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Dyeing and Adsorption Studies of Madder (*Rubia tinctorum*) on Wool Fabrics

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In this study, the dyeing behavior of wool fabrics with madder has been studied. Three well-known types of adsorption isotherms i.e. the Nernst, Freundlich and Langmuir isotherms were used to fit the data. It was found that the adsorption isotherm of madder on wool fabrics follows Freundlich type of adsorption. The exponent α in Freundlich isotherm equation ($C_f = kC_s^{\alpha}$) was obtained 0.61 corresponding to 0.5 for the direct dyes on cellulosic fibers. The effect of salt and pH on dyeing of wool samples was also investigated by the use of color characteristics measurements. The results showed that the color strength of the sample dyed at pH 4.5 was considerably higher than that of the samples dyed at pH 7 and 9. The difference between the *K*/*S* of the samples dyed at pH 7 and 9 was not significant, however, the color characteristics of the samples changed due to pH variation in dyebath. Also, addition of salt in the dyebath increased the madder adsorption. The *b** value of the dyed sample did not change as a result of salt addition but the *L** and *a** values showed variations to some extent.

Keywords: wool, madder, dyeing, color strength, natural dye.

1. INTRODUCTION

The use of natural dyes, extracted from natural resources including plants, animals, insects and minerals, for dyeing, painting and using as cosmetics dates back to millennia [1, 2]. During a few last decades, revival and application of natural dyes has gained a great deal of attention [3–6]. Most recently, Shahid et al. has reported advanced applications of natural dyes during the past fifteen years [7]. For instance, the authors have mentioned to use of natural dyes, indigo and madder, for making organic electronics devices showing acceptable properties.

Different reasons for widely grown researches on natural dyes including production of new and luxurious products, protection of the environment, achievement of better range of price, discover of new income sources, remain of resources for future generations, attention to health aspects and respect to governmental regulations, etc. were categorized into four groups: novelty, economics, personal reasons and ethics [1].

The root of madder plant or *Rubia tinctorum L.* has been used as one of the oldest natural dyes to dye and print natural fibers such as wool, cotton and silk [8]. A variety of madder species are being cultivated all over the world [8, 9]. Cuoco et al. have recently proposed a novel and cost-effective extraction method by using ultrasonic power, as well as identified the coloring constituents of madder roots by liquid chromatography coupled with a photodiode array detector. The Anthraquinonic aglycone and heterosidic dyes compounds were identified by retention time and UV-visible spectra: alizarin (1,2-dihydroxyanthraquinone), purpurin (1,2,4-trihydroxyanthraquinone), lucidin (1,3-dihydroxy-2-hydroxymethylanthraquinone), rubiadin (1,3-dihydroxy-2-methylanthraquinone), xanthopurpurin (1,3-dihydroxyanthraquinone), pseudopurpurin (1,2,4-trihydroxy-3-carboxyanthraquinone), lucidin primeveroside, ruberythric acid (alizarin primeveroside), galiosin (pseudopurpurin primeveroside) and rubiadin primeveroside [8].

During the past two decades, researchers have interested to investigate natural dyes, especially madder [10–13], for dyeing of synthetic fibers. Also, the use of new techniques including plasma [13, 14] for dyeing natural and synthetic fibers with natural colorants were studied. Gupta et al. have used Indian madder, *Rubia cordifolia*, for dyeing of nylon multifilament fibers. After purifying of color matters extracted from the powdered roots of madder plant by using chromatography technique, the authors completely investigated the adsorption kinetics and thermodynamics of purpurin on nylon fibers. Nernst adsorption isotherm was found for purpurin on nylon [11].

Farizadeh et al. [15, 16] have recently investigated the dyeing behavior of wool fibers with Iranian madder, cultivated in Fars Province. The kinetic and thermodynamics studies of madder adsorption on wool fibers were studied. The results showed that the adsorption isotherm is similar to types of Langmuir and Freundlich. Activation energy (16.01 kJ/mol) measurement of adsorption also proved that adsorption of madder on wool fibers occurs as physisorption. Determination of the standard affinity, enthalpy and entropy of dyeing at different temperatures indicated that the dyeing of wool fibers with Iranian madder is an exothermic process. The pseudo- second-order model fitted the adsorption kinetics studies of madder on scoured and mordanted wool fibers.

The aim of this study is to investigate the dyeing of wool fabrics with Iranian madder from the viewpoint of adsorption isotherm and dyebath conditions (salt effect and pH).

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2. EXPERIMENTAL

2.1. Materials

The powdered form of the madder cultivated in central areas of Iran was used in this research. Woven wool fabrics (twill 2/1, 356 g/m^2, 7 warps/cm, 9 wefts/cm) were used for dyeing. The samples were scoured before use by treating with a non-ionic surfactant solution of 2 g/l of Epicol ESB70 (Qingdao Anke Chemicals Co., China) at 40 °C for 15 min; the samples were then rinsed thoroughly with acetic acid to neutralize alkali. Other chemical materials were purchased from Merck Chemical Co.

2.2. Instruments

Absorbance measurements were carried out 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). *CIEL*, a*, b*, C*, h°* color coordinates and reflectance spectra of wool fabrics dyed with the madder were measured using a Texflash spectrophotometer (Datacolor Co., Switzerland). All color characteristics were measured under illuminant D_{65} using the CIE 1964 10° standard observer and specular component excluded.

2.3. Dye extraction process

Dye extraction was carried out using 1 g – 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 filtered by using a vacuum pump. The residues from filtration were extracted again for 15 min and then filtered. The filtrate was standardized to 1000 ml by evaporation and then used for experiments.

2.4. Absorbance test

To obtain the wavelength of maximum absorbance (λ_{max}) of the extracted madder, six different concentrations of the dye solutions, i. e. 1, 2, 3, 4, 5 and 8 g/l were prepared. Absorbance spectra of solutions were determined using UV-240 spectrophotometer over the range of 350 nm to 800 nm (see Fig. 1). The wavelength of maximum absorbance of the madder was determined as an important dye characteristic. From Fig. 1, it is found that λ_{max} for the madder used is 408 nm.

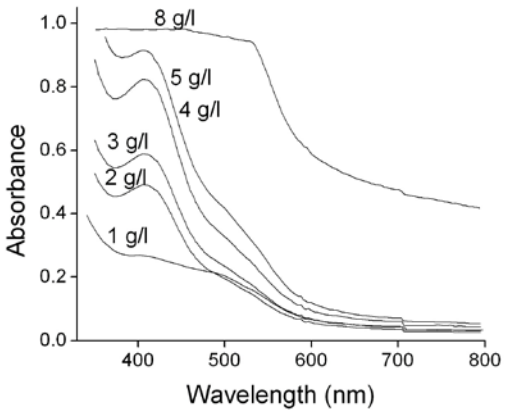

Fig. 1. Absorbance spectra obtained from different concentrations of the madder in distilled water

2.5. 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-visible spectrophotometer at 408 nm and the calibration curve obtained, shown in Fig. 2.

2.6. Adsorption isotherm

Adsorption isotherm was carried out using wool fabric (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 containing (1.5 – 155) % (o.w.f.) madder using a liquor ratio of 20 : 1 at pH 7 for 8 hours at 95 °C. After dyeing finished, the amount of dye remaining in dyebath was determined by using the absorbance measured at 408 nm and the calibration curve shown in Fig. 2. The amount of dye adsorbed on the fabrics was calculated by subtracting the dye amount remaining from the initial dye amount in dyebath.

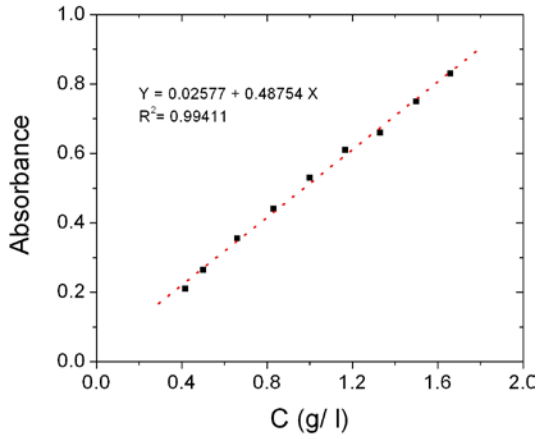

Fig. 2. The calibration curve of the madder in distilled water

2.7. 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). Dyeings were performed according to Fig. 3. After dyeing, all 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.

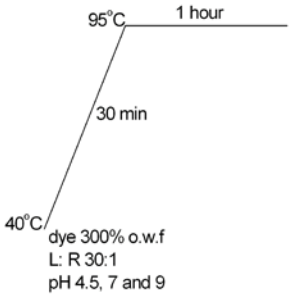

Fig. 3. Dyeing method of wool samples with the madder

2.8. Color measurements

The color strength $(K/S)_\lambda$ of dyed samples was determined by using Kubelka-Munk equation (Eq. 1).

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

where R_λ is the reflection factor of the samples at wavelength λ. K and S are the absorption and scattering coefficients, respectively [17].

3. RESULTS AND DISCUSSION

3.1. Adsorption isotherm of the madder on wool fabrics

Adsorption isotherms provide useful information on the dyeing mechanism. Three types of adsorption isotherm, usually referred to as the Nernst (Eq. 2), Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherms, have been considered [18].

$$C_f = kC_s, \quad (2)$$

where C_f is dye adsorbed onto fiber (g/kg or mol/kg), C_s residual dye in the bath (g/l or mol/l), and k a constant or partition coefficient.

$$C_f = \frac{KC_{\max}C_s}{1+KC_s}, \quad (3)$$

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

$$C_f = k'C_s^\alpha, \quad (4)$$

where k' and α are constant values.

Nernst adsorption isotherm is attributed to the distribution of a solute between two immiscible solvents and is linear up to the point corresponding to the dye saturating the fiber and the water [18]. Since wool is a hydrophilic protein fiber [18], Nernst adsorption isotherm was not considered in this work. The results obtained from the equilibrium dyeing of wool fabrics with the madder as well as the curves fitted using Freundlich and Langmuir adsorption isotherm equations (Eqs. 3, 4) are shown in Figs. 4 and 5, respectively. It can be seen that the coefficient of determination, R^2, obtained from fitting using Freundlich equation is 0.86 while for Langmuir 0.88. These coefficients of determination indicate that the adsorption of the madder on wool follows Type Langmuir. The linear forms of adsorption isotherm equations (Eqs. 5, 6), however, are widely used to determine the constant values (K, $C_{\max}$, k', α)[18].

$$\left(\frac{1}{C_f}\right) = \frac{1}{C_{\max}} + \frac{1}{KC_{\max}}\left(\frac{1}{C_s}\right); \quad (5)$$

$$(\log C_f) = \log k' + \alpha(\log C_s). \quad (6)$$

In this work, the coefficients of determination of the linear forms of adsorption isotherms were also obtained and it was found that the coefficient of determination of the linear form of the Freundlich was significantly higher than that of the Langmuir (Figs. 6, 7). It seems that the adsorption of the madder on wool at pH 7 is similar to direct dyes onto cellulosic fibers conform to Freundlich type of adsorption. Hydrogen bonding and van der Waals forces contribute mostly in Freundlich adsorption. The Iranian madder, from *Rubia tinctorum* family [19], contains hydroxyl and carbonyl groups [8], which can be attached with polymer chains in wool via hydrogen bonding. On the other hand, madder contains anthraquinonic skeleton dyes [8], which result in van der Waals forces between the madder and polymer chains in wool. The value α in (Eq. 4) was also calculated 0.61 corresponding to 0.5 for the adsorption of anionic dyes on cellulosic fibers [18].

Langmuir adsorption isotherm is often used for the adsorption of a solute on absorbant's specific sites [18]. In this study, the coloring matters existing in the madder have no electrical charge and chemical interaction and hence Langmuir adsorption isotherm could not be used to describe the equilibrium state in wool dyeing.

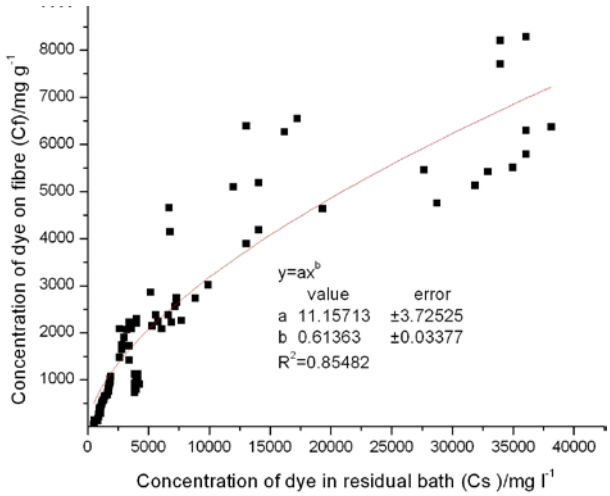

Fig. 4. Freundlich adsorption isotherm for the madder on wool fabric

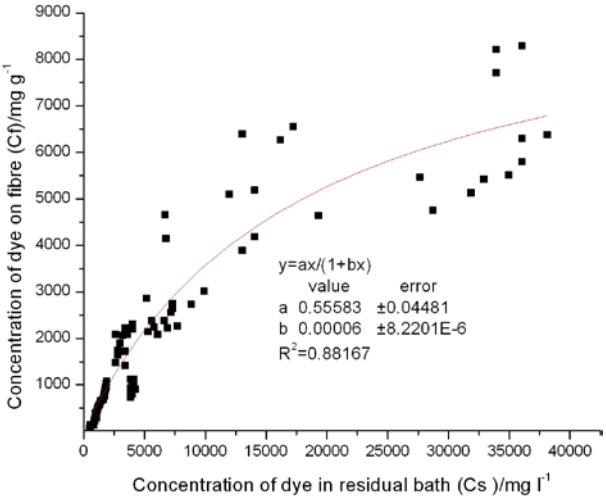

Fig. 5. Langmuir adsorption isotherm for the madder on wool fabric

3.2. Effect of dyebath pH on adsorption of the madder on wool fabrics

For this purpose, 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 L : R of 30 : 1. The results obtained have been shown in Table 1 and Fig. 8. It can be seen that adsorption of the madder onto wool

fabrics has considerably increased at acidic pH. In addition, the sample dyed at pH 4.5 showed the lowest L^* (Lightness; zero means black and 100 means white) and the maximum color difference ($\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} = 45.1$) compared with the samples dyed at pH 7 and 9. According to Table 1, the a^* (positive and negative values indicate redness and greenness, respectively) and the b^* (positive and negative values indicate yellowness and blueness ,respectively) and $h°$ (hue angle = $\tan^{-1}(b^*/a^*)$) values of all dyeings confirm that the samples placed in the first quarter (red-yellow) of *CIEL*a*b** color space. A reduced amount of chromaticity ($C^* = \sqrt{(a^*)^2 + (b^*)^2}$, indicating the color purity of the dyeing) and $h°$ of the sample dyed at pH 4.5 corresponds to the greater dullness and redness, respectively.

The hydrolysis of proteins in wool can be catalyzed by acids and alkalis and damage to wool can be significantly increased in hot solutions, especially under alkaline conditions [18], therefore, pH 4.5 is appropriate for dyeing of wool fabrics. Farizadeh et al. [15] also found that *K*/*S* in wool fabrics dyed with madder increased with decreasing of pH and attributed it to Keto-enol tautomerism of carbonyl groups of madder in acidic media, leading to higher hydrogen bonding with carboxyl groups of wool fibers. Additionally, the increase in absorbance of extracted Iranian-madder solutions [15] and the coloring components, purpurin and nordamncanthal, solutions in Indian madder [11, 20] proves that the solubility of madder increases with increasing of pH. Therefore, it is expected that adsorption of the madder onto wool fabrics decreases with increasing of pH. Nagia et al. [21] also have reported the same result when dyeing wool fibers with natural anthraquinone dyes extracted from *Fusarium oxysporum*; they attributed the increased dyeability to the ionic interaction of hydroxyl groups in dye molecules and the protonated terminal amino groups in wool as pH decreased.

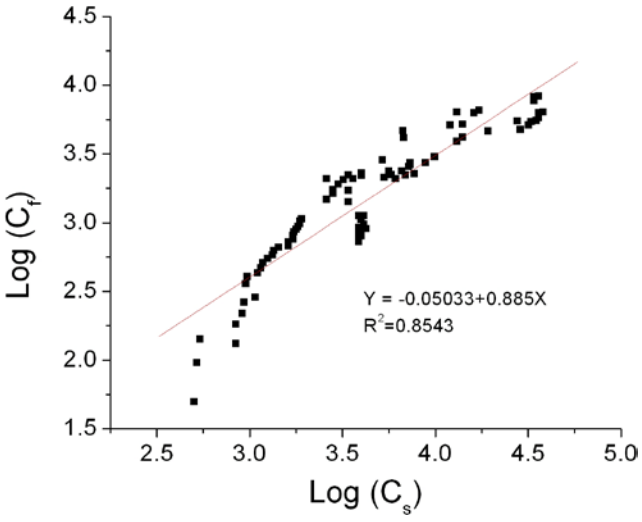

Fig. 6. Linear form of Freundlich adsorption isotherm for the madder on wool fabric

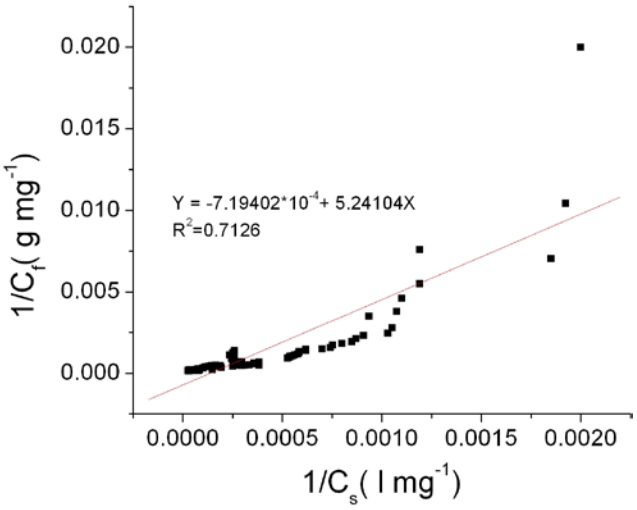

Fig. 7. Linear form of Langmuir adsorption isotherm for the madder on wool fabric

Fig. 8 shows that the color strength of the sample dyed at pH 9 is higher than that of the sample dyed at pH 7. Also, this difference can be seen from the color characteristics of the samples in Table 1. This could be attributed to ionization of hydroxyl groups in the madder at pH 9 leading to extension of resonance. Therefore, the sample dyed at pH 9 appears redder compared to that dyed at pH 7.

Table 1. Colorimetric data (*CIEL*a*b**, *C**, *h*°) and ΔE^*_{ab} of wool fabrics dyed with the madder at different pH

Dyebath pH	L^*	a^*	b^*	C^*	$h°$	ΔE^*_{ab}
Undyed sample	69.8	3.1	18.1	18.4	80.2	–
4.5	27.4	18.1	14.9	23.5	39.4	45.1
7	43.1	15.7	17.8	23.8	48.5	29.5
9	39.1	19.0	16.0	24.8	40.0	34.7

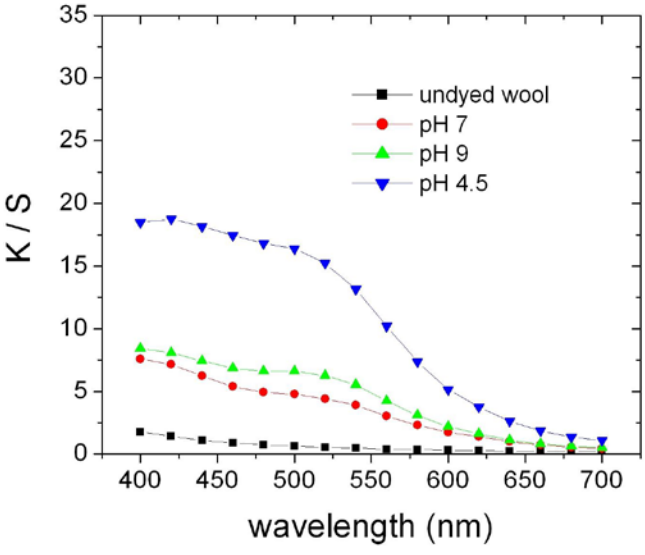

Fig. 8. The color strength of samples dyed with the madder at different pH

3.3. Effect of salt on adsorption of the madder on wool fabrics

For this purpose, two dyebaths were prepared: one bath containing 2.5 % o.w.f. oxalic acid (pH 4.5) and the other containing 4 % o.w.f. Glauber's salt and 4 % o.w.f. acetic acid (pH ~5). As can be seen from Table 2 and Fig. 9, dyeing in the presence of the salt increased the adsorption of the madder on wool fabric. It is expected that addition of the salt to the dyebath increased the exhaustion by rendering the dye even less hydrophilic. On the other hand, the addition of salt in dyebath increased *C** value. In the case of dyeing of modified acrylic fibers, it has been stated that the addition of salt (sodium sulfate) up to 1 g/l slightly increased the color strength of the dyed fabrics after which further increase in the salt concentration did not roughly change the color strength of samples dyed with madder [10].

As can be seen from Table 2, addition of salt in the dyebath did not affect the *b** value while the *L** and *a** values changed as a result of salt addition.

Table 2. Colorimetric data (*CIEL*a*b*, C*, h°*) and ΔE^*_{ab} of wool fabrics dyed with the madder

Dyebath pH	*L**	*a**	*b**	*C**	*h°*	ΔE^*_{ab}
4.5	25.0	23.8	17.7	29.7	36.5	–
~5	24.0	28.1	17.7	33.2	32.3	4.4

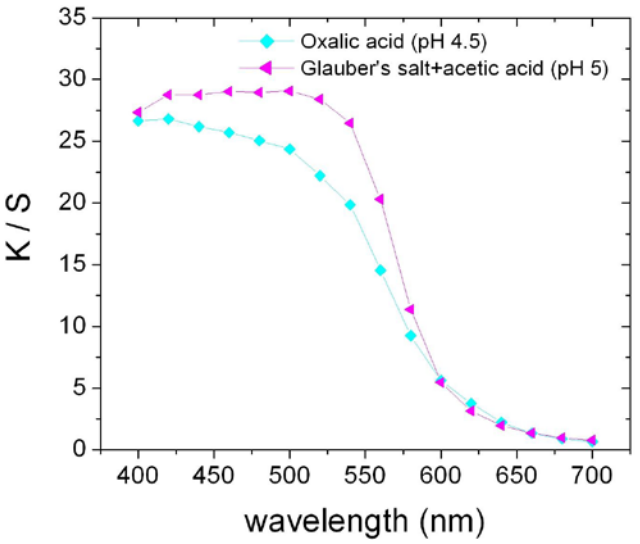

Fig. 9. The effect of salt on the color strength of dyed sample

4. CONCLUSIONS

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 fabrics is the Freundlich type of adsorption. Also, the color characteristics measurements confirmed that the adsorption of madder on wool fabrics significantly increased at pH 4.5 compared to dyeings at pH 7 and 9. The difference between color strength of the samples dyed at pH 7 and 9 was not significant. However, different color characteristics of the samples were found due to pH variation in dyebath. Addition of salt in the dyebath also increased the madder adsorption. The *b** value of the dyed sample did not change as a result of salt addition while the *L** and *a** values showed variations to some extent.

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