ISSN: 1304-7981 Number: **2**, Year: **2013**, Pages: **1-7** **http://jnrs.gop.edu.tr**

Gaziosmanpasa University
Graduate School of Natural and Applied Sciences
Journal of New Results in Science

Received: 29.01.2013
Accepted: 25.02.2013

Editors-in-Chief: Naim Çağman
Area Editor: Yakup Budak

Investigation of Dyeing Properties of Pine Wood Samples with *Allium Cepa* That Pretreated by Willow Extract

Ferda Eser[a] (ferda.eser@gop.edu.tr)
Adem Önal[1,a] (adem.onal@gop.edu.tr)
Arzu Ünal[b] (arzu.de@hotmail.com)

[a]Gaziosmanpasa University, Natural Dyes Application and Research Center 60250 Tokat, Turkey
[b]Gaziosmanpasa University, Science and Art Faculty, Department of Chemistry 60250 Tokat, Turkey

Abstract – In this work, willow (1 kg) pieces were allowed for 21 days at room temperature and 27 numbers of pine wood samples were mordanted for 12 h in willow extract. These mordanted samples were dyed with dyestuff obtained from dried onion shell by boiling in deiyonized water, at pH=4, 7 and 8 using pre-mordantation, together-mordantation and last-mordantation methods. The solutions of $CuSO_4 \cdot 5H_2O$, $AlK(SO_4)_2 \cdot 12H_2O$ and $FeSO_4 \cdot 7H_2O$ were used as mordanting agents**.** Dyeing conditions and other characteristics were determined. In generally, with high fastness authentic colours were obtained.

Keywords *–*
Allium cepa, willow, mordant, dyeing, fabric, fastness.

1. Introduction

Wood is an important sustainable, economical, renewable and biodegradable natural resource with diverse application [1]. Furniture industry is the most used area of the wood. At the production process, wood was treated with synthetic dyes and glazed finely. According to the literature reports, destruction of wood material which was dyed with chemical dyes harm to the environment [2]. It is known that interior decoration materials containing VOC (volatile organic compounds) were harmful to human health that such substances are around 150 [3]. Because of synthetic dyes cause allergies for people indoors, tendeny to natural dyestuffs start to increase day by day. In USA, EPA (Environmental Protection Agency) was reported that VOC have high-level risk, so water-based and inorganic pigments should be used immediately [4]. Because of the results that mentioned above, the importance of natural preservatives that don't harm the environment and human

[1]***Corresponding Author***

health have increased steadily and remarkable studies have done in this area in recent years [5-7].

Especially, in the studies including dyeing of cellulosic and protein-based fibers with natural dyes, it is stated that the fibers which were dyed with walnut peel exhibited antimicrobial property. Turkish red and buckthorn are the indispensable sources of the art of hand-weaving. It is known that 400 year old carpets and kilims which were dyed with natural dyes have been exhibited in Topkapi and Mevlana Museums, in Turkey [8].

In our study, trashed shells of onion were used as dyestuff source. Onion, which belongs to the Liliaceae family, is being used in salads and meals every day, around the World. From ancient times, onion shells have been using in dyeing of wool and egg in Anatolia. Khaki, green, oil green and their tones were obtained from the dyeing of wool with onion shell using different mordants. Onion shell has a dyestuff called Quercetin as given in Fig 1. which has a good dyestuff property because of its chromophore and oxochrome groups [9].

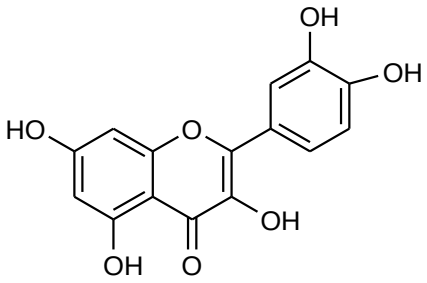

Figure 1. Chemical structure of Quercetin

Studies on onion shell have been done and published in the laboratory of Natural Dyes Applicatin & Research Center, Gaziosmanpasa University, since 1997. Over 100 different colors and their tones were obtained from the dyestuff extract of onion shell [10-12]. Another study was carried out in dyeing of cotton and wool fiber pre-treated with willow extract and high fastness values were acquired in the same laboratory [13].

In this study, the dried shells of onion were evaluated in terms of dyestuff source in dyeing of wooden material. For this purpose, pre-mordantation, together-mordantation and last-mordantation processes of wood materials were performed using $CuSO_4 \cdot 5H_2O$, $AlK(SO_4)_2 \cdot 12H_2O$ and $FeSO_4 \cdot 7H_2O$ mordants at different pH values. As a result, surface dyeing of wood material was achieved succesfully and a new water-based dyestuff source that friendly to human health was revealed.

2. Experimental

2.1. Materials

Yellow pine (*Pinus sylverstis* L.) which is used in furniture and joinery industry was used in the concept of the study. For this purpose, sanded wood samples were used which are in the size of 2.5x5 cm. Acetic acid (CH_3COOH) and sodium hydroxide (NaOH) were used of

analytical grade for regulating the pH of dye-bath. Cupper sulphate ($CuSO_4 \cdot 5H_2O$, ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and aluminium potassium sulphate ($AIK(SO_4)_2 \cdot 12H_2O$) were purchased from Merck and used as mordanting agent. Onion shells were supplied from bazaar of Tokat that native to Tokat region, in June 2012.

2.2. Extraction of Dyestuff From Onion and Willow

Extraction of dyestuff from onion shell: Onion shells were dried at room temperature and extraction of dyestuff from onion shells was performed using soxhlet apparatus. For this purpose, 100 g of onion shell was refluxed with 2 L of distilled water until colorless.

Extraction of willow: 1 kg branch of willow supplied from Tasliciftlik Campus in Tokat was cut into small pieces and fermented in 5 L of distilled water, at room temperature. After 3 weeks, the light pink solution was filtered and used for pre-mordantating of wood samples.

2.3. Dyeing of Wood

This process was performed by $CuSO_4$, $FeSO_4$, $AIK(SO_4)_2$ mordants using three dyeing methods including pre-mordantating, together-mordantating and last-mordantating methods at pH=4, 7 and 8 by allowing the samples in onion shell extract for 12 h, at room temperature.

Pre-mordantating method: The wood samples which were pre-treated with willow extract at room temperature, for 24 h were allowed to dyeing in 100 mL of dye bath for 12 h, at room temperature after letting the samples 0.1 M, 100 mL of mordant salts for 6 h.

Together-mordantating method: Wood samples which were pre-treated with willow extract were put into the 100 mL of dyebath and 0.1 M of mordant (in solid state which is equivalent to 0.1 M mordant solution) was added. pH was adjusted using acetic acid or sodium hydroxide solution and the samples were allowed for 12 h for dyeing.

Last-mordantating method: On the contrary to pre-mordantating method, wood samples were allowed to 12 h incubation in 100 mL of dyebath solution that the pH value was adjusted with acetic acid or sodium hydroxide. At the end of the period, samples were taken out of the beaker and each sample was put into a beaker containing 0.1 M 100 mL of mordant solution for 6 h, at room temperature.

2.4. Determination of Fastness and Color Codes

Fastness tests of the dyed wood samples were carried out according to the method of water dripping. For this purpose, the dyed samples were allowed to stand under running water (1 drop/sec) for 120 min. After the end of the period, the wet samples were compared with the first sample in terms of color loss and the results showed that there was no loss of color in the samples.. Color codes of dyed samples were determined using Pantone Color Quide [14].

3. Results and Discussion

The aim of the study is to obtain high fastness values with onion (*Allium cepa* L.) shell in the presence of willow extract. Therefore, the dyestuff was extracted from onion shell and the dyeings were performed using $FeSO_4$, $AlK(SO_4)_2 \cdot l2H_2O$, $CuSO_4$ mordants by pre-mordantating, together-mordantating and last-mordantating methods. Before dyeing process, all wood samples were pretreated with willow extract for 24 h at room temperature in order to improve the fastness and brightness of the samples.

The results of the studies including dyeing conditions, color codes were given in Table 1.

Table 1. Dyeing conditions and color codes of dyed samples

Dyeing method	**pH**	**$FeSO_4$**	**$CuSO_4$**	**$AIK(SO_4)_2$**
Pre-mordantating	4	16-1148 Nugget	17-0843 Brown mist	16-0947 Bright gold
	7	15-1516 Peach beige	18-1016 Cub	14-1031 Rattan
	8	17-1418 Yinger snop	18-0832 Plantation	15-1142 Honey gold
Together-mordantating	4	17-1048 Apple cinnomon	19-0414 Forest night	14-1121 Sheep skin
	7	14-1127 Desert mist	18-0920 Kongoroo	14-1120 Apricot
	8	13-0939 Golden cream	18-1321 Brownie	12-0817 Cream
Last-mordantating	4	16-1334 Ton	18-1110 Maclig biscue	12-0825 Popcorn
	7	18-1421 Cagnac	18-1031 Taffee	14-1133 Apricot nectar
	8	16-1323 Marcaroone	19-0622 Military olive	15-1234 Gold earth

According to the experimental results, different brown tones were obtained from the dyeings carried out with $CuSO_4$ mordant using pre-mordantating method at different pH values. The color obtained at pH 7 is lighter than pH 4 and pH 8. The color obtained from pH 4 is darker than the color obtained with pH 8. Dyeings, which were carried out with $CuSO_4$ mordant by together-mordantating were showed that the colors of wood samples are closed each other despite different pH values.

The three colors that acquired with $CuSO_4$ according to last-mordantating method at pH 4, 7 and 8 are the tones of brown and tobacco.

Pre-mordantating of samples using $FeSO_4$ gave the colors of oil black at pH 4 and 7; greenish brown at pH 8. The colors are getting lighter from pH 4 to pH 8 in last-mordantating method.
Orange and its tones are obtained from the dyeing of samples with $AIK(SO_4)_2$ mordant according to pre-mordantating method at pH 4, 7 and 8. Light orange and its tones are gotten with same mordant, by together-mordantating process. The colors channge to yellowish orange, light brown and pinkish orange using last-modantating method, at different pH values, with same mordant.

Dark colors were obtained by pre-mordantating and together-mordantating and light colors were gained by last-mordantating method in the presence of $FeSO_4$ mordant. Dark colors were obtained using $AIK(SO_4)_2$ mordant by pre-mordantating method. The colors obtained by together and last-mordantating methods are lighter than those of pre-mordantating method.

Dyeing mechanism

First, material treats with mordant salt in pre-mordantating method and then dyeing is performed by addition of dyestuff solution. Color tones change by mordantating method. This is because of the light absorption wavelenght variation of the complex which occur during bonding of dyestuff and wood molecules. According to the mordantating method, the sequence of bonding of ligand (dyestuff)-central atom (mordant cation) can be considered as given below :

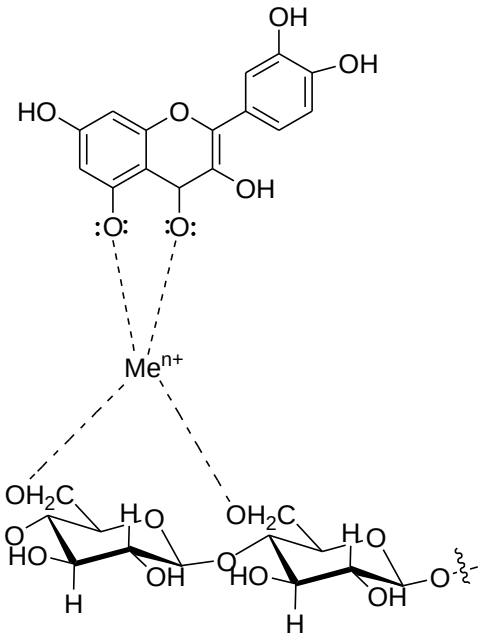

Figure 2. Dyeing mechanism of cellulose

Pre-modantating: [wood + mordant cation] (1)…….Dyestuff (2)
Together-mordantating : [wood + dyestuff + mordant] (all of them mix simultaneously)
Last-mordantating : [wood + dyestuff] (1)…….Mordant (2)
(1) and (2) show the sequence of process.

The predicted mechanism of together-mordantating is given below (Fig. 2). As it shown that metal cation of the mordant forms a stable complex via coordinate covalent bonding with oxochrome groups (-C=O and –OH) of the dyestuff (quercetin) at one side and selulose units of the wood material at another side (Fig. 2).

4. Conclusion

According to the results, the best mordant was determined as $CuSO_4$, followed by $FeSO_4$ and $AIK(SO_4)_2$ mordants and the most suitable dyeing method was determined as pre-mordantating for the dyeing of wood samples with onion shell in the presence of willow extract. As the result of the experimental works, it was observed that the dyestuff was penetrated to the wood at least 1.5 mm. Colors obtained from three mordants can be used in furniture industry and these colors and their tones are similar to the authentic tones of old buildings. Therefore, it is concluded that the colors obtained from he study can be used in the restoration of old wooden structures by General Directorate of Foundations. It is suitable to use in children's room furniture because of the harmless property of the naturally dyed wood samples. So, it is important to make common studies with industrialists in furniture and decoration area. In the light of the results which were obtained by our group before, it can be said that willow extract can be used as a natural mordant agent in order to obtain bright colors from the dyeing of both fiber and wood material.

Further investigations are going on.

References

[1] Jayashree, Pandey, K.K., Nagaveni, H.C., Mahadevan, K.M., 2011. Fungal resistance of rubber wood modified by fatty acid chlorides, International Biodeterioration&Biodegradation, 65(6), 890-895.
[2] Kutroğlu, A. (1895). Kimyasal odun maddelerininçevre sağlığına etkileri. Ahşap malzemenin korunması semineri. 21-22 Kasım 1984. Ankara.
[3] Salthammer, T., Schwarz, A., Fuhrmann, F. (1998). Atmosferic Environment, 33, 75-78.
[4] Salthammer, T., Bednarek, M., Furhmann, F., Funarki, R., Tanabe S.I. (2002). J.of Photochhem.and Photobiol. A: Chemistry, 152, 1-9.
[5] Edwarards, H.G.M., Farmell, D.W., Daffner, L. (1996). Spectrochemical acta Part A: Moleculer spektroscopy, 52, 1609-1648.
[6] Wheals, B.B., Wright, M.M. (1987). J. of Analyiyticac and Applied prolysis, 11, 195-211.
[7] Göktaş, O., Mammadov, R., Duru, M.E., Baysal, E., Çokak, A., Özen, E. (2006). Ekoloji, 15, 16-23.
Önal, A. (1996). Tr. Journal of Chem., 3, 194-203.
[9] Önal, A. (1996). Tr. Journal of Chem., 3, 203-214.
[10] Önal, A. (1997). J. of Kocaeli University, 10, 35-47.
[11] Çoban, S. (1992). Genel olarak Standart, standardizasyon ve tekstilde Kullanılan Haslık Kontrolleri. Tekstil ve Konfeksiyon, 2, 341-346.

[12] Önal, A., Tüzen, M. (1999). Bull. of Pure and Appl. Science, 18, 41-44.
[13] Kavak, F., Seyfikli, D., Önal, A. (2010). Rasayan Journal of Chemistry, 3, 1 – 8.
[14] Önal, A. (2000). Doğal Boyar maddeler (Ekstraksiyon-Boyama), Gaziosmanpaşa Üniv. Fen-Edebiyat Fakültesi, Yayınları No: 7, Tokat.