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Improvement of Dye Extraction from Common Walnut Stain and Optimization of Wool Dyeing Conditions

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Abstract

Different conditions for extracting juglone from the pigment of common walnut have been investigated. Means of improving dye exhaustion and fixation rates on wool yarn and fabric have also been studied. The different extraction procedures investigated were decoction, short-term and long-term aqueous maceration, and aqueous maceration at 40°C in neutral and alkaline media. Optimal dye extraction was achieved in alkaline solution at pH 10 at 40°C for 2 h. Dyeing was investigated in solutions of various pH. The dye exhaustion rate was considerably increased when an acidic dye bath was used. Post- oxidation has been tested as a means of improving the juglone fixation rate and it's washing fastness on wool yarn and fabric.

Keywords: Common Walnut*; *Exhaustion*; *Fixation*; *Dyeing*; *Juglone*; *Maceration*; *Oxidation*; *Wool

Introduction

Walnuts contain a principal colorant called juglone, an isomer of lawsone, which occurs in the leaves, root, and bark of *Juglans regia L.* (common walnut). Juglone, with a dark reddish-brown color, is mostly used to dye fabrics and hair, and is known as C.I. Natural Brown 7 (FIG.1.) [1]. It belongs to the naphthoquinone family of chromophores. It is a direct dye, which means that no mordant is necessary when it is used with protein fibers. Cellulose may also be dyed, but a mordant is required in this case.

Juglone can produce a brown-to-black, colorfast stain that is resistant to ultraviolet fading, making it an ideal outdoor wood stain. Although any walnut variety will produce a stain, the best choice is hulls from the black walnut tree (Juglansnigra), which is characterized by long, compound leaves.

The best time to gather the nuts is when they are still green: newly fallen or ready to fall off the tree. If the nuts rot and turn black on the ground, the dye will be partly decomposed. The dried nuts contain far less dye than fresh/frozen walnuts [2].

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Ali et al. found that dye produced by the alkaline extraction of henna leaves (laws one as the principal colorant) had better color strength than that extracted with distilled water. The dye fastness of the alkaline extract was good, and was not significantly improved by the use of a mordant. It was also inferred that the natural dye has good potential to act as co-partner with synthetic dye [3,4].

Benli et al. investigated the dyeing with nutshell-derived and other natural dyes of cotton fabrics that had been bioprepared using different enzymes under ultrasonic cavitation. It was observed that ultrasound- assisted biopreparation of cotton fabric provided favorable pretreatment results. Coloration of these fabrics could be achieved by deploying the natural dyes in the same bath as used for the biopreparation [5]. Fabrics dyed with the assistance of ultrasound showed significantly higher color efficiencies than those subjected to enzymatic pretreatment and dyed without the use of ultrasound. With dyes derived from nutshell and pomegranate peel, the use of ultrasound during the finishing process resulted in better light fastness values [6-9].

Natural juglone has been identified as a hydrojugloneglucoside ($C_{16}H_{18}O_8$), hydrolysis of which yields glucose and a hydrojuglone (1,4,5-trihydroxynaphthalene). Oxidation of the latter yields juglone (5- hydroxy-1,4-naphthoquinone, $C_{10}H_6O_3$) (FIG. 2 and 3). Juglone is only slightly soluble in hot water, but freely soluble in chloroform, benzene, ethanol, and diethyl ether [10].

The aim of this study was to identify a means of extracting more of the coloring component with less expenditure in terms of environmentally unfriendly organic solvents. Several extraction procedures were investigated: decoction, short-term and long-term aqueous maceration, and aqueous maceration at 40°C in neutral and alkaline media (FIG. 2). The alkaline medium was chosen in view of the acidic chemical nature of juglone.

The dyeing conditions were also investigated, varying the pH of the medium. Furthermore, in order to improve the fixation of the dye and its washing fastness on wool yarn and fabric, post-oxidation was tested.

Materials and Methods

Wool fiber features

Wool fiber was obtained from Timahdit, Morocco. Brown fleece was compacted and homogenized to give a medium-weight fleece of 1.9 kg. The fiber fineness was 44–50 on the Bradford scale, and the average fiber length was 9.6 cm.

Natural dye

Juglone dye was extracted from the pigment of the common walnut tree, which grows in the north of Morocco. The extraction method was based on water-solubilizing at high temperature of the dried and powdered walnut stain [1,11-13]. The dye was extracted by maceration in water at low temperature, as described below.

Chemicals

The alkaline reagent sodium carbonate (Na_2CO_3) and the acidic reagent acetic acid (CH_3COOH) were of analytical grade and were obtained from Sigma Aldrich GmbH & Co. (Germany). Hydrogen peroxide (H_2O_2) was purchased from Solvapur Co. (Casablanca, Morocco). A Marseille-type soap was prepared from vegetable oil obtained from a supermarket.

Spectrophotometry

An ultraviolet/visible spectrophotometer (Thermo, Helios Epsilon) was used to scan the range 325– 1100 nm with a spectral bandwidth of 1nm.

pH meter

A Henne AD1000 pH meter was used. This multimeter can measure pH, oxidation–reduction potential, and temperature.

Bath

A 250-mL flask was used. Heating was by a thermostated hotplate (Scilogex MS-H280-Pro).

Filter

Sample solutions in this study were filtered through paper.

Dye extraction methods

Extraction by decoction: Common walnut stain (3 g) was decocted in distilled water (50 mL) at 75°C for 1 h. The blend was then filtered through paper.

Extraction by long-termmaceration: Common walnut stain (3 g) was placed in a covered bath containing distilled water (50 mL) and macerated for 24 h at room temperature. The blend was then filtered through paper.

Extraction by short-termmacerating: Common walnut stain (3 g) was placed in a bath containing distilled water (50 mL) at 40°C for 2 h. The blend was then filtered through paper.

Extraction by short-term macerating in alkaline medium: Common walnut stain (3 g) was placed in a bath containing distilled water (50 mL) with 10 g/L sodium carbonate (pH 10) at 40°C for 2 h. The blend was then filtered through paper and neutralized with acetic acid.

Different yarn dyeing processes with walnut stain extract

Preparation of dye extract: Common walnut stain (6 g) was stirred in distilled water (100 mL) with 10g/L sodium carbonate (pH 10) at 40°C for 2 h. The blend was then filtered through paper and neutralized with acetic acid. The dye solution well-preserved to the dyeing phase.

Dyeing in solutions of different pH: Four yarn samples of 0.5 g, one of which was considered as a reference sample, were placed in respective baths containing dye extract (25 mL) (prepared as described in Section 2.5.1) and acetic acid at pH 3, 4, or 5 (the reference dye bath was kept at pH 7) at 90°C for 1 h, with a ratio of 1:50. At the end of the dyeing, the dye baths were allowed to cool to 40°C, and the yarns were withdrawn.

Soaping: The dyed yarns were soaped with 0.5 g/L Marseille soap at 60°C for 15 min, with a liquid ratio of 1:50.

Dyeing process and post-oxidation of yarn and fabric with walnut stain extract

Preparation of dye extract: Common walnut stain (9 g) was stirred in distilled water (150 mL) with 10 g/L sodium carbonate (pH 10) at 40°C for 2 h. The blend was then filtered through paper and neutralized with acetic acid. The dye solution well-preserved to the dyeing phase.

Dyeing in a solution at pH 4: Two yarn samples of 0.5 g and two fabric samples of 0.75 g were placed together in baths containing 50 mL of dye for yarns or 75 mL of dye for fabrics (extract prepared as described in Section 2.6.1) in acetic acid at pH 4 at 90°C for 1 h, with a ratio of 1:50. At the end of the dyeing, the dye baths were allowed to cool to 40°C, and the yarns were withdrawn.

Rinsing: One of the dyed yarns and one of the dyed fabrics were placed in respective baths containing 25 mL or 37.5 mL of distilled water at 45°C for 15 min.

Oxidation: The second dyed yarn and the second dyed fabric were placed in respective baths containing 4 mL of hydrogen peroxide in 25 mL or 37.5 mL of distilled water, and acetic acid at pH 4, at 45°C for 15 min.

Soaping: The dyed yarns and the dyed fabrics were soaped as indicated above, with 0.5 g/L Marseille soap at 60°C for 15 min, with a liquid ratio of 1:50

Spectral analysis

Spectrophotometer calibration: The spectrophotometer was calibrated by using distilled water as a background blank.

Measurement of dye exhaustion and fixation rate

Aliquots (1 mL) were removed from each dye bath and diluted to 20 mL with distilled water for measurement. The absorbance intensities, measured at 400 nm, are shown in TABLES 4 and 5.

Colorimetric

The reflectance (R%) values of dyed samples were measured on Thermo scientific SPE instrument (D_{65}/10°), and colour yields (K/S) of dyed samples were calculated by the Kubelka–Munk equation :

$$K/S=(1-R^2)/2R$$

Where R is the reflectance value at the maximum absorption wavelength (nm), K is the absorption coefficient, and S is the scattering coefficient.

Washing fastness

Washing fastness was determined at 40°C over 30 min according to ISO 105-C6:A1S [14].

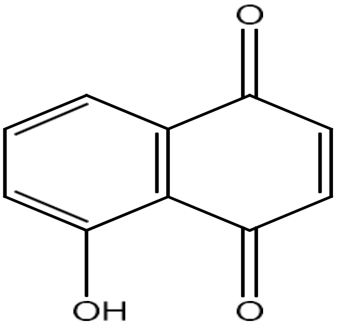
Results and Discussion

Dye extraction methods from walnut stain

TABLE 1 shows the relative absorbances of juglone dye extracted from walnut stain by different methods.

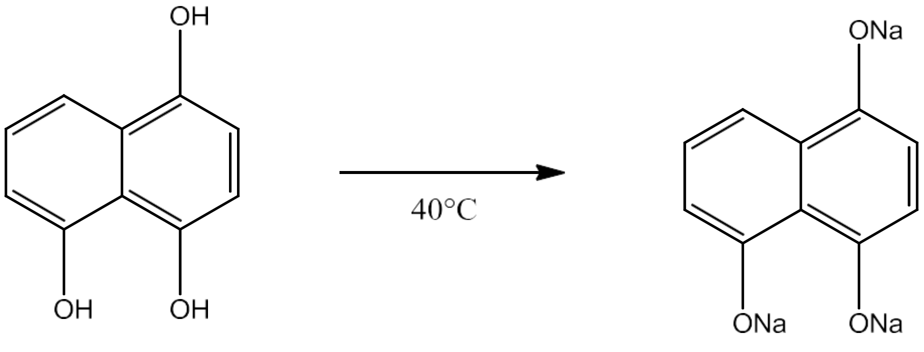
TABLE 1. **Absorbances of juglone extracted by different methods.**

Conditions for the extraction of juglone from walnut stain	**Dye absorbance**
Extraction by decoction	1.248
Extraction by long-term maceration	0.963
Extraction by short-term maceration	1.102
Extraction by short-term maceration in alkaline medium	1.278



C.I. Natural Brown 7

FIG.1. **Chemical structure of juglone (5-Hydroxy-1,4-naphthoquinone).**



Hydrojuglone(1,4,5-trihydroxynaphthalene)

Juglone salt(1,4,5-trisodiumoxynaphthalene)

FIG.2. **Dissolution reaction of hydrojuglone in alkaline medium.**

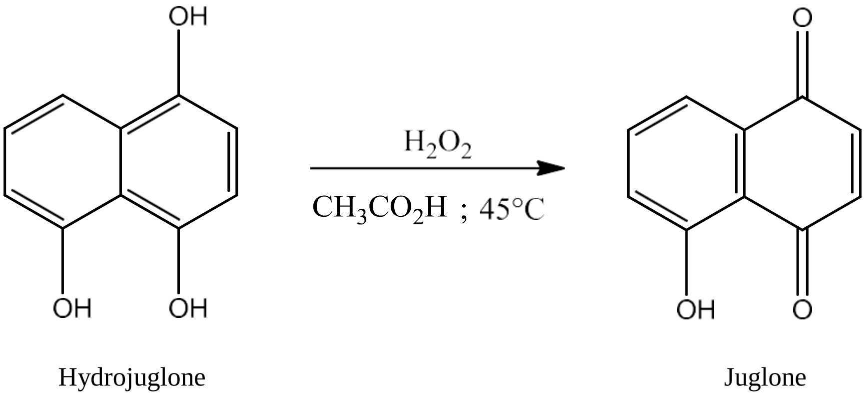


FIG.3. **Oxidation reaction of hydrojuglone in acid medium.**

The results show that higher dye absorbance was attained when using the extraction method of short- term maceration in alkaline medium. This indicated that the solubility of juglone dye was increased in the alkaline medium. Moreover, macerating at 40°C achieved a higher dye solubility than long-term maceration at room temperature. Incubation at 40°C is favorable for enzymatic hydrolysis of the hydrojugloneglucoside, which is converted into the hydrojugloneaglycone [1]. This dye extraction process was identified as optimal because it was more profitable within shorter treatment times.

Different yarn dyeing processes with walnut stain extract

Measurement of dye exhaustion rate in different dyeing processes: TABLE 2 shows the relative absorbances of juglone measured before and after its application in solutions of different pH.

TABLE 2. **Measurement of dye exhaustion rates and K/S in different dye baths**

Dye bath pH	**Initial dye bath (Abs_i)**	**Final dyebath (Abs_f)**	**Dye exhaustion rate $\{[(Abs_iAbs_f)/Abs_i]□100\}$**	**K/S**
7	1.004	0.393	60.8%	0.78
3	1.004	0.196	80.4%	2.05
4	1.004	0.312	68.9%	1.11
5	1.004	0.383	61.8%	0.81

Measurement of dye fixation rates in different dyeing processes: Table 3 shows the results of fixation measurements of juglone applied in different dyeing processes.

TABLE 3. **Measurement of dye fixation rates in different dye baths.**

Dye bath pH	**Residual soaping bath (Abs_s)**	**Dye fixationrate{[(Abs_i– Abs_f– Abs_s)/Abs_i]□100}**	**K/S**
7	0.038	57.0%	0.66
3	0.035	76.9%	1.66
4	0.053	63.6%	0.87
5	0.079	53.9%	0.58

The dyeing processes in the acidic media, particularly that at pH 3, led to higher dye exhaustion (E= 80.4% , K/S= 2.05) and fixation rates (F=76.9%, K/S=1.66) . This can be explained in terms of increased affinity of juglone for wool fiber when the active sites on the wool bear more positive electrical charge. Besides, the dye fixation rate was also increased because of extensive hydrogen- bonding between the hydroxyl group of juglone and quaternized amino groups on the wool fiber.

ElcinGûnesa and RizaAtav were obtained less dyeing uptake with nutshell extract on wool expressed by K/S value of 0.6 [11]. This due to the different conditions used in extraction and dyeing process.

The extraction conditions were achieved in boiling temperature for 30 min, and the dyeing conditions were carried out at the pH 5.7. However, their dyeing uptake was increased using mordant such as alum ($KAl(SO_4)$), especially in the presence of ferrous sulfate ($FeSO_4$) whose the color turns from reddish to greenish.

Dyeing process and post-oxidation of yarn and fabric with walnut stain extract

Measurement of dye exhaustion rate: TABLE 4 shows the relative absorbances of juglone measured before and after its application in dyeing processes at pH 4.

TABLE 4. **Measurement of dye exhaustion rate.**

	Initial dye bath (Abs_i)	**Final dye bath (Abs_f)**	**Dye exhaustion rate {[(Abs_i– Abs_f)/Abs_i]□100}**
Yarn dye bath at pH 4	0.824	0.475	42.3%
Fabric dye bath at pH 4	0.824	0.564	31.5%

Measurement of dye fixation rates with post-oxidation: TABLE 5 shows the results of fixation measurements of juglone in dyeing processes at pH 4 after post- oxidation.

TABLE 5. **Measurement of dye fixation rates in different dye baths.**

	Residual oxidation bath/residual rinsing bath (Abs_o/Abs_r)	**Residual soaping bath with post-oxidation (Abs_s)**	**Dye fixation rate $\{[(Abs_i – Abs_f – Abs_o – Abs_s)/Abs_i]□100\}$**
Yarn dyed with post-oxidation	0.027	0.019	36.7%
Yarn dyed without post-oxidation	0.046	0.019	34.4%
Fabric dyed with post-oxidation	0.024	0.016	26.6%
Fabric dyed without post-oxidation	0.040	0.020	24.2%

The results clearly show that post-oxidation increased the dye fixation rate on the yarn and fabric. This can be attributed to improved fastness of the dye after oxidation, whereby it is converted into a water-insoluble form inside the fibers.

Washing fastness

The results of measurements on the dyed yarn and fabric are presented in TABLE 6.

TABLE 6. **Washing fastness of dyed yarn and fabric with and without post-oxidation.**

Samples	**Washing fastness (assessing staining)**						**Washing fastness (assessing change in color)**
	WO	**PAC**	**PES**	**PA**	**CO**	**CA**	
Dyed yarn With post-oxidation	4	4-5	4-5	4	4	4	4–5
Dyed yan	4	4-5	4-5	4	4	4	4–5

without post-oxidation							
Dyed fabric With post-oxidation	3-4	3-4	4	4-5	4-5	4	4-5
Dyedfabricwithoutpost-oxidation	3-4	3	3-4	4-5	4-5	3-4	4-5

The values from these experiments confirm solid fixation of the dye following post-oxidation. The washing fastness was improved on the dyed fabric, although it remained constant on the dyed yarn. As described previously, the juglone dye is converted into an insoluble form inside the fibers after post- oxidation. The good washing fastness on the dyed yarn can be mainly attributed to a high degree of hydrogen-bonding and van der Waals bonds established within the fibers. Consequently, post-oxidation of the dyed yarn had no further influence on its washing fastness.

Conclusion

This study has indicated that optimal extraction of juglone is achieved in alkaline solution at pH 10 at 40°C for 2 h. The optimal dyeing conditions have been identified as a solution at pH 3. Increasing the acidity to pH<3 is not recommended in order to avoid damage to wool fibers at high temperature. Post- oxidation has been confirmed to improve the dye fixation rate on wool yarn and fabric as well as its washing fastness. Juglone dye is converted into an insoluble form inside the fibers of a fabric after post- oxidation. However, the good washing fastness on the dyed yarn can mainly be attributed to a high degree of hydrogen-bonding and van der Waals bonds established inside the fibers.

REFERENCES

1. HarBhajan S, Kumar Avinash B. Handbook of Natural Dyes and Pigments. 2014.
2. Catharine E. Natural Dye: Experiments and Results. Blog on September 11. 2016.
3. Ali S, Tanveer H, Rakhshanda N. Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. J Clean Prod. 2009;171:61-66
4. Bhuyan R, Saikia CN, Das KK. Extraction and identification of colour components from the bark of Mimusops elengi and Terminalia arjuna and evaluation of their dyeing characteristics on wool. Indian Journal of Fibre & Textile Research. 2004; 29:470–6.
5. Benli H, Bahtiyari, M.İ. Cellulose. 2015;22: 867.
6. Aly AS, Moustafa AB, Hebeish A. Bio-technological treatment of cellulosic textiles. J Clean Prod. 2004;12:697–705.
7. Aniş P, Davulcu A, Eren HA. Enzymatic pre-treatment of cotton. Part 1. Desizing and glucose generation in desizing liquor. Fibres Text East Eur. 2008;4(69):100–103.
8. Karaboğa C, Körlü AE, Duran K, et al. Use of ultrasonic technology in enzymatic pretreatment processes of cotton fabrics. Fibres Text East Eur. 2007;15(4):97–100.
9. Moore SB, Ausley LA. Systems thinking and green chemistry in the textile industry: concepts, technologies and benefits. J Clean Prod. 2004;12:585–601.
10. Alihosseini F, Sun G. Functional Textiles for Improved Performance, Protection and Health. 2011.

11. Gûnesa E, Atav R. The use of nutshell firstly as a natural dye for cotton and wool and then as a natural adsorbent for colour removal of basic dye effluent. Coloration Technology. 2017;3:88-93.
12. Dument E. Teindre avec les plantes (les plantes tinctoriales et leur utilisation)', Ed. Ulmer. 2010.
13. Marquet M. Guide des teintures naturelles. Ed. Belin. 2011.
14. International Standard Organization. Tests for colour fastness. Part C06: Colour fastness to domestic and commercial laundering, Test no.105-C06. 2010.