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Properties of wool dyed with pinecone powder as a by-product colorant

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The properties of the pinecone, an Iranian natural and low cost agricultural by-product, have been studied for its potential use in textile dyeing. In this research, wool fibres due to their high affinity towards the aqueous extract of natural dyes have been used and their dyeability with powdered pinecone is studied. The effects of two different variables, including dye concentration and mordant type on the color properties of dyed wool fibres are investigated. To determine the functional group of pinecone colorant, FTIR test is also performed. The colorimetric properties (color strength, color difference, color coordinates CIE Lab) and the color fastness (wash and light) results are considered for quantifying evaluation of dye concentration and mordant type effects. The results show that the wool possesses high affinity towards pinecone dyeing solution, and the used mordant methods exhibit different shades ranging from beige to brown with good fastness.

Keywords: Dyeing, Pinecone, Protein fibre, Wool

1 Introduction

Since the today's worldwide awareness is going towards the human health, natural materials are considered as acceptable alternatives to the synthetic products for different applications especially in dyeing and chemical industries. Natural dyes due to their biodegradable properties and a wide variety of soft shades are generally compatible with synthetic dyes[1-3]. Natural colorants are generally known as pigments or dye molecules, which could be obtained from plant, animal, or mineral sources. There are some noticeable characteristics related to the natural dyes that make them available for dyeing applications in textile industries including color fastness properties, a wide range of color shades and the ability of dyeing on various textile samples.

Recently, many studies have been developed to discover such novel natural sources with high potential application in textile and other color industry. Agricultural and forest by-products are now considered as one of the cost-effective natural sources[3-5]. The most common natural dyes used in textile application as listed in Color Index are flavonoid compounds[6] , among which pinecone is one of the common by known natural sources[7]. The chromophoric component of pinecone colorant consists of phenolic benzoic units partly connected with each other through pi-electron conjugate systems[8]. Although, there are numerous literature wherein studies have been focused on cationic and acidic dyes removal from water by using pinecones [9-11], but the studies on using the pinecone as a natural dye for dyeing of the textile substrate, especial wool, are almost limited.

The black pine (*Pinus nigra*) is a species of pine occurring across large areas of Iran[12]. Pinecones could be extracted from the large evergreen tree, which is often planted as an ornament in parks and forest. This natural colorant with a rounded spirally arranged structure has a 5–10 cm length. The epidermal and sclerenchyma cells component of pinecone contain cellulose, hemicellulose, lignin, resin, and tannins in their wall cells which contain polar functional groups such as alcohol, aldehyde, ketone, carboxylic, phenolic, etc.[13]. Generally, on the forest footpaths, the pinecones are considered as municipal waste, which could only be collected and transported.

In this study, the color properties of dyed wool using pinecone, an Iranian natural low cost agricultural by-product has been investigated. For this reason, different dyeing processes are carried out using 25, 50, and 100 % (owf) of powdered pinecone. Pre-mordanting of wool with mordants is carried out to obtain dyed samples with good color fastness, high depth of shade and variety of color shades.

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The common metal salts based on aluminum, chromium, copper, iron, and tin are used through the dyeing process. The CIE lab values, color strength *K/S*, color differences, and wash & light fastness values are measured to study the dyeing properties.

2 Materials and Methods

2.1 Materials

In this study, the brown 5cm long pinecones were collected locally from Isfahan University of Technology campus, Isfahan, Iran. As far as the impurity and surface-adhered particle removal is concerned, the pinecone samples were initially washed several times with distilled water and then dried at 110°C overnight. The dried materials were then cut and ground by using a crusher to achieve the cone powder used in wool dyeing.

Five grams of commercially available wool were inserted to the aqueous solutions (3 and 5 %owf) containing aluminum, potassium dichromate, stannous chloride, copper, and iron (II) sulfate as mordants of commercial grade, procured from Merck Company (Germany).

2.2 Apparatus

In this research, a Polymat dyeing machine (AHIBA AG, PM 100 Dietikon/ Zurich) was used. The mordanting and wash fastness tests were also applied on the wool specimen. Additionally, the specimens' color measurements were performed by using a Spectra Flash 60 (Datacolor International) reflectance spectrophotometer. Using Heraeus Xenotest 150S, the light fastness of samples was also determined. It should be noticed that blue and gray scales were used for evaluating the light and wash fastness respectively.

2.3 Dyeing Procedure

Initially, the raw wool was scoured until the impurity such as oil and dust could be removed from the. Wool (5 g) was then washed for 20 min in an aqueous solution containing $1 gL^{-1}$ of non-ionic detergent with a liquor ratio of 40:1 at 50°C. After washing, the samples were rinsed in cold water and dried at room temperature.

In this study, we used pre-mordanting methods for dyeing the wool. The mordanting step followed by dyeing step was carried out using the following experimental conditions:

Mordanting		**Value**
Alum, stannous chloride, potassium dichromate, ferrous sulfate, copper sulfate	:	3-5 % owf
Liquor- to- material ratio	:	30:1
Temperature	:	100°C
Time	:	45 min

Dyeing		**Value**
Powdered pinecone	:	25, 50 and 100 % owf
Liquor- to -material ratio	:	30:1
Temperature	:	100°C
Time	:	60 min
*p*H (HCO_2H)	:	4

The metal salts were dissolved in hot water, and then the wool was treated with this solution using a liquor-to-material ratio of 30:1 for 45 min. The heat was increased slowly over 20 min up to boiling temperature and then kept in that condition for about 45 min. The samples were then rinsed, squeezed and allowed to dye.

The mordanted samples were dyed with pinecone powder (25, 50, and 100 %owf) in liquor -to- material ratio of 30:1 for 1 h (*p*H was adjusted at 4 with acetic acid). The bath temperature was increased over 20 min to boiling point and then was kept as such for 1 h (Fig. 1). The dyed specimen was rinsed in cold water and washed with $1 gL^{-1}$ of non-ionic detergent (Nekanil LN) at 60°C for 15 min in a bath of liquor-to-material ratio 20:1. Finally, the dyed samples were rinsed and dried at room temperature.

2.4 Colorimetric Assay

A Tex flash spectrophotometer (Data color corp.) was used to measure the spectral reflectance of the dyed. Three measurements were made on each sample. The relative color strength of dyed expressed as *K/S* was measured by the light reflectance technique using Kubelka- Munk equation. The CIE

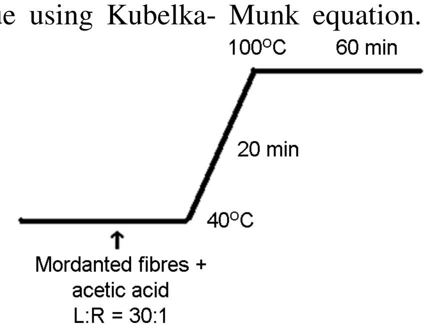

Fig. 1—Dyeing method of mordant wool

lab values (L^*, a^*, b^*, C^*, h°) were also recorded for all dyed samples along with controlled sample. Chroma is a measure of intensity or saturation of color. The hue angle (h°) is expressed on 360° grid to show the tonality of color. Red colors are represented by h° values around 0° (or 360°); blue colors are described by values at about 270° (or -90°). Yellow and green colors are illustrated with the hue angle at around 90° and 180° (or -80°) respectively[14].

Color differences (ΔE) for mordanted samples in comparison with unmordanted samples were measured using the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad \ldots(1)$$

where $\Delta L = L^*_{mordanted} - L^*_{unmordanted}$; $\Delta a = a^*_{mordanted} - a^*_{unmordanted}$; and $\Delta b = b^*_{mordanted} - b^*_{unmordanted}$; wherein 'L' , 'a' and 'b' describe lightness, redness and yellowness of color respectively.

2.5 Color Fastness

The wash and light fastness of the dyed fibres was determined according to ISO-105-C01 and ISO-105-B02 standards respectively. For wash fastness test, the fibres were washed in a standard soap solution at 40℃ for 30 min with the liquor-to-fibre ratio at 1:50. The color changes observed in samples were compared with a reference to the original and the gray scale from 1 (poor) to 5 (best) were allocated to the dyed samples accordingly. A sample with a wash fastness rating at 3 indicates a considerable alteration in color after washing. The degree of staining on the adjacent yarns was measured after drying. The light fastness test results were also rated from 1 (poor) to 8 (best) according to the color changes occurred in wool dyed samples

3 Results and Discussion

3.1 Chemical Structure

The FTIR spectrum of pinecone is shown in Fig. 2. The results show the indicative broadband of unbounded –OH group at 3100-3600 cm^{-1} and the –CH stretching (C sp^3) at 2927 cm^{-1}. The carbonyl (-C=O) stretching is observed at 1639 cm^{-1}, and the carboxylate anion (-COO-) appears at 1447 cm^{-1}. The peak at 1382 cm^{-1} is attributed to C-H bending of the methylene group, and the phenol peak (C-O stretching) appears at 1265 cm^{-1}. The absorption peak at 1030 cm^{-1} represents the C-O-C linkage of the ester group. Hence, FTIR spectra analysis shows the presence of chemical groups like –CH, -OH, -CO and –C=O in the extracted pinecone colorant.

3.2 Color Measurements

3.2.1 CIE Lab

Natural dyes need mordant additives to be fixed on the fibre surfaces. In this study, alum, potassium dichromate, and stannous chloride as the brightening mordants and cupric and ferrous sulfate as the dulling mordants were used. It is well known that each color has its own distinct appearance, based on three elements, namely hue, chroma and lightness value. The color assessment results of un-dyed and dyed specimen are given in Table 1.

Based on the hue angle value, the color of the crude wool has a light yellow shade (h°=81. 71). As these are dyed with powdered pinecone, tonality of color would be changed from yellow to pale brown. This color change behavior could be shown according to the change of a* value from 2.69 to 7.22 which means that the greenness effect becomes weaker whilst the redness effect become stronger.

The results also indicate that different range of colors from pinecone colorant could be obtained by using different types of mordants. It is clear that final color, their brilliance, and color fastness properties are not only dependent on the dye itself but also on the used mordants' concentration. From the experiment results, it is obvious that the pre-mordanted with 3 % owf metal salts do not have good dye absorption; also, the shade is similar for various mordants. Hence, the results of this experiment are not shown here.

The L* of dyed wool without using mordants (using 25 % owf dye) is found 68.57 which clearly indicates the best dye absorbency on the surface. The high value of the dye absorption tendency of wool in

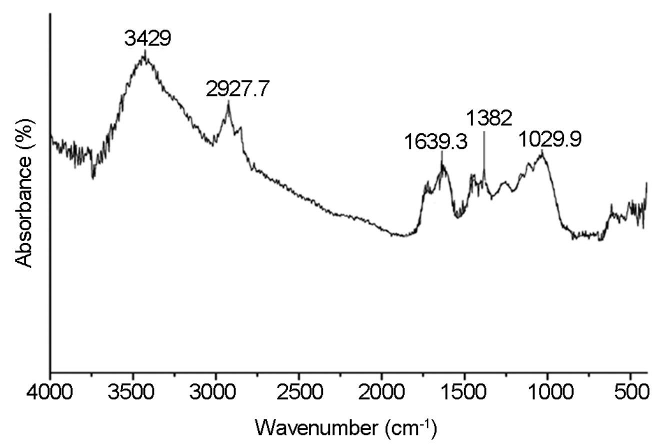

Fig. 2—FTIR of pinecone powder

Table 1—Colour values of wool dyeing using mordants and dye

Dye % owf	Mordants	CIELab					Color
		L	a	b	C	h	
Raw wool		77.27	2.69	18.42	18.62	81.71	Light beige
25	Alum	59.81	6.53	22.17	23.11	73.58	Beige
	$SnCl_2$	59.38	7.96	21.36	22.79	69.56	Reddish beige
	$CuSO_4$	38.43	3.39	15.25	15.63	77.44	Yellowish green
	$FeSO_4$	38.24	7.46	20.23	21.57	69.76	Reddish brown
	$Na_2Cr_2O_7$	55.94	3.13	16.78	17.07	79.43	Dark yellow
50	Alum	59.76	7.73	17.74	19.35	66.47	Light greenish brown
	$SnCl_2$	51.67	10.99	25.65	27.91	66.79	Reddish beige
	$CuSO_4$	31.02	2.24	14.39	14.56	81.14	Dark green
	$FeSO_4$	37.82	4.11	13.79	14.39	73.42	Dark greenish brown
	$Na_2Cr_2O_7$	43.19	6.88	20.34	21.47	71.31	Greenish brown
100	Alum	58.88	-0.03	8.82	8.82	90.20	Light yellow
	$SnCl_2$	57.03	2.06	9.65	9.87	77.97	Light brown
	$CuSO_4$	44.82	1.55	7.56	7.71	78.37	Dark reddish brown
	$FeSO_4$	41.65	0.42	8.43	8.44	87.13	Dark greenish brown
	$Na_2Cr_2O_7$	52.27	1.19	10.76	10.82	83.66	greenish brown

L− lightness (0= black, 100= white), a−red/green; b− yellow/blue, C− chroma; and h− hue angle (0-360°).

the case of using mordant-free color bath contains 50 %owf pinecone colorant, as the L* value of about 65.89 indicates the affinity towards the pinecone dye molecules. The results show that the lightness value is decreased for the entire specimen treated with different mordants. The ferrous and copper sulfate exhibit the lowest L* value of dyed specimen. It is well known that using ferrous sulfate as mordant would result in darkening and browning the color shade, whereas the stannous chloride gives brighter color than any other mordant. The mordants with higher L* values show lighter shades, while a lower L* value of mordants leads to provide darker shades for wool. The results show that wool becomes blackish, when iron is employed as the mordanting agent. The chromaticity (C*) of premordanted sample decreases as dye concentration increases. According to Table 1, it can be seen that the presence of some mordants including ferrous and copper at 50% and 100 % owf dye could decrease the fibre chromaticity.

As it has been mentioned before, the type of used mordant could affect the color shades of the dyed samples. The alum and tin give beige and light brown color; chrome provides dark yellow to light greenish brown; iron presents reddish brown to greenish brown, and copper yields yellowish green to reddish brown.

Pinecone gives a brown and reddish yellow on wool. As shown in Fig. 3, all mordanted specimens dyed with pinecone are found in red–yellow range of CIELab color space. It has been seen that the dyed wool without mordant and the dyed wool with tin have the higher redness and lower hue angle. It is obvious from Fig. 3 that the brown shade of pinecone is relatively shifted towards a more reddish brown color by increasing the percentage of pinecone from 25 % to 100 %owf. Figure 3 (a) clearly shows that the raw wool, the dyed un-mordanted wool and the dyed Cr-wool have nearly the same color coordinates (a* and b*). It can be observed from Fig. 3 (b) that the differences between the colors coordinates of dyed wool with different mordants are meaningful. It can be clearly seen in Fig. 3 (c) that the dissimilarity of color coordinates between raw and dyed samples are high, whereas a* and b* of the dyed mordanted sample are approximately in the same range.

Figure 4 shows the absorption spectra of a residual dye in the dye-bath (50 %owf). It is observed that the absorbance tendency of residual dye in dyebath containing copper and ferrous is noticeably less than that of the other mordants. Considering the Lambert-Beer's Law, since the solution absorbency is directly related to the color bath concentration, the dye uptake of pre-mordanted wool with iron and copper is higher than that of other mordanted fibres. Also, the decrement of residual dye absorbency in dyebath results in increasing the dyebath exhaustion. So, the low absorbance values of residual dye in the dyebath

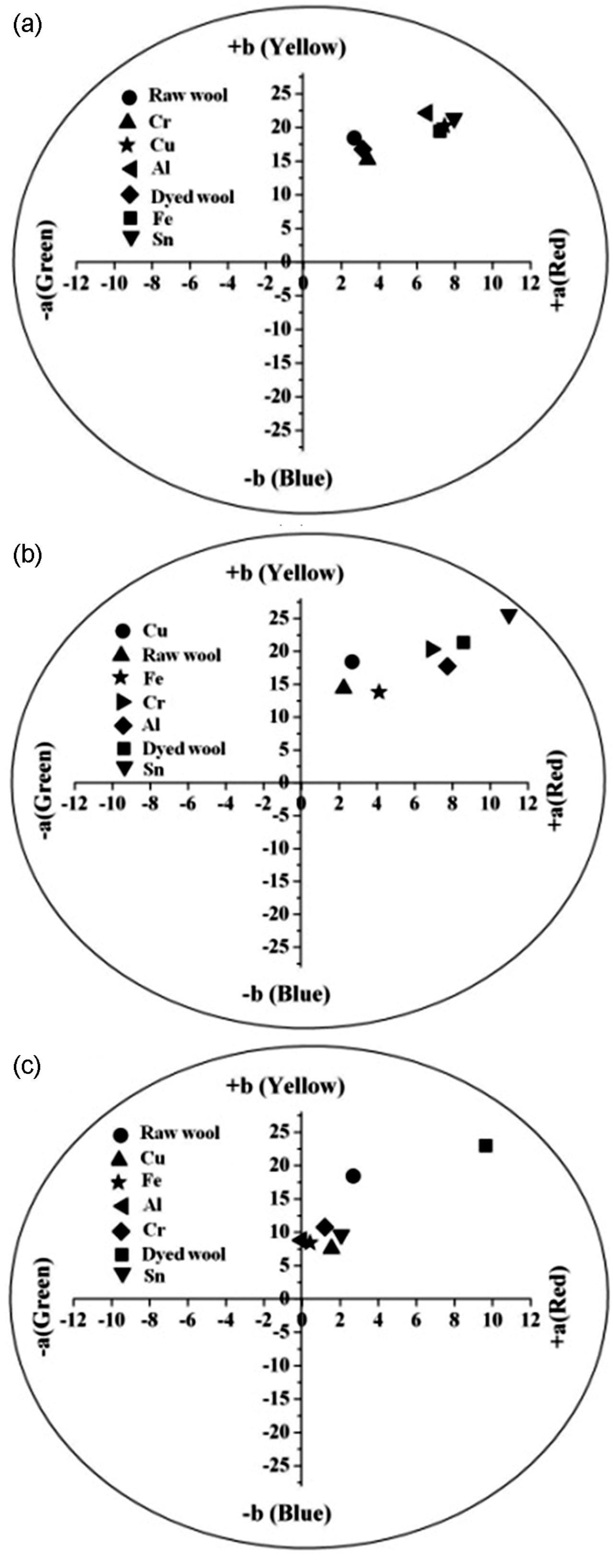

Fig. 3—Effect of mordant on a*-b* of dyed fibre with (a) 25, (b) 50 and (c) 100% owf dye

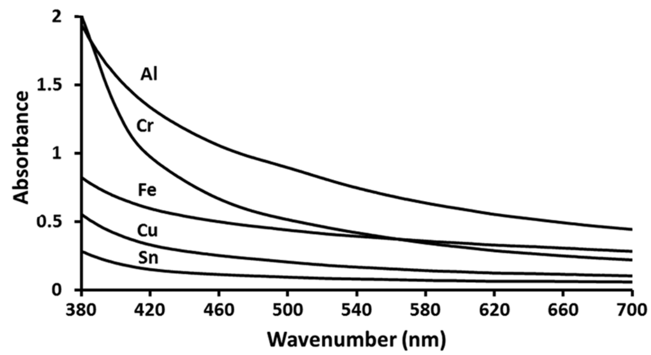

Fig. 4—Absorbance spectra of pinecone dye solution (50% owf) after dyeing

of pre-mordanted wool with ferrous and copper are indicating high percentage dyebath exhaustion of these mordants.

3.2.2 Color Differences (ΔE)

Delta E (ΔE) is defined as the difference between two colors in a L*a*b* color space. The ΔE value rating 3.5-5 means a good and clear color difference between the samples, and the values more than 6 refer to the samples with a brilliant color difference. The color differences of dyed un-mordanted wool are shown in Table 2. According to ΔE values, the difference between raw wool and dyed un-mordanted wool is higher than eight values. The results show that the increasing dye concentration directly affects delta E values. In addition to this, the color differences between dyed samples having 25, 50 and 100 %owf dye are significant. So, the pinecone concentration is very effective on enhancing the shade depth of color.

3.2.3 Color Strength (K/S)

It is well known that different mordants not only cause differences in hue color and L*, but also could significantly change *K/S* values. As can be seen from Fig. 5, the color absorption is improved by increasing dye concentration. Color absorption of wool is extremely affected by the used mordants; this may be because of the maximum absorption and easy formation of metal- complexes with the fibres. In the mordanting process, the deep shades are obtained with copper (*K/S*= 19.6 at 100 % owf dye) and ferrous sulfate (*K/S*= 11.4 at 100 % owf dye) respectively. The lowest *K/S*value is obtained using stannous (*K/S*= 7.87 at 100 % owf dye). According to Saravanan[5] and Johti[15], it has been reported that iron and stannous show the highest and lowest *K/S* values in dyeing wool with barks of *Ficus religiosa* respectively.

Table 2—Color differences of dyed wool

Parameter	Equation	ΔE
ΔE_{25}	$\sqrt{(L_{25}-L_{Raw})^2+(a_{25}-a_{Raw})^2+(b_{25}-b_{Raw})^2}$	9.86
ΔE_{50}	$\sqrt{(L_{50}-L_{Raw})^2+(a_{50}-a_{Raw})^2+(b_{50}-b_{Raw})^2}$	13.14
ΔE_{100}	$\sqrt{(L_{100}-L_{Raw})^2+(a_{100}-a_{Raw})^2+(b_{100}-b_{Raw})^2}$	17.10
ΔE_{100-25}	$\sqrt{(L_{100}-L_{25})^2+(a_{100}-a_{25})^2+(b_{100}-b_{25})^2}$	7.56
ΔE_{100-50}	$\sqrt{(L_{100}-L_{50})^2+(a_{100}-a_{50})^2+(b_{100}-b_{50})^2}$	4.06
ΔE_{50-25}	$\sqrt{(L_{50}-L_{25})^2+(a_{50}-a_{25})^2+(b_{50}-b_{25})^2}$	3.58

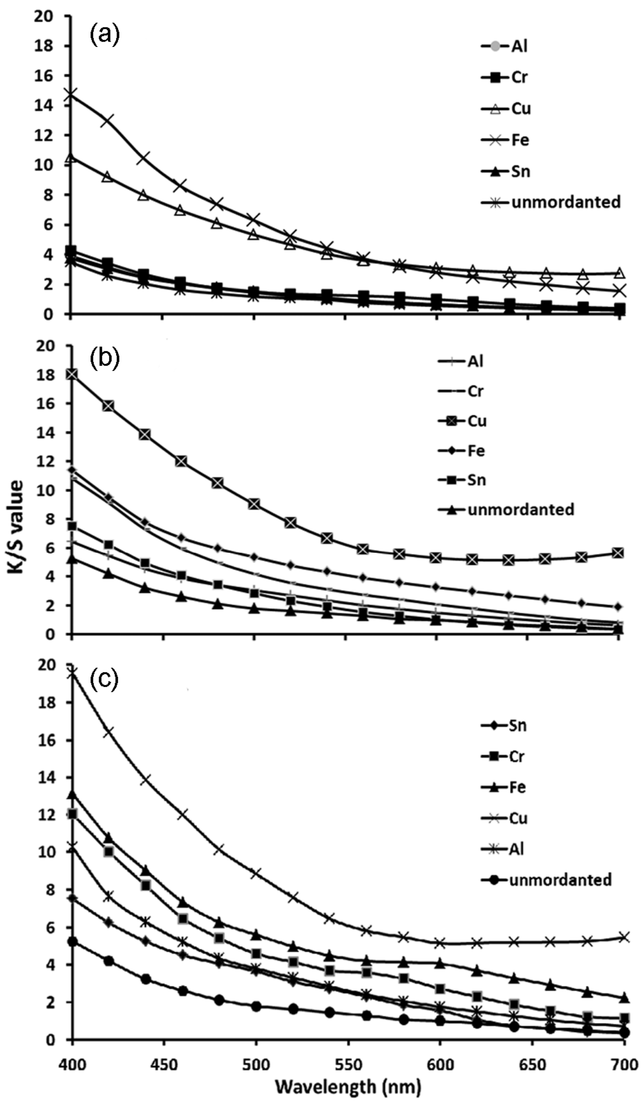

Fig. 5—*K/S* values of wool dyed fibre using (a) 25, (b) 50 and (c) 100% owf dye

3.2.4 Color Fastness Properties

The wash and light fastness results of mordanted and un-mordanted wool dyed with pinecone are presented in Table 3. The color fastness results for the latter type of dyed wool reveal that the wash fastness is well rated from 4 to 5 (the 5 is the highest rating). The affinity of wool can attribute this result to a pinecone. The light fastness of un-mordanted wool is to be medium (3-4 on the standard blue scale, whereas 8 is the highest rating). The samples dyed with pre-mordanting method show a good light fastness rating of 5- 7 (8 is the highest rating). As the dye concentration is increased, there is an improvement in the light fastness by ½ to 1 grade. The use of copper or ferrous sulfate gives high resistance to fading, whereas stannous chloride or alum does not. The high fastness of this dyed sample may be due to ligands of pinecone such as OH and COOH, making a complex with a metal ion from the mordant.

Table 3—Fastness properties of dyed wool fibres

Dye % (owf)	Mordants	Fastness		Staining	
		Light	Wash	Wool	Cotton
25	Nil	3	3	4	4
	Alum	4	3-4	4-5	4-5
	$SnCl_2$	3-4	3	4	4
	$CuSO_4$	4-5	4	4-5	5
	$FeSO_4$	4-5	3-4	4-5	5
	$Na_2Cr_2O_7$	4	3-4	4-5	5
50	Nil	3-4	4	4	4
	Alum	4	4	4-5	4
	$SnCl_2$	3-4	3-4	4	4
	$CuSO_4$	5-6	4-5	4-5	4-5
	$FeSO_4$	5	4	4-5	4-5
	$Na_2Cr_2O_7$	4-5	3-4	4	4
100	Nil	3-4	3-4	4	4
	Alum	4	4	4	4-5
	$SnCl_2$	4	3-4	4	4
	$CuSO_4$	6	4-5	4-5	4-5
	$FeSO_4$	5-6	4	4-5	4
	$Na_2Cr_2O_7$	5	3-4	4	4

4 Conclusion

This study shows that the pinecone, an agricultural by-product, can be used for dyeing wool. Application of pinecone on wool obtains a wide range of colors including beige, pale to dark green and brown shades with adequate fastness. A study on the effect of mordant concentration reveals that 5% owf of mordant gives good shade for wool. An increment of dye concentration from 25% to 100 % owf results in an increase in dye uptake. The results show that the premordanted wool with different mordants enhances the color and fastness properties. The best dye uptake and fastness properties are obtained with ferrous and copper sulfate. It can be found that the development of dyeing wool by pinecone colorant is very interesting due to renewable and abundant properties of this natural colorant source.

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