

Synthesis, Characterization and Dyeing Assessment of Novel Acid Dyes on Wool Fabric IV

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Summary: We report synthesis and performance evaluation of a series of novel acid dyes based on diazotized substituted aryl amines and employing substituted naphthalene sulfonic acids as coupling component. The synthesized dyes were thoroughly characterized using UV-visible, IR, ¹HNMR spectroscopy, elemental analysis and negative MALDI-TOF mass spectrometric analysis. The effectiveness of these dyes was evaluated by applying them on wool fabric using a standard exhaust dyeing procedure. The results for washing, light, perspiration and rubbing fastness of the dyed fabric demonstrate excellent fixation, binding strength and fastness properties which indicate that they are suitable for industrial wool dyeing operations.

Keywords: Acid dyes, Wool dyeing, Substituted aryl amines, Substituted naphthalene sulfonic acids, MALDI-TOF mass spectroscopy.

Introduction

Wool is a commercially relevant natural fiber with unique set of properties that enabled it to become one of the major apparel fibers with a vast area of application ranging from textile clothing, upholstery and insulation industry [1-3].

Dyeing is a major value addition step in wool processing essential for its effective utilization in fabric industry [4]. Several approaches and coloring compounds have been explored and commercialized for imparting color to the wool fibers [4-6]. Among them, acid dyes are considered to be a logical choice because wool exhibit cationic character owing to the presence of ionizable amino groups as part of the main chain peptide bonds connecting the amino acid units together [6, 7].

Acid dyes have established their effectiveness and are extensively utilized in commercial wool dyeing operations [4, 6]. Belonging to a large family, they are so named because the original members of this family require them to be applied under acidic conditions [4, 5, 8]. The name is further justified as most of the commercial acid dyes are merely sodium salts of organic acids with the anion part essentially comprising a chromophore [5-7]. In Aqueous solutions, acid dyes split into colored negative and uncolored positive fragments and thus

interact with the fibers that have, or can be induced to have ionizable sites such as amino and carboxyl groups which can be ionized to NH³⁺ and COO⁻ respectively [8]. Wool under acidic conditions is such a fiber and dye uptake involves an anion exchange process in which the dye molecules displace smaller anions associated with the ammonium ions in the fiber [4, 8].

Despite of their success and vast applications in commercial wool dyeing, acid dyes suffers from some shortcomings [9-11]. For instance, they exhibit poor to moderate fastness properties, lower dye bath exhaustion and less penetration at lower temperatures² [9, 10]. Besides, high temperatures used in conventional dyeing operations can potentially impart some unfavorable properties such as weak fiber structure, lower strength and elongation at break of yarns and poor fabric abrasion resistance [11]. There is thus a strong need to explore and develop novel acid dyes possessing better dyeing properties.

In our ongoing efforts to explore novel and more efficient dyes with superior properties and functionalities, we reported several dyes which can potentially be commercialized for the industrial applications [12-14]. In continuation of our previous

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research, the present study focused on the synthesis, characterization and exploring the dyeing performance of three novel acid dyes derivatives. These dyes were synthesized using substituted aryl amines and substituted naphthalene sulfonic acids as diazo and coupling components, respectively. The structural characterization was performed using UV-visible, IR, ^1H NMR spectroscopy, elemental analysis and negative MALDI-TOF mass spectrometric analysis. To elucidate the dyeing performance, the synthesized dyes were applied on wool fabric where they exhibit excellent fixation, binding strength and fastness properties. This indicates that they are suitable to be applied on commercial wool dyeing operations.

Experimental

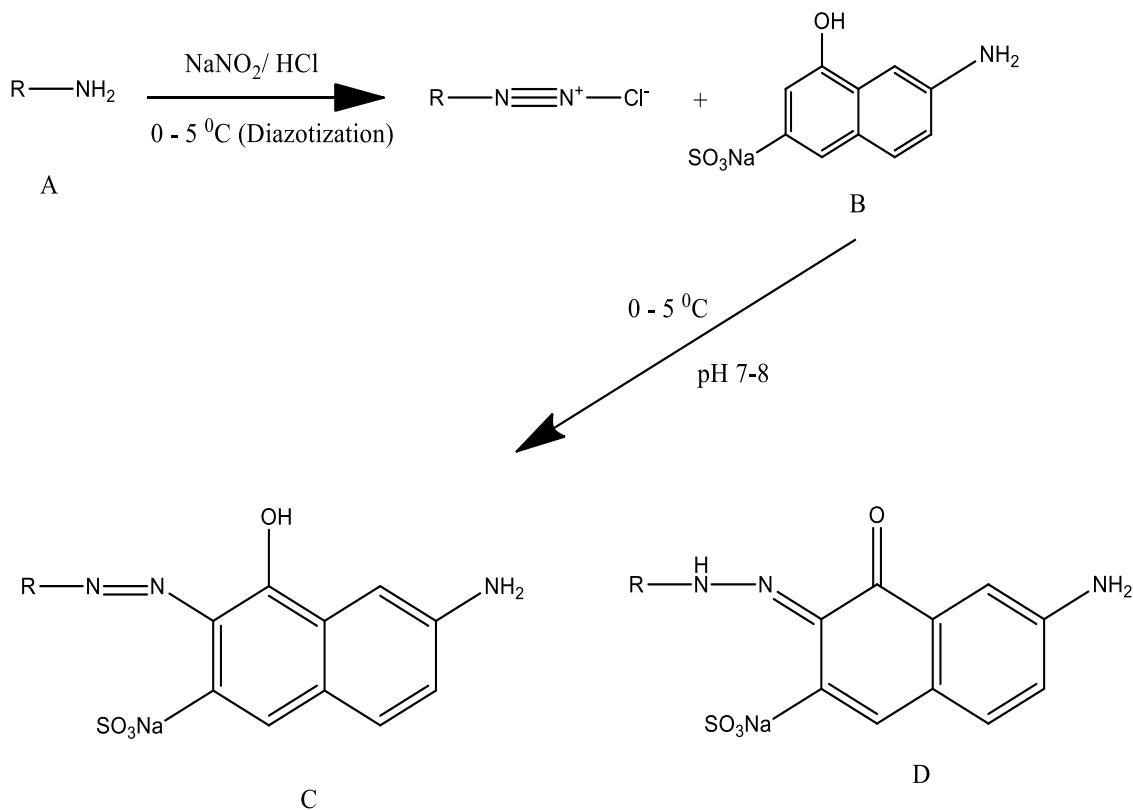
Material and Characterizations:

All reagents and solvents used in this study were of technical grade. Thin layer chromatography was performed on TLC plates coated with silica gel PF 254 (Merck). UV-visible spectroscopy was

recorded in de-ionized water on a Spectromiczo Bausch & Lomb spectrophotometer. FTIR spectra were all recorded on a Jasco A-30 spectrometer using KBr discs (Sigma Aldrich). ^1H NMR spectroscopy was performed on a Bruker AM 300 spectrophotometer using deuterated dimethyl sulfoxide (DMSO) as solvent (Sigma Aldrich). All the fabric samples were dyed on an I.R dyeing machine (Roaches Int.). Color fastness properties were explored using SDC test methods and CIE color coordinates L^* , a^* , b^* were all recorded on a Datacolor Spectroflash-650 instrument.

Table-1: Diazo and Coupling Components.

Dyes Code	Diazo Component (A)	Coupling Component (B)
C10	3-Amino sulfonic acid	2-Amino-8-naphthol-6- sulfonic acid (Gamma acid)
C11	4-Aminoacetophenone	2-Amino-8-naphthol-6- sulfonic acid (Gamma acid)
C12	3-Aminoacetophenone	2-Amino-8-naphthol-6- sulfonic acid (Gamma acid)



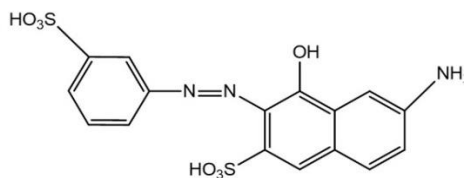
Scheme-1: General Synthesis Route for Acid Dyes [12, 13].

Synthesis of Dyes

Three different acid dyes were synthesized by employing substituted aryl amines and aminohydroxy-naphthalene sulfonic acid as diazo and coupling components, respectively. The details of the synthesis procedure have already been reported in our earlier publication [12, 13]. The diazo (A) and corresponding coupling components (B) used are all listed in Table-1 and a general synthesis route is depicted in Scheme-1 where the structures C representing the dye molecule and D representing the isomeric form [15, 16]. The resulting dyes were thoroughly characterized using FTIR, UV-Visible, ¹HNMR and MALDI-TOF (negative ion mode) mass spectroscopy and their structures are described in Scheme 2.

*Analytical and Spectral Data**2-Amino-8-naphthol-7-(3-Aminosulfonyl-diazinyl)-6-sulfonic acid (C10)*

MALDI-ToF (negative) analysis: Mol. Formula C₁₆ H₁₃ N₃ O₇ S₂, Mol. Weight: 423.24, Mass found by MALDI spectra: 422.880, Species Observed: M-H. UV: at λ_{max}: 530nm; log ε = 3.99. IR: (measured in KBr on a Jasco A30 instrument): (cm⁻¹): ν_{max} 3421 (N-H stretch), 1566 (N=N), 1191(S=O), 1051 (S-O). ¹HNMR (300 MHz, DMSO-d6): δ, ppm: 7.39 (1H, s), 7.44 (1H, s), 7.94-8.02 (2H, m), 8.867 (1H, s).



2-Amino-8-naphthol-7-(3-Aminosulfonyl-diazinyl)-6-sulfonic acid (C10).

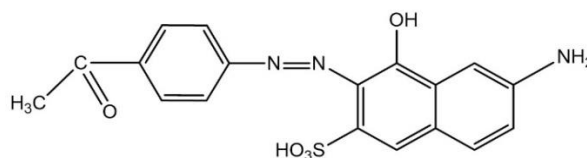
*d*6): δ, ppm: 7.39 (1H, s), 7.44 (1H, s), 7.94-8.02 (2H, m), 8.867 (1H, s).

2-Amino-8-naphthol-7-(4-Aminoacetophenyl-diazinyl)-6-sulfonic acid (C11)

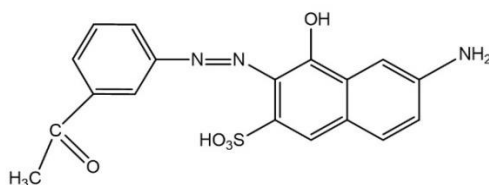
MALDI-ToF (negative) analysis: Mol. Formula C₁₈ H₁₅ N₃ O₅ S, Mol. Weight: 385.395, Mass found by MALDI spectra: 384.777, Species Observed: M-H-H₂O. UV: λ_{max}: 510nm, log ε = 4.08. IR: (measured in KBr on a Jasco A30 instrument): (cm⁻¹): ν_{max} 3418 (N-H stretch), 1595 (N=N), 1196(S=O), 1051 (S-O). ¹HNMR (300 MHz, DMSO-*d*6): δ, ppm: 2.7 (1H, S), (7.52 (1H,s) , 7.18 (1H,d, *J*=7.2Hz), 7.77-7.89 (2H,m) , 8.14 (1H,d, *J*=8.4 Hz) , 12.53 (s, br, OH).

2-Amino-8-naphthol-7-(3-Aminoacetophenyl-diazinyl)-6-sulfonic acid (C 12)

MALDI-ToF (negative) analysis: Mol. Formula C₁₈ H₁₅ N₃ O₅ S, Mol. Weight: 385.395, MALDI spectra: 384.740, Species Observed: M-H. UV: λ_{max}: 512nm, log ε = 4.2. IR: (measured in KBr on a Jasco A30 instrument): (cm⁻¹): ν_{max} 3425 (N-H stretch), 1570 (N=N), 1215 (S=O), 1052 (S-O). ¹HNMR (300 MHz, DMSO-*d*6): δ, ppm: 2.67 (3H, s), 7.17 (d, *J*=9.3Hz), 7.52(S,1H), 7.72(1H,b,*J*=7.8-8.1Hz), 7.85-7.99 (1H,m), 8.32 (1H,s), 12.49 (br, s, OH).



2-Amino-8-naphthol-7-(4-Aminoacetophenyl-diazinyl)-6-sulfonic acid (C11)



2-Amino-8-naphthol-7-(3-Aminoacetophenyl-diazinyl)-6-sulfonic acid (C 12)

Scheme-2: Structural formulas of Synthesized Acid Dyes.

Application of acid dyes on Wool fabric:

For the application of the synthesized dyes (C10-C12), a conventional exhaust dyeing procedure was adopted [12]. Briefly, scoured and bleached wool fabric was dyed with a 1% of the synthesized dye (C10, C11 and C12), based on weight of fabric (o.w.f.) employing a liquor to fabric ratio of 1:20. The pH of the dyeing bath was maintained in the range of 2.5 to 3.5 throughout the dyeing process. Initially, the temperature of dye bath was gradually raised to around 60°C followed by the addition of Glauber's salt. The temperature was then raised further to around 90 °C and the dyeing was continued for another 30 minutes. Finally, the dye bath was dropped to remove the dyed fabric which was thoroughly washed with cold water, soaped in a 2 g/L nonionic detergent at 50 °C followed by rinsing. The resulting washed and dyed fabric thus obtained was then air-dried before being used for any further characterizations.

Evaluation of the Fastness properties

The dyed fabric was subjected to various fastness properties using the standard ISO procedures and SDC laboratory consumables. The methods used are; ISO 105-C06 C2S:1994 (E) for washing fastness, ISO 105 B02:1988 (E) for light fastness, ISO105-X12:1993 (E) for rubbing fastness and ISO 105-E04:1994 (E) for color fastness to perspiration. The CIE Lab values of all the samples were recorded. The change of shade values were assigned by comparing the test specimen with a standard color grey scale where the color change was represented by various ratings in the range of 1 to 5. The rating 1 was assigned to the highest change in shade representing maximum color loss and poor performance of the dye. Similarly, rating 5 was assigned to no change of shade, representing excellent dyeing performance of the dye. For evaluating the degrees of staining, a multi-fiber staining fabric comprising of cellulose acetate (CA), cotton (CO), polyamide (PA), polyester (PES), polyacrylic (PAC) and wool (WO) was used as adjacent fabric. The resulting degrees of staining were assigned using a standard grey scale for staining.

Evaluation of the dyebath exhaustion and color strength:

The uptake of dye by the wool fabric was determined by measuring the absorbance at λ_{\max} of the dye bath before and after the dyeing process using a standard UV/visible spectrophotometer. Assuming A_1 and A_2 representing the dye bath absorbance before and after dyeing, respectively, the percentage of dye bath exhaustion (% E) can be calculated using [17]:

$$\% E = \frac{A_1 - A_2}{A_1} \times 100 \quad (1)$$

For measuring the color yield of dyed fabric (before and after wash), the samples were subjected to light reflectance measurements. The color strength (K/S) values were then assessed using the Kubelka-Munk equation [18]:

$$K/S = \frac{(1-R)^2}{2R} \quad (2)$$

where K and S represent the sorption and scattering coefficients, respectively, and R is the decimal fraction of the reflectance.

Results and Discussion

The dyeing performance of three novel sulfonic acid dyes (C10-C12) was explored in this work. These dyes were synthesized following a procedure mentioned in the experimental section, using the diazo and coupling components mentioned in table-1. The structure elucidation was performed using various analytical techniques already mentioned in the experimental section. The resulting structures of the dyes are depicted in Scheme 2. Following an exhaust dyeing procedure, wool fabric was dyed with the synthesized dye. From the UV-visible spectroscopy, the λ_{\max} values of the resulting shades were found to be between 510 nm to 530 nm which correspond to the shades from orange to red.

Table-2: Color Parameters of dyed wool fabric before and after washing with a nonionic detergent at 50 °C.

Sample Name		L*	a*	b*	C*	h*	X	Y	Z	x	y
C-10	Before Wash	19.75	15.91	3.11	16.22	11.06	3.73	2.93	2.69	0.3989	0.3133
	After Wash	18.60	14.29	2.69	15.16	10.00	3.13	2.16	2.55	0.3992	0.2755
C-11	Before Wash	18.59	17.43	2.82	17.66	9.20	3.50	2.65	2.46	0.4066	0.3078
	After Wash	17.48	16.55	2.12	16.15	8.80	3.10	2.22	2.35	0.4041	0.2894
C-12	Before Wash	23.54	27.99	10.78	29.99	21.06	5.93	3.96	2.54	0.4770	0.3188
	After Wash	22.15	26.16	9.34	28.70	20.33	5.55	3.13	2.15	0.5124	0.2890

The resulting values of CIE L* a*, b* C* for the (pre and post-washed) dyed fabric using synthesized dyes (C10, C11 and C12) are all listed in Table-2. These values clearly indicate that the dyeing resulted in shades of moderate depths. L* values for all the three dyes are in the range of 17 to 22. For each of the dye explored the values of the color parameters for pre and post-washed (at 50 °C using a nonionic detergent) fabric are close to each other which indicates excellent fixation and fastness properties [19].

As can be seen from Table-2, among the three dyes tested, C12 exhibit highest values of the color parameters. Remarkably, compared to C11, the values of the color parameters obtained for the dye C12 are significantly higher. These two dyes were synthesized using aminoacetophenone diazo components having amino substituent at different positions (Scheme 2, Table-1). This result is in line with what was observed earlier by other researchers [20, 21] and clearly indicates that the position of substituent has marked influence on the dyeing. Similar trends were observed for the values of the color parameters CIE L* a*, b* c* recorded for light exposure and alkaline perspiration (Table-3 and 4, respectively). These results demonstrate that wool can be successfully dyed with the synthesized dyes C10, C11 and C12 under standard exhaust dyeing conditions.

To demonstrate the effectiveness of the dyes C10, C11 and C12 on wool further, we explored their washing, light, perspiration and rubbing fastness. For this, standard tests based on ISO procedures [22-27] were performed and the results obtained are all listed in Table-5 and 6. The change of shade values and degrees of staining were assigned using a standard

grey scale as already mentioned in the experimental section.

It can be seen from the values of various fastness properties obtained for the dyed fabric that all the three dyes tested performed well in the fastness tests (except light fastness test) as the resulting grey scale ratings are mostly 4 and above (Table-5). Dye C11 and C12 however give fastness ratings of 3-4 on polyamide representing fair to good performance. This may likely attributed to the higher affinity of the dye molecules for these fibers causing more transference during the test. Remarkably, the grey scale ratings obtained for the fabric dyed with dyes C11 and C12 are very close to each other which is likely due to their structural similarities (Scheme 2). As mentioned earlier, both these dyes were synthesized using two different isomers of aminoacetophenone as diazo component and a common 2-amino-8-naphthol-6- sulfonic acid (Gamma acid) as coupling component (Table-1). Among the three dyes tested, the fabric dyed with C10 give highest grey scale ratings of 4-5 to 5, demonstrating exceptional fastness properties. This may likely attributed to the presence of additional sulfonic acid substituent in its structure providing additional binding site with the fiber (Scheme 2). This additional sulfonic substituent was inherited from the diazo component 3-Amino sulfonic acid (Table-1 and Scheme 2). In the light fastness test, all the three dyes showed moderate to low light fastness properties as represented by the ratings in the range of 4 to 4-5 (light fastness scale). On the basis of the data presented in Table-5 and 6, it can be safely concluded that the synthesized dyes C10, C11 and C12 performed well on wool substrate.

Table-3: Color parameters of dyed wool fabric before and after light exposure.

Sample Name		L*	a*	b*	C*	h*	X	Y	Z	x	y
C-10	Untreated	19.75	15.91	3.11	16.22	11.06	3.73	2.93	2.69	0.3989	0.3133
	Treated	18.21	14.75	2.95	15.15	10.81	3.30	2.18	2.18	0.4308	0.2845
C-11	Untreated	18.59	17.43	2.82	17.66	9.20	3.50	2.65	2.46	0.4066	0.3078
	Treated	17.40	16.55	2.11	16.75	8.11	2.46	2.45	2.17	0.3474	0.3460
C-12	Untreated	23.54	27.99	10.78	29.99	21.06	5.93	3.96	2.54	0.4770	0.3188
	Treated	22.15	26.47	9.05	28.17	20.25	4.91	3.77	2.27	0.4484	0.3442

Table-4: Color parameters of dyed wool fabric subjected to alkaline perspiration.

Sample		L*	a*	b*	C*	h*	X	Y	Z	x	y
C-10	Untreated	19.75	15.91	3.11	16.22	11.06	3.73	2.93	2.69	0.3989	0.3133
	Treated Alkaline	18.10	14.75	2.76	15.11	10.17	3.19	2.11	2.24	0.4230	0.2798
C-11	Untreated	18.59	17.43	2.82	17.66	9.20	3.50	2.65	2.46	0.4066	0.3078
	Treated Alkaline	17.48	16.12	2.13	16.58	8.90	2.95	2.16	2.00	0.4149	0.3037
C-12	Untreated	23.54	27.99	10.78	29.99	21.06	5.93	3.96	2.54	0.4770	0.3188
	Treated Alkaline	22.13	25.41	9.24	27.00	20.16	4.78	3.15	2.25	0.4695	0.3094

Table-5: Results of various fastness properties of dyes C10, C11 and C12 on wool fabric.

Dye Code	Change in Shade	Multi-fiber Fabric					Crocking		Light Fastness	
		CA	CO	PA	PES	PAC	WO	Dry		Wet
C-10	4-5	5.0	4-5	4-5	5.0	5.0	4-5	5.0	4-5	4-5
C-11	4.0	4-5	3-4	3.0	5.0	5.0	4-5	5.0	4-5	4.0
C-12	4.0	5.0	4-5	3-4	5.0	5.0	4-5	5.0	4-5	4-5

Table-6: Results of various fastness properties of dyes C10, C11 and C12 on wool fabric.

Dye Code	Fastness To							% Dye Fixation by K/S values	Dye Exhaustion (% E)
	Light hours	Wash		Perspiration alkaline		Rubbing			
	100	y	s	y	s	dry	wet		
C-10	4-5	4-5	4-5	4-5	4.0	5.0	4-5	79.82	62.23
C-11	4.0	4.0	3-4	4-5	4.0	5.0	4-5	94.53	60.38
C-12	4-5	4.0	4-5	4-5	4-5	5.0	4-5	91.79	78.98

y = test was performed before washing, s = test was performed after washing.

The percentage of dye bath exhaustion (% E) by the wool fabric under the conditions specified in the experimental section was also calculated. The percentage of dye bath exhaustion is an important dyeing parameter representing the amount of dye transferred from the liquid phase to the solid substrate [17]. The values of % E were calculated for each dye (C10, C11 and C12) by measuring the absorbance (at λ_{\max}) of the dye bath, before and after the dyeing process. As can be seen from Table-6, all the three dyes exhibit moderate dye exhaustion under the condition employed. The % E values obtained are 62.23 % for C10, 60.38 % for C11 and 78.98 % for C12. The relatively larger value recorded for C12 can be explained on the basis of its relatively smaller molecular size which gave rise to the adsorption of maximum number of molecules on the fiber surface. The % E values obtained for C10, C11 and C12 under the dyeing conditions employed are in fair agreement with the values reported in literature for similar dyes [28]. The expected dye uptake on wool fabric can however be improved considerably for the dyeing of wool fibers by optimizing several parameters involved in the whole dyeing process [28]. It is worth recalling that compared to other protein based fibers such as silk and nylon, amorphous nature and presence of considerably higher number of amino groups in wool enable it to accommodate higher dye uptake and acquire comparatively darker shades. Thus, judicious selection of dyeing parameters and the appropriate use of dyeing auxiliaries can lead to considerable improvement in the apparent dye uptake by the wool fiber [29, 30]. For instance, use of cationic agents, wetting agents and certain electrolyte may enhance diffusion, dye penetration and rate of dye uptake [26]. The values of the percent dye fixation on to the fabric are listed in Table-6. These values were calculated for each dye from their corresponding color strength values obtained using Data Color Spectrophotometer. The minimum dye fixation on wool, dyed fabric C10 is 79.82% and maximum dye fixation on wool dyed fabric C11 is 94.53%.

We previously reported the synthesis of nine derivatives of acid dyes using substituted aryl amines as diazo component and amino-hydroxy substituted naphthalene sulfonic acid as coupling component

[14]. The results obtained for the dyes C10, C11 and C12 are comparable with those reported earlier.

Conclusion

We presented the synthesis, characterization and dyeing assessment of three novel acid dyes based on substituted aryl amines as diazo component and aminohydroxy-naphthalene sulfonic acid as coupling components. Wool was selected as substrate fabric owing to its commercial relevance and the dyes were applied using a conventional exhaust dyeing procedure.

From the results presented, it can be concluded that the synthesized dyes C10, C11 and C12 are effective for the dyeing of wool under standard exhaust dyeing conditions. Besides, UV-Vis spectroscopy revealed that the λ_{\max} values of the resulting shades were in the range of 510 nm to 530 nm which correspond to the shades from orange to red. All the three dyes performed reasonably well in the washing, light, rubbing and perspiration fastness studies as evident from the grey scale ratings values of mostly 4-5 and 5. The structure of the dye molecule and the position of the sulfonic acid substituent were found to have considerable influence on the dyeing performance.

In conclusion, all the three dyes explored performed reasonably good in the dyeing of wool fabric. In future, we will further optimize the dyeing parameters to enhance the performance of these dyes for applications in commercial dyeing operations.

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References

1. R. S. Asquith in *Chemistry of Natural Protein Fibers*. Springer Science & Business Media; Dec 6 (2012).
2. M. Feughelman, *Natural Protein Fibers. J. App. Poly. Sci.* **18**, 489 (2002).

3. W. S. Simpson, G. Crawshaw, editors, *Wool: Science and Technology*, Elsevier; (2002).
4. D. M. Lewis, J. A. Rippon, editors, *The Coloration of Wool and other Keratin Fibres*. John Wiley & Sons; May 20 (2013).
5. D. R. Waring, G. Hallas, *The Chemistry and Application of Dyes*, Springer Science & Business Media, Nov 11 (2013).
6. K. Hunger, *Industrial Dyes: Chemistry, Properties, Applications*, John Wiley & Sons, Sep 24 (2007).
7. F. J. Wortmann, G. Wortmann, H. Zahn, Pathways for dye diffusion in wool fibers. *Tex. Res. J.* **67**, 720 (1997).
8. R. L. Bruce, N. V. Broadwood, D. G. King, Kinetics of Wool Dyeing with Acid Dyes *Tex. Res. J.* **70**, 525 (2000).
9. I. Holme, Challenge and Change in Wool Dyeing and Finishing. *Rev. of Progress in Coloration and Related Topics.* **33**, 85 (2003).
10. D. M. Lewis, Damage in Wool Dyeing. *Rev. of Progress in Coloration and Related Topics.* **19**, 49 (1989).
11. S. Muhammad, A. Abdulmalik, S. Habibu, and M. Ladan, Influence of Auxiliaries in Dyeing of Wool with Acid Dyes. *Int. J. Tex. Sci.* **4**, 78 (2015).
12. Z. Akhtar, S. I. Ali, M. Farooq, S. Zubair, R. Parveen and K. M. Khan, Application of Acid Dyes on Silk Fabric and Fastness Properties Part II. *J. Chem. Soc. Pak.* **40** (2018).
13. Z. Akhtar, M. R. Kazmi, S. I. Ali, N. Abbas and R. Parveen, Application of Acid Dyes on Nylon Fabric and Evaluation of Fastness Properties Part III. *J. Chem. Soc. Pak.* **40**, 898 (2018).
14. Z. Akhtar, M. Farooq, M. R. Kazimi, R. Parveen, S. I. Ali, A. Karim and K. M. Khan, Syntheses and Application of Sulfonic Acid Dyes on Wool Fabric. *J. Chem. Soc. Pak.* **38**, 127 (2016).
15. J. Musnickas, V. Rupainyte, R. Treigiene and L. Rageliene, Dye Migration Influences on Colour: Characteristics of Wool Fabric Dyed with Acid Dye. *Fibres Text. East. Eur.* **13**, 65 (2005).
16. D. P. Law, A. B. Blakeney and R. Tkachuk, The Kubelka–Munk Equation: Some Practical Considerations. *J. Near Infrared Spectroscopy.* **4**, 189 (1996).
17. Q. Zhang, Research on Improving the Wet Fastness of Reactive Dyes for Wool Dyeing. in *Proceedings 12th Int. Wool Res. Conf., Vols I and II*, 531 (2010).
18. H. M. Patel, and B. C. Dixit, Synthesis, Characterization and Dyeing Assessment of Novel Acid Azo Dyes and Mordent Acid Azo Dyes based on 2-Hydroxy-4-Methoxybenzophenone-5-Sulfonic Acid on Wool and Silk Fabrics. *J. Saudi Chem. Soc.*, **18**, 507 (2014).
19. B. C. Dixit, H. M. Patel, D. J. Desai and R. B. Dixit, Studies on Dyeing Performance of Novel Acid Azo Dyes and Mordent Acid Azo Dyes based on 2, 4-Dihydroxybenzophenone. *J. of Chem.* **6**, 315 (2009).
20. *Color Fastness to Rubbing, Standard Methods for Determination of the Color Fastness of Textile and Leather*, the Society of Dyers and Colorist 5th Edition, PP.X12/1 (1990).
21. Color fastness to perspiration, Standard Methods for the determination of the color fastness of textiles and another, The Society of Dyers and Colorists, fifth edition, 1990, PP EO4/1.
22. ISO 105 - CO6: 2010 - Textiles – Tests for Colour Fastness - Part CO6: Colour Fastness to Domestic and Commercial Laundering (2010).
23. ISO 105 - BO2: 2013 – Textiles – Test for Colour Fastness - Part BO2: Colour Fastness to Artificial Light: Xenon arc Fading Lamp Test (2013).
24. ISO 105 - EO3: 2010 – Textiles – Test for Colour Fastness - Part EO3: Colour Fastness to Chlorinated Water (2010).
25. ISO 105-E04:2013 Textiles -- Tests for Colour Fastness - Part E04: Colour Fastness to Perspiration (2013).
26. S. Muhammad, A. Abdulmalik, S. Habibu and M. Ladan, Influence of Auxiliaries in Dyeing of Wool with Acid Dyes. *Int. J. Tex. Sci.* **4**, 78 (2015).
27. P. Alexander, R. F. Hudson, The Kinetics of Wool Dyeing: Part I: Simple Acid Dyes *Tex. Res. J.* **20**, 481 (1950).
28. M. Periolatto, F. Ferrero and G. Migliavacca, Low temperature Dyeing of Wool Fabric by Acid Dye After UV Irradiation. *J. Tex. Instit.* **105**, 1058 (2014).
29. P. Alexander, R. F. Hudson, The Kinetics of Wool Dyeing: Part I: Simple Acid Dyes *Tex. Res. J.* **20**, 481 (1950).
30. M. Periolatto, F. Ferrero and G. Migliavacca, Low temperature Dyeing of Wool Fabric by Acid Dye After UV Irradiation. *J. Tex. Instit.* **105**, 1058 (2014).