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Investigation of the dyeing properties of the colorant extracted from *Juglans regia* L. leaves on cellulosic and protein fabrics

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Abstract: Dyeing properties of different fabric species were investigated using leaf extract of *Juglans regia* L. For this purpose, wool and cotton fabrics were dyed using brown napthaquinone colorant extracted from walnut leaves by pre-mordanting, meta-mordanting and post-mordanting methods in the presence of ferrous sulfate ($FeSO_4.7H_2O$), copper(II) sulfate ($CuSO_4.5H_2O$) and alum sulfate ($AlK(SO_4)_2.12H_2O$) at medium pH. Color codes were determined with Pantone Color Guide, and K/S and *L* a* b** values were determined using color measurement spectrophotometer, and also washing-, crocking-fastness levels were evaluated using gray scale. High fastness colors were obtained in general in the present study.

Keywords: *Juglans regia* L., mordant, wool, cotton, fastness.

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INTRODUCTION

The use of natural dyes generally obtained from different parts of plants such as flowers, leaves, bark, roots, and stems has began in China and Central Asia, and these dyes were used to dye various materials such as clothes, rugs, and carpets (1). Synthesis, processing, and use of synthetic dyes are considered highly harmful to the environment and human health. They may cause carcinogenic, toxic, and allergic effects, especially on humans. Therefore, natural dyes and pigments can be considered as very important alternatives to synthetic dyes (2–4). In addition, there is a growing interest in recent years for the use of natural dyes by researchers due to their biodegradable, non-allergenic, non-toxic, and environmentally friendly properties (5, 6). Natural dyes, as reported by multiple studies, have several biological properties such as antibacterial and insecticidal functions, possibly due to their natural origin (7). Due to their low cost, wastes obtained from plants can be considered as important raw materials for the textile industry (8). Considering all these advantages, different national and international institutes conduct researches to improve the extraction of colors from natural resources (9). There are many studies in the literature on natural dyeing for different fiber types (10–12).

Natural products are used in many areas of the industry due to their biological activities and versatile applications (13–15). *Juglans regia* L. is commonly known as walnut tree and belongs to *Juglandaceae* family. *Juglans regia* L. is mostly grown in uncultivated, temperate regions and poor soil and, is cultivated commercially in geographical regions including Western South America, United States, Asia and Southern Europe (16). In addition, Turkey, in terms of manufacture and import of walnut, has a very important place in the world.

Chemical interactions that occur between plant species are called allelopathy, and organic compounds that play a role in allelopathy are called allelochemicals. One of these allelochemicals is Juglone (Figure 1), which is responsible for walnut allelopathy (17). It was reported that juglone is the main coloring component which is found in walnut husks, root, leaves, and stem bark (18, 19). Apart from natural dyeing, walnuts have been found to be beneficial in alternative medicine and are used to treat various ailments such as infectious diseases, diuretic, asthma, skin diseases, stomach-ache and eczema, traditionally (20).

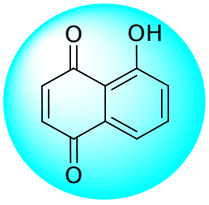

Figure 1: Chemical structure of Juglone (5-Hydroxy-1,4-naphthoquinone)

In the present study, the dyeing properties of different fabric species were investigated using leaves extract of *Juglans regia* L. For this purpose, pre-mordanting, meta-mordanting and post-mordanting methods were performed using ferrous sulfate ($FeSO_4.7H_2O$), copper sulfate ($CuSO_4.5H_2O$), and alum ($AlK(SO_4)_2.12H_2O$) at a medium pH. Color codes and K/S values were determined and high fastness of dyed samples were obtained in general.

EXPERIMENTAL SECTION

Reagents and Equipments

All chemicals and mordants ($CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $AlK(SO_4)_2.12H_2O$) were obtained from Sigma Aldrich. Distilled water was used in all steps of the study. Extraction was performed using soxhlet apparatus. The color properties of the dyed samples were evaluated by Premier Colorscan SS 6200A Spectrophotometer in terms of CIELab values (*L**, *a**, *b**, *C**) and color strength (*K/S*) values. While washing fastness values were determined according to ISO 105-C06 standards, dry and wet crock fastness of dyed fabrics were determined according to ISO 105-X12 method (21).

Methods

Natural Dye Extraction and Mordanting

In the present study, fresh (green) *Juglans regia* L. leaves used as a natural dye source was collected from Tokat (Turkey). 50 g of green walnut leaves was refluxed on soxhlet apparatus in distilled water until it becomes colorless. This procedure was repeated until 5 liters of color extract is obtained, and finally all extracts were combined (22). Ferrous sulfate, copper sulfate, and alum sulfate were used as mordants, and the dyeing procedures were performed as pre-mordanting, meta-mordanting, and post-mordanting. Pre-mordanting, meta-mordanting, and post-mordanting methods were applied as performed in our previous studies (23, 24).

RESULTS AND DISCUSSION

Determination of color performance

After dyeing, the samples were exposed to sunlight for 200 h and, light fastness of dyed samples were rated on 1–8 grey scale. After dyeing, the dyed fabric samples were taken out and soaping was done (30 min at 45 °C). The dyed samples were washed several times to remove unfixed surface dye. The pre-, meta- and post- mordanting dyed samples were investigated for different properties such as color strength, washing fastness, and light fastness. The wash fastness was determined by keeping the liquor to material ratio at 50:1. Color strength was expressed as K/S values of the dyed samples using the Kubelka-Munk equation (25):

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

where K is the absorption coefficient, R is the reflectance of the dyed sample and S is the scattering coefficient.

K/S and *L*, a*, b** values of wool and cotton fabrics are given in Table 1. *L** is the lightness or luminance value, which ranges from 0 to 100, and the higher lightness value represent lower color yield. The lower *L** values indicate that the sample become darker than that of the control sample. *a** values run from negative (green) to positive (red) and *b** values run from negative (blue) to positive (yellow) (26).

Table 1: K/S and *L*a*b** values of cotton and woolen fabrics.

Fabric	Mordant	*L**	*a**	*b**	K/S
Cotton	$FeSO_4$	50.09220	3.2035	11.6849	8.84863
Cotton	$FeSO_4$	38.2095	-0.6540	5.8743	13.6510
Cotton	$FeSO_4$	57.8050	5.4138	22.5157	8.16812
Cotton	$CuSO_4$	61.0601	1.8038	10.6227	3.37569
Cotton	$CuSO_4$	50.4130	4.3318	11.3770	6.78419
Cotton	$CuSO_4$	67.9525	0.3574	9.5092	2.17486
Cotton	$AlK(SO_4)_2$	63.2240	1.9043	12.8670	4.61283
Cotton	$AlK(SO_4)_2$	70.2700	2.5259	10.1383	3.08468
Cotton	$AlK(SO_4)_2$	70.2642	0.8801	7.5420	1.79238
Wool	$FeSO_4$	62.2755	-0.0560	5.2680	2.52778
Wool	$FeSO_4$	65.9266	0.1176	5.3012	2.12176
Wool	$FeSO_4$	57.9216	0.2145	11.7485	5.41675
Wool	$CuSO_4$	65.6697	1.4781	10.1613	2.16557
Wool	$CuSO_4$	53.0520	4.0574	12.9911	5.9045
Wool	$CuSO_4$	68.3023	-0.0140	9.1994	1.76316
Wool	$AlK(SO_4)_2$	70.7843	1.1885	10.0900	2.12717
Wool	$AlK(SO_4)_2$	69.6861	0.5437	11.1085	3.62508
Wool	$AlK(SO_4)_2$	70.8454	0.7576	7.9840	1.56455
Unmordant cotton	-	69.7925	1.3569	9.0152	2.15633
Unmordant wool	-	1.6091	0.9240	6.0562	2.18797

As seen in Table 1, different intensity and brightness or color tones were obtained in the dyed cotton fabrics. Predominantly greenish yellow and brown tones were obtained. The value of *a** is negative and the color has shifted to brown with ferrous sulfate. The highest K/S (13.65) value is obtained for ferrous sulfate using meta mordanting method.

For dyeing of woolen fabrics, yellow, khaki and brown color tones are obtained and the highest K/S (5.90) value is obtained for copper sulfate using meta mordanting method.

Fastness values and color codes of dyed cotton samples are given in Table 2.

Table 2: Fastness values and color codes of dyed cotton samples.

Method	Mordant	pH	Light fastness	Washing fastness	Rubbing (wet/dry)	Color code (Pantone)
T1	$FeSO_4$	4.50	5/6	4	4 – 5	1265CS C:0 M:7 Y:100 K:55
T2	$FeSO_4$	4.50	6	5	4 – 4/5	112CS C:0 M:14 Y:100 K:53
T3	$FeSO_4$	4.50	5/6	4	4 – 4/5	105CS C:65 M:55 Y:98 K:0
T1	$CuSO_4$	3.55	5/6	5	4 – 5	103CS C:0 M:7 Y:100 K:30
T2	$CuSO_4$	3.55	5	3	4 – 4/5	117CS C:0 M:25 Y:100 K:23
T3	$CuSO_4$	3.55	6	3/4	4 – 4	104CS C:0 M:6 Y:100 K:42
T1	$AlK(SO_4)_2$	5.20	5	3/4	4/5 – 5	110CS C:0 M:19 Y:100 K:15
T2	$AlK(SO_4)_2$	5.20	5	4	4 – 5	109CS C:0 M:8 Y:100 K:3
T3	$AlK(SO_4)_2$	5.20	5	4	4 – 5	4535CS C:0 M:4 Y:25 K:22
	Unmordant	7.25	5/6	4	4 – 4/5	605CS C:0 M:0 Y:90 K:18

T1: Pre- mord., T2: Meta- mord., T3: Post- mord., Wash and rubbing 5 (maximum) to 1 (very poor) and Light 8 (maximum) to 1 (very poor)

For dyeing experiments, using $FeSO_4$ wet, dry rubbing and washing fastness values are 4.5, approximately. Light fastness values are between 5–7. These results are generally considered acceptable. For $CuSO_4$, all fastness values are found to be very good except washing and light fastness.

When the dyeing was made with $AlK(SO_4)_2$, all results are 4.0 and over. Fastness values are 4.0 and higher for unmordanting dyeings.

Fastness values and color codes for dyed woolen fabrics are given in Table 3.

Table 3: Fastness values and color codes of dyed woolen fabrics.

Method	Mordant	pH	Light	Wash	Rubbing (wet/dry)	Color code
T1	$FeSO_4$	4.50	6	3/4	4/5	111CS C:0 M:16 Y:100 K:45
T2	$FeSO_4$	4.50	6/7	4	5/5	365CS C:13 M:0 Y:94 K:74
T3	$FeSO_4$	4.50	6	3/4	4/5	382CS C:23 M:0 Y:95 K:0
T1	$CuSO_4$	3.55	5/6	3	4/5	4515CS C:0 M:8 Y:46 K:40
T2	$CuSO_4$	3.55	4/5	4	4/5	451CS C:2 M:0 Y:38 K:45
T3	$CuSO_4$	3.55	4	2/3	4/5	103CS C:0 M:7 Y:100 K:30
T1	$AlK(SO_4)_2$	5.20	4/5	3	5/5	105CS C:65 M:55 Y:98 K:45
T2	$AlK(SO_4)_2$	5.20	4/5	3	4/5	1265CS C:0 M:31 Y:98 K:64
T3	$AlK(SO_4)_2$	5.20	4/5	2/3	4/5	398CS C:4 M:0 Y:100 K:40
	Unmordant	7.25	5/6	4/5	5-4/5	618CS C:0 M:3 Y:77 K:44

T1:Pre- mord., T2: Meta mord., T3: Post mord., Wash and rubbing 5 (maximum) to 1 (very poor) and Light 8 (maximum) to 1 (very poor)

In Table 3, it can be seen that the wash fastness values of ferrous sulfate is higher than those of copper sulfate and alum. However, the wash fastnesses are low and other fastnessess are high for last mordanting for copper sulfate. In addition, the wash fastnesses are low and other fastnesses are at a good level for alum. Fastness values for unmordanted dyes are 4.0 and above.

Predicted dyeing mechanism

Treatment with mordant salts of the natural fabrics, facilitates the bonding of dye, changes the color tone and increases the fastness. As a result permanent colors are obtained. If we discuss the dyeing mechanism, Al^{3+} and Fe^{2+} ions have six coordination numbers, and they are able to make complexes in the octahedral configuration. The proposed mechanism for dyeing of wool and juglone are given in Figure 2 (27). The unoccupied regions of the metal ions can be filled with H_2O molecules, oxochrome groups of the dyestuff or free amino and carboxyl groups of wool fabric.

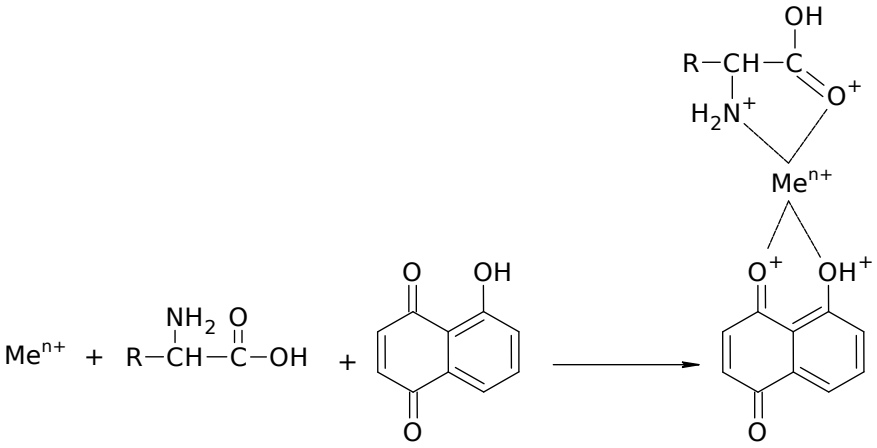

Figure 2: Proposed mechanism of dyeing of wool fabric with 5-hydroxy-1,4-naphthalene dione.

Cotton has a cellulosic structure, here, coordinated covalent bonding occurs between $-CH_2O-$ groups of cellulose and metal cation (Me^{n+}: Fe^{2+}, Cu^{2+}, Al^{3+}). The suggested mechanism for dyeing of cotton is given in Figure 3.

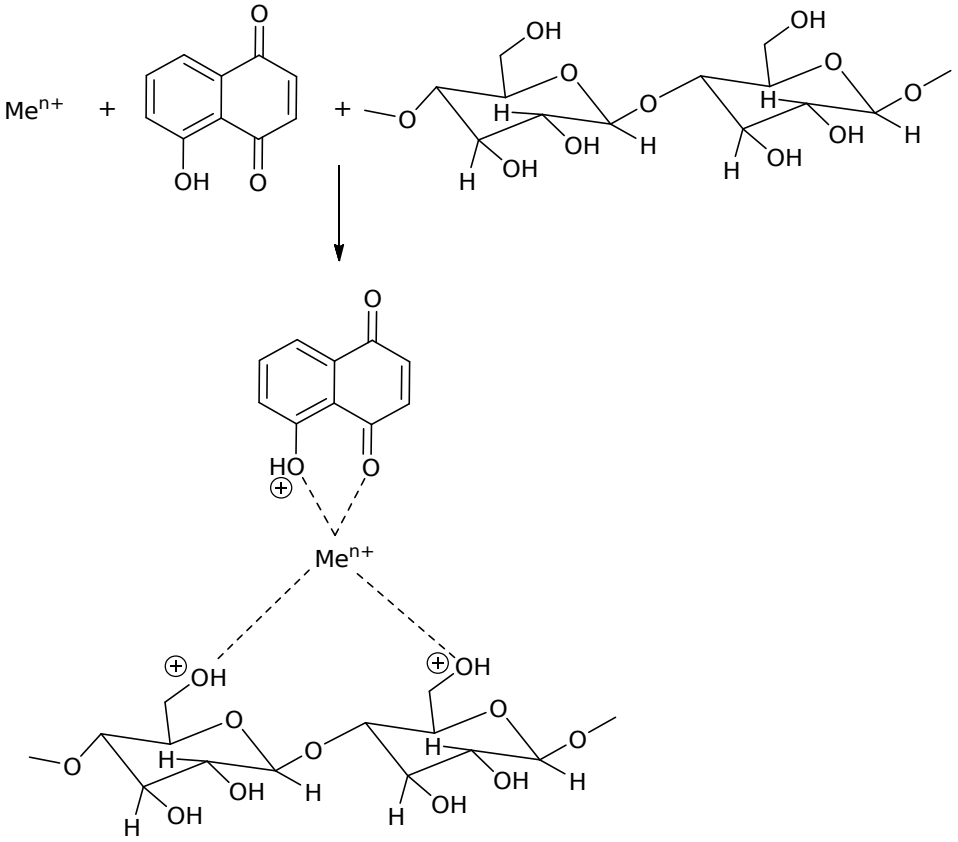

Figure 3: Proposed mechanism of dyeing of cotton fabric with 5-hydroxy-1,4-naphthalene dione.

CONCLUSIONS

In this study, the *Juglans regia* L. leaves were used for dyeing of cotton and wool fabrics. Natural dye solution was extracted and applied to the selected fabrics by pre- mordanting, meta-mordanting, and post- mordanting techniques using the following metal salts, copper sulfate, ferrous sulfate, and alum. We obtained brown, yellow, green, khaki color tones, and they have high fastness colors.

The color tones were observed to change when the dyeing techniques and mordant were changed. Darker colors were obtained for all three mordants in the meta-mordanting method. However, lighter color tones were obtained for all three mordants in the post- mordanting. Yellow and khaki tones were obtained in the dyeing of cotton fabric; while green and brown tones were obtained in dyeing of woolen fabric. The dyeing efficiency in terms of mordant can be ordered as Ferrous sulfate > Copper sulfate > Alum > unmordant.

Consequently, data obtained in the present study showed that *Juglans regia* L. leaves can be used as a natural dyestuff source in dyeing of cotton and woolen fabrics with suitable mordants.

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