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Colorimetric Properties of Wool Dyed with Cochineal: Effect of Dye-Bath pH

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ABSTRACT

In the present work an evaluation was carried out on the effect of dye-bath pH and mordant type on the obtained shades and fastness properties in wool dyeing with cochineal. In this way wool samples were first mordanted with four different mordants and subsequently dyed with cochineal at different dye-bath pH values of 1 to 9. Colorimetric evaluations were carried out and the fastness properties of the dyed samples were assessed. Changes in the chemical structure of the dye in different pH conditions were also discussed. It was found that the pH of the dye-bath has a great effect on the obtained shades. Based on the results, a combination of dyeing in different values of dye-bath pH from 1 to 9 along with mordanting with various mordants can considerably develop a range of obtainable hues in dyeing of wool with cochineal. Based on the obtained results, the studied different pH conditions have not significant effect on the fastness properties. Prog. Color Colorants Coat. 7(2014), 129-138 © Institute for Color Science and Technology.

1. Introduction

Cochineal (C.I Natural Red; CI 75470) is a natural dye of insect origin that has been used for centuries for dyeing textiles. Its main source is the dried bodies of the females of the Coccus cacti scales which live on a species of cactus (Nopaleacoccinellifera) mainly in Central America and Mexico [1-5].

The main coloring agent in all cochineals is a derivative of anthraquinones so called carminic acid (Scheme 1) that can be used as mordant dye with the carbonyl and the adjacent phenol groups participating in the fiber–mordant–dye complex [2, 3].

Armenian cochineal contains the highest proportion of (up to 95%) carminic acid. However the various species have characteristic fingerprints of anthraquinone minor components (including the laccaic acid, kermesic acid and flavokermesic acid) which allow them to be distinguished [2].

The anthraquinone chromophore contains four

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*Corresponding author: pvalipour2003@yahoo.com hydroxy groups which two of them positioned in direct neighborhood of one central oxo group. The first dissociation step occurs at carboxylic group in the position 2 (pK0=2.9), which is the most acidic site. The following acid-base equilibrium (pK1=5.4) involves the 6-hydroxyl group since the 5- and 8- OH groups (pK2=8.7 and pK3=12.2) are less acidic due to their position with respect to the carbonyl, which reduce the hydrogen mobility through hydrogen bonding [6].

The color of carminic acid in solution changes with pH, since the phenolic groups are rather acidic. Thus, at low pH, carminic acid is pale orange, changes to red at slightly acidic and neutral pH, and finally turns violet in alkaline solution. These solutions have little intrinsic color below pH 7, where the quinone ring has greatest photo stability showing a pale-straw tint at pH near 4 [3].

Another important characteristic of carminic acid is the property of forming complexes with several metals ions. In fact, the metal ions can act as acceptors to electron donors to form co-ordinate bonds with dye molecule, which is insoluble in water [7].

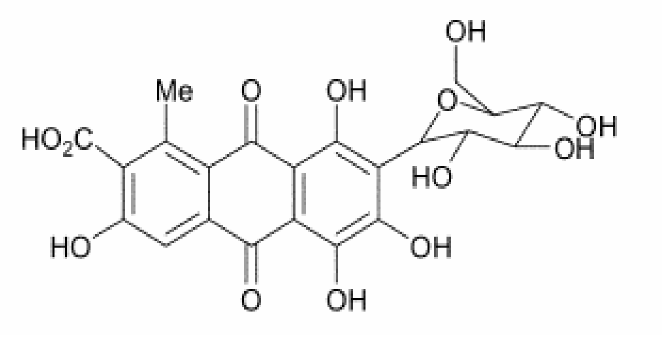
Complexation shifts the maximum absorption in the visible range to higher wavelengths, with an apparent increase in color intensity. Generally, mordants form chemical bonds between the dye molecules and the proteins of the fibers, which usually used in order to increase the absorption and fixing efficiency and prevent fading against washing and exposure to light.

In most recipes, mordants are used on the fiber before dyeing (pre-mordanting) but they can also be used during (simultaneous or meta-mordanting) and after dyeing (after-mordanting) [8-12]. Using a different mordant with the same dyestuff may produce different shades, for example, iron is usually used for darkening the colors, copper sulfate also makes the shades darker but can give shades which are otherwise very difficult to obtain, tin brightens the colors and, chrome is good for obtaining yellow shades.

Conventionally, in textile coloration, cochineal produces a range of scarlet, pink and other red hues. The obtained shade is changed by the mordants, the fiber and the pH of dyebath. Alum mordants make dyed fiber by cochineal more purple and less red but Tin has the opposite effect. There are a number of recipes for dyeing with cochineal and producing various shades [8-10].

The literature survey indicates that there have been relatively few works investigating the effect of dye-bath pH and the mordant on the obtained color in cochineal dyeing. It was previously shown that the sensitivity of natural pigments to pH is an effective parameter in de-acidifcication of dyes and the pH change can induce structural modification to the chromophoric system [11]. Montazer et al studied the colorimetric properties of wool dyed with natural dyes after treatment with ammonia [12]. They found that after-treatment of wool dyed with natural dyes, ammonia tends to change their color and the color change is not reversible by subsequent treatment with acid.

As the color of carminic acid changes with pH, in natural dyeing with cochineal, the parameter of pH is expected to be effective on the final shade. The present work discusses the effect of dye-bath pH on chemical structure of the dye, obtained colorimetric values and the fastness properties of dyed samples.



Scheme1: Chemical structure of carminic acid.

2. Experimental

2.1. Materials

A commercial material of cochineal dye was used. The wool used for dyeing was twill fabric: weight 205 gm^{-2}, 72 ends per inch, 64 picks per inch. The nonionic detergent used for the scouring of wool was obtained from the Shirley Development Ltd. Ferrous sulfate [$FeSO_4$], Aluminum potassium sulfate (Alum) (KAl $(SO_4)_2.12H_2O$) , Copper Sulfate [$CuSO_4.2H_2O$] and Potassium dichromate ($K_2Cr_2O_7$) , Sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3) and Acetic acid (CH_3 COOH) were supplied by Merck.

2.2. Scouring

The wool samples were first scoured with 0.5% nonionic detergent for 30 min at 50ºC. The L.R. (Liquor ratio) of the scouring bath was kept at 40:1. The scoured material was thoroughly washed with clean water and dried at room temperature.

2.3. Mordanting

A pre-mordanting procedure was used in which the scoured wool yarns were mordanted prior to dyeing by treating with different mordants at boil for 45 min. The liquor ratio was 40:1 and the concentration of mordants was 5% on weight of the samples. The pH was adjusted using acetic acid at 5. The mordanted material was then rinsed with water thoroughly, squeezed and dried.

2.4. Dyeing

Cochineal powder was mixed with a required amount of water and boiled for one hour. The extract was cooled to room temperature (25°C) and filtered. The filtrate was then used as the dye solution at concentrations of 5% (o.w.f) for dyeing of the wool samples. The liquor-goods ratio was 40:1. The pH of different acidic and alkaline dye- baths was adjusted with proper amount of sulfuric acid, acetic acid or sodium hydroxide. Samples were introduced into dyeing solutions at room temperature. Temperature was raised to the boiling point and dyeing continued at the boil for 1 hr. At the end of the dyeing period, the dye bath solution was removed and the rinsing procedure started. Excess dye was removed by rinsing with cold water.

2.5. Colorimetric evaluation:

The spectral reflectance of the dyed samples was measured using a (Texflash spectrophotometer, (Datacolor Corp.). The K/S values were calculated by the Kubelka-Munk equation. (Eq.l) [12- 14].

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

where R is the reflectance of dyed fabric at wavelength (λ), K is the absorption coefficient, and S is the scattering coefficient. CIELAB coordinates [13,14] (L* , a*, b*, C*) where, L* defines lightness; a* denotes the red/green value; and b* the yellow/blue value and C* is the saturation) were calculated from the reflectance data for 10^{o} observer and illuminant D_{65}.

2.6. Fastness properties

The dyed samples were tested according to ISO standard methods. The specific tests were as follows: ISO 105-X12(1987), color fastness to rubbing; ISO 105-C02 (1989), color fastness to washing; and ISO 105-B02 (1988), color fastness to light (carbon arc).

2.7. UV/Vis absorption spectra:

The absorption spectra of dye solutions were recorded by a UV-Vis CINTRA 10 spectrophotometer within the visible spectrum between 400 and 700nm.

3. Results and discussion

3.1. Colorimetric evaluations:

The absorbance spectra of cochineal dye solution at different pH values are shown in Figure 1. As can be seen the wavelength of maximum absorption as well as the intensity of absorption in λ_{max} change with pH. Generally, cochineal dye solution exhibits a reddish orange color in acidic media and a reddish purple color in alkaline media. The CIELAB color values of cochineal dye solution at different pH values are also shown in Figure 2.

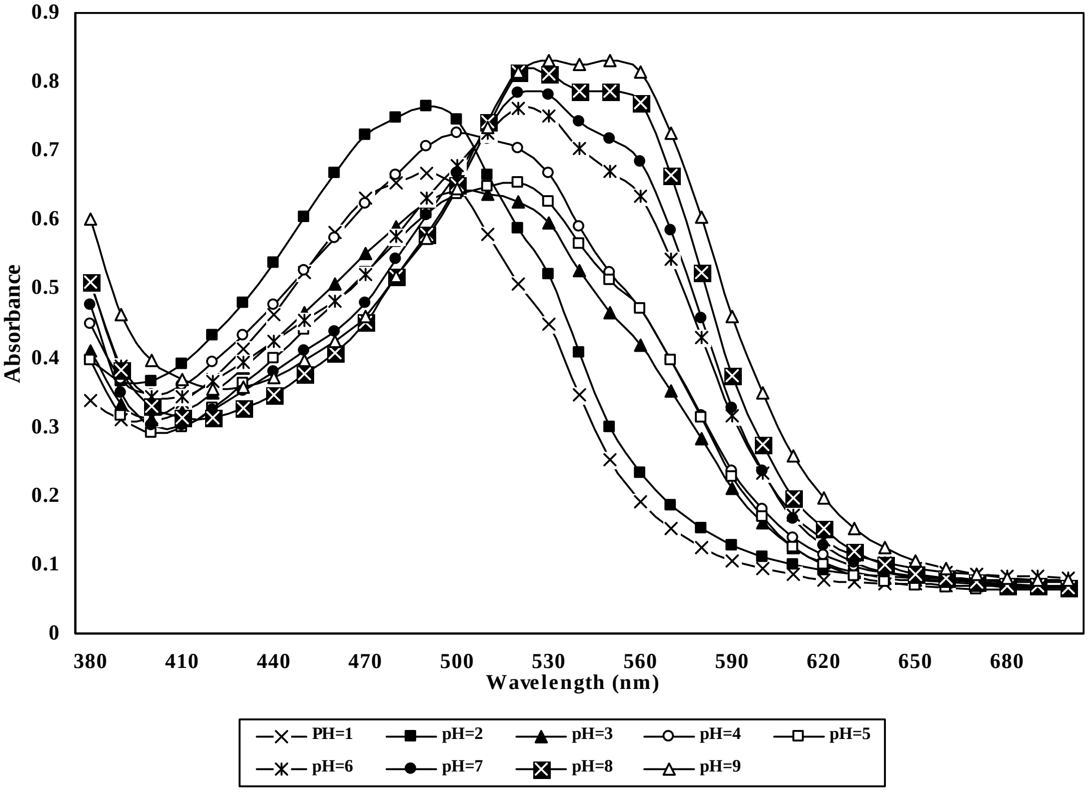


Figure 1: The effect of pH level on absorbance spectra of cochineal dye solution.

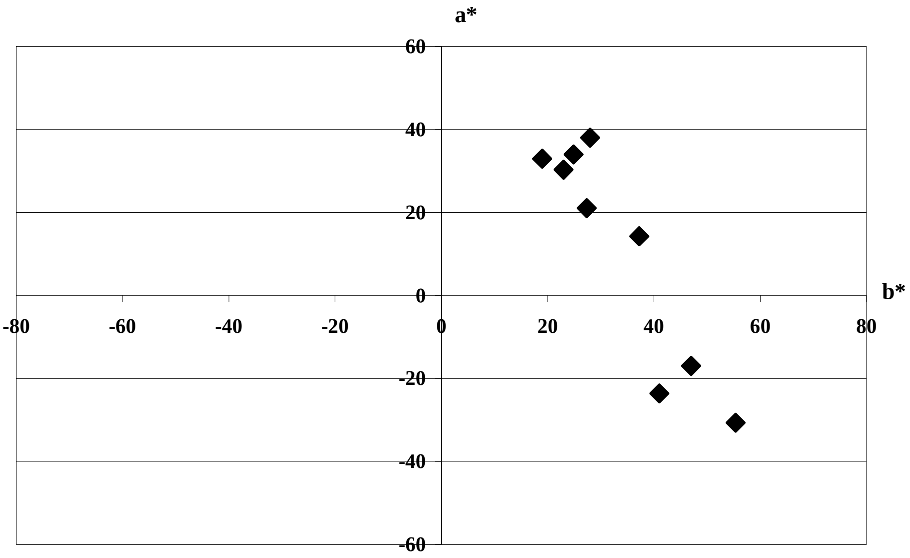


Figure 2: Location of CIELAB color values of cochineal dye solution at different pH values.

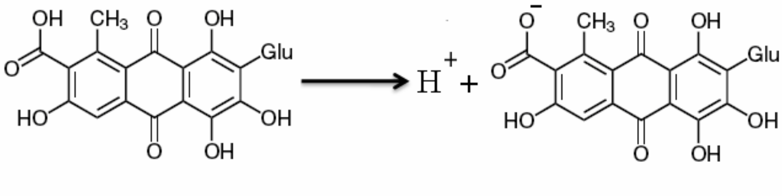
Carminic acid as an anthraquinone glycoside is expected to dissociate in water, so that two forms coexist at pH=7, the fully protonated acid (CAH) and the deprotonated anion (CA-) (Scheme 2).

These keto-enol pair structures enable two single proton transfers and one double proton transfer and therewith suggest the coexistence of the normal form (CAH) and three tautomers (T1, T2, T3) as shown in Scheme 3.

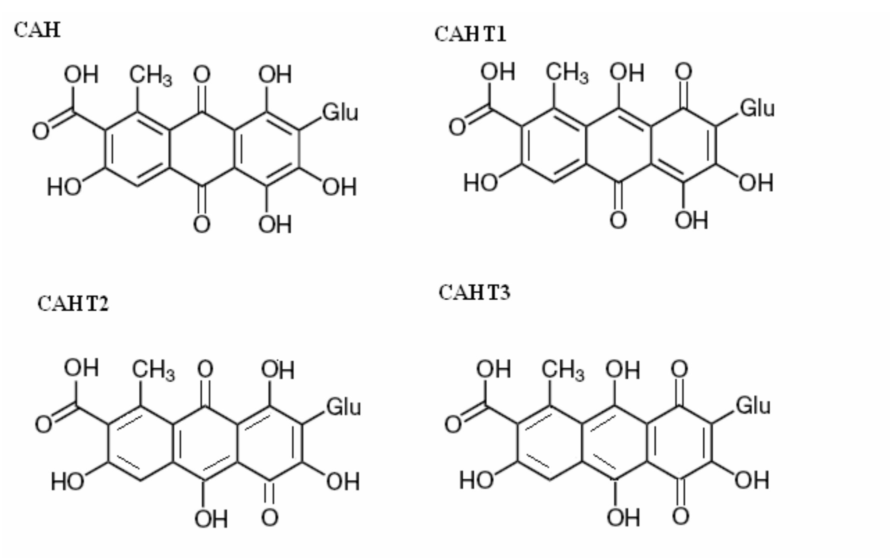
In the alkaline condition, the carboxylic acid group of the carminic acid is converted to carboxylate ion, and this affects the energy levels of π-, π*- and n molecular orbital in the adjacent conjugated system, and unexpectedly modifies the color.

In strong alkaline conditions, the hydroxyl groups at the sttared positions in the carminic acid structure are also attacked, giving a variety of possible resonant structures and this in turn affects the color (Scheme 4). The presence of both carboxyl and hydroxy groups in anthraquinone structure of cochineal is probably responsible for its behavior in different pH conditions.

Figure 3 shows the effect of different mordants on (K/S) spectra of wool samples dyed with cochineal. The behavior of the dye after dyeing on wool may be explained by the chelating ability of the mordant. Metal ions provide a bridge between the dye and wool by forming coordination complexes with functional groups of the dye molecule (OH, C=O) on the one hand and with the functional groups of the wool protein (NH_2, COOH) on the other hand. The wavelength of the absorbed light is inversely proportional to the energy difference between highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). So, the HOMO and LUMO have π- bonding and π*-antibonding characters, respectively.

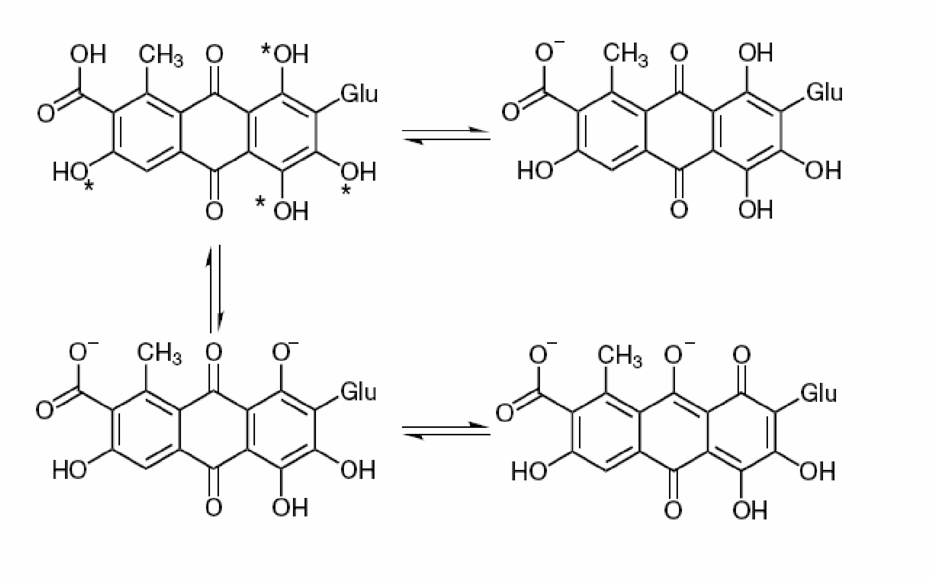


Scheme 2: The fully protonated (CAH) and the deprotonated anion (CA-) of Carminic Acid.



Scheme 3: The normal form (CAH) and the three tautomers (T1, T2, T3) in the Carminic acid.

Metals have relatively low energy levels, and their incorporation into a delocalized system results in a lowering of overall energy. Thus the type of mordant used and the intensity of the metal- ligand interaction affect the absorbance of the metal complex and the resulted color.



Scheme 4: The four possible resonant structures of Carminic acid.

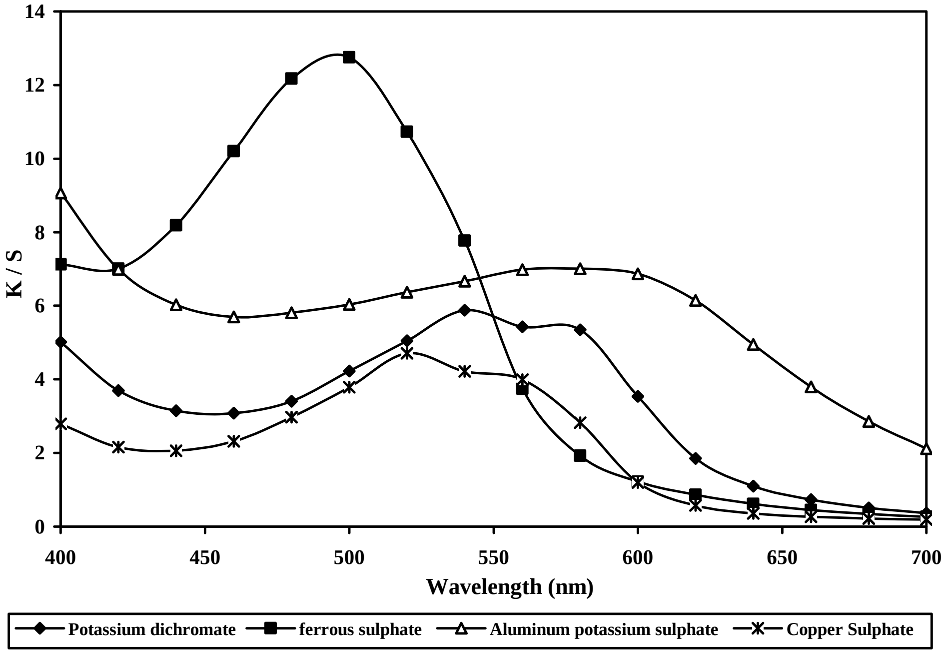


Figure 3: Effect of different mordants on K/S spectra of wool samples dyed with cochineal.

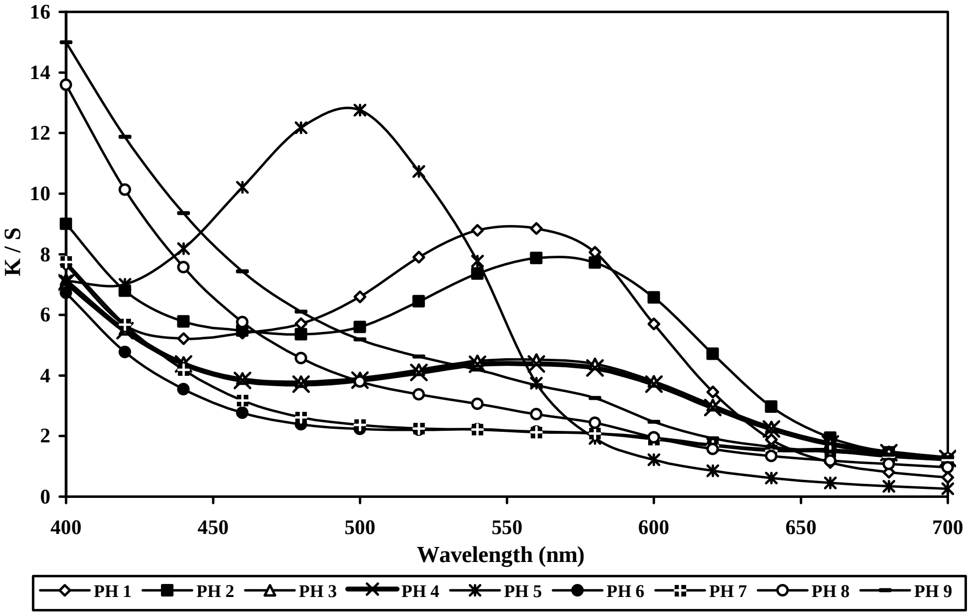


Figure 4:The (K/S) spectra of Iron pre-mordanted samples dyed with cochineal at different values of dye bath pH.

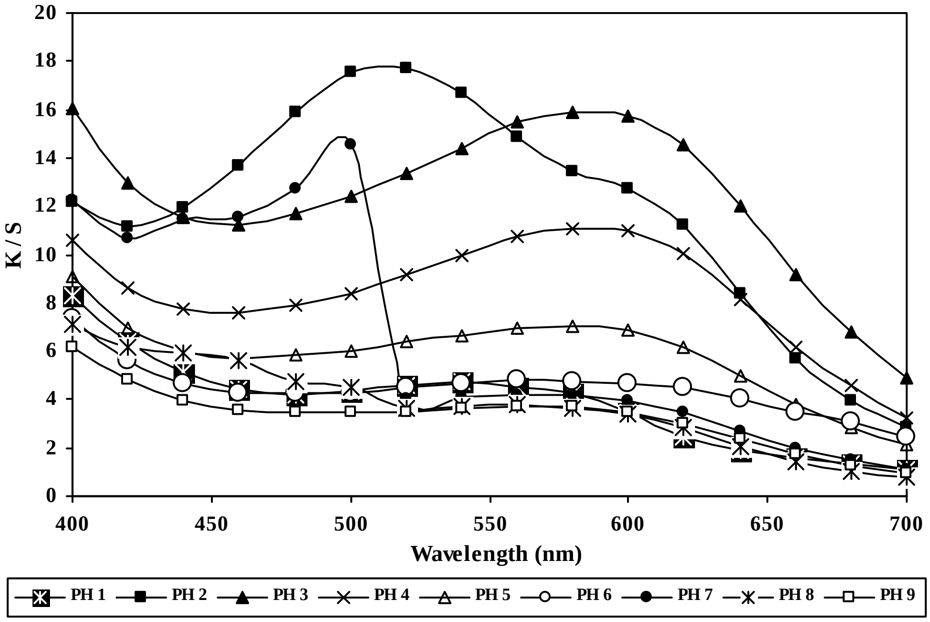


Figure 5: The (K/S) spectra of Alum pre-mordanted samples dyed with cochineal at different values of dye bath pH.

Figures 4 and 5 show the absorbance (K/S) spectra of samples dyed with cochineal, pre-mordanted with Ferrous sulfate and Alum at different values of dye-bath pH. It can be seen that cochineal dyeing at different conditions of pH can produce different shades on the wool sample as it affects the shape of K/S spectra of the dyed sample.

In general, higher dye uptake (K/S values) on the wool in acidic conditions could be attributed to the structural features of the dye and the fiber, where the electrostatic forces between the positively charged end amino groups of the fiber and the dye molecules could be expected to play a dominant role in the increased dye adsorption.

The CIELAB locations of the various obtained shades in dyeing of wool with cochineal at different pH values and by pre-mordanting with the Ferrous sulfate, Aluminum potassium Sulfate, Copper sulfate and Potassium dichromate are shown in Figure 6. It can be noted that the implementation of dyeing process at different values of dye-bath pH could extensively broaden the range of obtainable shades.

3.2. Fastness evaluation

Results for fastness properties of dyeing with cochineal at different pH values and by using different mordants are given in Table 1. When all the dyed samples were subjected to wash fastness evaluation, it was observed that except Alum pre-mordanted samples, almost all showed good-to- excellent (4-5) and excellent (5) washing fastness. However the samples mordanted with alum, particularly when dyed at acidic conditions, showed lower washing fastness properties. Generally, the samples mordanted with Potassium dichromate had the best rubbing fastness properties among all. Iron pre-mordanted samples showed the weakest light fastness properties followed by Alum. Light fastness of the samples was found to reach the fair values of 7-8 according to the blue scale standard while the sample dyed using copper mordant was found to have the best light fastness properties among others.

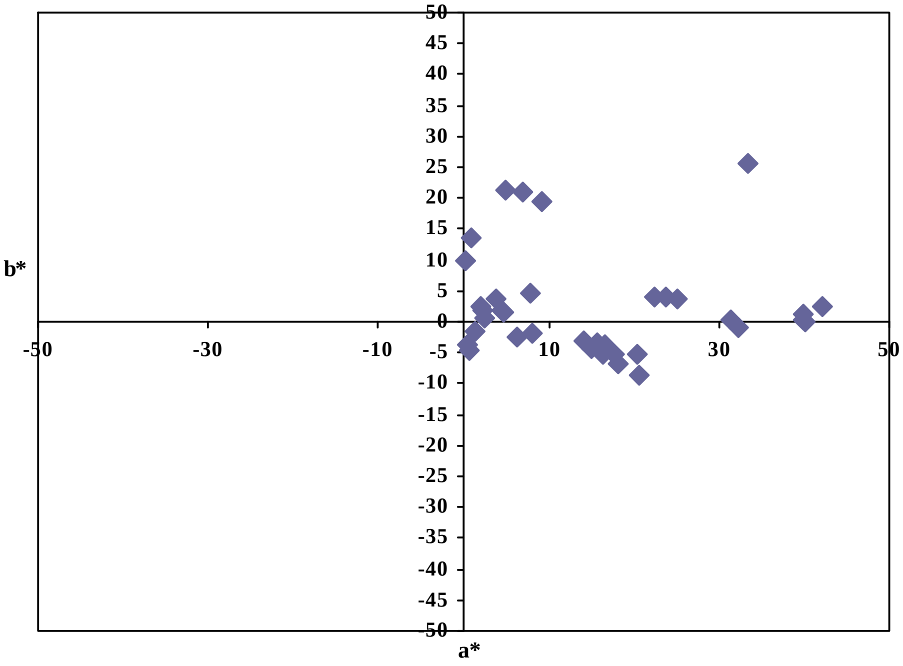


Figure 6: Location of CIELAB color values of wool samples dyed with cochineal and different mordants at different pH values.

Table 1: Fastness properties of wool samples dyed with cochineal and different mordants at different pH values.

Fastness		pH Mordant	1	2	3	4	5	6	7	8	9
Washing		Alum	3	3	3	4	4-5	4-5	4-5	4-5	4-5
		Iron	4-5	4	4-5	5	5	4-5	5	5	4
		Copper	4-5	4-5	4-5	5	4	4-5	5	5	4-5
		Potassium dichromate	5	5	4-5	4-5	5	5	4-5	4-5	5
Light		Alum	7.5	7	7.5	7	8	8	7.5	8	7.5
		Iron	8	7.5	6	7.5	7	5	7	7.5	6.5
		Copper	8	8	8	8	8	8	8	8	8
		Potassium dichromate	8	8	8	8	7.5	7.5	7	7	7
Rubbing	Wet	Alum	3	3.5	3	3	3	4	4	3	4
		Iron	3	3	3	2.5	3	3.5	3	3	4
		Copper	3	3	3	3	4.5	3	4	4	3
		Potassium dichromate	4.5	4.5	4.5	4	4	4.5	4	4	4.5
	Dry	Alum	2	2	2	2	2	3	2	2	2
		Iron	1	2	1	1.5	1.5	1.5	2	2.5	1.5
		Copper	2.5	2.5	2.5	2.5	2.5	2.5	2	2	2
		Potassium dichromate	4.5	3.5	3.5	3	3	3	3	3	3

4. Conclusion

There are a number of limiting problems in natural dyeing which one of them is the limited range of attainable shades from natural coloring materials. In this way, from the ancient times, natural dyers have used some inventive techniques in order to increase the diversity of shades in natural dyeing. For instance, the application of different mordanting agents, combinatory dyeings and post- treatment of dyed samples are some conventional techniques for producing various beautiful shades from natural dyestuffs. In the present work, the intrinsic sensitivity of cochineal to pH was used to increase the range of attainable hues in cochineal dyeing of wool. It was observed that the combination of dyeing in different values of dye-bath pH along with mordanting with various mordants can considerably develop a range of obtainable hues in dyeing of wool with cochineal. Thus, implementation of dyeing process at different values of dye-bath pH gave a variety of beautiful shades. Moreover, the produced shades differ from mordant to mordant. Based on the obtained results, generally the effect of dye-bath pH on the fastness properties of dyed samples was not significant.

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