

USAGE OF WILLOW EXTRACT AS MORDANT AGENT AND DYEING OF WOODEN AND FIBER SAMPLES WITH ONION (*Allium cepa*) SHELL

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ABSTRACT

The present work examines the usage of willow extract as a natural mordanting agent during dyeing of wooden and fiber samples with onion (*Allium cepa*) shell as a natural dyestuff source under different conditions. The naked willow was cut into small pieces and allowed for 20 days in distilled water. At the end of the period, the solution was filtered and stored at room temperature until usage. The extraction of dyestuff from dried shell of onion was performed using soxhlet apparatus in distilled water. Cotton, wool, feathered-leather and wood samples were dyed using pre-mordanting, together mordanting and last mordanting methods at fix pH value (pH=4,5-5) in the presence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mordants. To investigate the best dyeing conditions, 9 wool, 9 cotton, 9 feathered-leather fibers, and 18 wood samples were dyed according to the methods that mentioned above. Before the dyeing experiments all the samples were first kept into willow extract for 24h and then they put into the Artificial Animal Urine System (AAUS) for 24h. The optimum dyeing conditions were determined and the importance of willow extract as a mordant agent was evaluated in terms of fastness of dyed samples. The results of the present study suggest that the use of willow extract is not only enhance the fastness but also increase the brightness of the dyed samples.

Keywords : Onion (*Allium cepa*), willow extract, mordant, natural fibers, wood

INTRODUCTION

Natural dyes which presents in plants are less harmful on humans and environment so they play an important role to be a better alternative source to synthetic dyes¹⁻⁷.

Dyeing of natural fibers have great practical importance to develop processes of obtaining high fastness values. To improve the colour quality of the fibers, a lot of methods have been tried from ancient times. The technology used in the production of natural dyes was known in China as early as 3000 B.C. and among the Indians, Phoneicians, Hebrews, and Venetians in the 13th century A.D. and later was passed on to the Greeks and Romans. It was also known in Africa, Mexico, and Peru^{8,9}.

The dyestuff in the onion (*A. cepa*) shell is quercetin¹⁰ (Figure 1.) which exhibits good dyeing properties because of its auxochrome group (-OH) together with other chromogen groups.

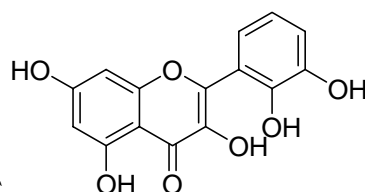


Fig.-1: Chemical structure of quercetin

In this study, a new mordant source-the willow extract-was used together with AAUS in dyeing of wool, cotton, feathered-leather fibers and wood materials with the shell of onion. The dyeing processes were carried out using pre-mordanting, together-mordanting and last-mordanting methods with Fe(II), Al(III) and Cu(II) salts.

EXPERIMENTAL

Preparation of mordant solutions and dye-bath

The shells of onion (*A. cepa*) were supplied from the dining hall of Gaziosmanpasa University in June, 2008. It was dried in shade, cleaned and powdered by grinder before the experiments. To prepare the natural mordant solution, the stem of willow (*Salix alba*) was cut into small pieces and it was left for 20 days at room temperature. 10 L of distilled water was used for 1 kg of willow. At the end of the time, the solution was filtered and all samples were kept in this solution for 1 day before dyeing procedures.

Extraction of onion shells was performed by soxhlet apparatus with distilled water. 1 L of distilled water was used (for 100 g plant material) then the dyestuff was transferred to the aqueous media.

Reagents and equipments

All chemicals used in this work, were purchased from Merck. Distilled water was used for all steps. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Merck. Extraction was performed by using soxhlet apparatus. Colour codes were determined by Pantone Colour Guide. The wash-, crock (wet, dry)- fastness of all dyed samples were established according to ISO 105-C06 and to CIS¹¹, respectively, and fastnesses were determined by Atlas Weather-ometer, a Launder-ometer and a 255 model crock-meter, respectively.

Dyeing procedures

Dyeing procedures of wool, cotton, feathered-leather and wood samples with artificial animal urine system (AAUS)

The undyed materials were kept into AAUS included NH_3 (3%, v/v), CaC_2O_4 (3%, m/v) and urea (3%, m/v) for 24 h, at room temperature after treatment with willow extract for 24 h before dyeing procedures¹². At the end of the time, the samples rinsed with distilled water and dyed according to the dyeing methods that mentioned below.

Pre-mordanting method

The undyed material (1 g) which was treated with willow solution and AAUS for 24 h at room temperature, separately, was heated in 0.1 M mordant solution (100 mL) for 1 h at 90°C. After cooling of sample, it was rinsed with distilled water and put into dye-bath solution (100 mL). It was heated at 90°C for 1 h, at the end of the period, the dyed material removed, rinsed with distilled water and dried.

Together-mordanting method

Both mordant (in solid state which equivalent to 0.1 M mordant solution) and dyestuff solution poured into a flask and the sample placed in this mixture. The complication was heated at 90°C for 1 h. After cooling, it was rinsed and dried.

Last-mordanting method

On the contrary to pre-mordanting method, the undyed material (1 g) was first treated with dyestuff solution for 1 h at 90°C. After cooling the sample, it was rinsed with distilled water and put into 0.1 M mordant solution (100 mL) and heated for 1 h at 90°C. Finally, the dyed material was rinsed with distilled water and dried.

RESULTS AND DISCUSSION

Proposed dyeing mechanism

As the 3-hydroxy group (3-OH) and 4-oxo group (Fig. 2a, Fig. 3a and Fig. 4a) have more acidic protons, they are the first sites to be involved in the complexation processes. Another complexation can occur with 3'- and 4'-OH groups (Fig. 2b, Fig. 3b and Fig. 4b)¹³.

The dyeing mechanisms of wool and feathered-leather with quercetin by pre-mordanting (1), together-mordanting (2) and last-mordanting (3) methods can be considered as follows¹²:

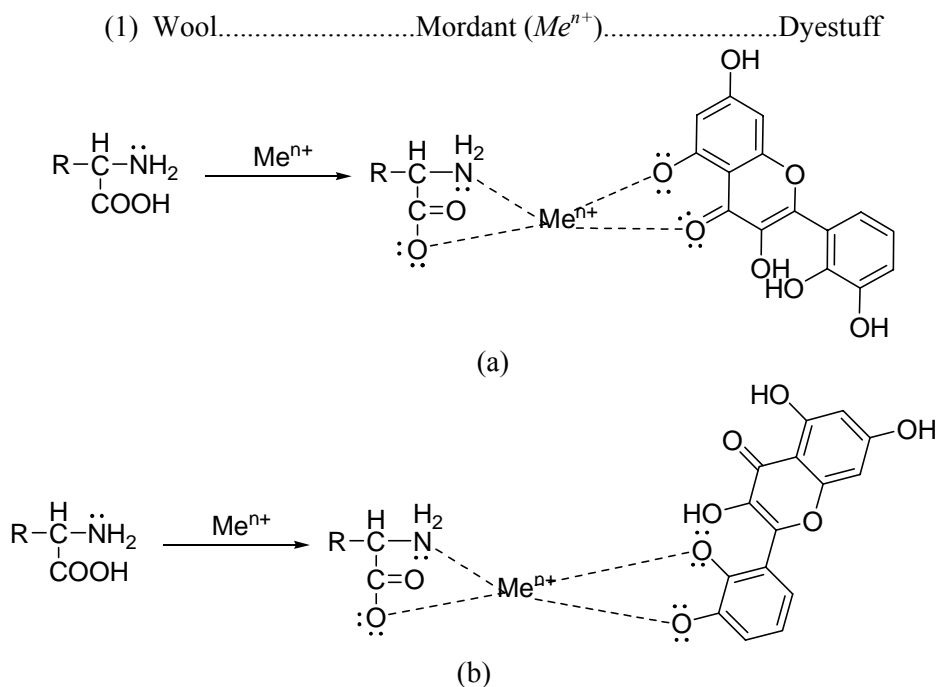


Fig.-2: Proposed mordant-dye complex according to pre-mordanting method in dyeing of wool fibers

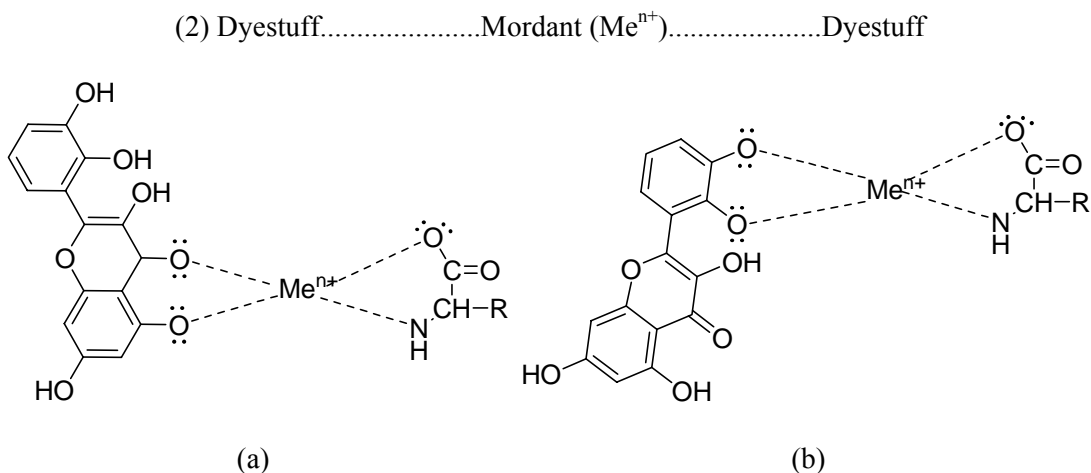
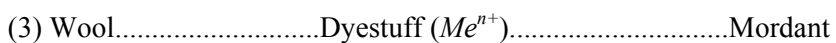


Fig.-3: Proposed mordant-dye complex according to together-mordanting method in dyeing of wool fibers



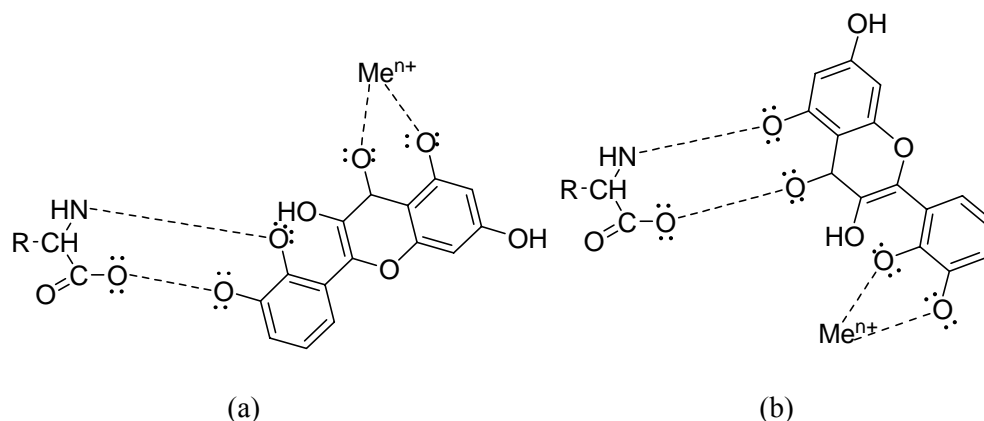


Fig.-4: Proposed mordant-dye complex according to last-mordanting method in dyeing of wool fibers

Because of cotton and wood have cellulosic structure, coordinate covalent bonding occurs between CH_2O -groups of cellulose and metal cation. The suggested mechanism is given below (Figure 5a and 5b) :

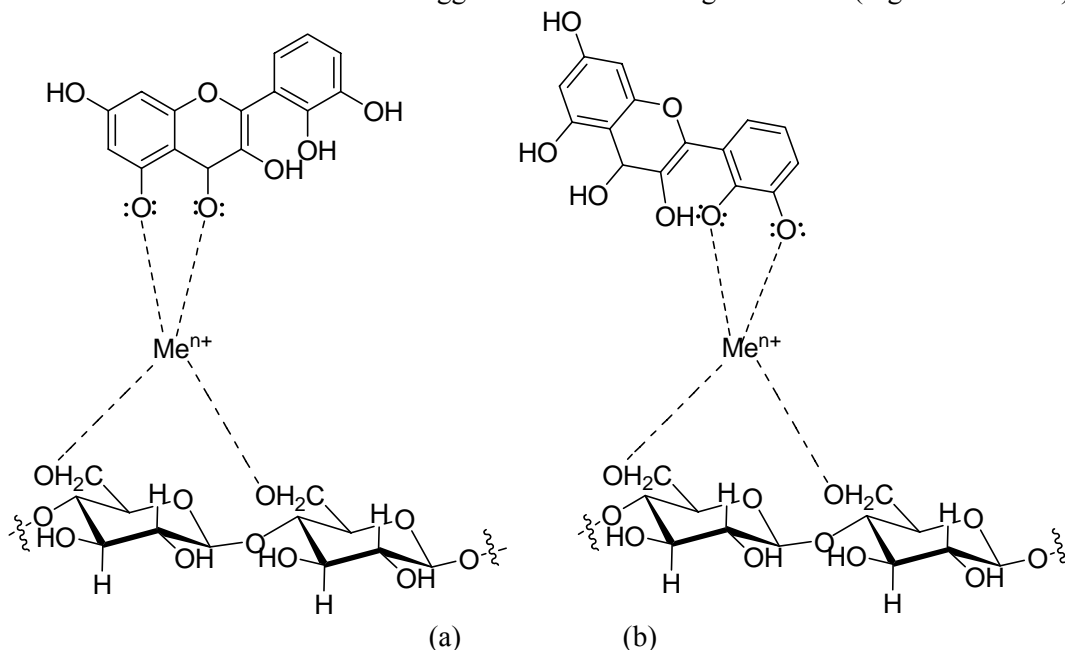


Fig.-5: Proposed mordant-dye complex according to together-mordanting method in dyeing of cotton and wood

As seen from the curves in Fig. 6 the average fastness for wool samples decreases in the order of $\text{Fe(II)} > \text{Cu(II)} > \text{Al(III)}$. Best values for wool samples obtained by using last-mordanting method with Fe(II) and Al(III) mordants.

It can be clearly observed from the Fig. 7, there is no considerable difference between together- and last-mordanting method with the use of Fe(II) and Al(III) mordants in dyeing of cotton fibers.

The highest fastness values for feathered-leather is obtained using Fe(II) mordant with together- and last-mordanting methods (Fig. 8)

In general, from the figures 1, 2 and 3, the most effective mordant agent is Fe(II) and the most convenient dyeing procedure is last-mordanting method. This situation can be explained by the high stability of Fe(II) complex. Based on the results it can be noted that treatment of natural fibers with willow extract assists to strenght the coordinate covalent bonding of Fe(II) salt to natural fiber.

When evaluated the dyed samples, green and its tones were obtained in the presence of pre- and together-mordanting methods with wool samples by all mordant salts, and, brown and its tones were obtained by last-mordanting method.

In dyeing of cotton fibers brown and cream tones were occurred. According to the experimental results, however, the colours of dyed cotton samples are faded when it is compared with dyed wool and feathered-leather fibers.

Bright green and cream colours were obtained in dyeing of feathered-leather, in general.

In addition, wood samples were dyed according to pre-mordanting, together-mordanting and last-mordanting methods with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. First, all samples were dyed only these mordant salts and onion shell extract (Dyeing procedure-I). Subsequently, the raw wood samples pre-treated with willow extract for 24 h and then AAUS for 24 h, at room temperature, respectively. At the end of the period the samples were dyed according to the three mordanting methods with using Fe(II), Al(III) and Cu(II) salts (Dyeing procedure-II). Brown, green and cream tones were obtained both dyeing processes (I and II) of wood samples but there is a great difference between the brightness of wooden samples according to the first and second dyeing processes. In the second procedure, excellent bright colours and colour tones were obtained in the presence of willow extract and AAUS.

The effect of AAUS was explained by Onal¹³ in 1996. Shortly, the components of AAUS (ammonia, urea, oxalate) have a great importance on the fastness of dyed fibers. Ammonia helps the expanding of fiber misels so it facilitates the penetration of dye to the fiber. Urea serves as a pH regulator. And last, oxalate plays an important role during the formation of complex structure which occurs between dye and natural fiber. It makes this complex very stable and so the fastness values of the dyed samples increases in the presence of AAUS.

Another material which was used to improve the fastness and quality of the fibers is willow extract. Using of willow extract in dyeing of fibers was performed first time by our group. This extract has a big role on the brightness of the colour. The water-extraction products of wood are carbohydrates, pectins, proteins, tanens and mineral compounds. The effect of willow extract may due to the hydrogen bonding between sellulosic structure of wood and tanens¹⁴.

All the fastness values and colour codes are presented in Table I, Table II, Table III for wool, cotton and feathered-leather samples, respectively.

It can be clearly seen that wet and dry fastness values are very good for dyed wool and cotton fibers but the best wash-fastness values are obtained with cotton fibers (Table 1 and Table 2). These mordants and dyeing procedures are not as effective as in feathered-leather (Table 3).

CONCLUSIONS

Best dyeing conditions of wool materials are obtained with Al(III) and Cu(II) mordants using last-mordanting method. Generally green and brown colour tones were obtained for wool samples. On the contrary to wool, the highest fastness values obtained for cotton fibers with Fe(II) according to all mordanting methods. The colours of cotton fibers are brown and cream tones. Bright green and cream tones are obtained for feathered-leather. Fe(II) salt with together or last-mordanting method, Al(III) salt with pre- and last-mordanting methods give the best results for this type of fiber. Not only AAUS but also willow extract contributes the brightness of natural fibers and wood materials. AAUS and willow extract are more effective on wood materials than natural fibers. Green, brown and cream colours are observed by using dyeing procedure-II.

Consequently, onion shell can be evaluated as an important natural dyestuff source. It can be used in dyeing of either cellulose or protein fibers. In addition, in this study, the results show that willow extract and AAUS are effective mordants for obtaining high fastness values. Further investigations are going on.

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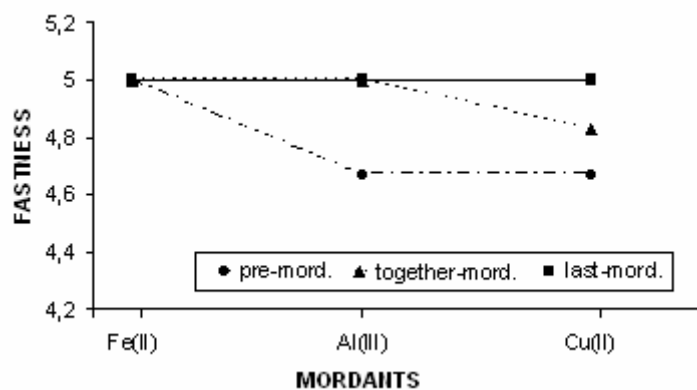


Fig.-6: The variation of average fastness for wool with respect to the mordant agent

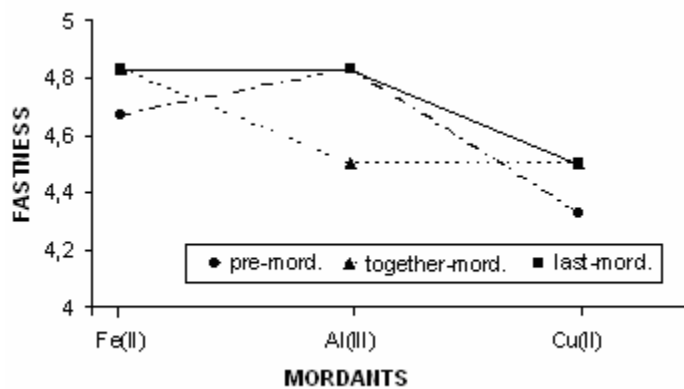


Fig.-7: The variation of average fastness for cotton with respect to the mordant agent

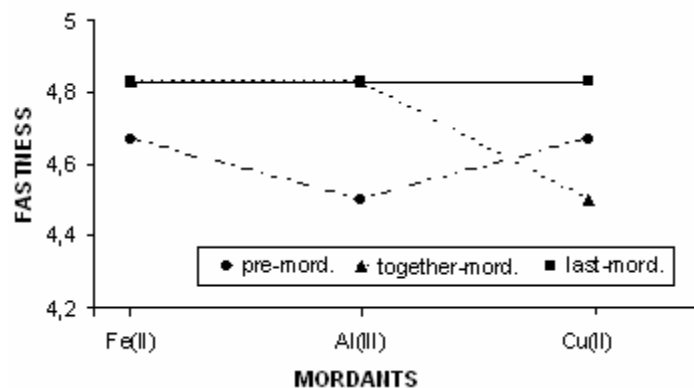


Fig.-8: The variation of average fastness for feathered-leather with respect to the mordant agent

Table-1: Fastness values and colour codes of dyed wool fibers

Mordant	Dyeing Method	Wash-Fastness	Crock Fastness		Colour Code
			Wet	Dry	
FeSO ₄ .7H ₂ O	Pre-mordanting	4	5	5	16-1105 TP
	Together-mordanting	4-5	5	5	18-0601 TP
	Last-mordanting	4-5	5	5	15-1132 TP
CuSO ₄ .5H ₂ O	Pre-mordanting	4	5	5	14-0108 TP
	Together-mordanting	3-4	5	5	13-0917 TP
	Last-mordanting	4-5	5	5	16-1323 TP
AlK(SO ₄) ₂ .12H ₂ O	Pre-mordanting	3-4	5	5	13-0932 TP
	Together-mordanting	4-5	5	5	17-0929 TP
	Last-mordanting	4-5	5	5	13-1014 TP

Table-2: Fastness values and colour codes of dyed cotton fibers

Mordant	Dyeing Method	Wash-Fastness	Crock Fastness		Colour Code
			Wet	Dry	
FeSO ₄ .7H ₂ O	Pre-mordanting	5	5	5	16-1105 TP
	Together-mordanting	5	5	5	18-0601 TP
	Last-mordanting	5	5	5	15-1132 TP
CuSO ₄ .5H ₂ O	Pre-mordanting	4-5	5	4-5	14-0108 TP
	Together-	4-5	5	5	13-0917 TP

	mordanting				
	Last-mordanting	5	5	5	16-1323 TP
AlK(SO ₄) ₂ .12H ₂ O	Pre-mordanting	4	5	5	13-0932 TP
	Together-mordanting	5	5	5	17-0929 TP
	Last-mordanting	5	5	5	13-1014 TP

Table-3: Fastness values and colour codes of dyed feathered-leather

Mordant	Dyeing Method	Wash-Fastness	Crock Fastness		Colour Code
			Wet	Dry	
FeSO ₄ .7H ₂ O	Pre-mordanting	4	5	5	16-1105 TP
	Together-mordanting	4-5	5	5	18-0601 TP
	Last-mordanting	4-5	5	5	15-1132 TP
CuSO ₄ .5H ₂ O	Pre-mordanting	3-4	4-5	5	14-0108 TP
	Together-mordanting	3-4	5	5	13-0917 TP
	Last-mordanting	3-4	5	5	16-1323 TP
AlK(SO ₄) ₂ .12H ₂ O	Pre-mordanting	4-5	5	5	13-0932 TP
	Together-mordanting	4	4-5	5	17-0929 TP
	Last-mordanting	4-5	5	5	13-1014 TP

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