

Dyeing Studies of Wool Fibers with Madder (*Rubia Tinctorum*) and Effect of Different Mordants and Mordanting Procedures on Color Characteristics of Dyed Samples

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Abstract: In this work, the dyeing behavior of wool fabrics with madder was studied. The effect of different mordants (potassium dichromate, stannous chloride, alum, ferrous sulfate, lime, copper(I, II) sulfate, cobalt chloride, and nickel chloride) with three mordanting procedures (pre-, meta-, and post-mordanting) on color characteristics of the dyed samples was also investigated. The adsorption of madder on wool fibers was found to follow Freundlich type of isotherm. The addition of salt and acid (pH 4.5) to the dyebath increased the dye adsorption. Mordanting with different mordants and mordanting procedures showed a variety of color characteristics of the dyed wool fabrics. The results showed that all color characteristics of the dyed samples were in the first quadrant of CIE $L^*a^*b^*$ color space. Mordanting with potassium dichromate, ferrous sulfate, and copper(I, II) sulfate showed the darker shades and lower chromaticity values while stannous chloride and alum gave the lighter shades and higher chromaticity values. The minimum color difference (ΔE) was obtained from mordanting with the chlorides of cobalt and nickel. The wash and light fastness of the mordanted samples were higher than those of the un-mordanted one.

Keywords: Wool, Madder, Mordant, Fastness properties, Natural dye

Introduction

Natural dyes and pigments have been used in dyeing, painting, and making cosmetics for millennia [1]. During the last decades, revival and application of natural dyes have achieved a great deal of attention [2-5]. During the past fifteen years, Shahid *et al.* [6] have reported advanced applications of natural dyes.

The successful introduction of a new and luxurious product depending on the marketing strategy, protection of the environment, a better range of price, new income sources, resources for future generations, health aspects and governmental regulations are a number of reasons for the increasing interest in natural dyes [1].

Madder was used for dyeing and printing natural fibers such as wool, cotton, and silk [7]. At the present, different types of madder are being cultivated around the world [7,8]. Cuoco *et al.* [7] have recently found a novel and cost-effective extraction method using ultrasonic power; they identified the coloring constituents of madder roots by liquid chromatography coupled with a photodiode array detector.

In recent decades, researchers have been interested to study natural dyes, especially madder, for dyeing of synthetic fibers [9-12]. Also, advanced techniques including plasma for dyeing of natural and synthetic fibers with natural colorants were studied [12]. El-Shishtawy *et al.* [9] used madder, *Rubia tinctorum* L., and alum and ferrous sulfate (as mordants) for dyeing of modified PAN fibers. Gupta *et al.* [10] have investigated the dyeing of nylon multifilament fibers with Indian madder (*Rubia cordifolia*). It was found

that the major component of Indian madder is purpurin (*ca.* 66 %) while contains little or no alizarin. In the case of European madder (*Rubia tinctorum*), the major colorant constituent is alizarin.

Recently, other workers have studied the kinetics and thermodynamics of adsorption of Iranian madder on wool fabric. After obtaining the optimum condition for extraction, alizarin, purpurin, and 1,4-dihydroxyanthraquinone were identified as the main coloring compounds for Iranian madder by using HPLC and TLC techniques. The results showed that the adsorption isotherm was near to Types Langmuir and Freundlich. Activation energy of the adsorption (16.01 kJ/mol) also showed the physisorption nature of the dyeing of wool fibers with madder. Results obtained from the standard affinity, enthalpy and entropy of the dyeing indicated that the dyeing of wool fibers with Iranian madder was an exothermic process. The adsorption kinetics studies of the madder on scoured and mordanted wool fibers were fitted with pseudo-second-order model [13,14].

Other researchers have discussed the light, wash [3-5,15] and rub [3] fastness properties of natural dyes on natural fibers. Also, Gupta *et al.* [11] have studied the effect of different mordants on light and wash fastness properties of nylon fabrics dyed with purpurin and munjistin. Cristea and Vilarem [16] improved the light fastness of cotton fabrics dyed with natural dyes such as madder, weld, and woad, using ultraviolet antioxidants.

The effect of enzymes, protease [17] and Laccase [18], and multilamellar liposomes prepared from Soya lecithin [19] on dyeing of wool fiber with madder, as well as the effect of ammonia on madder-dyed wool fiber [20] have been investigated. It was found that the color strength of the

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madder-dyed samples increased in the optimum range, despite the fact that wash and light [17,19] and dry rub [19] fastness properties did not significantly change. In the case of madder-dyed samples treated with ammonia [20], fading in light fastness tests increased and wash fastness improved along with a bathochromic shift.

The aim of this study is to investigate the dyeing properties of wool fabrics with madder and the effect of different mordants and mordanting procedures on the color characteristics of dyed samples.

Experimental

Materials

The powdered form of the madder cultivated in central areas of Iran and woven wool fabrics (356 g/m², 7 warps/cm, 9 wefts/cm) were used in this work. The samples were scoured before dyeing by treating in a solution of 2 g/l of a non-ionic surfactant (Epicol ESB70 from Qingdao Anke Chemicals Co., China) at 40 °C for 15 min; the samples were rinsed thoroughly with acetic acid to neutralize alkali. Potassium dichromate, stannous chloride, alum, ferrous sulfate, lime, copper(I, II) sulfate, cobalt chloride, nickel chloride, oxalic acid, and sodium carbonate were purchased from Merck Chemical Co.

Instruments

Absorbance measurements were determined using a UV-240 (Shimadzu Co., Japan) UV-visible spectrophotometer. All dyeings were carried out in a Ahiba-Polymat Laboratory scale dyeing machine (Ahiba1000, Datacolor Co., Switzerland). CIE L^* , a^* , b^* , C^* , h° color coordinates and reflectance spectra of the samples were measured by a Texflash spectrophotometer (Datacolor Co., Switzerland). All color characteristics were measured under illuminant D₆₅ using the CIE 1964 10° standard observer and specular component excluded.

Methods

Dye Extraction Process

Dye extraction was carried out using 1-8 g of the madder powder in 1000 ml distilled water at pH 7 for 30 min at 95 °C. After cooling, the obtained mixture was filtered by using a vacuum pump. The residues from filtration were extracted exactly as above for 15 min and then filtered. The filtrate was standardized to 1000 ml by evaporation and then used for experiments.

Calibration Curve

For this purpose, different concentrations of the madder were prepared from 2 g/l extracted madder solution. The absorbance of the solutions was measured by using the UV-240 spectrophotometer at the wavelength of maximum absorbance (408 nm), and the calibration curve was plotted.

Adsorption Isotherm

Adsorption isotherm was carried out using wool fabrics

(5 g), which had been wetted out in cold tap water, sealed in stainless steel dye pots of 100 ml capacity housed in a Ahiba-Polymat Laboratory scale dyeing machine, using 1.5-155 % (o.w.f.) madder, and a liquor ratio of 20:1 at pH 7 for 8 h at 95 °C. After dyeing was finished, the amount of dye remaining in the dyebath was obtained by using the absorbance measured at 408 nm and the calibration curve. The amount of dye adsorbed on the fibers was calculated by subtracting the dye amount remaining in the dyebath from the initial dye amount used.

Dyeing

Dyeing of wool fabrics was carried out using 300 % (o.w.f.) madder, a 30:1 liquor ratio and at pH 4.5 (2.5 % oxalic acid), pH 7, pH 9 (2.5 % sodium carbonate). The dyeings were carried out according to Figure 1. After dyeing, all the samples were treated with a solution of 2 g/l of Epicol ESB70 at 95°C for 15 min; then rinsed thoroughly in tap water, and finally dried at room temperature.

Mordanting

Mordanting of the samples was carried out in three different procedures; pre-, meta-, and post-mordanting. The process was started at 40 °C, and the temperature was raised to 95 °C within 30 min and continued for 1 h. In pre- and post-mordanting, mordanting of the samples was carried out separately in fresh baths. Table 1 shows the required amounts of mordants and auxiliaries used for mordanting procedures.

Fastness Properties Measurements

The wash and light fastness of the samples were determined according to the ISO 105-C06: 1994 (E) and ISO 105-B02: 1994 (E), respectively. For light fastness, the samples were tested using an air-cooled xenon arc lamp for a period of 24 h. In the case of wash fastness, the degree of color change and staining were assessed according to the ISO 105-A05: 1996 (E) and ISO 105-A04: 1989 (E), respectively.

Color Measurements

In this work, the color strength, $(K/S)_\lambda$, of the samples was determined by using Kubelka-Munk equation (equation (1)).

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1-R_\lambda)^2}{2R_\lambda} \quad (1)$$

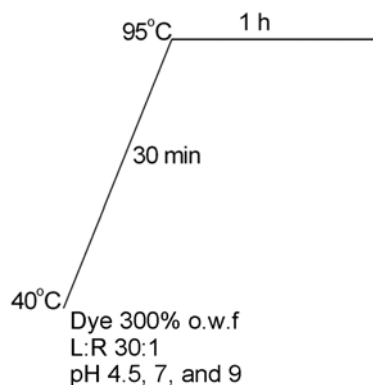


Figure 1. Dyeing method.

Table 1. The required amounts of mordants and auxiliaries used for mordanting of wool fabrics

Procedure	Mordants								
	Cr	Sn	Al	Fe	Ca	Cu ¹⁺	Cu ²⁺	Co	Ni
Post-mordanting	Oxalic acid (2.5 %)	Cream of tartar (2.5 %)	Cream of tartar (5 %)	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)
	Potassium dichromate (2.5 %)	Stannous chloride (3 %)	Alum (10 %)	Ferrous sulfate (1.8 %)	Calcium oxide (10 %)	Cu ₂ SO ₄ (1.8 %)	CuSO ₄ (1.8 %)	Cobalt chloride (3.6 %)	Nickel chloride (3.6 %)
				Oxalic acid (2.5 %)				Oxalic acid (2.5 %)	Oxalic acid (2.5 %)
Meta-mordanting	Same as post-mordanting	Same as post-mordanting	Same as post-mordanting	Cream of tartar (3.6 %)	Same as post-mordanting	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)	Same as post-mordanting	Same as post-mordanting
				Oxalic acid (2.5 %)		Cu ₂ SO ₄ (1.8 %)	CuSO ₄ (1.8 %)		
				Ferrous sulfate (1.8 %)		Oxalic acid (2.5 %)	Oxalic acid (2.5 %)		
Pre-mordanting	Cream of tartar (2.5 %)	Same as post-mordanting	Same as post-mordanting	Same as post-mordanting	Same as post-mordanting	Same as post-mordanting	Same as post-mordanting	Cream of tartar (3.6 %)	Cream of tartar (3.6 %)
	Potassium dichromate (2.5 %)							Cobalt chloride (3.6 %)	Nickel chloride (3.6 %)

where R_λ is the reflectance of the samples at wavelength λ . K is the Kubelka-Munk absorption coefficient and S is the Kubelka-Munk scattering coefficient [21].

The visual perception of depth (D_I) for the samples was determined using the Integ method (equation (2)):

$$D_I = \sum_{\lambda=400}^{700} \left(\frac{K}{S} \right)_\lambda E_\lambda (\bar{x}_\lambda + \bar{y}_\lambda + \bar{z}_\lambda) \tag{2}$$

where E_λ is the relative spectral energy distribution of the used illuminant and $\bar{x}_\lambda, \bar{y}_\lambda, \bar{z}_\lambda$ are the CIE color-matching functions at the related λ [21].

Results and Discussion

Adsorption Isotherm of the Madder on Wool Fibers

Adsorption isotherms provide useful information on the dyeing mechanism. Three types of adsorption isotherm referred to as the Nernst (equation (3)), Langmuir (equation (4)), and Freundlich (equation (5)), have been considered in dyeing processes [22].

$$C_f = k C_s \tag{3}$$

where C_f (g/kg or mol/kg) and C_s (g/l or mol/l) are amount of dye on the fiber and in the residual dyebath, respectively, and k is a constant.

$$C_f = \frac{K C_{\max} C_s}{1 + K C_s} \tag{4}$$

where K is the ratio of rate constants for adsorption and desorption, and C_{\max} is the maximum number of adsorption sites occupied by the dye molecules in the fiber.

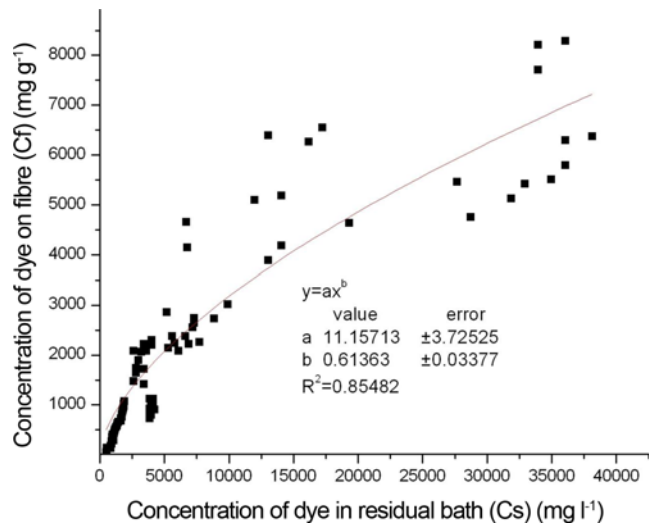


Figure 2. Adsorption isotherm for the madder on wool fibers.

$$C_f = k' C_s^\alpha \tag{5}$$

where k' and α are constant values.

The Nernst adsorption isotherm describes the distribution of a solute between two immiscible solvents and is linear up to the point corresponding to the dye saturation on the fiber. Since wool is a hydrophilic protein fiber [22], the Nernst adsorption isotherm was not considered in this work. Figures 2 and 3 show that the results from the equilibrium adsorption of madder on wool fibers were largely fitted by the Freundlich and Langmuir adsorption isotherms (equations (4) and (5)), respectively. The correlation coefficient obtained from fitting data to the Freundlich and Langmuir equations are 0.86 and 0.88, respectively. These correlation coefficients indicate

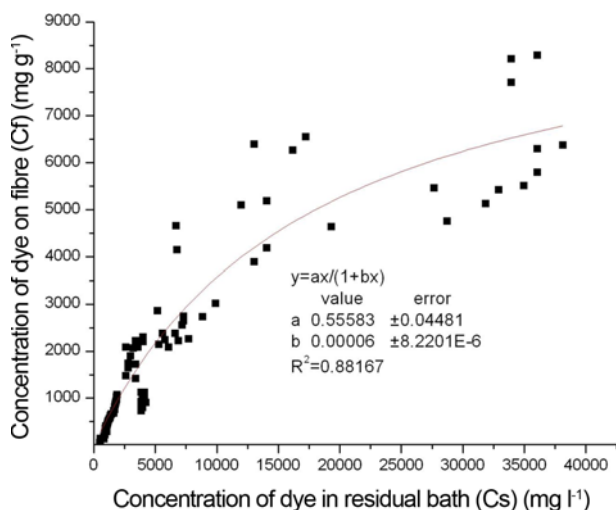


Figure 3. Adsorption isotherm of dyeing madder on wool fibers.

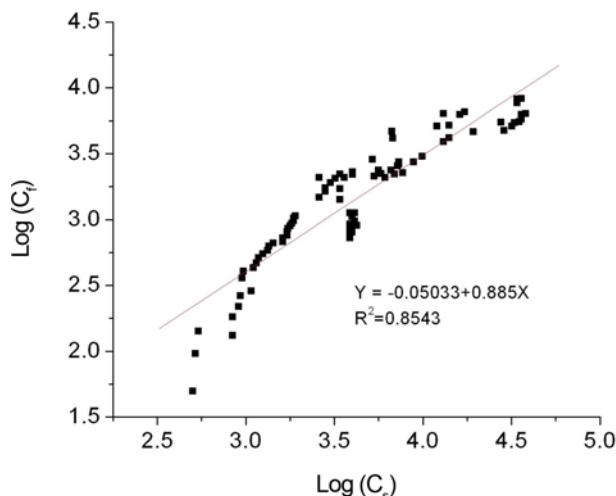


Figure 4. Linear form of Freundlich adsorption isotherm for the madder on wool fibers.

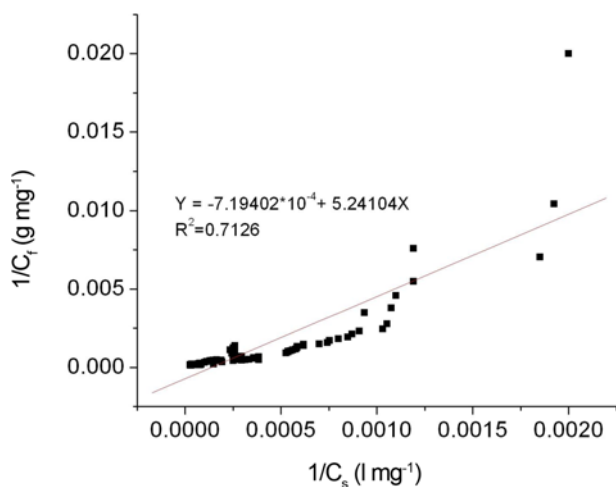


Figure 5. Linear form of Langmuir adsorption isotherm for the madder on wool fibers.

that adsorption of the madder on wool fibers follows the Langmuir isotherm. However, the linear forms of adsorption isotherm equations (equations (6) and (7)) are widely used to determine the constant values (K, C_{max}, k', α) [22].

$$\frac{1}{C_f} = \frac{1}{C_{max}} + \frac{1}{KC_{max}} \left(\frac{1}{C_s} \right) \tag{6}$$

$$\text{Log}C_f = \text{Log}k' + \alpha(\text{Log}C_s) \tag{7}$$

Therefore, from equations (6) and (7), the correlation coefficient of the linear forms of the adsorption isotherms was obtained. It was found that the correlation coefficient of the linear form of the Freundlich adsorption isotherm was significantly higher than that of the Langmuir adsorption isotherm (Figures 4, 5). It seems that adsorption of the madder on wool at pH 7 is similar to adsorption of direct dyes on cellulosic fibers, conforming to the Freundlich adsorption isotherm. Hydrogen bonding and van der Waals forces contribute in the Freundlich adsorption. Iranian madder, from *Rubia tinctorum* family, contains hydroxyl and carbonyl groups [23], which can be attached with polymer chains in wool via hydrogen bonding. On the other hand, madder contains anthraquinonic skeleton dyes [7] which result in van der Waals adsorption between the madder and polymer chains in wool. Also, as a result of fitting the data in Figure 2 to the Freundlich adsorption isotherm equation (equation (5)), the value of 0.61 was obtained for α , which is similar to 0.5 for the adsorption of anionic dyes on cellulosic fibers [22].

The Langmuir isotherm implies the presence of specific sites in the solid on which adsorption can take place [22]. In this work, the coloring matters existing in the madder have no electrical charge and chemical interaction with wool fiber and therefore Langmuir adsorption isotherm cannot be used to describe the equilibrium state in adsorption of the madder.

Effect of Dyebath pH on Adsorption of the Madder on Wool Fibers

The wool fabrics were dyed at different pH 4.5, 7, and 9 using the extracted solutions from powdered madder (300 % o.w.f.) at a LR of 30:1. The results obtained have been shown in Figure 6. It can be seen that adsorption of the madder on wool fibers has considerably increased at acidic pH.

The hydrolysis of proteins in wool can be catalyzed by acids and alkalis and wool damage can be significantly increased in hot solutions, especially under alkaline conditions [22], therefore, pH 4.5 was applied for dyeing of wool fabrics. Farizadeh *et al.* [13] also found that K/S for wool fabrics dyed with madder increased with decreasing of pH which attributed to keto-enol tautomerism of carbonyl groups of the madder in acidic media, leading to higher hydrogen bonding with carboxyl groups of wool fibers. In addition, the increase in absorbance of the extracted solutions of

Iranian-madder [13] and the coloring components (purpurin and nordamncanthal) in Indian madder [10,24] proves that the solubility of madder increases as pH increases. Therefore, it is expected that adsorption of the madder on wool fibers

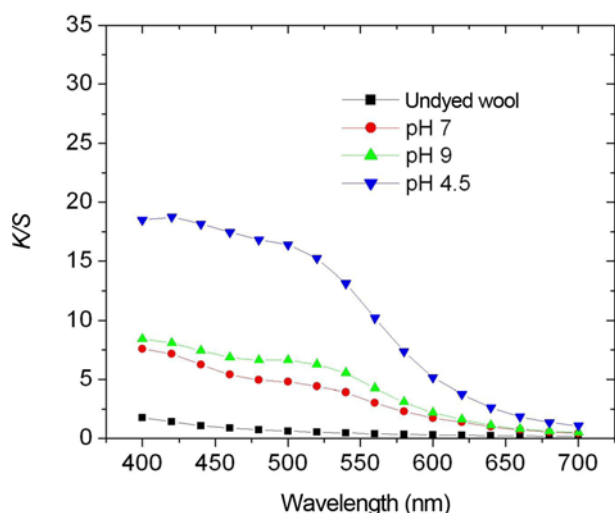


Figure 6. Color strength from dyeing madder on wool fibers at different pH.

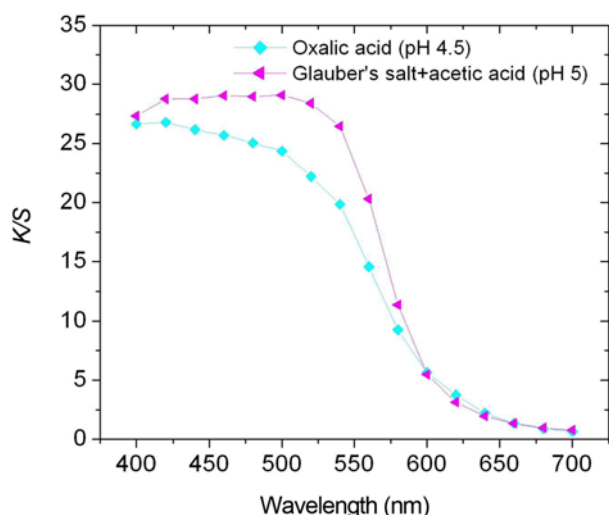


Figure 7. Color strength of the samples dyed with the madder in the presence and absence of salt.

Table 2. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with potassium dichromate with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	15.88	10.97	4.04	11.69	20.23	45924
Meta-mord.	19.15	18.65	7.87	20.24	22.87	39044
Pre-mord.	21.79	22.70	11.07	25.26	26.00	34484
Post-mord. ^a	15.22	10.17	3.55	10.77	19.24	48305

^aUse of salt in dyebath.

decreases with increasing of pH values. Nagia *et al.* [25] also reported the same result when wool fibers were dyed with natural anthraquinone dyes extracted from *Fusarium oxysporum*; they found that as pH decreased, the dyeability increased due to the ionic interaction of hydroxyl groups in the dye molecules and the protonated terminal amino groups in wool.

Effect of Salt on Adsorption of the Madder on Wool Fibers

To evaluate the effect of salt on the adsorption, two dyebaths were prepared containing: (1) 2.5 % o.w.f. oxalic acid (pH 4.5), hereafter referred to as the control sample, and (2) 4 % o.w.f. Glauber's salt and 4 % o.w.f. acetic acid (pH 5). As can be seen from Figure 7, dyeing in the presence of the salt increased the adsorption of madder on wool fabric. It is expected that addition of the salt to the dyebath increased the exhaustion by rendering the dye molecules even less hydrophilic. In dyeing of modified acrylic fibers with madder, it has been stated that the addition of sodium sulfate up to 1 g/l slightly increased the color strength of the dyed fabrics. However, further increase in the salt concentration did not roughly change the color strength of the samples [9].

Effect of Different Mordants and Mordanting Procedures on the Color Characteristics of Wool Fabrics Dyed with Madder

Most of the natural dyes have poor fastness properties on natural and synthetic fibers. Consequently, use of metal salts as mordants to acquire deep shades, as well as to acquire acceptable fastness properties has been considered [22]. In this study, potassium dichromate, stannous chloride, alum, ferrous sulfate, lime, copper(I, II) sulfate, cobalt chloride, and nickel chloride were used as mordanting agent.

Table 2 and Figure 8(a) show the colorimetric data of madder-dyed samples when using potassium dichromate in three mordanting procedures. It can be seen from Table 2 that the color characteristics (a^* , b^* , h°) of all dyed samples are located in the first quarter of CIE $L^*a^*b^*$ color space.

It can be seen from Figure 8(a) that the color strength of madder samples mordanted with potassium dichromate was higher than the control sample (except for the pre-mordanted one). In accord with Table 2 and Figure 8(a), addition of Glauber's salt also improved the dyeability and color

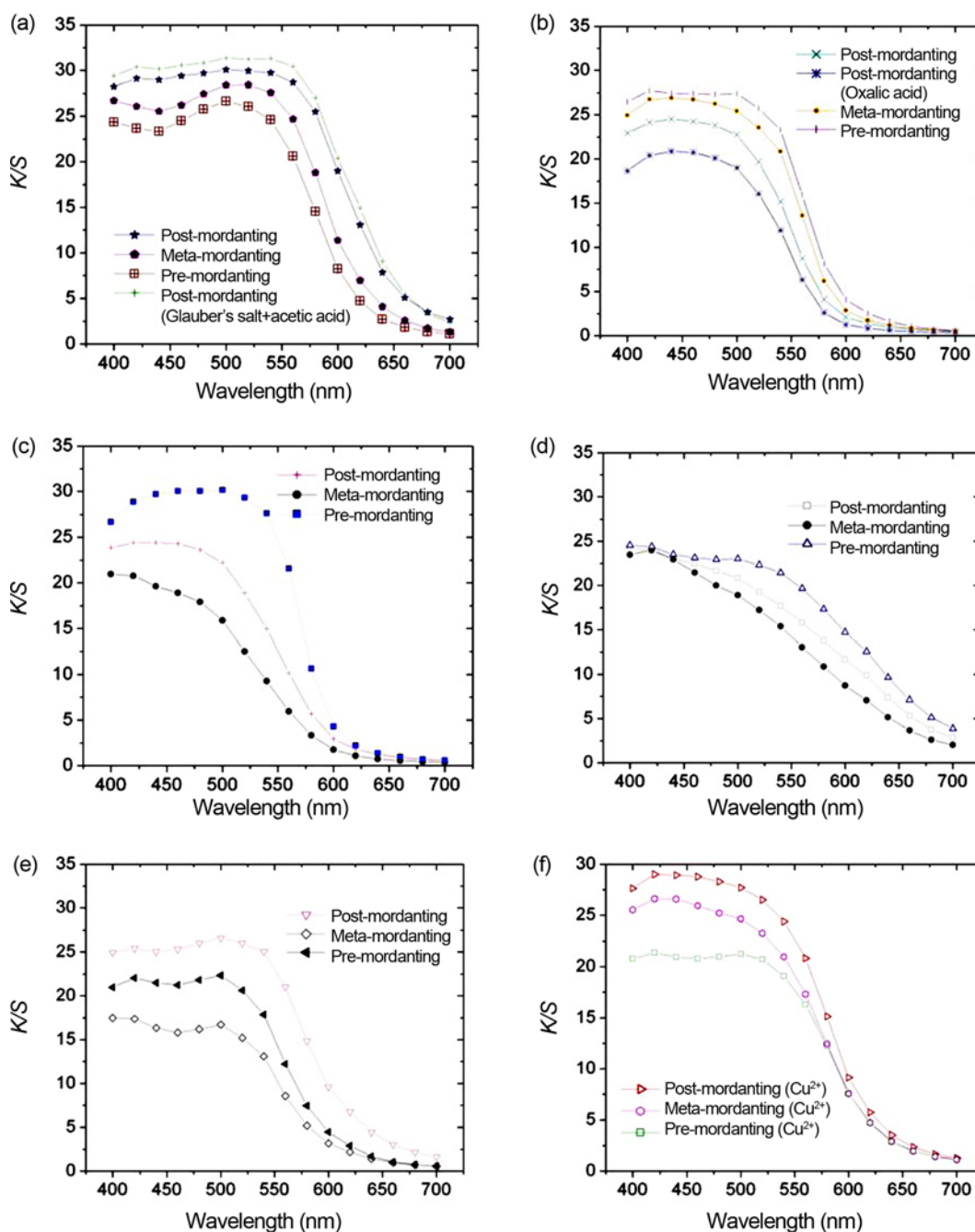


Figure 8. Color strength of the samples mordanted with (a) potassium dichromate, (b) stannous chloride, (c) alum, (d) Ferrous sulfate, (e) calcium oxide, (f) copper(II) sulfate, (g) copper(I) sulfate, (h) cobalt chloride, and (i) nickel chloride.

characteristics of the sample in post-mordanting process. Furthermore, Figure 8(a) shows a bathochromic shift in chromium mordanting compared to the control sample. The color of pre- and meta-mordanted samples were red and brownish-red (higher C^* values), respectively, while the post-mordanted samples gave brown shades (smaller C^* values). In post-mordanting, the color strength of the samples at the wavelengths between 400 and 500 nm increased

significantly compared to other mordanting procedures. As a summary, in the case of chromium mordanting, the deeper shades on wool fibers achieved using post-mordanting.

Variations in colorimetric data, namely ΔL^* ($=L^*_{\text{mordanted sample}} - L^*_{\text{control sample}}$), ΔC^* ($=C^*_{\text{mordanted sample}} - C^*_{\text{control sample}}$), $\Delta K/S_{\lambda_{\text{max}}}$ ($=K/S_{\lambda_{\text{max}}}(\text{mordanted sample}) - K/S_{\lambda_{\text{max}}}(\text{control sample})$) and the color differences, $\Delta E = \sqrt{\Delta L^{*2} + (a^*_{\text{mordanted sam.}} - a^*_{\text{control sam.}})^2 + (b^*_{\text{mordanted sam.}} - b^*_{\text{control sam.}})^2}$, of the samples mordanted with different metal salts and

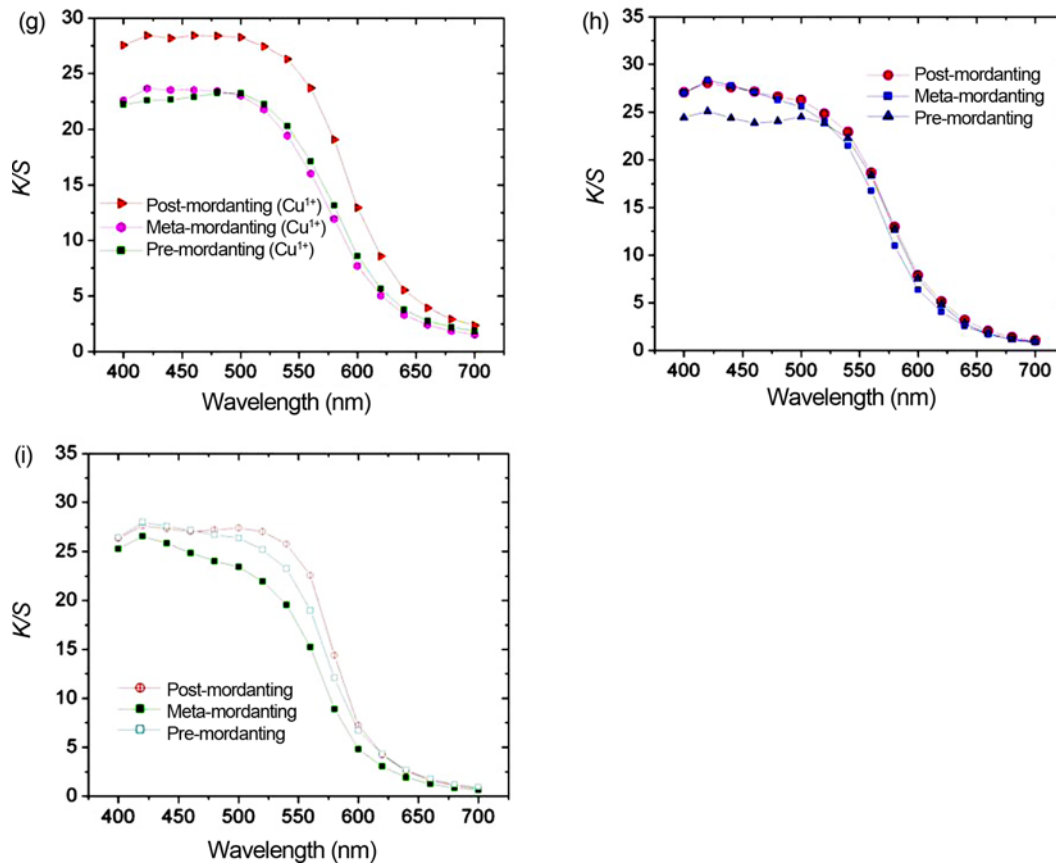


Figure 8. Continued.

Table 3. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with stannous chloride with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	33.10	32.98	30.39	44.85	42.67	26942
Meta-mord.	29.53	33.05	25.94	42.02	38.13	31545
Pre-mord.	26.52	29.73	21.27	36.56	35.58	33882
Post-mord. ^a	38.12	36.51	36.12	51.36	44.69	22186

^aUse of oxalic acid in mordanting bath.

mordanting procedures have been shown in Figure 9.

It can be seen from Figure 9 that, mordanting with chrome shows relatively lower lightness, color purity and higher values of color difference as compared to other mordants used. In post-mordanting with chrome salt, an increased Integ values were found, indicating a broader $K/S-\lambda$ curve or an increase in the area under the $K/S-\lambda$ curve, and therefore the duller color was obtained (Table 2-9). Furthermore, it was found that, in chromium pre-mordanting, variations of the colorimetric data were lower than other chromium mordanting procedures. The same result was also reported with Mikropoulou *et al.* [4] in madder-dyeing of wool fabric when mordanted with chrome.

The results obtained from dyeing wool fabrics with the madder when using stannous chloride in three mordanting procedures have been presented in Table 3 and Figure 8(b). Also, the effect of oxalic acid in the mordanting bath was studied. It was found that all the color characteristics of madder-dyed samples were located in the first quarter of the CIE $L^*a^*b^*$ color space when mordanted with stannous chloride (Table 3). Figure 8(b) shows that the higher $(K/S)_{\lambda_{\max}}$ was obtained by using pre-mordanting method with stannous chloride. Therefore, the mordant type and mordanting procedure could affect the color characteristics of the samples. Gupta *et al.* [11] also reported the same result on purpurin-dyed nylon fabrics mordanted with stannous

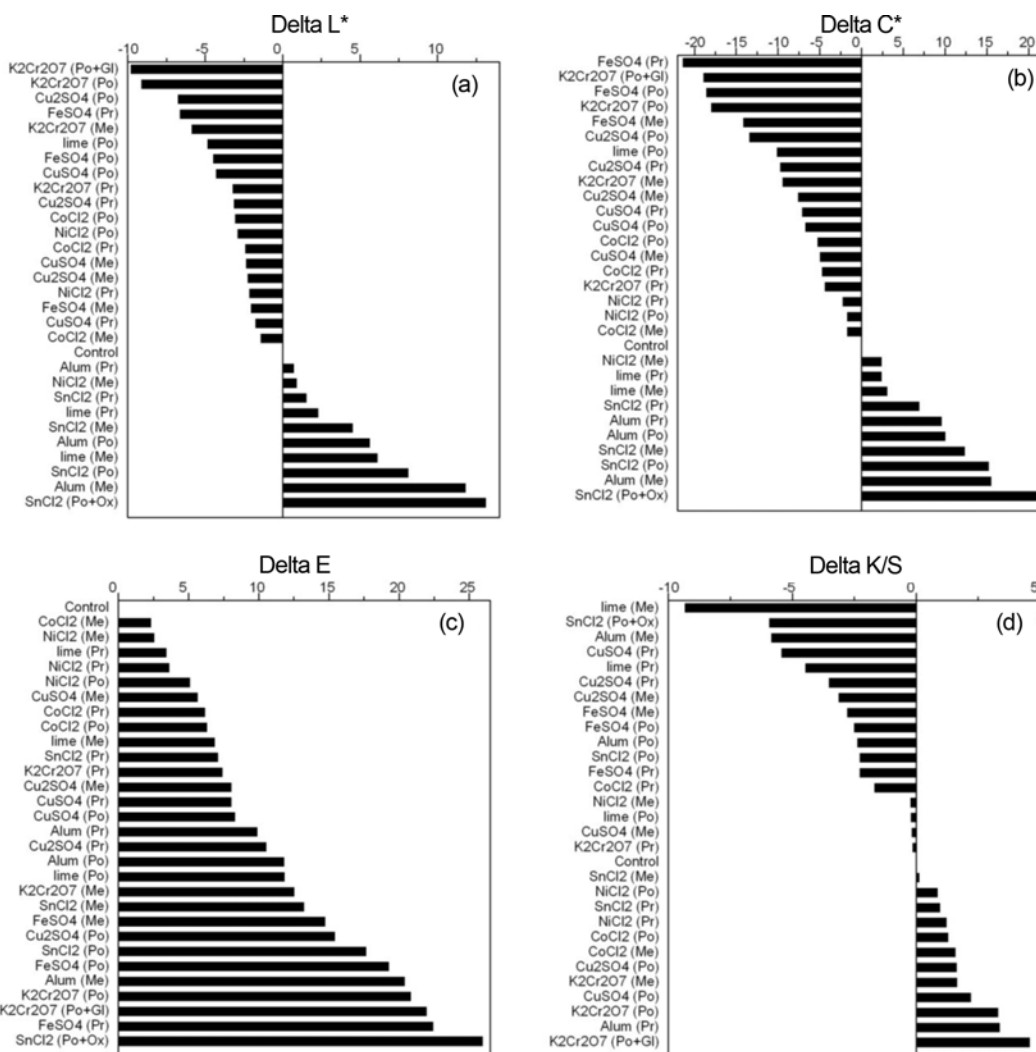


Figure 9. Variations of colorimetric characteristics of the samples mordanted with different mordants.

Table 4. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with alum with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	30.61	29.89	26.08	39.67	41.11	27497
Meta-mord.	36.81	31.37	32.48	45.15	46.00	20405
Pre-mord.	25.72	33.02	21.23	39.25	32.73	38190

chloride. It can be seen from Figure 8(b) that there is no significant difference between the color strength of pre- and meta-mordanted samples. From economic aspect, the use of meta-mordanting would be preferred. It was found that stannous chloride gives the brighter red shades in comparison with chromium mordant. The use of oxalic acid in post-mordanting bath decreased the color strength of the sample while a gorgeous and transparent red color was obtained. Mordanting with stannous chloride resulted in higher L^* and C^* values than the other mordants used in this study (Figures 9(a), (b)).

Table 4 and Figure 8(c) show the colorimetric characteristics from dyeing wool fabrics with the madder and mordanted with alum in three different procedures. In the case of alum, the higher color strength was obtained for the sample by pre-mordanting procedure (Figure 8(c)). This result is well consistent with that of alum pre-mordanted nylon fabrics dyed with purpurin [11] and wool fabrics dyed with madder [3]. A significant bathochromic shift was found for pre-mordanting with alum compared to the other mordanting procedures. Tables 3 and 4 and Figures 9(a) and 9(b) show that meta-mordanting with alum and post-mordanting with

stannous (in the presence of oxalic acid) exhibits almost the same shade of bright red.

Iron salts are known to be significant in alteration the resulting colors with a shift towards dark shades. In old times, some European dyers used natural dyes with mud or silt rich in iron salts to obtain a dark color on fiber [26].

The results obtained from dyeing wool fabrics with the madder and mordanted with ferrous sulfate in three different mordanting procedures have been shown in Table 5 and Figure 8(d). In the case of ferrous sulfate, all the three mordanting procedures produce a brown color similar to the post-mordanting with potassium dichromate. Figure 8(d) shows that the sample pre-mordanted with ferrous sulfate has the greater color strength than those post- and meta-mordanted.

Figure 9(b) shows that the significant darkness in hue was obtained with ferrous sulfate in pre-mordanting procedure as compared to other metal mordants used in this work. Therefore, the iron salt can be an applicable alternative to heavy metals (e.g., chrome) to obtain dark shades.

The use of mordants such as Co, Sn or Cr salts have caused environmental pollution with the effluents released from the dyeing process due to the waste water limits specified for the amounts of heavy metals [5]. Szymczyk *et al.* [27] have synthesized new iron-complexed azo dyes that iron could be substituted with metals such as chrome and

cobalt.

Table 6 and Figure 8(e) show the colorimetric data of dyeing wool fabrics with the madder and mordanted with lime in three different procedures. For pale shades (e.g., lemon tints), lime was used in dyeing of wool and silk with weld [4]. Moreover, in madder-dyeing, chalk or lime was used with an organic fatty compound by a pretreatment process. Based on the standard procedure, an aqueous dispersion of the slightly acidic powdered colorant and alum was alkalinized by use of chalk or lime [4]. It can be seen from Figure 8(e) that mordanting with lime gave the higher color strength in post-mordanting procedure. A brownish-red color for post-mordanting and a red color for meta- and pre-mordanting was obtained. A significant bathochromic shift was observed in mordanting with lime (Figures 6 and 8(e)).

Figure 9(d) shows that meta-mordanting with lime gives the lowest color strength comparing to other mordants used in this study.

The results obtained from madder-dyed wool fabrics mordanted with copper(I, II) sulfate in three different mordanting procedures have been shown in Figures 8(f), 8(g), and Table 7. The levelling in the madder-dyed samples mordanted by using CuSO_4 and Cu_2SO_4 decreased significantly when comparing to other mordants used in this work, especially in the case of meta-mordanting. Figures 8(f) and 8(g) show that post-mordanting with copper(I, II) sulfate

Table 5. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with ferrous sulfate with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	20.54	7.99	7.65	11.07	43.76	31720
Meta-mord.	22.97	10.74	11.21	15.53	46.24	28665
Pre-mord.	18.37	6.92	4.52	8.26	33.13	35420

Table 6. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with lime with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	20.17	17.32	9.04	19.54	27.57	36049
Meta-mord.	31.12	26.00	19.83	32.70	37.34	20168
Pre-mord.	27.30	26.21	18.44	32.05	35.13	27090

Table 7. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with copper(I, II) sulfate with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
				Cu_2SO_4		
Post-mord.	18.26	14.35	7.57	16.22	27.83	40784
Meta-mord.	22.76	18.43	12.14	22.07	33.38	31302
Pre-mord.	21.86	17.17	10.12	19.93	30.50	31597
				CuSO_4		
Post-mord.	20.72	19.51	12.03	22.93	31.66	38478
Meta-mord.	22.66	20.52	13.73	24.69	33.78	33981
Pre-mord.	23.26	19.69	10.98	22.54	29.15	29058

increased the color strength values compared to other mordanting procedures.

It can be seen from Figures 8(f) and 8(g) that the samples post-mordanted with Cu_2SO_4 and CuSO_4 have almost the same color strength values. However, according to Table 7, the chromaticity and Integ values for the former as compared to those for the latter notably decreased and increased, respectively. In other words, post-mordanting with Cu^{1+} ion salt gives a darker color.

The results obtained from dyeing wool fabrics with madder

and mordanted with cobalt chloride in three different procedures have been shown in Table 8 and Figure 8(h). It was found that the lower color strength value obtained for pre-mordanted sample while the higher C^* value obtained for the meta-mordanted one. It can be seen from Figure 9(c) that meta-mordanting with cobalt chloride exhibits the minimum color difference.

The results obtained from dyeing wool fabrics with the madder and mordanted with nickel chloride in three different procedures can be seen in Table 9 and Figure 8(i). There is

Table 8. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with cobalt chloride with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	21.94	20.44	13.31	24.39	33.06	35891
Meta-mord.	23.60	22.83	16.15	27.97	35.27	34521
Pre-mord.	22.61	21.60	12.46	24.94	29.98	32976

Table 9. Colorimetric data and Integ value of wool fabrics dyed with the madder and mordanted with nickel chloride with three different procedures

Procedure	L^*	a^*	b^*	C^*	h°	Integ value
Post-mord.	22.09	24.45	13.55	27.95	28.99	37203
Meta-mord.	25.91	25.94	18.77	32.02	35.89	31266
Pre-mord.	22.85	23.04	14.86	27.41	32.82	35570

Table 10. Light fastness properties of madder-dyed samples

Unmordanted	Procedure	Mordanted								
		Cr	Sn	Al	Fe	Ca	Cu^{1+}	Cu^{2+}	Co	Ni
5-6	Post-mordanting	7 7-8 ^a	6-7 6-7 ^b	6-7	6-7	7	7	7	6-7	7
	Meta-mordanting	7	7	5	6-7	4-5	6-7	6-7	6	5
	Pre-mordanting	6-7	7	6	7-8	4-5	6-7	7	6-7	7

^aUse of salt in dyebath and ^buse of oxalic acid in mordanting bath.

Table 11. Wash fastness properties of madder-dyed samples

Unmordanted	Procedure	Mordanted									
		Cr	Sn	Al	Fe	Ca	Cu^{1+}	Cu^{2+}	Co	Ni	
1	Post-mordanting	3.0 2.5 ^a	1.5 1.5 ^b	2.5	1.0	3.0	2.5	2.0	1.5	2.0	Change in color
	Meta-mordanting	2.5	2.0	1.5	1.0	2.5	2.5	2.0	1.5	1.5	
	Pre-mordanting	2.5	1.5	2.5	1.0	2.5	2.5	2.0	1.5	1.5	
2-3	Post-mordanting	4 3-4 ^a	3 3-4 ^b	3-4	3-4	2-3	3	2-3	3	2-3	Staining on wool
	Meta-mordanting	4	3	3-4	4	3-4	3-4	3	2	2	
	Pre-mordanting	3-4	2-3	3	3-4	3-4	3-4	3	2-3	1-2	
4	Post-mordanting	4-5 4-5 ^a	4-5 4-5 ^b	4	3-4	4-5	4-5	4	3-4	3-4	Staining on cotton
	Meta-mordanting	4-5	4	4-5	4-5	4-5	4-5	4-5	4	3-4	
	Pre-mordanting	4-5	3-4	3	4-5	4-5	4-5	4-5	4-5	3-4	

^aUse of salt in dyebath and ^buse of oxalic acid in mordanting bath.

no significant difference between the color characteristics of post- and pre-mordanting with NiCl_2 .

Figure 9 shows that colorimetric characteristics of the dyed samples mordanted with nickel chloride are similar to those of the control sample, especially in the meta-mordanting procedure.

Color Fastness

Tables 10 and 11 show that, light and wash fastness of the mordanted samples were higher than the un-mordanted one. In addition, staining of the mordanted samples on wool and cotton fabrics reduced in comparison with that of the un-mordanted one. In post-mordanting with chrome, the dyeings have been carried out in the presence (shown as *a* in Tables 10 and 11) and absence of salt. Fastness results show that addition of the salt increased the light fastness while wash fastness of the sample decreased to some extent (from 3 to 2.5). Moreover, post-mordanting with stannous chloride was carried out in the presence of oxalic acid (shown as *b* in Tables 10 and 11) or cream of tartar. Similar wash and light fastness properties were obtained for the samples post-mordanted in the presence of oxalic acid or cream of tartar.

Conclusion

In this work, the dyeing behavior of wool fabrics with Iranian madder was studied. It was found that the adsorption isotherm of the madder on wool fibers is the Freundlich type of adsorption. Also, the addition of acid and salt to the dyebath increased the adsorption.

The effect of different mordants- namely, potassium dichromate, stannous chloride, alum, ferrous sulfate, lime, copper(I, II) sulfate, cobalt chloride, and nickel chloride- with different mordanting procedures on the color characteristics of the dyed wool fabrics was also investigated. In this case, bright red to deep brown shades were obtained by using different mordants and mordanting procedures. Mordanting with potassium dichromate, ferrous sulfate and copper(I, II) sulfate showed the darker ($\Delta L^* = L^*_{\text{mordanted sample}} - L^*_{\text{un-mordanted sample}} < 0$) shades and lower chromaticity ($\Delta C^* = C^*_{\text{mordanted sample}} - C^*_{\text{un-mordanted sample}} < 0$) values while mordanting with stannous chloride and alum resulted in the lighter ($\Delta L^* > 0$) shades and higher chromaticity ($\Delta C^* > 0$) values. It was found that the chlorides of cobalt and nickel give the minimum color difference (ΔE) with the un-mordanted dyed sample. The wash and light fastness properties of the samples increased as a result of mordanting.

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