinical Medicine

ISSN 2515-8260 Volume 08, Issue 02, 2021

Synthesis of Novel anti UV- Reactive Dyes and their applications on textile fabric

Saadia Abd Elmegied ,Magda M. Kamel; Badria M. Youssef, Safia A. Mahmoud

Textile Research Division, National Research Centre, 33 El Bohouth St. (Former El Tahrir St.), Dokki, Giza, Egypt, P.O.12622
Corresponding author email: sa_abdelraoof@yahoo.com

Abstract: New anti UV- reactive dyes (1-4) were synthesized from its structure was confirmed by 1HNMR and IR spectroscopy and their dyeing behavior and ultraviolet (UV) protection on cotton and wool fabrics were investigated. From the study, we can see that the exhaustion value reached over 85%, the T (UVA) and T (UVB) were 3.3% and 3.4%, respectively. The fabric dyed with anti UV- reactive dyes had very good ultraviolet radiation protection. The effects of varying dyeing conditions were investigated. Fabrics dyed with anti-UV dyes were tested for color strength (K/S), rate of fading (ΔE) values. The dyed fabrics also showed very good light fastness and good to excellent washing, rubbing, and perspiration fastness. In this paper our work aiming to reduce the undesirable photodegradation effects of UVR on dyed fabrics by applying these new anti UV- reactive dyes.

Keywords: synthesis; characterization; reactive dyes; dyeing; color strength (K/S), UV absorbers; wool - cotton fabric.

1. INTRODUCTION:

One of the most important problems nowadays is that more ultraviolet rays reach earth due to the low thickness of the ozone layers. Long-term exposure to this radiation can lead to a series of dermatological diseases such as acceleration, aging skin, acne ,and skin cancer. The ultraviolet radiation (UVR) is composed of three types: UV-A (315–400 nm), UV-B (290–315 nm), and UV-C (100–290 nm)[1]. Ultraviolet (UV) protection of fabrics can be greatly improved by coloring because most dyes have an absorption strip extending from the visible spectrum (400-700 nm) to the invisible UV spectrum (280-400 nm). The UV protection provided by the dyes is determined by the absorption site and its intensity in the ultraviolet spectrum, which is mainly governed by the chemical composition of the dyes rather than the class of dyes [2–8]. Several factors may affect the absorption of ultraviolet radiation (UVR) for the fabrics, such as the chemical composition of the fabric in addition to the depth of color may be of the utmost importance and also protection against ultraviolet radiation increases with increasing concentrations of dye in general [9–12]. Dark-colored fabrics enjoy UV protection better than light colors, provided that the fabric has the same chemical composition [13-19]. However, light-colored clothing may occupy several factors that may affect the first place as summer clothing because it is less absorbent to sunlight compared with dark-colored fabrics [20-22]. The need to increase the efficiency of light-colored fabrics towards UV

protection has become another challenge. One of the most important solutions to improve the protection of ultraviolet UV fabrics by producing a more compact fabric structure.

Various treatments have been used to improve the color strength and stability properties of the dyed fabrics such as ultraviolet, ultrasound, and gamma rays [23-24]. However, the effect of radiation therapy has been used in a limited way to evaluate the stability properties of dyed fabrics with natural and synthetic dyes.

In many recent studies, the emphasis has been on the formation of dyes containing ultraviolet absorption groups and their application to fiber dyeing to improve the UV protection properties of fabrics [25, 26]. For example, dispersed dyes [27-29] and reactive dyes. Rarely did they care about the acid dye, which is important with silk as ultraviolet protection. Exposure to high doses of ultraviolet radiation, which causes damage to the human skin, may lead to burns, skin damage, and skin cancer [30-33] .

The dyes were widely studied in terms of their UV protection, which included direct dyes, reactive dyes, acid dyes and, azo dyes. With all these studies, the results have not been shown to confirm that any class of dyes can provide better UV protection and this variation in dyes is not only chemical composition but also application conditions which in turn can alter the fiber properties. Among all these types of dyes are the reactive dyes which can be used widely because of their strong stability for washing.

It is worth mentioning that the number of reactive groups and their effectiveness affect dyeing properties such as substantively, exhaustion, fixation, and washing-off after dyeing [34], where these dyes are colored compounds containing functional groups that interact with the nucleophilic groups such as OH, SH, and NH2 found in tissue fibers [35].

2. Experimental

2.1. Materials and instrumentation

2.1.1. Fabric

Cotton fabric: Mill-scoured and bleached cotton fabric, 130 g/m2, was obtained from Misr El-Mahalla Co., Egypt. The fabric was treated with a solution containing 3 g/l non-ionic detergent (Hostapal CV, Clariant, Egypt) and 5 g/l sodium carbonate at a liquor ratio 50:1 under boiling for 1h, after which time it was thoroughly rinsed and dried at room temperature.

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, after which time it was thoroughly rinsed and dried at room temperature.

2.1.2. Chemicals

Aminobenzene-2-sulphonic acid, 3-aminophenol, and 3-nitro aniline were provided by Isma Dyestuff and Chemical Co., Egypt.Cyanuric chloride was supplied by Merck. All other chemicals and auxiliaries used in the study were of laboratory reagent grade and applied

without further purification. All other chemicals used in study were of laboratory reagent grade and applied without further purification.

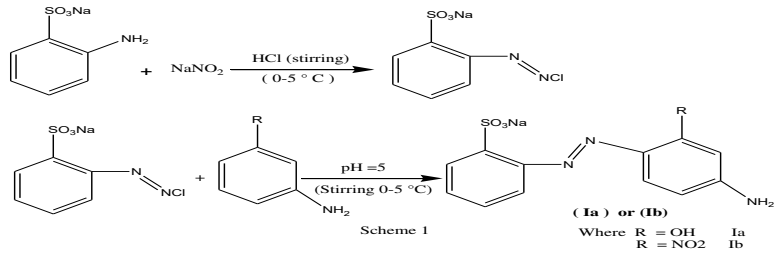
FT/IR spectra were recorded using JASCO FT/IR- 4700 spectrometers with high resolution 0.4 cm-1 using the ATR accessory. The 1HNMR spectra were recorded at room temperature on a Bruker Advance II 400 spectrometer at 400.13 MHz the samples were dissolved in hexadeuterio

2.2. Synthesis of dyes (1-4)

The procedures used for the synthesis of new reactive dyes (1 –4), shown in Schemes (1-4), are represented by the initial preparation of dye intermediates (I–V) given below.

2.2.1. Sodium (E)-2-((4- amino -2-hydroxy (nitro) phenyl)diazenyl) benzene sulfonate Ia and Ib respectively

A neutral solution of 2-aminobenzene sulfonic acid (orthanilic acid; 90%; 0.05mol)was diazotized using sodium nitrite in a concentrated hydrochloric acid at 0ºC; the pH was maintained at 5–6 by simultaneous addition of 2 M sodium carbonate solution while cooling at 0–5 ºC. The resulting solution of diazonium salt was then added with continuous stirring to 3-aminophenol (0.05mol) and 3-nitro aniline to produce[Sodium (E)-2-((4- amino -2-hydroxy phenyl)diazenyl) benzene sulfonate(**Ia)**],[Sodium (E)-2-((4- amino -2-nitro phenyl) diazenyl) benzene sulfonate (**Ib)**] respectively in scheme 1. The precipitated product, formed upon the addition of 10% w/v sodium chloride, was filtered off, washed with 10% brine solution, and dried in an oven at 50 ºC.



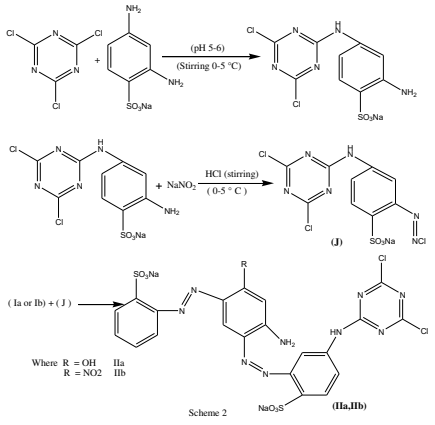
Scheme 1

2.2.2. Synthesis of IIa and IIb

Cyanuric chloride (3.7 g, 0.05mol) was stirred in acetone (50 ml) at a temperature below 5ºC for a period of an hour. A neutral solution of metaphenylene diamine sulphonic acid (0.05

ISSN 2515-8260 Volume 08, Issue 02, 2021

mol) was then added in small lots in about an hour. Neutral pH was maintained below 5ºC through this reaction. The reaction was then stirred at 0–5ºC for further four hours when a clear solution was obtained. The pH was maintained at 5–6 by simultaneous addition of 2 M sodium carbonate solution.The solution was stirred for a further 2h at 0-5 ºC. To this solution, hydrochloric acid (36 %; 5ml; 0.05mole) was added and then cooled to 0-5 ºC. A solution of sodium nitrate (0.05mole) dissolved in water (10 ml) was added over 20 min .The reaction mixture was stirred for 1 h at 0-5 ºC to give [Sodium 2-(chloro diazinyl)-4E(4,6dichloro 1,3,5triazine 2-ylamino)benzene sulphonate](J).The diazo solution (J) was coupled with Ia (0.05 mole) and Ib (0.05 mole) at pH 5–6 and stirred at 0-5 ºC for 4h to yield (IIa) and (IIb) respectively , in scheme 2 .

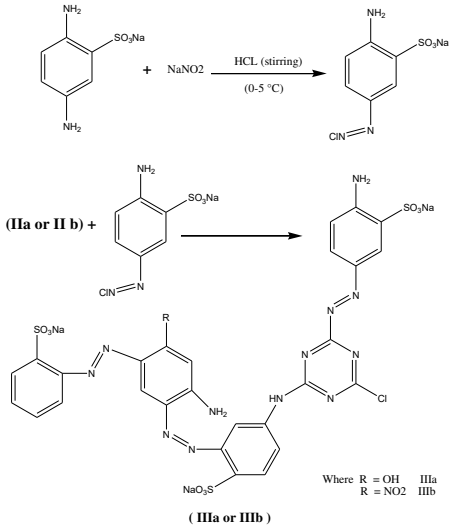


Scheme 2

2.2.3. Synthesis of (IIIa,IIIb)

A neutral solution of paraphenylene diamine sulphonic acid (0.05 mol) was diazotized using sodium nitrite in a concentrated hydrochloric acid at 0ºC; the pH was maintained at 5–6 by simultaneous addition of 2 M sodium carbonate solution while cooling at 0–5 ºC. The solution of diazonium salt of paraphenylene diamine sulphonic acid (0.05 mol) was dissolved in acetone (30 ml) drop wisely added to the solution (IIa, IIb) over 20 min.The reaction mixture was stirred for 1 h at 0-5 ºC and maintained pH 5-6 to give (IIIa, IIIb) respectively in scheme 3.

ISSN 2515-8260 Volume 08, Issue 02, 2021

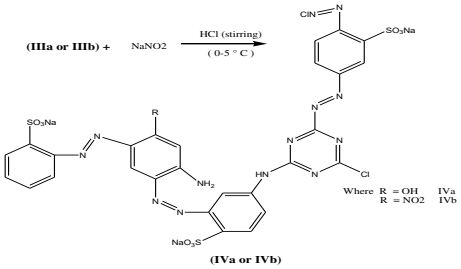


(IIIa or IIIb)

Scheme 3

2.2.4. Synthesis of dyes1-4

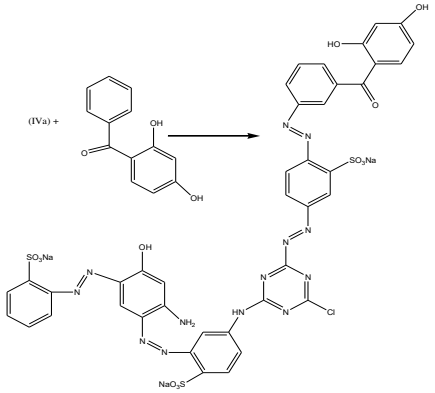
A neutral solution of (IIIa, IIIb0.05mole) was diazotized using sodium nitrite in a concentrated hydrochloric acid at 0ºC; the pH was maintained at 5–6 by simultaneous addition of 2 M sodium carbonate solution while cooling at 0–5 ºC to give (IVa, IVb) respectively, drop wisely added a neutral solution of 2,4dihydroxybenzophenone (0.05mole) and resorcinol (0.05mole)on (Iva) to give dye 1 and dye 2 respectively and drop wisely added a neutral solution of 2,4dihydroxybenzophenone (0.05mole) and resorcinol (0.05mole)on (IVb) to give dye 3 and dye 4 respectively.



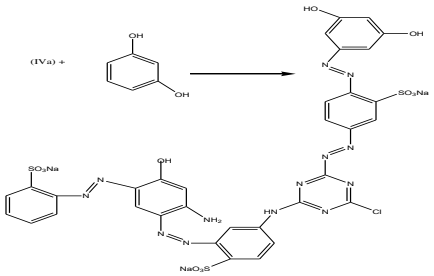
(IVa or IVb)

Scheme 4

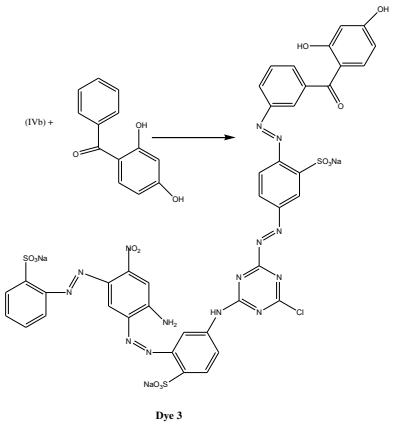
ISSN 2515-8260 Volume 08, Issue 02, 2021



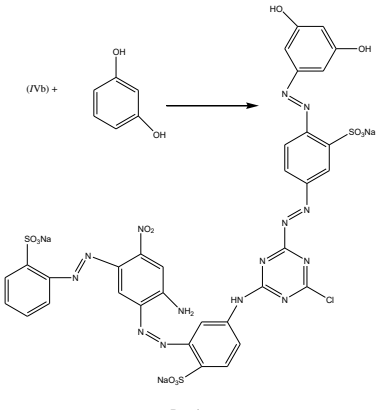
Dye 1



Dye 2



Dye 3



Dye 4

ISSN 2515-8260 Volume 08, Issue 02, 2021

2.3. Dyeing procedure

2.3.1. Dyeing of cotton

The synthesized (1-4), reactive dyes, were applied with 60 g/l sodium sulphate followed by add 20 g/l sodium carbonate. The dyeing was conducted with sodium sulphate at 40°C for 30 min and then allowing fixation in sodium carbonate for a further 60 min at 60°C. After thorough rinsing, the dyed samples were extracted with 50% aqueous DMF at the boil for 15 min.

2.3.2. Dyeing of wool

All the reactive dyes (1-4), were applied at various pH 3-7 using 5% o.w.f. ammonium sulphate. Each dyeing was performed at 50°C, allowing the temperature of the dye bath to raise to the boil over 30 min. The dyeing was continued at the boil for a further 60 min. At the end of the dyeing process, the samples were thoroughly rinsed and air-dried.

2.4. Dyeing measurements

Measurements and testing dye exhaustion uptake of dye by the cotton and the wool yarn was measured by sampling the dye bath before and after dyeing. The dye concentration (g/l) of the dye bath was measured on a Shimadzu UV-2401PC UV-visible spectrophotometer at the λmax value using a calibration curve previously obtained using known dye concentrations (g/l). The percentage of dye bath exhaustion (%E) was calculated using Eqn 1[36]:

$$\%E = [1-C2/C1] \times 100$$

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

The relative color strength (K/S) and CIELAB coordinates (L*a*b*c* h*∂e*) of the dyed fabrics were also measured using a Hunter lab's Ultra Scan PRO spectrophotometer (USA) under illuminant D65, 10standard observer [37]. The K/S value of dyed fabrics was measured by the light reflectance technique using Kubelka-Munk Eqn (2) (Judd et al., 1975). The reflectance (R) of the dyed fabrics was measured according to the following equation.

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

where,

R = Decimal fraction of the reflection of the dyed fabric

K = Absorption coefficient, and S = scattering coefficient

2.5. Fastness testing

Dyed cotton and wool samples with 2% shade (o.w.f) after washing-off using 2 g/l nonionic detergents at 80^{o}C for 15 min was tested by standard ISO methods [38]. Wash fastness [ISO 105-C02 (1989)], and fastness to perspiration [ISO 105-E04 (1989)] were evaluated using the visual ISO greyscale for both color change. Light fastness (Xenon arc) was evaluated using ISO 105-B02.

2.6. Ultraviolet Protection

The ultraviolet protection factor (UPF) was determined according to AS/NZS 4399:1996 standard procedure. The ultraviolet transmission through the fabric was determined by a Cary Varian 300 UV-Vis spectrophotometer under AATCC 183:2010 UVA Transmittance [39,40] .

3. Results and discussions

3.1. Synthesis

The dyes 1, 2, 3 and 4were prepared by coupling reaction of 2,4dihydroxybenzophenone and resorcinol with diazotized IVa, IVb respectively in basic solution. The chemical structures of these dyes were confirmed by 1HNMR and IR spectroscopy.

The chemical structures of dye 1 were confirmed by

IR ((KBr) υmax/cm-1):3426-3600(3OH), 3500(NH),3300-3310(NH_2) , 1600-1610 (2C=O) and 1550-1590 (4N=N).

^{1}HNMR: d H (ppm) in [2H6] DMSO: 4, 42 (s, 2H, NH_2), 7,26-7.45(m, 9H, $3C_6H_3$), 7.60-7.82(m, 8H, $2C_6H_4$), 7.70-7.92(s,2H, C_6H_2),8.2(s, 1H, NH) and9,78-10.23(s, 3H, 3OH).

The chemical structures of dye 2 was confirmed by IR ((KBr) υmax/cm-1): 3100-3480 (3OH), 3300(NH) 3200(NH_2), and 1520-1580 (4N=N).

^{1}HNMR: d H (ppm) in [2H6] DMSO: 5, 4 (s, 2H, NH_2), 7, 11-7.54 (m, 9H, $3C_6H_3$), 7,60-7,82(m, 4H, C_6H_4), 8.01-8.20(m, 2H, C_6H_2),8,5(s, 1H, NH) and9,98-10.50(s, 2H, 3OH).

The chemical structures of dye 3 was confirmed by IR ((KBr) υmax/cm-1): 3600-3620(2OH), 3300(NH),3350(NH_2), 1650 (C=O), 1490-1570 (4N=N).

^{1}HNMR: d H (ppm) in [2H6] DMSO: 5,1 (s, 2H, NH_2), 7, 24-7.51(m, 9H, $3C_6H_3$),7.56-7.71 (m, 8H, $2C_6H_4$), 7.8-8.2 (m, 2H, C_6H_2)9,2(s, 1H, NH)9,06-10,5(s, 2H, 2OH).

The chemical structure of dye 4 was confirmed by IR ((KBr) υmax/cm-1): 3400-3550(2OH), 3400 (NH), 3430(NH_2), 1488-1600(4N=N),

^{1}HNMR: d H (ppm) in [2H6] DMSO: 5, 6 (s, 2H, NH_2), 7,32-7,59 (m, 9H, $3C_6H_3$),7,6 -7,9(m, 4H, C_6H_4), 8.02-8,7(m, 2H, C_6H_2),8,9(s, 1H, NH),9.80 -10,6(s, 2H, 2OH).

3.2. Dyeing application on cotton(c) and wool (w) fabrics.
3.2.1. Effect of concentration of Na_2So_4 on K/S, value of cotton fabric dyed with dye [1-4].

Cotton fabrics were dyed with reactive dyes (1-4), (2% o.w.f). The dyeing was conducted with different concentrations of sodium sulphate 20%, 40%, 60% at 60°C for 30 min and then allowing fixation in sodium carbonate for a further 60 min at 80°C and 60°C respectively. The effect of different concentrations of salt [Na_2So_4] on both values of K/S, L, a, b, and ΔE of cotton fabric dyed with reactive dyes (1-4), are shown also in tables (1-4). From tables (1-4) it can be seen that the K/S values of cotton fabric dyed with reactive dyes (1-4) the maximum K/S value was obtained at (60%) of salt [Na_2So_4] concentration. Also, from a table (1-4) it is observed that by increasing the concentration of salt [Na_2So_4] from (20,40,60%) the K/S values have been increased, this is due to as the concentration of salt [Na_2So_4] increase the dye uptake also increase, Also the color difference (ΔE) values of cotton fabric dyed with reactive dyes (1-4), are given all in tables (1-4). From this tables, in the table (1&2) it can be seen that by increasing the concentration of salt Na_2So_4 there is no significant color difference (ΔE) between the samples, in the table (2&3)up to (40%) as increasing in Na_2So_4concentration the increasing in color difference (ΔE) takes place.

Table (1): Effect of different concentration of Na_2So_4 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye1.

Conc. of Na_2So_4%	K/S	L	a	b	ΔE
20%	3.61	52.43	22.39	22.22	42.40
40%	3.80	50.76	22.25	21.11	42.93
60%	3.93	52.28	22.25	22.70	42.69

Table (2): Effect of different concentration of Na_2So_4 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye2.

Conc. of Na_2So_4%	K/S	L	a	b	ΔE
20%	2.71	73.94	7.29	12.88	16.21
40%	2.72	73.69	7.63	14.73	17.93
60%	4.02	66.18	13.59	23.62	30.33

Table (3): Effect of different concentration of Na_2So_4 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye3.

Conc. of Na_2So_4%	K/S	L	a	b	ΔE
20%	2.45	73.02	7.55	11.97	16.07
40%	2.55	72.01	8.39	12.29	17.21
60%	2.81	69.32	10.49	15.64	21.98

Table (4): Effect of different concentration of Na_2So_4 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye4.

Conc. of Na_2So_4%	K/S	L	a	b	ΔE
20%	2.34	74.85	5.10	9.86	12.49
40%	2.53	74.89	5.07	10.79	13.19
60%	2.80	73.84	5.27	11.99	14.71

3.2.2. Effect of concentration of Na_2Co_3 on K/S, value of cotton fabric dyed with dye [1-4].

The dyeing of Cotton fabrics with reactive dyes (1-4),(2% o.w.f), was conducted with sodium sulphate 20% at 60°C for 30 min and then allowing fixation in sodium carbonate[5,10,15,20%] for a further 60 min at 80°C and 60°C respectively. The color strength (K/S) were measured and cited in Tables (5-8).

The effect of different concentrations of Na_2Co_3 on both values of K/S, L, a, b, and ΔE of cotton fabric dyed with reactive dyes (1-4) are listed in Tables (5- 8). From Tables (5- 8) it can be seen that as the concentration of Na2Co3 increases from 5% to20%, the colour strength [K/S] also increases. Above 10% dye Na_2Co_3 concentration the colour strength values nearly levels off or a very slight improvement takes place.

Also, from tables (5-8), it can be seen that the color difference (ΔE) values of cotton fabric dyed with reactive dyes (1-4) increasing as the concentration of Na_2Co_3 increases from (5%) to (20%).

Table (5): Effect of different concentration of Na_2Co_3 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye1.

Conc. of Na_2Co_3%	K/S	L	a	b	ΔE
5%	1.50	65.58	10.36	21.73	28.21
10%	2.42	70.95	7.25	17.98	28.84

15%	2.44	70.10	7.55	18.22	29.52
20%	2.97	69.85	7.99	18.76	34.59

Table (6): Effect of different concentration of Na_2Co_3 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye2.

Conc. of Na_2Co_3%	K/S	L	a	b	ΔE
5%	2.77	65.46	11.70	21.46	34.79
10%	2.78	63.91	12.94	22.02	36.39
15%	3.12	62.41	13.58	22.85	38.03
20%	3.54	60.27	14.55	23.46	39.99

Table (7): Effect of different concentration of Na_2Co_3 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye3.

Conc. of Na_2Co_3%	K/S	L	a	b	ΔE
5%	2.49	73.09	7.74	14.68	24.52
10%	2.86	68.53	11.27	19.80	31.84
15%	3.34	67.24	12.80	21.67	34.45
20%	3.61	63.10	16.22	25.43	40.62

Table (8): Effect of different concentration of Na_2Co_3 on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye4.

Conc. of Na_2Co_3%	K/S	L	a	b	ΔE
5%	4.75	49.82	24.82	24.34	50.98
10%	5.36	48.02	24.71	24.00	51.91
15%	6.94	44.63	25.67	24.26	54.89
20%	9.74	39.41	25.74	23.01	57.90

3.2.3. Effect of dye concentration on K/S, value of cotton fabric dyed with dye [1-4].

The dyeing of Cotton fabrics with different concentration of reactive dyes (1-4)),(0.5-2%o.w.f), were conducted with sodium sulphate 20% at 60°C for 30 min and then allowing fixation in sodium carbonate[10%] for a further 60 min at 80°C and 60°C respectively. The color strength (K/S) were measured and cited in Tables (9-12).

Tables (9-12) show that as the dye concentration increase from 0.5% to2%, the color strength also increases. Above 1% dye concentration the color strength values nearly level off or a very slight improvement takes place.

ISSN 2515-8260 Volume 08, Issue 02, 2021

Also, the color difference (ΔE) values of cotton fabric dyed with different concentrations of reactive dyes (1-4), are given all in tables (9-12). From these tables, it can be seen that by increasing concentration of dye concentration the increase in color difference (ΔE) takes place.

In tables (9-12) it can be seen that up to (1.5%) of dye concentration there is no significant color difference (ΔE) between the samples.

Table (9): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye1.

Conc. of dye %	K/S	L	a	b	ΔE
0.5%	15.82	37.19	19.48	29.29	2.86
1%	19.61	30.59	17.99	22.70	9.61
1.5%	19.83	30.18	17.62	22.21	10.30
2%	20.03	27.79	16.70	19.24	14.20

Table (10): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye2.

Conc. of dye %	K/S	L	a	b	ΔE
0.5%	20.49	25.82	16.32	16.35	17.68
1%	23.83	22.74	13.44	11.80	23.65
1.5%	25.32	21.37	11.87	9.73	26.46
2%	26.50	21.25	11.83	9.76	26.52

Table (11): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye3.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	9.67	48.56	24.89	34.64	13.56
1%	12.03	44.86	26.06	35.42	11.69
1.5%	13.35	43.18	27.45	35.37	11.55
2%	13.99	41.99	27.93	34.18	10.77

Table (12): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of cotton fabric dyed with dye4.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	19.61	28.89	22.93	18.79	13.99
1%	22.51	24.98	19.50	15.03	18.94
1.5%	22.80	23.75	18.31	12.89	21.42
2%	22.81	23.06	16.81	11.77	22.80

ISSN 2515-8260 Volume 08, Issue 02, 2021

3.2.4. Effect of dye concentration on K/S value of wool fabric dyed with dyes [1-4].

Wool fabrics were dyed with reactive dyes (1-4). The dyeing method carried out at various dye concentration (0.5-2% o.w.f), using 5% o.w.f. ammonium sulphate at pH3 and L.R 1:50 at 100 0C for 60 min. The color strength (K/S) were measured and cited in Tables (13-16).

Tables (13-16) show that as the dye concentration increases from 0.5% to3%, the color strength also increases. From tables (13-14) it is obvious that the color strength values of wool fabric dyed with reactive dye 1, 2 above 2.5% dye concentration nearly levels off or a very slight improvement takes place. In the case of wool fabric dyed with reactive dyes 3 and 4 higher improvements in color strength values take place when the concentration of dye more than 2%, as shown in tables (15-16).

Also, the color difference (ΔE) values of cotton fabric dyed with reactive dyes (1-4), are given in all tables (5-8). From these tables, it can be seen that up to (2.5%) of concentration of dye in the table (13&14), as increasing in dye concentration there is no significant color difference (ΔE) between the samples, in the table (15&16) as increasing in concentration of dye, the color difference (ΔE) between the samples also increases.

Table (13): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of wool fabric dyed with dye1.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	2.48	67.33	10.24	34.25	31.20
1%	3.37	62.69	13.13	34.64	34.79
1.5%	4.82	58.16	15.83	36.06	39.36
2%	6.03	56.51	16.81	38.41	42.37
2.5%	7.87	53.07	18.50	38.82	45.36
3%	8.56	51.33	18.58	38.01	45.92

Table (14): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of wool fabric dyed with dye2.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	1.37	71.62	6.58	26.69	21.85
1%	4.01	56.73	14.69	31.46	35.40
1.5%	4.06	58.33	15.38	32.12	36.34
2%	4.57	58.67	16.57	32.38	38.18
2.5%	5.76	54.05	16.89	33.47	40.76
3%	5.78	55.26	17.47	35.18	40.81

ISSN 2515-8260 Volume 08, Issue 02, 2021

Table (15): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of wool fabric dyed with dye3.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	2.40	74.93	3.89	22.20	15.86
1%	4.38	68.73	9.78	30.89	27.71
1.5%	6.10	65.60	11.99	34.33	32.71
2%	6.65	65.15	13.49	34.89	33.97
2.5%	8.64	62.27	15.46	39.37	39.62
3%	11.10	59.95	17.45	41.04	42.84

Table (16): Effect of different dye concentration on both of K/S, L, a, b, and ΔE value of wool fabric dyed with dye4.

Conc. of dye%	K/S	L	a	b	ΔE
0.5%	4.45	59.82	18.04	34.59	38.44
1%	6.21	55.87	20.47	36.07	42.81
1.5%	10.71	51.46	22.30	40.07	48.86
2%	12.64	49.46	24.11	40.56	51.23
2.5%	14.59	48.56	24.99	41.87	53.04
3%	18.82	44.01	26.09	39.53	55.02

3.2.5. Effect of PH on K/S value of wool fabric dyed with dyes [1-4].

Wool fabrics were dyed with reactive dyes (1-4). The dyeing method carried out at various dye concentration (2.5% o.w.f), using 5% o.w.f. ammonium sulphate at PH (4-9) and L.R 1:50 at 100 ^{0}C for 60 min. The color strength (K/S) were measured and cited in Table (17).

From table (17) wool samples dyed with A and B intermediate and reactive dyes 1-4 give the highest color strength(K/S) values at pH 4 for dyes 1,2and 4 while the highest color strength(K/S) values for dye 3 were obtained at pH 5.

Also, the color difference (ΔE) values of wool fabric dyed with reactive dyes (1-4), are given in table (17). From this table, it can be seen that as increasing in PH the color difference (ΔE) decreased.

Table (17): Effect of PH on both of K/S, L, a, b, and ΔE value of wool fabric dyed with dyes (1-4).

Dye		PH4	PH5	PH6	PH7	PH8	PH9
D1	K /S	4.91	4.34	3.56	3.05	2.42	2.32
	L	59.11	60.89	62.01	61.7	65.7	65.01
	a	14.69	13.44	11.82	12.46	9.27	10.02
	b	37.59	37.55	34.59	30.5	30.52	28.8
	ΔE	39.35	37.9	34.42	31.91	28.45	29.79
D2	K /S	5.3	4.66	4.61	3.3	2.55	2.47
	L	56.13	56.84	56.31	60.66	62.3	63.61

ISSN 2515-8260 Volume 08, Issue 02, 2021

	a	15.89	15.18	17.41	14.41	13.5	13.07
	b	34.71	33.24	30.56	31.59	27.89	29.33
	ΔE	39.51	37.8	37.48	34.08	30.22	30.24
D3	K /S	5.36	7.15	5.15	4.47	4.15	3.88
	L	62.62	58.85	64.26	65.2	65.4	67.29
	a	15.81	19.24	13.83	12.97	12.94	10.96
	b	40.6	43.89	37.51	36.69	36.85	36.02
	ΔE	46.17	40.5	36.43	35.05	35.01	32.81
D4	K /S	18.14	15.36	13.11	11.02	9.38	8.44
	L	45.11	46.84	48.04	51.83	53.06	54.89
	a	25.28	24.6	23.2	21.29	19.95	19.49
	b	40.07	39.71	39.62	41.42	40.76	40.65
	ΔE	54.12	52.47	50.98	48.97	47.2	45.89

.

From table (18) it can be observed that with increasing time of irradiation of dyed wool and cotton samples, The UPF value decreases for all dye intermediates A and B.

For dyed samples with dyes (1 - 4), it can be observed that the UPF of samples dyed with dye2 is less than that with dye1, dye3, and dye4. following the order dye1 > dye3> dye4>dye2. This can be attributed to the presence of carbonyl group in 2,4-dihydroxy benzophenone in Dye1 and Dye3.

The UPF value for wool and cotton fabric dyed with anti-UV dyes (1-4) is higher than that for samples dyed with dye intermediates A and B. This can be explained by the presence of an anti-ultraviolet functional finishing group in the structure of the dyes.

Table (18): The effect of Time of Irradiation on UPF value of wool and cotton fabric dyed with anti-UV dyes (1-4) and there intermediate A and B at optimum condition

Time of Irradiation In hrs	UPF											
	Intermediate A		Intermediate B		Dye 1		Dye 2		Dye 3		Dye 4	
	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton
0h	220.4	37.6	227.9	26.4	1330.5	73.98	827.7	45.09	1284.2	59.23	1247	47
35h	198.05	30.1	187.2	21.8	1262.4	67.1	496	34.21	539.9	50.8	911.4	33.2
70h	183.35	29.0	169.58	21.05	1247	56.1	433.2	32.8	517.5	45.9	744.4	26.9
105h	178.19	24.1	161.0	20.9	714.9	51.6	401.4	32.2	464.3	45.0	727.4	25.9
140h	153.91	23.3	148.45	20.0	616.7	46.8	391.91	30.6	251.9	42.1	469.5	23.4

175h	140.59	22.3	139.79	16.7	498.4	45.7	296.9	29.1	204.2	39.0	434.1	21.4

3.3 Fastness properties

The fastness properties for washing, rubbing, perspiration, and light of the dyed cotton and wool fabrics which dyed with dyes (1-4) and their intermediate are A and B showed in the table (19). It can be seen that the fastness properties of cotton and wool fabric dyes with anti-UV reactive dyes better than dyed with their intermediate. The results of fastness properties showed that dry crocking of dyed cotton and wool dyed with intermediate A and B and anti-UV reactive dyes (1-4) give better results than wet. On the other hand fastness to washing and perspiration ranged from good to very good results. Finally, light fastness property ranges from good to very good.

Table (19): Fastness Properties of cotton and wool samples dyed with dye intermediates (A, B) and anti-UV reactive dyes (1-4) at optimum condition

Dyes	Crocking fastness		Washing fastness			Acidic perspiration			Alkaline perspiration			Light fastness
	Dry	Wet	St.*	St.**	Alt.	St.*	St.**	Alt.	St.*	St.**	Alt.	
	COTTON FABRIC											
A	2-3	2	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3	4
B	2-3	2	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3	4
Dye1	4 -5	4	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	5
Dye2	4 -5	4	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	5
Dye3	4 -5	4	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	5
Dye4	4 -5	4	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	5
	WOOL FABRIC											
A	3-4	3	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5
B	3-4	3	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5
Dye1	4 -5	4	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	6-7
Dye2	4 -5	4	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	6-7
Dye3	4 -5	4	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	6-7
Dye4	4 -5	4	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	4 -5	6-7

4. CONCLUSIONS

This study has successfully synthesized four new reactive dyes, where their dyeing behavior and ultraviolet (UV) protection on cotton and wool fabrics were investigated, the results

revealed that the UPF value for wool and cotton fabric dyed with anti-UV synthesized dyes (1-4) is higher than that for samples dyed with dye intermediates A and B, and the dyeing application on cotton and wool fabrics was showing a high affinity to the fabric with excellent fastness properties.

5. ACKNOWLEDGMENT

We thank the National Research Center, Giza, Egypt for financial support either through chemicals or analyzes through the project 11090324 (Innovation Colorants and Development of Textile Auxiliaries and New Materials via Frontiers Sciences), as we work as a team to thank the Central Laboratory of Textile Industries Division for allowing us to measure on the devices To produce this work in a distinct form.

6. REFERENCES

1- Omer Kamal Alebeida ; Tao Zhao. Review on. developing UV protection for cotton fabric. The Journal of The Textile Institute, 2017 VOL . 108, NO . 12, 2027–2039.

2. Chakraborty, JN.; Sharma, V. ; Gautam, P. Enhanced protection in textiles against UV radiations.Asian Textile J 2012, 21, 57–61.

3. Gorensek, M. ; Sluga, F. Modifying the UV blocking effect of polyester fabric. Text Res J 2004, 74, 469–474.

4. Rosinskaya, C.; Djani, M.; Kizil, Z. et al. Improvement of UV protection with cotton fabrics dyed with binary mixtures of the reactive dyes. MelliandInt 2003,9, 147–148.

5. Veatch, KD. ;Gatewood, BM. Influence of light exposure on the UV protection of direct, reactive, acid, and
disperse dyes on cotton and nylon fabrics. AATCC Rev 2002, 2,47–51.

6. Palacin, F. Textile finish protects against UV radiation.Melliand Textil berichte Int Text Rep 1997, 78, 113–115.

7. Riva, A.;Algaba, I. Pepio, M. et al. Modeling the effects of color on the UV protection provided by cotton woven
fabrics dyed with azo dyestuffs. IndEngChem Res 2009,48,9817–9822.

8. Czajkowski, W. ; Paluszkiewicz, J. Synthesis of bifunctional monochlorotriazine reactive dyes increasing UV protection properties of cotton fabrics. Fibres Text East Eur2008, 16, 122–126.

9. Yadav, R. ;Karolia, A. ; Mairal, A. Effect of Acacia Catechu on UV protection of cotton, polyester and P/C
blend fabrics. Colourage2009, 56,50–55.

10. Wilson CA, Gies PH, Niven BE, et al. The relationship between UV transmittance and color - visual description
and instrumental measurement. Text Res J 2008; 78:128–137.

11. Srinivasan,M. ;Gatewood, BM. Relationship of dye characteristics to UV protection provided by cotton fabric. Text Chem Color Am Dyest Rep 2000,32, 36–43.

12. Grifoni ,D.;Bacci, L. ;Zipoli, G. et al. Laboratory and outdoor assessment of UV protection offered by flax and
hemp fabrics dyed with natural dyes. Photochemistry and Photobiology2009,85, 313–320.

13. Colin M.H.Driscoll. Artificial protection against solar radiation -fabrics. Photosciences2001, 3, 457-486

14. Sarkar, AK. An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants. BMC
Dermatol2004, 4, 15–22.

15. Gies, HP.; Roy, CR.; Elliott, G. et al. Ultraviolet radiation protection factors for clothing. Health Phys1994, 67,
131–139.

16. Gies, P. Photoprotection by clothing. **Photodermatol Photoimmunol Photomed** 2007; 23: 264–274.

17. Pailthorpe ,MT. Textiles and sun protection: the current situation. Austral as Text 1994, 14, 54–66.

18. Gies, HP.; Roy, CR.; Toomey, S. et al. Protection against solar ultraviolet radiation. Mutat Res FundamMolMech Mutagen 1998, 422,15–22.

19. Zhang, Z.;Thomas, B.; Wong, C. et al. Fast measurements of transmission of erythema effective irradiance through clothing fabrics. Health Phys 1997, 72, 256–260.

20. Dubrovski, PD. ;Brezocnik, M. Prediction of the ultraviolet protection of cotton woven fabrics dyed with reactive dyestuffs. Fibres Text East Eur2009,17,55–59.

21. Akaydin, M. Research of UV permeability properties of basic weft knitted structures. Sci Res Essays 2010, 5,
2169–2178.

22. Dubrovski PD and Golob D. Effects of woven fabric construction and color on ultraviolet protection. Text
Res J 2009; 79: 351–359.

23.Fazal, R., Adeel, S., Qaiser, S., Bhatti, I.A., Shahid, M., 2012. Dyeing behaviour of gamma irradiated cotton fabric using Lawson dye extracted from henna leaves (Lawsoniainermis). Radiation Physics and Chemistry 81 (11), 1752–1756.

24.Bhatti, I.A., Adeel, S., Rehman, F., Irshad, M., Abbas, M., 2012a. Effect of mercerization and gamma irradiation on the dyeing behaviour of cotton using stilbene based direct dye. Radiation Physics and Chemistry 81 (7), 823–826.

25. Sun, Y.; Zhao, D.; Freeman, H. S. Synthesis and properties of disperse dyes containing a built-in triazine stabilizer. Dyes and
Pigments 2007, 74 (3), 608-614
.
26.Czajkowski, W.; Paluszkiewicz, J. Synthesis of Bifunctional Monochlorotriazine Reactive Dyes Increasing UV-Protection
Properties of Cotton Fabrics.Fibres Text East Eur 2008, 16 (5), 122-126.

27. Dixit, B. C.; Patel, H. M.; Desai, D. J. Synthesis and application of new mordent and disperse azo dyes based on 2,4-
dihydroxybenzophenone. J Serb ChemSoc 2007, 72 (2), 119-127.

28. Freeman, H. S.; Mason, M. E.; Lye, J. Disperse dyes containing a built-in oxalanilide stabilizer. Dyes and Pigments 1999,
42 (1), 53-63.

29.Maradiya, H. R.; Patel, V. S. Studies of novel monomeric and polymeric azo disperse dyes. Journal of Applied Polymer
Science 2002, 84 (7), 1380-1389.

ISSN 2515-8260 Volume 08, Issue 02, 2021

30. Afaq, F.; Mukhtar, H. Effects of solar radiation on cutaneous detoxification pathways. J PhotochPhotobio B 2001, 63 (1-3),
61-69.

31. Greenlee, R. T.; Murray, T.; Bolden, S.; Wingo, P. A. Cancer statistics, 2000. Ca-Cancer J Clin 2000, 50 (1), 7-33.

32. Huang, H. F.; Ma, W.; Tang, B. T.; Zhang, S. F. Properties of a novel acid dye 1-amino-4-[(6-nitro-2-benzothiazolyl)amino]-
9,10-anthraquinone-2-sulfonic acid with anti-UV capability. Chinese Chem Lett 2010, 21 (4), 417-420.

33. Feng, X. X.; Zhang, L. L.; Chen, J. Y.; Zhang, J. C. New insights into solar UV protective properties of natural dye. J Clean
Prod 2007, 15 (4), 366-372.

34.Wai-yin Wong1, Jimmy Kwok-cheong Lam1, Chi-wai Kan1 andRon Postle2Influence of reactive dyes on ultraviolet
protection of cotton knitted fabricswith different fabric constructionsTextile Research Journal2016, Vol. 86(5) 512–532

35.Bahi, A., Jones, J.T., Carr, C.M., Uligin, R.V., Shao, J., 1992. Surface characterization of chemically modified wool. Journal of Textile Research 77, 937–945.

36-Tarek, A., El-Sedik, M., Abd El-Megied, S., Hassan, I.,Yehya, Y. and Radim, H. (2016), “Synthesis, spectral
study and application of solid state fluorescent reactive disperse dyes and their antibacterial activity”, Arabian
Journal of Chemistry.

37-Fatma, A.M., Mousa, A.A., Farouk, R. and Youssef, Y.A.(2015), “Union dyeing of wool/polyester blend fabric using
sulphatoethylsulphone dye derivative of C.I. Disperse Yellow23”, International Journal of ChemTech Research, Vol. 8 No. 8,
pp. 112-120.

38-Society of Dyers and Colourists (1990), Methods of Test for Colour Fastness of Textiles and Leather, British Standards
Institution.

39-. Khattab, T.A.; Fouda, M.M.; Abdelrahman, M.S.; Othman, S.I.; Bin-Jumah, M.; Alqaraawi, M.A.; Fassam, H.A.;
Allam, A.A. Development of Illuminant Glow-in-the-Dark Cotton Fabric Coated by Luminescent Composite
with Antimicrobial Activity and Ultraviolet Protection. J. Fluoresc. **2019**, 29, 703–710.

40. Pisitsak, P.; Hutakamol, J.; Jeenapak, S.; Wanmanee, P.; Nuammaiphum, J.; Thongcharoen, R. Natural dyeing
of cotton with xylocarpus granatum bark extract: Dyeing, fastness, and ultraviolet protection properties. Fibers Polym. **2016**, 17, 560–568.