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Extraction of Total Dyestuff from Walnut Leaves (*Juglans regia* L.) and Its Dyeing Conditions for Natural Fibres

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The dyestuff of total dyestuff in walnut leaves (*Juglans regia* L.) was extracted by the reported method and used in dyeing of woollen strips, feathered-leather and cotton using three types of mordanting methods at various pH values. In order to determine the most proper mordant and pH value from the point of view of the wash, crock and light fastness in dyeing of the above samples by walnut, some selected transition element salts such as $CuSO_4{\cdot}5H_2O$, $FeSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ were used as mordant agent at various pH. The experimental results indicate that dyed samples with the highest fastness were obtained by Cu(II) for the samples except for cotton and by Al(III) for only cotton at pH = 8 in the pre-mordanting method. The results also reveal that the wallnut plant containing juglone dyestuff will probably be an important raw material in the dyeing process of natural textile fibres.

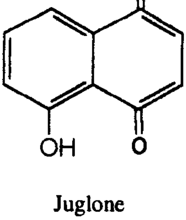
Key Words: Extraction, Dyestuff, Walnut leaves, *Juglans regia* L., Natural fibres.

INTRODUCTION

Natural dyes have high importance in producing hand-made carpets, kilim and similar industrial dyeing applications because of their advantage of high colour-fastness, cheapness, long-term colour stability and authentic properties. Now-a-days, the natural dyes are being produced in Asian countries such as Turkey, Iran, India, Azerbaijani and natural dye products are being used in most countries of the world[1].

There are many industrial plants which contain natural dyes. Walnut leaves (*Juglans regia* L.) are one of them. It is known as a natural dyestuff source. Its leaves contain 1.1–3.3% juglone[2,3]. At the same time, the seeds of walnut are also used as a traditional remedy for treating cough, stomach ache and cancer in Asia and Europe[4].

The dyestuff in the tannin of walnut is juglone (8-hydroxy-1,4-naphthoquinone)[5]. The molecular structure of this compound is given below:



Juglone

It is expected that juglone exhibits dyeing properties for wool, feathered-leather and cotton because of its auxochrome group (—OH) together with chromogen group (C=O and benzene ring).

Wool molecules consist of amino acid units, which contain free amino and carboxylic groups[3]. During the dyeing of wool, hydrogen bonds occur between the auxochrome groups of dyestuff and amino groups.

The literature survey reveals that not much study has been done on the dying properties of juglone. So the present paper is an effort for determining the dying capacity of juglone for wool, feathered leather and cotton from the point of view of their fastness.

In order to investigate the most proper mordant and pH value in terms of the wash-, crock- and light-fastnss in dyeing the above samples by juglone and some selected transition metal salts such as $CuSO_4{\cdot}5H_2O$, $FeSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ were used as mordant agenst at various pH.

Dyeing procedures were carried out at various pH values by three types of mordanting methods, pre-mordanting, together-mordanting and last-mordanting. 48 woollen strips, 35 cotton strips and 16 feathered-leather strips were dyed using transition element salts as mordant agents.

EXPERIMENTAL

Extraction of Juglone: Walnut leaves were picked up in Tokat city (Turkey) in June 2003. Before the experiment the leaves were dried in shade and then powdered. 20 g of plant material was extracted by maceration in 250 mL of chloroform for 1 h, at room temperature. The chloroform solution was filtered and evaporated under reduced pressure at 50°C to give a dry residue. The total dyestuff was determined to be 1.1–3.3%[2]. It was dissolved in 200 mL of distilled water for using in dyeing procedures[6].

Dyeing procedure of wool: The dyeing procedures of wool were carried out by using the three types of mordanting methods: pre-mordanting, together- mordanting and last-mordanting.

Pre-mordanting: White fowl woollen strips (1 g) were placed into 100 mL of 0.1 M mordant solution and heated for 1 h at 90°C. After cooling, it was rinsed, dried and placed in a 100 mL dye-bath. After heating for 1 h at 90°C, it was allowed to cool. The dyed product was rinsed with distilled water and dried. This process was carried out at pH 2, 4, 6, 8 successively for each mordant.

Together-mordanting: Mordant (equivalent to a concentration value of 0.1 M), 100 mL of dyestuff solution and 1 g of woollen strips were placed in a 250 mL Erlenmeyer flask. This mixture was heated for 1 h at 90°C. After cooling, it was filtered, rinsed with distilled water and dried. This process was carried out at pH 2, 4, 6, 8 successively for each mordant.

Last-mordanting: First, 1 g of woollen strips were heated in 100 mL of dye-bath for 1 h at 90°C. After cooling, the woollen strips were filtered and dried. Then these were put in 100 mL of 0.1 M of mordant solution and heated for 1 h at 90°C. Finally, these were filtered, rinsed with distilled water and dried. This process was also carried out at pH 2, 4, 6, 8 for each mordant.

The woollen strips dyed by each of these three methods were kept in a 100 mL solution of NH_3 (3%) to increase the fastness of the colours.

Dyeing procedure of Feathered-Leather : At first, dyeing of feathered-leather was carried out using both pre-mordanting and together-mordanting methods. The third procedure, *i.e.*, last mordanting did not give positive results since the temperature of the dye-bath should have been between 35–40°C during dyeing since the feathered-leather loses its water and shrinks at higher temperatures. At lower or higher temperatures, good results cannot be obtained. The dyeing procedure for feathered-leather was achieved using the two methods given as below.

Pre-mordanting: The white feathered-leather treated with $K_2Cr_2O_7$ (*ca.* 15 cm^2) was heated for 1 h at 35-40°C in 100 mL of 0.1M mordant solution in a 300 ml of Erlenmeyer flask. After cooling, it was added into 100 mL of dyestuff solution and shaken at frequent intervals for 1 h at 35-40°C. After completion of the dyeing process the dyed feathered-leather was filtered, rinsed with distilled water and dried.

Together-mordanting: The feathered-leather following pre-mordanting was added to 100 mL of dyestuff solution and mordant agents were mixed in a 250 mL Erlenmeyer flask. This mixture was shaken at frequent intervals for 1 h at 35–40°C and finally the dyed feathered-leather was filtered, rinsed with distilled water and dried.

The length of the feather in the feathered lamb-leather used in this work was approximately 1.5 cm. For these two methods, the dyeing pH was selected as 2 and 4. This situation has been discussed in the last section.

Dyeing procedure of cotton: Cotton has structure and properties different from wool and leather. It consists of glycoside units and there can occur coordinative and intermolecular hydrogen bonding with the mordant agent and dyestuff. In this work, the best dyeing was obtained with pre-mordanting and together-mordanting methods.

Pre-mordanting: Cotton (1.5 g, 50 cm^2) was heated for 1 h at 95°C in 100 mL of 0.1 M mordant solution. After cooling, the cotton was taken out, rinsed with distilled water and dried. It was put into 100 mL of dye-bath and heated for 1 h at 95°C. It was allowed to cooland then filtered. Finally, the dyed-cotton was rinsed in distilled water and dried.

Together-mordanting: 100 mL of dyestuff solution was added to the cotton and mordant agent (equivalent to the 0.1 M value) and heated for 1 h at 95°C. After cooling, it was taken out, rinsed with distilled water and dried.

Last-mordantating: Cotton (1.5 g, 50 cm^2) was dyed in 100 mL of dyestuff solution for 1 h at 95°C. After filtering, it was heated in 100 mL of 0.1 M mordant solution for 1 h at 95°C. The dyed cotton samples were filtered, rinsed with distilled water and dried.

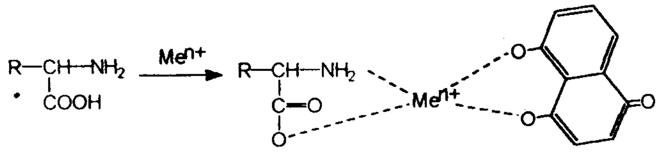
Fastness Tests: The crock-, light- and wash-fastness of all dyed samples were determined by a LHTP model Alas Laundero meter, a 255 model crock-meter and a Fadeometer (Xenotest), respectively. Colour codes were determined using Pantone Colour Guide[7]. Moreover, crock-, light- and wash-fastness were established according to DIN 54021, DIN 54004 and to ISO 105-C06, C1S, respectively[8, 9]

RESULTS AND DISCUSSION

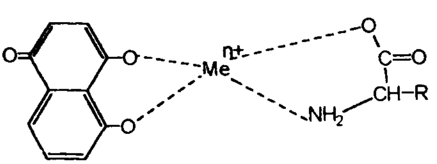
The dyeing processes of the woolen strips, feathered-leather and cotton with juglone dyestuff were carried out using some selected transition metals salts as mordant agents at various pH values by three methods. 48 woollen strips, 35 cotton strips and 16 feathered-leather samples were dyed at pH 2, 4, 6, 8; pH 2, 5, 8 and pH 2, 4, respectively.

The dyeing mechanisms of wool and feathered-leather with juglone by pre-mordanting (1), together-mordanting (2) and last-mordanting (3) can be considered as follows[10]:

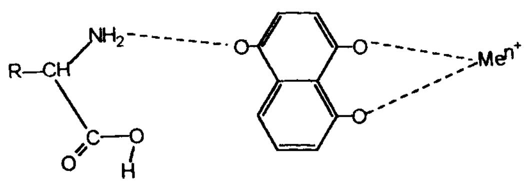
(1) Wool Mordant (Me^{n+}) Dyestuff



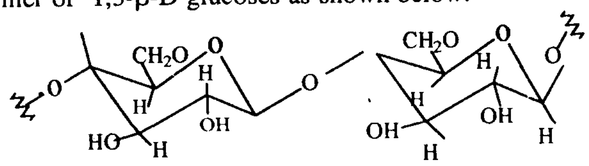
(2) Dyestuff Mordant (Me^{n+}) Wool



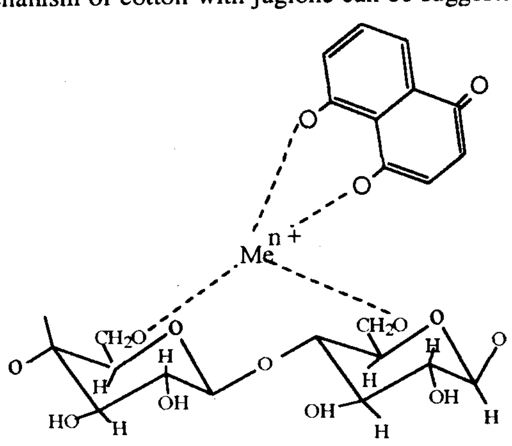
(3) Wool Dyestuff (Me^{n+}) Mordant



On the other hand, cotton contains 90% cellulose. The cellulose molecule is a linear polymer of 1,3-β-D glucoses as shown below:



Cotton can be dyed without using any mordant agent. However, when a mordant agent is used in the dyeing process, a lot of colour tones can be obtained. The dyeing mechanism of cotton with juglone can be suggested as below.



The relationships between fastness-pH for wool, feathered-leather and cotton, mordant-average fastness for wool, mordant-average fastness for feathered-leather and mordant-average fastness for cotton are shown in Figs. 1–4 respectively.

Fig. 1 shows the variation of fastness-pH for wool and feathered-leather samples. As seen in Fig. 1, for both wool and feathered-leather, the fastness increases when the pH is varied from 8 to 2. This result means that the dyeing with high fastness can be achieved in acidic pH range.

This is the expected result because in the acidic pH range, the proton of acid is bonded with free carboxyl group of amino acids in the structure of wool or feathered-leather and the anion of acid is bonded to nitrogen atom with positive charge in the structure[6]. Moreover, in the dyeing process by acidic dyestuff, the bonding tendency of dyestuff molecule to the wool decreases in the alkali medium ($pH \geq 8$). The dissociation of carboxyl groups increases by the alkaline effect and the anion of the dyestuff is to be free since the positive charged amino acid groups are bonded to the carboxyl anions. Therefore, the desired bonding does not occur in the alkaline medium.

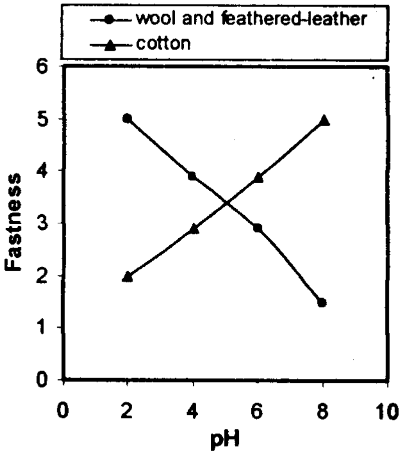


Fig. 1. The variation of fastness with pH

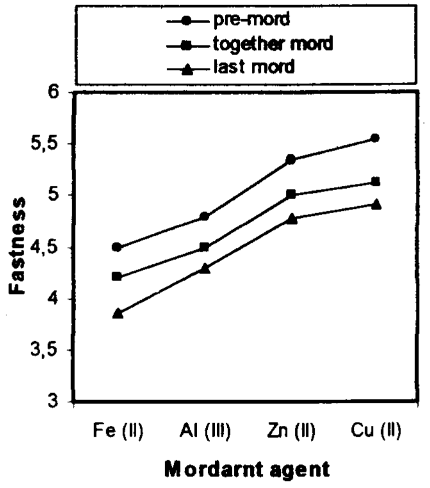


Fig. 2. The variation of average fastness for wool with respect to the mordant agent

On the other hand, as also seen in Fig. 1, the fastness for cotton increases with increase of pH. This is due to the fact that the oxygen atoms in cellulose units of cotton are free in slightly alkaline medium and the cellulose units are easily bonded to the metal cations of mordant agent.

The arithmetic average fastness values (wash, crock, light) of dyed wool samples *vs.* mordant salts is presented in Fig. 2. The highest fastness was obtained by the pre-mordanting method for each of the four metal salts, Fe(II), Al(III), Zn(II) and Cu(II).

The average fastness values of the all dyed samples by Cu(II) are 5.70, 5.13 and 4.85 for pre-modanting, together-mordanting and last-mordanting methods, respectively. The lowest fastness values were obtained by Fe(II) mordant which are 4.47, 4.22 and 4.19 for pre-mordanting, together-mordanting and last-mordanting methods, respectively. When we take into consideration the average fastness by mordanting methods, the effect of mordanting agents on the fastness of the investigated samples can be ordered as Cu(II) > Zn(II) > Al(III) > Fe(II). It is due to the fact that the Cu(II) mordanting agent forms a more stable complex with dyestuff molecules compared to the other mordant.

Fig. 3 shows the average fastness values for dyed feathered-leather samples by pre-mordanting and together-mordanting methods. Here, the last mordanting method was not used due to not being important in the dyeing of feathered-leather. The fastness values by Cu(II) change from 4.85 to 5.18 and by Fe(II) mordant agent from 3.48 to 4.13 in pre-mordanting and together-mordanting methods, respectively.

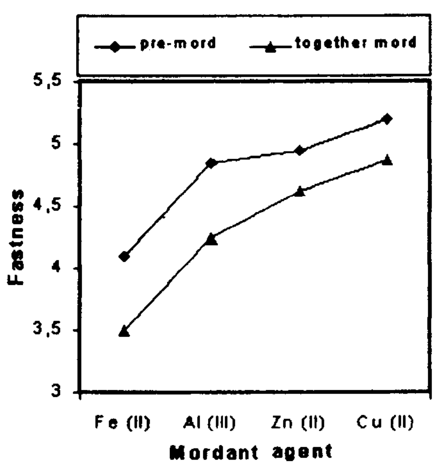


Fig. 3. The variation of average fastness for feathered-leather with respect to the mordant agent

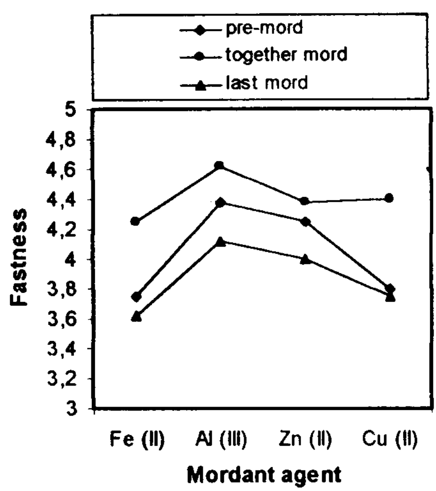


Fig. 4. The variation of average fastness for cotton with respect to the mordant agent

The average fastness values (wash, crock, light) of dyed cotton samples by Fe(II), Al(III), Zn(II) and Cu(II) for the three mordanting methods are shown in Fig. 4. The best result was obtained in the presence of Al(III) by together-mordanting method. The average fastness values by Al(III) are 4.38, 3.81 and 3.70 for the together-mordanting, the pre-mordanting and the last-mordanting.

On the other hand, the lowest fastness by Fe(II) was 4.23 for together-mordanting, 3.72 for pre-mordanting and 3.59 for last-mordanting. Thus, the effect of the mordanting agent on the fastness of the cotton samples can be sequenced as:

Al(III) > (Cu(II) > (Zn(II) > (Fe(II).

Conclusions

The results show that it is possible to dye natural fibres using mordanting methods by some transition metal salts at various pH values. Generally, different colours and colour tones and excellent fastness dyeings were obtained with juglone. The highest colour depth on cotton and protein fibres (wool and feathered-leather) were obtained at 90°C for 1 h for wool and cotton at 35°C and 40°C for 1 h for feathered-leather.

The best results were obtained using pre-mordanting method for both wool and feathered-leather by Cu(II) mordant salt at pH $\leq$ 4. In addition, the dyed samples with highest fastness were also obtained by Cu(II) for the samples except cotton and by Al(III) for only cotton at pH = 8 in the pre-mordanting method. However, a further experimental study should be made to investigate the reason for the highest fastness value obtained by Al(III) for cotton.

Consequently, if walnut (*Juglans regia* L.), which contains juglone dyestuff, is used for dyeing natural textile fibres, it will probably be an important raw material in terms of commercial use.

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