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Original Article**

INVESTIGATION OF USAGE IN DYEING OF TEXTILE OF POMEGRANATE (*PUNICA GRANATUM*) JUICE

Huseyin Efil^{1,a} <efilkimya@gmail.com>
Adem Önal^b <adem.onal@gop.edu.tr>
Ferda Eser^c <ferda.kavak@gop.edu.tr>
Uğur Çakır^d <ugur.cakir@gop.edu.tr>

^aScience school, Amasya, Turkey

^bNatural Dyes Application and Research Center, Gaziosmanpasa University, Tokat, Turkey

^cDepartment of Chemistry, Gaziosmanpasa University, Tokat, Turkey

^dErbaa Vocational High School, Gaziosmanpasa University, Tokat, Turkey.

Abstract - In this study, the dyeing properties of pomegranate (*Punica granatum*) juice were investigated. Its juice was obtained by extraction (cool press) to obtain the dyebath. Aluminium sulphate $Al_2(SO_4)_3$, Iron (II) sulphate ($FeSO_4$), Copper (II) sulphate ($CuSO_4$) salts and (NH_3 + calcium oxalate + urea) solution 3% g/v were used as mordants for mordanting of wool, viscose and linen fabrics. All fabrics were dyed at different pH values (4 and 7) using together mordanting, pre-mordanting and last mordanting methods). Consequently, 11 wool, 11 viscose and 11 linen fabric samples were dyed at two different pH degree (4 and 7). Color codes, fastness measurements and dyeing conditions were determined.

Keywords - Pomegranate, mordant, dyes, wool, viscose, linen

1. Introduction

Punica granatum belong to *Lythraceae* family which has slightly sour and some slightly sweet [1].

100 mL of *Punica granatum* juice meets 16% need of human in daily. This juice is rich respect to antioxidant called as pro-anthocyanidine [2]. Antioxidants have an most important in the pharmacological studies. Skin of *Punica granatum* fruit has tannin (between 30% - 28%) and is used in leather industry. In addition, fruit skin has also been using in dyeing of fabric, leather and making the ink [3]. In the skin of *Punica granatum* has tannic acid, parinaric acid, palmitic acid, stearic acid, oleic acid and linoleic acid [4-5].

Figure 1 is shown the chemical structure of tannin (tannic acid).

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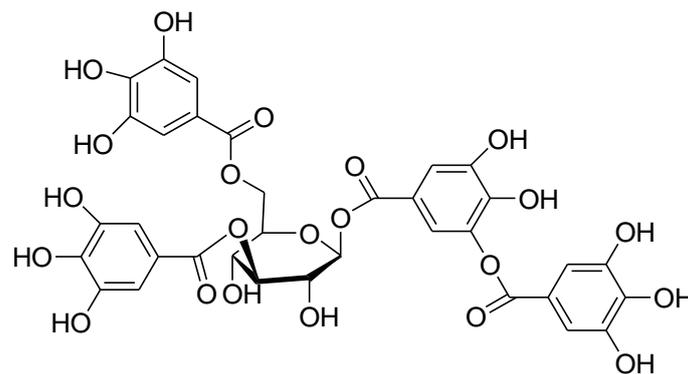


Figure 1. Molecule structure of tannic acid (Ferrell, Thorington and Richard, 2006).

Furthermore, the fruit of *Punica granatum* has been using to extend the life of containers.[6]. Its juice has B and K vitamines that is used in diet product [7]. In addition, its seeds are source of diet fiber [8]. Because of the high antioxidant values of skin, it is used the main source of pro-antocyanidine and kersetol either pharmaceuticals or other areas studies [9].

According to the literature surveys there is no enough research in dyeing of fabrics that using the fruit juice of *Punica granatum*. That is why, we aimed to investigate the dyeing properties or capacity of *Punica granatum* juice in dyeing of wool, linen and viscose fabric using some dyeing methods and mordant that described in experimental section.

2. Experimental

2.1. Reagents and equipments

All chemicals and mordants ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) used in this work, were purchased from Merck. Distilled water was used for all steps. *Punica granatum* juice was obtained mechanically (cool press). Color codes were determined by using Pantone Color Guide. The wash-, crock- (wet, dry) and light fastness of all dyed samples were carried out according to ISO 105-C06 and to CIS, respectively, and fastness levels were determined by Atlas Weather-ometer, a Launder-ometer and a 255 model crock-meter, respectively [10].

2.2. Fabrics

Wool and cotton and fabrics were chosen as the fabric types to be studied. The characteristics of the fabrics are shown in Table 1.

Table 1 - Characteristics of the used fabrics

Fibre type	Mass per unit area (g/m^2)	Surface type	Fabric density
Wool	180	weaved	Weft:28, warp: 30
Linen	150	knitted	Course:18, Wale:13
Viscose	140	knitted	Course:15, Wale:12

2.3. Natural dye extraction and mordanting

The juice of *Punica granatum* fruit used as a natural dye source in the present study; these were supplied from Tokat bazaar (Turkey). The raw materials was pressed and diluted with distilled water before using. (the rate of natural dye source to distilled water was 1:1) The colored solutions were filtered and used in the dyeing process.

The metal salts iron sulfate , copper sulfate and aluminum sulfate were used as mordants; the dyeing procedure of the textile fabrics is pre-mordanting (T1), together mordanting (T2), and after-mordanting (T3). The experimental plan is listed in Table 2.

Table 2 - Experimental plan

Treatment type (T)	Mordant	Dyeing pH	Wool	Viscose	Linen
Pre-mordanting (T1)	Iron sulphate	4-7	+	+	+
	Copper "	4-7	+	+	+
	Aluminium "	4-7	+	+	+
Together-mordanting (T2)	Iron sulphate	4-7	+	+	+
	Copper "	4-7	+	+	+
	Aluminium "	4-7	+	+	+
Last-mordanting (T3)	Iron sulphate	4-7	+	+	+
	Copper "	4-7	+	+	+
	Aluminium "	4-7	+	+	+

3. Dyeing

Three dyeing methods including pre-mordanting (T1), together-mordanting (T2) and last-mordanting (T3) were applied to the wool, linen and viscose fabrics.

In the T1 procedure, fabric was initially dipped into 0.1 M mordant solution (100 ml) and then resulting solution was heated for 1 h at 90°C. Then it was cooled and rinsed with double distilled water and then poured into the dye-bath solution (100 ml). Then further dyeing was carried out at 90°C for 1 h. Finally, the material after dyeing was removed, washed with double distilled water and finally dried at room temperature [11].

In the T2 procedure, both mordant (in solid form that is equal to 0.1 M mordant solution) and the dye residue was transferred in a conical flask and the sample was poured into the mixture. Then the mixture was heated at 90°C until 1 h. Then it was cooled and washed with distilled water, squeezed and finally it was dried [11].

In the T3 method, the non-colored material (1 g) was firstly given treatment with the dye solution for 1 h at 90°C. Then sample was cooled, washed twice with distilled water and poured into 0.1 M mordant solution (100 ml). It was heated for 1 h at 90°C and then, After dyeing, the washing of the dyed fabrics were carried out in cold, boiled, boiled with non-ionic detergents and cold rinsing[11].

3.1. Dyeing mechanism of the fabrics

Metal complex formation has been an outstanding property of textile dyeing from ancient times, since it was known that the technical performance, including fastness such as washing and light, of many natural dyes could be improved by treatment with definite metal ions, a method known as mordanting [12].

Al (III) and Fe (II) ions have a coordination number of six and they are able to make complexes in the octahedral configuration. So, in the proposed mechanisms which are given in Figure 2 the unoccupied sites of the metal ions may be occupied with H₂O molecules, oxochrome groups of the dyestuff or free amino and carboxyl groups of wool fabric [12]. Proposed mechanisms for dyeing of wool and cotton fiber with the extract of apple leaves are given in Figure2 and Figure 3.

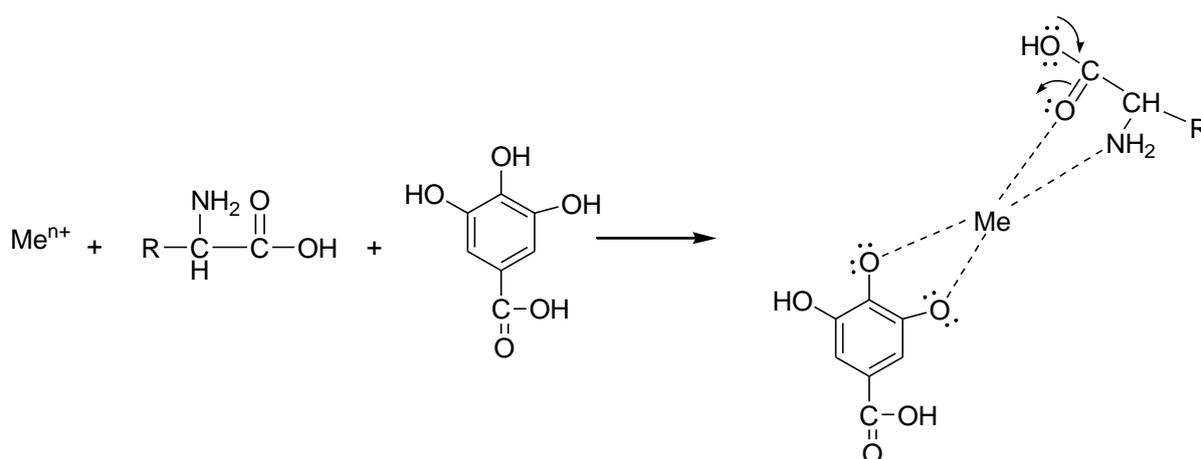


Figure 2. Proposed dyeing mechanism of wool (together mordanting.)

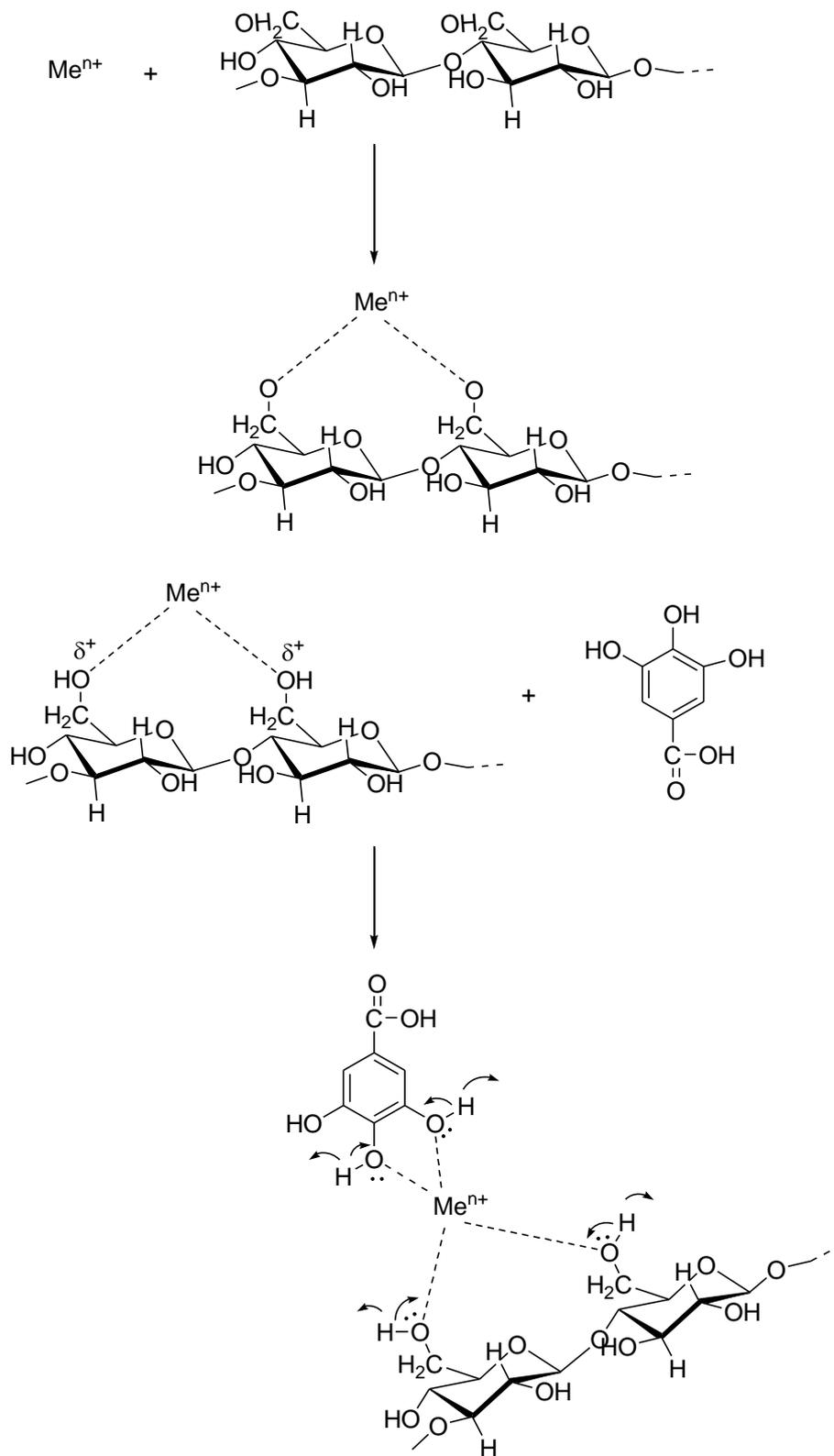


Figure 3. Proposed dyeing mechanism of linen (together mordanting.)

3.2 .Fastness results for viscose fabrics

Pre-mordanting, together mordanting and last – mordanting fastness values are given in table 1, table 2 and table 3, respectively.

Table 1. Fastness results of viscose fabrics with FeSO₄ mordant.

FeSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	3	4/5	5	7806-Y13R
	7	4/5	2	4/5	6	57005-Y20R
T2	4	3/4	4	4/5	6	6005-Y10R
	7	3/4	4	4/5	4	0505-Y0RS
T3	4	4/5	4	4/5	3	6005-Y10R
	7	4/5	4	4/5	2	6005-Y10R
Unmordant	4	1/2	3/4	4/5	5	0621-Y
	7	4/5	2	4/5	5	0621-Y
Urea+NH ₃ +Oxalate	4	1/2	3/4	4/5	4	0631-Y03R
	7	1/2	4/5	4/5	6	0505-Y05R

Table 2. Fastness results of viscose fabrics with AlK(SO₄)₂ mordant

AlK(SO ₄) ₂	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	4/5	4/5	1	S-1020-Y
	7	3/4	3/4	3/4	6	S-1030-Y
T2	4	4/5	4/5	4/5	6	S-1030-Y
	7	4/5	4/5	3/4	6	S-1020-Y
T3	4	4/5	4/5	4/5	2	1008-Y
	7	4/5	4/5	4/5	4	1008-Y

Table 3. Fastness results of viscose fabrics with CuSO₄ mordant

CuSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	3	4/5	6	S-2030-Y
	7	3/4	3	4/5	5	2894-Y32R
T2	4	4/5	4	4/5	6	6005-Y30S
	7	3/4	4	4/5	6	1952-Y30S
T3	4	4/5	4	4/5	6	3121-Y29R
	7	4/5	3/4	4/5	6	2013-Y32R

3.3. Fastness results for linen fabrics

Pre-mordanting, together mordanting and last – mordanting fastness values are given in table 4, table 5 and table 6, respectively.

Table 4. Fastness results for linen with FeSO₄ mordant

FeSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	3	4/5	5	7806-Y13R
	7	4/5	2	4/5	6	57005-Y20R
T2	4	3/4	4	4/5	6	6005-Y10R
	7	3/4	4	4/5	5	0505-Y0RS
T3	4	4/5	4	4/5	3	5005-Y10R
	7	4/5	4	4/5	6	6005-Y10R
Unmordant	4	1/2	3/4	4/5	5	0631-Y03R
	7	1/2	3	4/5	5	0539-G99Y
Urea+NH ₃ +Oxalate	4	1/2	3/4	4/5	4	0621-Y
	7	1/2	4/5	4/5	6	0611-G95Y

Table 5. Fastness results for linen with AlK(SO₄)₂ mordant

AlK(SO ₄) ₂	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	4/5	4/5	1	S-1020-Y
	7	3/4	3/4	4/5	5	S-1030-Y
T2	4	4/5	4/5	4/5	6	S-1030-Y
	7	4/5	3/4	4/5	6	S-1020-Y
T3	4	4/5	4/5	4/5	2	1008-Y
	7	4/5	4/5	4/5	4	1008-Y

Table 6. Fastness results for linen with CuSO₄ Mordant

CuSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	4/5	3	4/5	6	S-2030-Y
	7	3/4	3	4/5	6	2894-Y32R
T2	4	4/5	5	4/5	6	6005-Y10R
	7	3/4	4/5	4/5	6	1952-Y30S
T3	4	4/5	4	4/5	6	2013-Y32R
	7	4/5	4/5	4/5	6	2013-Y32R

3.4. Fastness results for wool fabrics

Pre-mordanting, together mordanting and last – mordanting fastness values are given in table 7, table 8 and table 9, respectively.

Table 7. Fastness results of wool fabrics with FeSO₄ mordant.

FeSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	1/2	1/2	1/2	1	S-5020
	7	1/2	1/2	1/2	4	7511-Y99R
T2	4	1/2	1/2	1/2	1	6128R
	7	1/2	1/2	1/2	1	4837-Y98R
T3	4	1/2	1/2	1/2	2	S-2030-Y90R
	7	1/2	1/2	1/2	3	S-2030-Y90R
Unmordant	4	1/2	1/2	1/2	5	1719-Y90R
	7	1/2	1/2	1/2	4	1719-Y90R
Urea+NH ₃ +Oxalate	4	1/2	1/2	1/2	5	1719-Y90R
	7	1/2	1/2	1/2	5	1719-Y90R

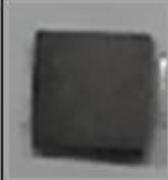
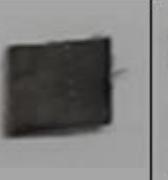
Table 8. Fastness results of wool fabrics with AlK(SO₄)₂ mordant

AlK(SO ₄) ₂	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	1/2	1/2	1/2	1	4837-Y98R
	7	1/2	1/2	1/2	5	7311-Y99R
T2	4	1/2	1/2	1/2	3	S-3040-Y20R
	7	1/2	1/2	1/2	6	S-3040-Y20R
T3	4	1/2	1/2	1/2	3	S-3010-Y20R
	7	1/2	1/2	1/2	4	S-3010-Y20R

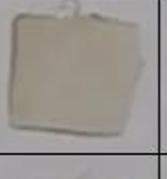
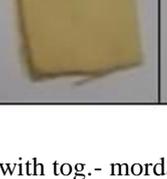
Table 9. Fastness results of wool fabrics with CuSO₄ mordant

CuSO ₄	pH	Rubbing			Light	Color Code
		Washing	Wet	Dry		
T1	4	1/2	1/2	1/2	1	S-3040-Y0R
	7	1/2	1/2	1/2	5	S-3040-Y0R
T2	4	1/2	1/2	1/2	3	S-3446-Y19R
	7	1/2	1/2	1/2	6	S-3446-Y19R
T3	4	1/2	1/2	1/2	3	1619-Y34R
	7	1/2	1/2	1/2	4	1619-Y34R

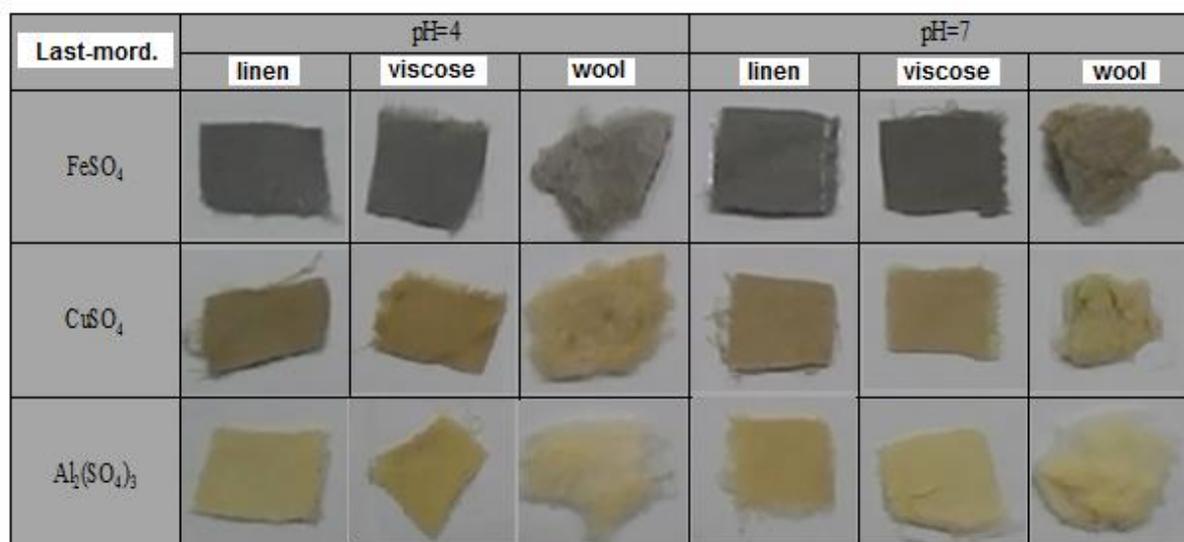
Dyed fabrics in this research are given in Picture 1, 2 and Picture 3, (urea+ammonia+oxalate) and unmordanting Picture 4, respectively.

Pre-mord.	pH=4			pH=7		
	linen	viscose	wool	linen	viscose	wool
FeSO ₄						
CuSO ₄						
Al ₂ (SO ₄) ₃						

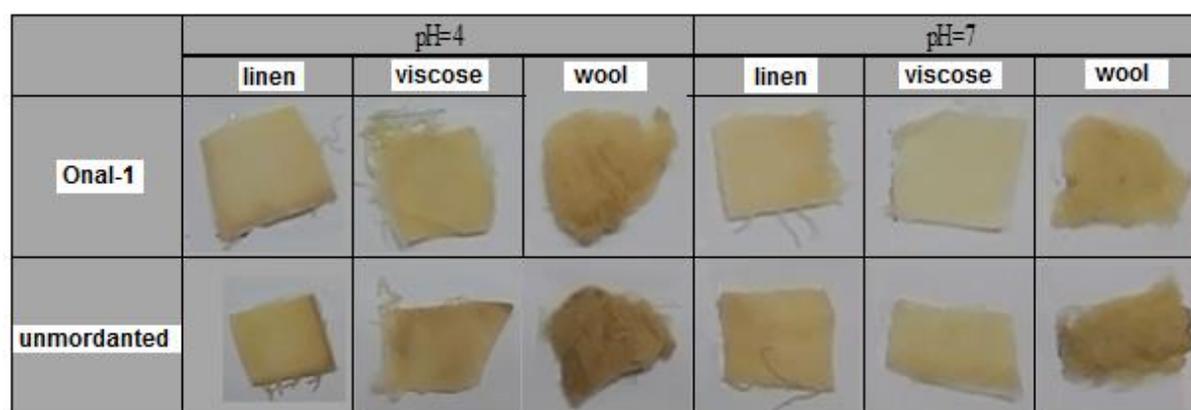
Picture 1. Dyed samples (linen, viscose, wool) with pre- mordanting method

Tog.-mord.	pH=4			pH=7		
	linen	viscose	wool	linen	viscose	wool
FeSO ₄						
CuSO ₄						
Al ₂ (SO ₄) ₃						

Picture 2. Dyed samples (linen, viscose, wool) with tog.- mordanting method



Picture 3. Dyed samples (linen, viscon, wool) with last mordanting method



Picture 4. Dyed samples with Önal-1 mordant and unmordanting method (wool,linen,viscose)

Dyed samples obtained using the FeSO₄ for each three methods are darker from each other mordant (AlK(SO₄)₂ and CuSO₄). In addition, the lowest fastness values are obtained for wool. High fastness values have been obtained pH 4, in generally. Pre- mordanting method is very proper for each three samples (wool, linen, viscose) in dyeing.

The occurred dyeing using (Urea+NH₃+CaC₂O₄) solution has higher fastness values at pH 4 and pH 7, and darker colors were obtained than other mordants. We say that this solution has great importance each of pH values (pH 4 and pH 7). In here, NH₃ opens micelles of fabric. Urea is increases the solubility of dyestuff, and oxalate is makes stable of the complex molecule formed between dye, mordant and fabric [13-14].

According to the results, light fastness values is highest for CuSO₄, in generally. However, there is no considerable difference for light fastness at pH 4 and 7.

Good light fastness results were obtained at pH 7. However, there is no any important difference for each of pH values (4 and 7).

4. Conclusions

In this study, the pomegranate juice was used for dyeing wool, viscose and linen fabrics. Natural dye solution was extracted and applied to the selected fabrics using pre, together, and last mordanting techniques. The dyeing results of the study showed that pomegranate juice can be used as a natural dyestuff source in dyeing of wool, linen and viscose fabrics with suitable mordants.

References

- [1] LaRue, J., H. (1980). *Growing Pomegranates in California*. California Agriculture and Natural Resources.
- [2] Özkal, N., Dinç, S. (1993). *Nar (Punica granatum L.) Meyva Kabuklarının Eczacılık Yönünden Değerlendirilmesi*. Ankara Eczacılık Fakültesi Dergisi.22(1-2)
- [3] Özgirgin, M., (1986). *Boyarmadde Kimyası*, cilt no:68, s. 72-75, Milli Eğitim Basımevi-İstanbul.
- [4] Gunstone, F., D., Harwood, J., L., Dijkstra A. J. (2007). *The Lipid Handbook with Cd-Rom*. 3rd ed. Boca Raton: CRC Press. ISBN 0849396883 | ISBN 978-0849396885.
- [5] Alfred, T. (2000). *Fats and Fatty Oils*. Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a10_173. ISBN 3-527-30673-0.
- [6] O'Grady, L., Sigge, G., Calep, O.J., Opara., L.(2014). Bioactive compounds and quality attributes of pomegranate arils(*Punica granatums L.*) processed after long – term storage. Department of Food Science, Faculty of Agri Sciences, Stellenbosch University, South Africa.
- [7] Jindal, K.,Sharma, R., C.(2004).Recent trendsin horticulture in the Himalayas. Indus Publishing. ISBN 81-7387-162-0.
- [8] Asme (2004).Drilling fluids processing handbook. Gulf Professional publishing is an imprint of Elsevier 30 Corporate Drive, Suite 400, Burlington, MA 01803,USA. Linacre House, Jordan Hill, Oxford, UK.
- [9] Karaca, E.,(2011). Nar suyu konsantresi üretiminde uygulanan bazı işlemlerin fenolik bileşenler üzerinde etkisi. Çukurova Üniversitesi Fen Bilimleri Enstitüsü Dergisi. 9-11.
- [10] Schubert,S., Lansky E., Neeman, I.(1999).Antioxidant and eicosanoid enzyme inhibition properties of pomegranate seed oil and fermented juice flavonoids. Journal of Ethnopharmacology, 66, (1), 11-17.
- [11] Onal, A. Extraction of dyestuff from onion (*Allium cepa L.*) and its application in the dyeing of wool, feathered-leather and cotton, Turkish Journal of Chemistry 20 (1996.) 3, 194-203
- [12] Raja A.S.M, G.Thilagavathi: Dyes from the leaves of deciduous plants with a high tannin content for wool, Coloration Technology 124 (2008.) 5, 285-289
- [13] Tutak M., H.Benli: Colour and fastness of fabrics dyed with wallnut (*Juglans regia L.*) base natural dyes, *Asian Journal of Chemistry* 23 (2011.) 2, 566-568
- [14] Bhattacharya S.D., A.K.Shah: Metal ion effect on dyeing of wool fabric with catechu, *Coloration Technology* 116 (2000.) 1, 10-12