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INVESTIGATION OF THE DYEING PROPERTIES OF *Sideritis trojana ehrend* IN THE FABRICS THAT PRE-TREATED WITH WILLOW EXTRACT

Adem Önal[a] <adem.onal@gop.edu.tr>
Nil Acar[a] <*nilacar88@hotmail.com*>
Ferda Eser[b] <ferda.kavak@gop.edu.tr>
Uğur Cakır[c] <ugur.cakir@gop.edu.tr>

[a]*Gaziosmanpasa Unıversity, Natural Dyes Application and Research Center, Tokat, Turkey*
[b]*Gaziosmanpasa Unıversity, Department of Chemistry, Art and Science Faculty, Tokat, Turkey*
[c]*Gaziosmanpasa University, Erbaa Vocational High School, Department of Textile, Tokat, Turkey*

Abstract - In this study, the usage of Sarıkız herb tea (*Sideritis trojana ehrend)* was examined in terms of textile dyeing. For this purpose, cotton and wool fabrics were treated with willow extract for 24 h, at room temperature. The pretreated samples were dyed with *S. trojana* extract in the presence of three mordants including alum ($AlK(SO_4)_2 \cdot 12H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and using three mordanting methods (pre-mordanting, meta-mordanting and post-mordanting). Fastness properties (rubbing and light) were also determined. Generally, high fastness values were obtained. The color strength values of the wool fabrics were found to be higher than that of cotton fabrics. It is concluded that, *S. trojana ehrend* has affinity to the wool fabrics, and can be used as an alternative source in the presence of willow extract in natural dyeing.

Keywords - *Sideritis trojana ehrend, mordant, dyeing, fastness, wool, cotton*

1. Introduction

Natural coloring agents have been used since beginning of the time to color wool, silk, cotton and leather [1]. Natural dyes are widely used in textile dyeing due to their ecofriendly properties [2-4]. In addition, those pigments are anti-allergic and harmless to human and environment [5]. Natural dyes and pigments can be considered as an important alternative to the harmful synthetic dyes and generally they give soft and lustrous pastel colors. It is known that, synthetic dyes are synthesized from petrochemical sources that resulted chemical substances which are hazardous to human health and environment. Thus, there is a growing interest to natural dyes due to their biodegradable, less toxic and eco-friendly properties in recent years [6, 7]. Therefore, necessity of lowered cost natural dyeing for production was canalized people to use of dyestuff containing wastes such as food, beverage and aerial parts of the plants [8].

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To color the fiber, generally different parts of plants have been used including bark, flowers, leaves and seed. Although bark of the plant is rich with coloring agent, usage of the bark could kill the plant. Bark is preferred in dyeing because of its high percentage of coloring agent. Therefore, leaves, flowers and seeds are used for the extraction of the dyestuff from the plant. The leaves of the plant provide abundant and easy availability source for dyeing industry [9].

S. trojana ehrend belongs to Labiatae family and grows in Kaz mountains in Turkey. It is called as Sarıkız herb tea. There are 45 genus, 546 type and 730 taxa in Turkey. [10]
S. trojana exhibits antioxidant and antimicrobial activity [11] and has been using as a natural tea.

Best to our knowledge, there is no study on the dyeing properties of *S. trojana*. It is reported that, the plant contains o- methyl- izo skultelarin-7-o-[(6- o- acetyl- Beta-allopyrazonyl-(1,2)]- beta- glucopiyranoside as coloring agent (Figure 1) [12].

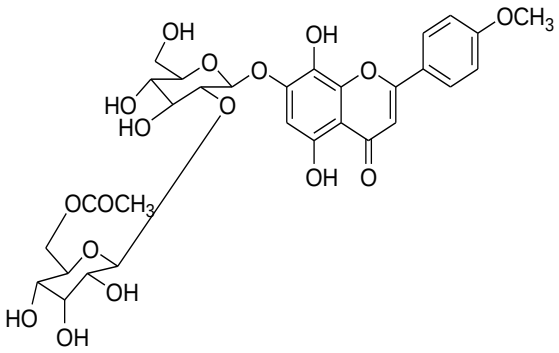

Figure.1. *O*- methyl- izo skultelarin-7-*o*-[(6- *o*- acetyl- *β*-allopyrazonyl-(1,2)]- *β*-glucopiyranoside

The dyestuff has oxochorome groups (carbonyl and hydroxide groups) which may be exhibited good dyeing properties.

2. Experimental

Fabrics

Scoured, bleached and mercerized plain weaved cotton fabric (240 g/m^2) and wool fabric (125 g/m^2) were purchased from Has Ozgen Textile Company (Tokat, Turkey).

Preparation of willow extract

Willow branches (1 kg) were soaked in distilled water (10 L) for 21 days at room temperature and then filtered. The filtrate was used in the pre-treatment processes.

Preparation of the mordant solutions and the dye-bath

To prepare wool and cotton samples for dyeing processes, the samples were treated with the water extract of willow, at room temperature for 24 h. The stem and the leaves of *S. tojana* were supplied from Plant Research Laboratory, Gaziosmanpasa University, in June, 2014.

The parts of the plant were dried and cleaned in order to remove the impurities. Soxhlet apparatus was used for the extraction of the plant. Plant material (100 g) was extracted with distilled water (1 L). Extraction was maintained at its boiling point, for 12 h. After the end of the period, the mixture was filtered and the clear solution was used as dye bath in the dyeing experiments.

Reagents and equipments

Analytically grade chemicals including alum ($AlK(SO_4)_2 \cdot 12H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) were supplied from Merck. Soxhlet apparatus was used for the extraction process. Premier Colorscan SS 6200A Spectrophotometer was used for the determination of CIELab values (L^*, a^*, b^*) and color strength (K/S) values. Kubelka-Munk equation was used for the expression of color strength values of the dyed samples as K/S values:

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

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

Fastness levels of the dyed fabrics were evaluated using rubbing (wet, dry) and light fastness tests and determined according to ISO 105-C06 and to CIS, respectively. For light fastness, dyed samples were exposure to bare sunlight for 200 h. After the end of the time, light fastness ratings of dyed samples were given on 1-8 grey scale. A 255 model crock-meter and Atlas Weather-ometer were used for the determination of rubbing and light fastness values, respectively. [13].

Dyeing procedures

Dyeing procedures of the wool and the cotton samples were carried out according to the dyeing diagram (Figure 2). The undyed materials were kept into willow extract for 24h, at room temperature before dyeing procedures. At the end of the time, the samples were rinsed with distilled water and dyed using pre-mordanting, meta-mordanting and post-mordanting methods.

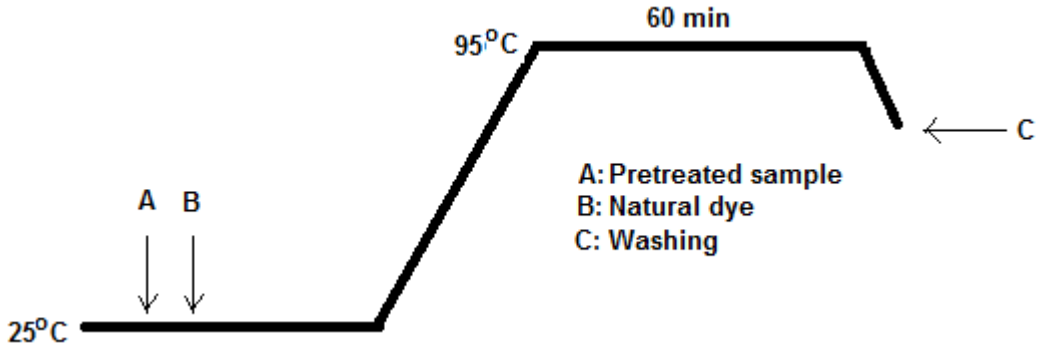

Figure 2. Dyeing diagram

Dyeing process was started at 25°C. Natural dye and the samples which were pretreated with willow extract were added and the temperature was increased to 95°C. Dyeing was continued

at the same temperature for 60 min. After the dyeing process, the dyed material was cooled and rinsed with distilled water [14].

Dyeing method

For pre-mordanting method, fabrics (pre-treated and unpretreated) were soaked into mordant solution (0.1 M, 100 mL) and heated for 30 min at 95ºC. Then, it was cooled and washed with distilled water. The fabric was then placed into the dye-bath solution (100 mL) and dyed at 95ºC for 1 h. At the end of the period, the dyed material was removed, rinsed with distilled water and dried.

In meta-mordanting method, both mordant (in solid form that is equal to 0.1 M mordant solution) and the dye residue was transferred to a conical flask and the fabric was poured into the mixture. Then the mixture was heated at 95ºC until 1 h. Then it was cooled and washed with distilled water, squeezed and finally it was dried.

For post-mordanting method, the non-colored material (1 g) was firstly treated with the dye solution for 1 h at 95ºC. Then the material was cooled, washed twice with distilled water and poured into 0.1 M mordant solution (100 mL). It was heated for 30 min. at 95ºC. After the end of the process, the dyed fabrics were rinsed with distilled water [15].

3. Results and Discussion

Proposed dyeing mechanism

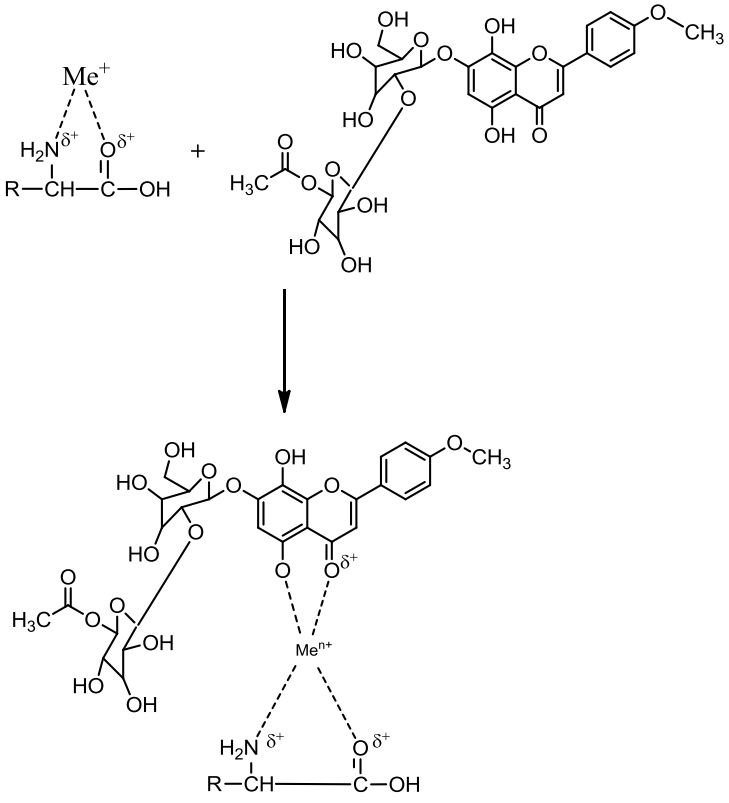

Figure 3. Proposed mordant-dye complex in the dyeing of wool fabrics

Wool structure contains both $–NH_2$ and –COOH groups. Therefore, it is expected that chemical interactions between *S. trojana* extract dye and the wool fabric occurred between –OH (hydroxyl) group of the dye molecule and oxygen and nitrogen atoms of the wool fabric via H-bonding (Figure 3).

The structure of mordant-dye complex that occurred in the dyeing of wool fabric with *S. trojana* extract can be considered as follows [15]:

Cotton consists of CH_2O- units. Due to its cellulosic structure, formation of complex is expected between CH_2O- groups of cellulose and metal cation via coordinate covalent bonding. The predicted structure is given below (Figure 4):

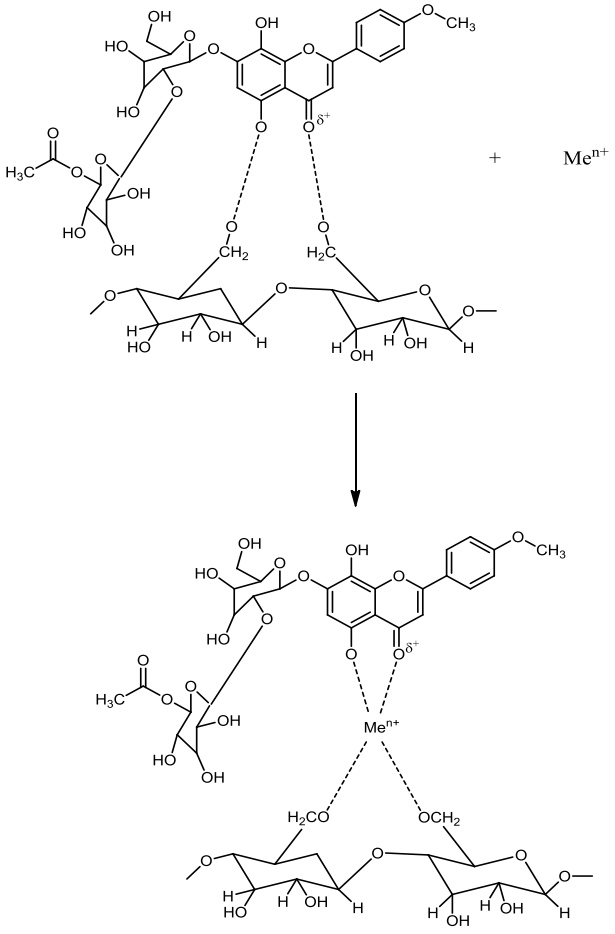

Figure 4. Proposed mordant-dye complex according to meta-mordanting method in the dyeing of cotton (Me^{n+}: mordant cation)

Fastness properties

Fastness values of the dyed fabrics are given in Table 1. Rubbing fastness of the dyed samples was determined in both dry and wet form. It is observed that rubbing fastness values were found higher in the dry form than in the wet form. Additionally, higher rubbing fastness rates were obtained with pre-mordanting method for cotton fabrics. The light fastness values of the dyed fabrics range between 3 and 7 i.e. moderate to excellent. There is no important difference between pH 4 and pH 8 in all mordanting methods and each three mordants in

terms of light fastness levels. Dyeing of wool and cotton fabrics in the presence of copper sulfate mordant exhibited higher light fastness values than the other mordants (Table 1).

Table 1. Light and rubbing fastness results for the dyed cotton and the wool samples

			Light fastness			Rubbing fastness					
						Dry			Wet		
			$CuSO_4$	$FeSO_4$	$AlK(SO_4)_2$	$CuSO_4$	$FeSO_4$	$AlK(SO_4)_2$	$CuSO_4$	$FeSO_4$	$AlK(SO_4)_2$
Pre-mord.	Cotton	pH:4	6	3	3	5	4	5	5	4	4/5
		pH:8	6	4	3	5	5	5	5	5	5
	Wool	pH:4	7	5	6	5	4	5	4/5	5	4
		pH:8	7	7	6	5	5	5	4/5	4/5	4/5
Meta-mord.	Cotton	pH:4	6	5	4	5	5	5	5	4/5	4/5
		pH:8	6	5	7	4/5	4	5	4	4/5	5
	Wool	pH:4	7	4	6	5	5	4/5	5	5	4/5
		pH:8	7	7	6	4	4/5	5	3/4	4/5	5
Post mord.	Cotton	pH:4	6	4	4	5	5	5	5	5	4/5
		pH:8	6	5	5	5	4/5	5	4/5	4/5	5
	Wool	pH:4	6	5	6	5	4	5	5	4/5	5
		pH:8	7	7	7	5	4	5	5	5	5

Determination of color strength and color coordinates

Table 2. The CIELab values for the dyed cotton samples

Dyeing method	mordant	Control samples (untreated and dyed with *S. trojana* extract)			Cotton samples (pre-treated with willow extract and dyed with *S. trojana* extract)		
		*L**	*a**	*b**	*L**	*a**	*b**
Pre-mord.	$CuSO_4$	71.7	4.4	37.7	64.5	7.5	26.2
	$FeSO_4$	67.7	6.7	23.1	69.3	4.4	20.3
	$AlK(SO_4)_2$	77.4	2.0	28.6	76.1	4.1	25.9
Meta-mord.	$CuSO_4$	71.9	2.8	27.8	65.5	5.1	26.5
	$FeSO_4$	55.1	8.3	25.0	55.1	4.1	16.4
	$AlK(SO_4)_2$	82.2	0.3	27.7	81.8	-2.1	16.2
Post-mord.	$CuSO_4$	78.1	-0.4	17.8	75.1	1.5	17.2
	$FeSO_4$	68.4	10.7	34.1	69.6	3.8	20.1
	$AlK(SO_4)_2$	86.6	-0.2	10.5	83.2	2.5	16.9

Evaluation of color parameters was performed using CIELab system. Results were given in Table 2 and Table 3, respectively. Lightness-darkness values of dyed fabrics symbolized with "*L*" and these values varied between 100 and 0, representing white to black; + values of *a** and *b** indicate redness and yellowness shade, respectively. Additionally, - values of *a** and *b** refer to greenness and blueness color tones, respectively. Lightness values of the dyed fabrics were found between 55-87 and 54-84, for cotton and wool fabrics, respectively. Darker color and color tones were obtained with pre-treatment processes in the dyeing of wool fabric. Cream and brown color and color tones were obtained in the dyeing of cotton fabrics. Cream and yellow color and color shades were achieved in the dyeing of wool fabrics. Additionally, it is observed that different mordants are not only affected the hue of the color but also color strength of the dyed fabrics.

Table 3. The CIELab values for the dyed wool samples

Dyeing method	mordant	Control samples (untreated and dyed with *S. trojana* extract)			Wool samples (pre-treated with willow extract and dyed with *S. trojana* extract)		
		*L**	*a**	*b**	*L**	*a**	*b**
Pre-mord.	$CuSO_4$	69.9	2.9	34.7	59.7	5.4	30.0
	$FeSO_4$	83.7	-0.6	9.3	54.4	2.9	14.2
	$AlK(SO_4)_2$	79.9	0.4	22.0	69.4	4.5	25.6
Meta-mord.	$CuSO_4$	71.6	1.3	23.7	71.9	4.7	28.4
	$FeSO_4$	67.1	3.6	16.2	55.9	2.9	13.8
	$AlK(SO_4)_2$	79.8	-0.6	13.4	65.8	3.9	28.4
Post-mord.	$CuSO_4$	79.9	-3.7	11.9	69.6	1.7	17.8
	$FeSO_4$	68.9	10.1	33.0	60.5	7.0	25.6
	$AlK(SO_4)_2$	63.0	5.9	20.5	79.7	-0.1	13.0

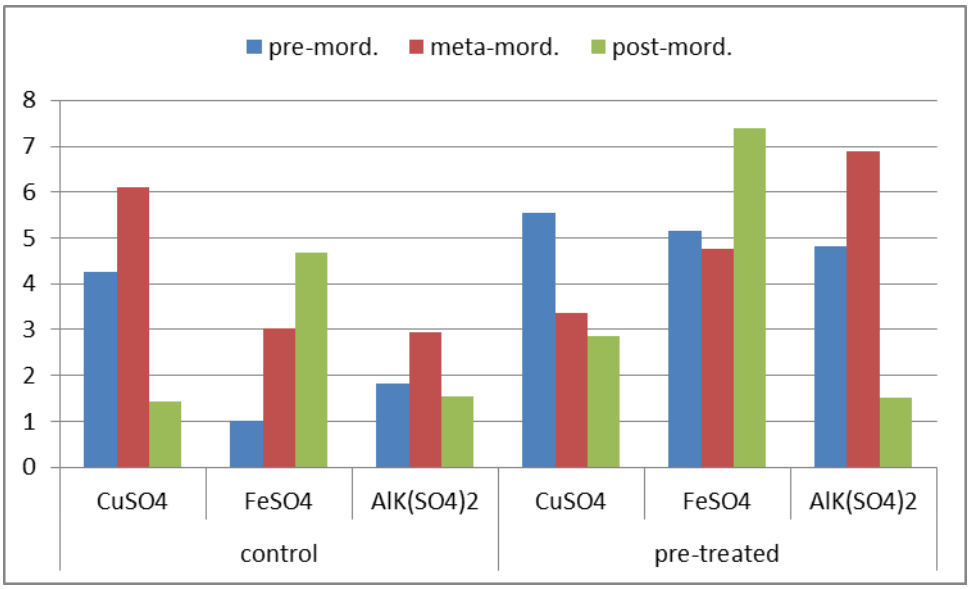

Figure 5. K/S values of the dyed wool samples

Influence of various mordants such as alum, ferrous sulfate and copper sulfate was investigated for wool and cotton fabrics (Figure 5 and Figure 6). The highest K/S value (8.5) was obtained in the presence of ferrous sulfate mordant for cotton fabric (Figure 5). The results also indicated that pre-treatment agent (willow extract) generally helps to increase the color strength of the dyed samples. It is observed that K/S values depend on the mordant type, dyeing method and pre-treatment process.

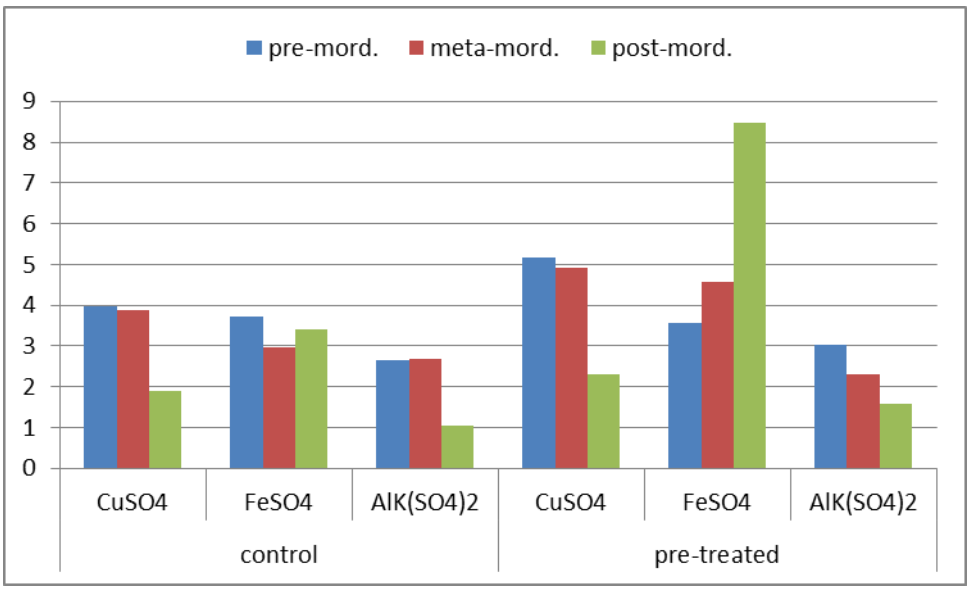

Figure 6. K/S values of the dyed cotton samples

4. Conclusions

The way to improve the quality of the dyeing is to use natural mordants such as willow extract. This extract plays an important role on the brightness of the colors. Willow extract contains salicylic acid and other tannins [16]. These components extend the pores of the fiber micelles during the pre-treatment process, and so, it facilitates to increase the affinity of the dye to the keratin. Therefore, high color fastness values were obtained in the presence of willow extract.

As a result, fastness values of the wool samples are found higher than that of cotton samples. Yellow, brown, cream color and color tones are obtained from the dyeing of the fabrics with *S. trojana* extract in the presence of willow extract pre-treatment. High fastness values are obtained for three mordanting methods with all mordants that used in the study.

Consequently, *S. trojana* is a proper natural source for dyeing of wool and cotton fabrics. Therefore, this plant may be used as a natural source in the production of the carpets and kilims.

References

[1] Samanta A.K., P.Agarwal: Application of natural dyes on textiles, Indian Journal of Fibre & Textile Research 34 (2009.) 384-399
[2] Kamat S.Y., D.V.Alat: Natural dyes-a dying craft?, The Indian Textile Journal 3 (1990.) 6, 66-70
[3] B.Glover: Are natural colors good for your health- are synthetic ones better, Textile Chemist and Colorist 27 (1995.) 4, 17-20
[4] Smith R., S.Wagner: Dyes and the environmental is natural better?, American Dyestuff Reporter 80 (1991.) 9, 32-34
[5] Moiz A., Ahmed M.A., Kausar N., Ahmed K., M. Sohail: Study the effect of metal ion on wool fabric dyeing with tea as natural dye, Journal of Saudi Chemical Society 14 (2010) 1, 69-76
[6] Mongkholrattanasit, R., Kryštůfek, J., Wiener, J. Dyeing and fastness properties of natural dyes extracted from Ecalyptus leaves using padding techniques. *Fiber Polym*, 11 (2010) 346.
[7] Erkurt, E., Ünyayar, A., Kumbur, H. Decolorization of synthetic dyes by White rot fungi, involving laccase enzyme in the process. *Process Biochem*, 42 (2007) 1429.
[8] Erdem İşmal, Ö., Yildirim, L., Ozdogan, E. Use of almond shell extracts plus biomordants as effective textile dye. Journal of Cleaner Poduction, 70, (2014) 61-67.
[9] Raja A.S.M, G.Thilagavathi: Dyes from the leaves of deciduous plants with a igh tannin content for wool, Coloration Technology 124 (2008.) 5, 285-289
[10] Topçu, G., Barla, A., Gören, A.C., Bilsel, G., Bilsel, M, Tümen, G., "Analysis of the Essential Oil Composition of *Sideritis albiflora* Using Direct Thermal Desorption and Headspace GC-MS Techniques", *Turk. J. Chem*., 29, (2005), 525-529.
[11] Atalay, B., Diken, M.E., Dogan, S. Biological activities of some Lamiaceae species. FEBS Journal, 281, (2014), 65-783.
[12] Şahin, F.P. *Bazı Siseritis* L. Türleri üzerinde Farmasötik botanik ve Fitokimyasal çalışmalar. Ph.D Thesis, Hacettepe University, Sağlık Bimleri Enstitüsü. 2003 Ankara Turkey.
[13] Wolfe, K.L., R.H. Liu: Cellular antioxidant activity (CAA) assay for assessing antioxidants, foods, and dietary supplements, Journal of Agricultural and Food Chemistry 55 (2007) 22, 8896-8907.
[14] Vankar, P.S., Shanker, R., Wijaypala, S. Dyeing of cotton, wool, silk with extract of Allium cepa. Pigm. Resin Technol, 38, 242 (2009).
[15] A. Önal. Doğal Boyar maddeler, Gaziosmanpaşa Üniversitesi, Fen Edebiyat Fakültesi Yayınları. Yayın no:07 Tokat-Turkey.
[16] Kavak, F., Önal A., Seyfikli D. Usage of willow extract as mordant agent and dyeing of wooden and fiber samples with onion (*Allium cepa*) Shell. Rasayan J of Chem. 3, 1 (2010).