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Woolen Fabric Dyeing with *Punica granatum* L. Rind by Using Different Mordants

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In Turkey, there exist about 150 dye plant species that could be used in dyeing. However, these plants are not sufficiently utilized in field of cultivation. Through extension of these plants cultivation in agriculture, required raw materials in vegetable dyeing could be met. Hand woven carpets and other products dyed with dye plants are important income from domestic and foreign tourism sources. The aim of the study was to determine dyeing properties of quercetin, which is extracted from *Punica granatum* L. rind, using different mordants and dyeing methods on wool fabrics. The effect of mixture of the tannic acid and some selected metal salts were investigated in six difference dyeing methods by using buffer solutions at pH 4 for 1 h at 98-100 ºC with closed bath dyeing technique. The colour coordinate of dyed samples were found to lie in the yellow-brown quadrant of the colour space diagram. Colour differences in CIE L*a*b* unit, optimum mordant, dyeing methods and K/S rates of dyed wool fabrics were determined. In this study, good lightfastness (3-8), rubbing fastness (4-5) approximately and antibacterial fibers were obtained.

Key Words: *Punica granatum* L., Quercetin, Tannic acid, Mordant salts, Wool fabric.

INTRODUCTION

Together with the development of technology and production of synthetic dyes, natural dyes started to lose their importance gradually. However, natural dyes, that have been brought to the agenda in recent years once again, started to be used in many fields again[1].

There are *ca.* 150 species of plants that could be used as vegetable dye source in Turkey[2]. The extension of the agriculture of these plants will not only provide economic revenue for producers, but also contribute to the development of handicrafts, provide many positive advantages and will not harm the environment, compared to synthetic dyestuffs.

Today, environment friendly products are on the agenda in the world. As well as harming the natural environment, fabric dyes made of synthetic dyestuffs could also contain unhealthy carcinogenic properties. Researchers tend towards natural dyes as an alternative for that. The use of natural colours increasingly spreads on a large area, such as textile, food, home textile and pharmaceutical industry[3].

As well as being seen in almost every region of Turkey, *Punica granatum* L. (Fig. 1) grows primarily in the Aegean, Mediterranean and Southeastern Anatolia regions. *Punica granatum* L. is very rich in terms of iron, potassium and especially vitamin C, was discussed in our study for the purpose of evaluating its waste rinds in the food industry. The rich tannin that exists in the *Punica granatum* L. rind is intensively used in leather processing industry, rinse of juices and prevention of zinc poisonings. Additionally, *Punica granatum* L. rind and flowers are used in the production of dyes and inks[4].

Fig. 1. Granatum plant and *Punica granatum* L. rind

Polyphenolic compounds (*e.g.*, quercetin and tannins) that exist in the *Punica granatum* L. rind enable it to be used in dyeing. The studies performed with *Punica granatum* L. rind reported in literature, was observed that the rinds were largely used in wool, silk, polyester dyeing and as a dyeing material in hair dyes[4-7] and also as a natural mordant. In the study, it was observed that when natural mordants that are extracted from some barks, mango leaves and *Punica granatum* L. rind were used, washing and rub fastness increased in small quantities; colour fastness and light fastness escalated in a noticeable way[8].

In dyeings performed with the *Punica granatum* L. rind extraction, generally different metal salts were used as mordant together with the pre-, together- and last- mordanting methods. However, a study in which tannic acid and metal salts are used collectively and is performed in accordance with the given methods has not been encountered.

Examining the studies in which tannic acid (Fig. 2) was used as mordant and which was performed in an attempt to dye different materials; it was observed that fibres which are extremely sensitive to washing are obtained when tannic acid is used together with metal salts[9], it reduces worms and other allergens on the carpets at a rate of over 64 %[10], gains an anti-bacterial property to silk fibres[11]. It was observed in another study that it has 100 % bacterial destruction property. It also gains a high light and washing fastness to the fabric[12].

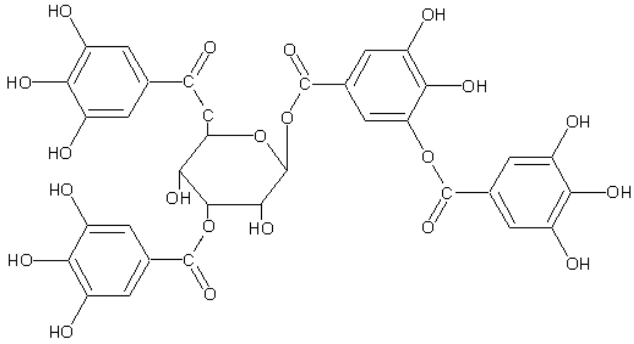


Fig. 2. Molecular structure of tannic acid

It is indicated in another study that, cotton fabrics gain a fine colour fastness and antiallergic and antibacterial properties when they are first treated with tannic acid and mordant salt and then with the dye extracted from meadow[13]. Kaimori and Sugimoto obtained a faint but durable colour when they treated the wool fabric firstly with tannic acid and aluminum sulphate and then with Alizarin Fast Blue ERL, at 100 ºC for 15 min[14].

The fact that tannic acid is known to be effective upon the mordant salts to increase their strength to be attached to the wool fabric and removal of allergens has made us head towards wool fabric dyeing with the method of mordanting with tannic acid[15].

Quercetin (Fig. 3) is one of the most commonly known flavonoids in the nature. In a study given in literature, it was indicated that the quercetin extracted from the mixture of bark containing onion and cone could be used as food colouring[16]. Different methods were used for the quantity determination of quercetin in various materials[17].

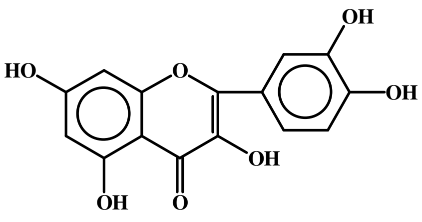


Fig. 3. Chemical structure of quercetin

In this study, the determination of quercetin on the *Punica granatum* L. rind was performed through using the derivative spectrophotometric method. It is indicated in literature that quercetin is a perfect chelating agent and forms a complex together with metal ions, such as Al^{3+}, Cd^{2+}, Mg^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+} and Ag^{+}. In literature, the antioxidant properties of the complexes formed by quercetin together with iron, aluminum, zinc and copper were studied[4]. The salts containing these ions were selected as mordants in the dyeing works that were implemented.

Sixty pieces of wool fabrics were dyed by means of using the quercetin extracted from the *Punica granatum* rind and the mordant salts of $Al(NO_3)_3\cdot 9H_2O$, $CdCl_2\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $Pb(CH_3COO)_2\cdot 3H_2O$, $Cu(CH_3COO)_2\cdot H_2O$, K_2CrO_4, $K_2Cr_2O_7$, $FeCl_3\cdot 6H_2O$, Ag_2SO_4 and $KAl(SO_4)_2\cdot 12H_2O$ at pH 4 by implementing six different methods separately. Determining the colour codes, colour measurement results and K/S values of the fabric samples that were dyed at 100 ºC, the tests of light fastness and rub fastness were performed.

EXPERIMENTAL

Mordants of $Al(NO_3)_3\cdot 9H_2O$, $CdCl_2\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $Pb(CH_3COOH)_2\cdot 3H_2O$, $Cu(CH_3COOH)_2\cdot H_2O$, K_2CrO_4, $K_2Cr_2O_7$, $FeCl_3$, Ag_2SO_4, $KAl(SO_4)_2\cdot 12H_2O$ were used in the study and acetic acid, sodium acetate were used in the preparation of the buffer solution. All the chemicals being used have analytical purity and are the products of E. Merck and Riedel firm. Distillate water was used in the preparation of the solutions.

Spectrophotometer (Philips PU 8700 UV-VIS), cuvette (Hellma, 100-QS), mechanic blender (Bosch 1210, 500W, 27000, 1/min), analytical scale (Sartorius, analytical A 200 S), water distillation device, pH paper, filter paper and technical glass materials. 100 % wool fabric with a grammage of 188 g/m^2 was obtained from Altinyildiz factory. Dyeing was carried out 1994 Roaches dyeing machine including 6-dyeing cans. The colour changes were measured with a spectraflash SF600 (Datacolor International, USA) and CIE L*a*b* data with Illuminant D65 at 10º observer, in Marmara University, Faculty of Technical Education, Department of Textile Studies. Lightfastness was evaluated by Standard test methods with light fastness, James H. Heal Co. Ltd. Hand-powered Crockmeter was used to determine the colour fastness to rubbing of the fabrics.

0.2 M $CH_3COONa\cdot 3H_2O$ solution: 27.2 g of $CH_3COONa\cdot 3H_2O$ was weighed and completed with distilled water to 1 L.

0.2 M CH_3COOH solution: 11.55 mL of CH_3COOH (99 %) was diluted with distilled water to 1 L.

pH = 4 Buffer solution: 90 mL 0.2 M of sodium acetate solution was added to 410 mL 0.2 M of acetic acid solution and completed with distilled water to 1 L.

Quercetin stock solution (100 µg/mL) : 0.01 g of pure quercetin and 25 mL of pure methanol were transferred to 100 mL of volumetric flask. Quercetin was rinsed until it completely dissolved and the solution was completed to the volume with the pure methanol.

Quercetin standard solutions: Being transferred to 10 mL of volumetric flasks from the stock solution at respectively 0.2, 0.4, 0.6, 0.8 and 1.0 mL, the quercetin was completed to the volume separately with the pure methanol and the standard solutions of the prepared quercetin were used for the drawing of the test conditions and standard curves.

Method

Dyestuff extraction from *Punica granatum* L. rind: For the purpose of extracting quercetin from the *Punica granatum* L. rind, 155 g of *Punica granatum* L. rind was homogenized in a beaker through being mixed in a mechanic mixer that has the property of scrapping with the pure methanol for 20 min. The suspension in the beaker was transferred to 1000 mL of volumetric flask by being filtered out of the coarse filter paper. Sample remnants remaining in the beaker were washed with methanol until they coloured no more and the process of filtering was sustained. 100 mL of acetic acid was added inside. The volume was completed to 1000 mL with methanol. Absorption and first derivation spectra of the colourful extract that dispersed as a result of the filtering process were drawn under operating conditions.

Drawing of spectra: Absorption (A) and first derivative absorption (^{1}D) spectra of the dye solution that was extracted from the *Punica granatum* L. rind and standard quercetin solutions were taken at the wavelength of 300-450 nm, band width of 2 nm, with a scanning rate of 500 nm/min and under high smoothing conditions.

Preparation of the calibration graphs: Peak to peak wavelength was used at the first derivative absorption spectra of the standard quercetin solutions prepared for the drawing of the calibration graph between the maximum at 354 nm and minimum at 393 nm.

Measurement: 0.1 mL of samples taken from clear filtrates that were obtained from the extraction which was performed as above were transferred to 10 mL of volumetric flask and completed to the volume with methanol. The first derivative absorption spectra of the prepared sample solutions were taken. The first derivative absorbance values of the maximum 354 nm and minimum 393 nm were assessed in these spectra and the sum of their absolute value was ($^1D_{354-393}$) inscribed.

Quercetin concentration which is the equivalent of the determined ^{1}D values was found through the related calibration curve and quercetin quantity in the *Punica granatum* L. sample was calculated.

Average quantity of quercetin was calculated by studying on three different *Punica granatum* L. samples.

Wool fabric dyeing with tannic acid: The researches performed on fabric dyeing with tannic acid, indicated that tannic acid increases the dyeing quality by means of enabling the mordant to be attached to the fabric better, forms a strong complex with proteins and has effects such as antibacterial and antibite. Besides, various dyeing methods have been encountered in literature researches, these methods are as follows[18]:

1. Tannic acid + Mordant → Dye
2. Dye → Tannic acid + Mordant
3. Tannic acid → Dye + Mordant
4. Tannic acid → Dye → Mordant
5. Tannic acid → Mordant → Dye
6. Mordant → Tannic acid → Dye

In this study we performed, the mordanting processes of the wool fabric partrides weighing 5 g that were prepared in accordance with the dyeing were completed with the buffer solution prepared at pH: 4 and various mordant salts through performing the six methods given above at 100 ºC for 0.5 h, in such a way that the colour intensity would be 2 % and their dyeing processes were completed at 100 ºC for 1 h in all dyeing methods. Materials were dyed in Roaches dyeing machine (closed system).

Wool fabric dyeing according to the method 1 (tannic acid + mordant → dye): In all dyeing processes, 1 g of mordant salt and 0.1 g of tannic acid were dissolved with the buffer solution at pH: 4 to be studied on, the volume was completed to 200 mL and the wool fabric partrides were boiled within the prepared solution at 100 ºC for 0.5 h, washed firstly with cold and then boiled hot distilled water and wrung properly. 25 mL of *Punica granatum* L. rind extract was completed to 200 mL with the pH: 4 buffer solution and the wool fabric partrides were boiled in the obtained dye solution at 100 ºC for 1 h once again. At the end of the boiling process, the wool fabric partrides were washed first with cold water and then boiled with distilled water again, wrung, laid on the filter papers and dried. Determining the colour codes of the dyed wool fabric partrides, their rubbing fastnesses and light fastnesses were retained. Colour differences of the dyed wool fabric partrides against the fabrics the fabrics dyed without mordant were determined and their K/S values were measured.

Other five dyeing methods, on the other hand, were dyed in the same way according to the line specified in its own method.

Effect of the mordant salt quantity on the wool fabric dyeing: Scaling 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5 g of $K_2Cr_2O_7$ salt separately by using the 2nd method (Dye → Tannic acid + Mordant), 0.1 g of tannic acid and 25 mL of *Punica granatum* L. rind extract were applied on the wool fabric partrides at the pH 4 for the purpose of determining the effect of the mordant quantity on the wool fabric. Rubbing and light fastnesses of the dyed wool fabric partrides were determined. Colour differences of the dyed wool fabric partrides against the dyed fabrics without mordant were determined and their K/S values were measured.

Effect of the tannic acid quantity on the wool fabric dyeing: Scaling 0.05, 0.1, 0,2, 0.3, 0.4, 0.5g of tannic acid separately by using the 2nd method (Dye → Tannic acid + Mordant), 1 g of $K_2Cr_2O_7$ salt and 25 mL of *Punica granatum* L. rind extract were applied on the wool fabric partrides at the pH 4 for the purpose of determining the effect of the tannic acid quantity on the wool fabric dyeing. Determining the rubbing and light fastnesses of the dyed wool fabric partrides, the colour differences of the dyed wool fabric partrides against the fabrics dyed without mordant were determined and their K/S values were measured.

Effect of the mordant salt type on the wool fabric dyeing: This study was performed in an attempt to determine the effect of different salts of the same metal ion on the wool fabric dyeing. Taking 1 g from the mordant salts of $Al(OH)_3$, $AlCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, 0.1 g of tannic acid and 25 mL of *Punica granatum* L. rind extract were applied on the wool fabric partrides at the pH 4 by using the 2nd method (Dye → Tannic acid + Mordant). Determining the rubbing and light fastnesses of the dyed wool fabric partrides, the colour differences of the dyed wool fabric partrides against the fabrics dyed without mordant were determined and their K/S values were measured.

Determination of the extracted colours: The reflectance values of the fabrics were measured by Datacolor Spectroflash SF 600 plus instrument with specular included mode and LAV 6.6 mm viewing aperture. The colour values of the fabrics were calculated with D65 illuminant/10° observer values and the CIE L*a*b* 1976 colour differences formula was used to express the colour dissrences. Each fabric was measured in three different areas, twice on each side of the fabric for consistency and the average value was calculated. The measurements were performed in areas of 2.5 mm. Since the colour differences of the dyed wool fabrics against the fabrics dyed without mordant were determined and the two samples were compared, the measurement was performed through reading firstly the sample accepted as standard and then the sample whose colour was about to be compared. At the end of the measurement, the differences between the colours that were compared with the standard on the screen were determined and the values of D* (colour difference), DL*, Da*, Db*, DC*, DH* were taken. Calculating how lighter or darker the compared colour was than the standard numerically, their K/S values being at 360-700 wavelength interval were measured.

Application of the light fastness on the dyed samples: The dyed wool fabric partrides, which were about to be applied light fastness, were placed into 12 cm × 6 cm of swatch cards in accordance with standards and then half of them were closed and placed into their places within the decolouring device carefully. The prepared blue swatch card was also placed into the decolouring device and the dyed samples where the light was turned on were exposed to light for 80 h in the modified device having an ambient temperature of 40 °C with a xenon arc fading lamp of 250 Watts. At the end of this period, light fastnesses of the wool fabric partrides were assessed in accordance with the grey and blue scale[19].

Application of the rubbing fastness on the dyed samples: Crockmeter was used for the determination of the colour fastnesses against rubbing. 5 cm × 5 cm of uncoloured, whited cotton fabrics having starch and other chemical materials removed were prepared as the rubb cloth and it was performed in two ways as dry and wet rubbing fastness[20].

RESULTS AND DISCUSSION

The absorption and 1st derivative spectra of the standard quercetin solutions prepared at the concentration range of 2-10 µg/mL were given in Figs. 4 and 5, respectively.

The average derivative absorbance values of the measure curve and the regression equation drawn between the concentration were found as:

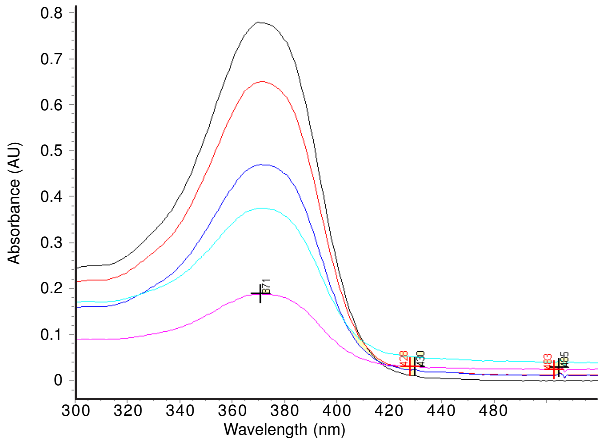


Fig. 4. Absorption spectra of standard solutions prepared for the calibration curve of the quercetin

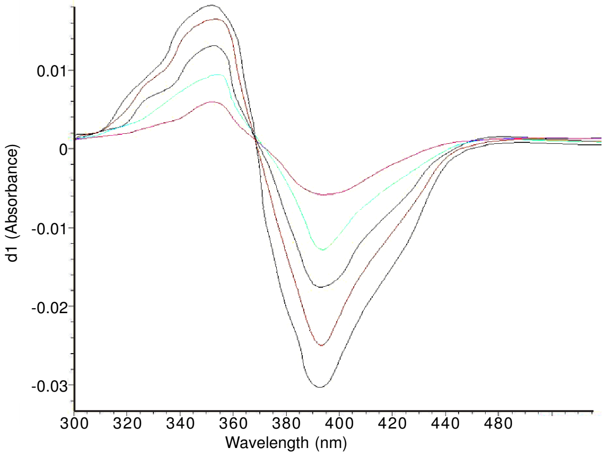


Fig. 5. 1st derivative spectra of the standard solutions prepared for the calibration curve of the quercetin

$$ {}^{1}D_{354\text{-}393} = 4.1092\ 10^{-5}C + 1.8094\ 10^{-3},\ r = 0.9992 $$

Absorption and first derivative spectra of the *Punica granatum* L. rind extract prepared as it is represented above under the working conditions are seen in Figs. 6 and 7. Obtaining the concentration values through the quercetin calibration curves being constituted, the quercetin quantity was found as 6.43 mg in 100 g of *Punica granatum* L. rind as a result of three parallel determinations.

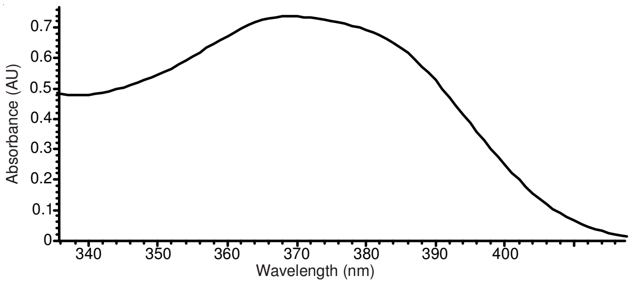


Fig. 6. Absorption spectrum of the *Punica granatum* L. rind extract

Quercetin is a natural dyestuff and dissolves in water. Sixty pieces of raw wool fabric partrides were dyed with buffer solutions prepared at pH: 4 by using six different dyeing methods by means of the mordant salts of K_2CrO_4, $Al(NO_3)_3 \cdot 9H_2O$, $CdCl_2 \cdot H_2O$, $MgCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $K_2Cr_2O_7$, $FeCl_3$, Ag_2SO_4 and $KAl(SO_4)_2 \cdot 12H_2O$,

TABLE-1
COLOR CODES OF THE DYED WOOL FABRIC PARTRIDES

pH = 4										
D65/10	L*	a*	b*	C*	h	X	Y	Z	x	y
$K_2Cr_2O_7$										
Method 1	60.05	0.22	16.31	16.31	89.22	26.77	28.18	20.3	0.3557	0.3745
Method 2	46.49	6.39	29.25	29.94	77.68	15.9	15.63	6.49	0.4182	0.4112
Method 3	45.36	5.35	28.61	29.11	79.4	14.9	14.8	6.17	0.4154	0.4126
Method 4	41.15	6.87	26.99	27.85	75.72	12.31	11.96	4.91	0.4219	0.4098
Method 5	50.17	2.14	20.35	20.46	84	17.99	18.56	11.05	0.378	0.3899
Method 6	55.39	0.77	20.28	20.29	87.84	22.27	23.31	14.58	0.3701	0.3875
K_2CrO_4										
Method 1	62.34	0.38	16.43	16.44	88.69	29.3	30.8	22.4	0.3551	0.3733
Method 2	48.62	6.62	28.96	29.71	77.13	17.58	17.29	7.52	0.4148	0.4078
Method 3	47.32	4.18	23.5	23.87	79.92	16.14	16.26	8.43	0.3952	0.3983
Method 4	38.6	9.13	27.75	29.21	71.78	11.08	10.43	3.93	0.4357	0.41
Method 5	46.02	5.27	24.72	25.28	77.96	15.36	15.28	7.45	0.4032	0.4011
Method 6	52.44	3.74	24.83	25.11	81.44	20.22	20.54	10.85	0.3918	0.3979
$Al(NO_3)_3·9H_2O$										
Method 1	77.4	1.51	33.7	33.74	87.43	50.05	52.21	27.7	0.3852	0.4017
Method 2	67.67	3.08	35.6	35.74	85.05	36.5	37.53	17.21	0.4001	0.4113
Method 3	74.54	2.49	27.58	27.69	84.84	45.95	47.55	28.48	0.3767	0.3898
Method 4	66.17	3.75	35.51	35.7	83.96	34.78	35.54	16.05	0.4027	0.4115
Method 5	71.77	2.47	28.76	28.87	85.09	41.87	43.31	24.7	0.3811	0.3942
Method 6	78.11	1.53	23.83	23.88	86.34	51.2	53.39	35.58	0.3652	0.3809
$CdCl_2·H_2O$										
Method 1	67.56	5.04	26.48	26.95	79.22	36.95	37.38	21.82	0.3843	0.3888
Method 2	64.6	5.76	28.85	29.42	78.71	33.41	33.55	17.91	0.3937	0.3953
Method 3	67.99	4.71	30.22	30.59	81.14	37.42	37.97	20.19	0.3915	0.3972
Method 4	65.23	6.22	29.22	29.87	77.98	34.32	34.34	18.26	0.3948	0.395
Method 5	67.45	5.1	28.67	29.12	79.92	36.82	37.23	20.51	0.3894	0.3937
Method 6	73.28	3.46	23.95	24.2	81.79	44.41	45.6	29.46	0.3717	0.3817
$MgCl_2·6H_2O$										
Method 1	66.42	6.08	25.9	26.61	76.78	35.79	35.87	21.05	0.386	0.3869
Method 2	66.64	5.59	27.46	28.02	78.49	35.92	36.16	20.42	0.3883	0.3909
Method 3	68.93	4.44	29.3	29.64	81.39	38.58	39.24	21.55	0.3882	0.3949
Method 4	65.47	6.21	28.7	29.36	77.8	34.62	34.65	18.73	0.3934	0.33937
Method 5	65.31	5.71	29.23	29.78	78.95	34.28	34.44	18.33	0.3938	0.3957
Method 6	75.87	3.44	21.51	21.78	80.92	48.33	49.67	34.41	0.365	0.3751
$Pb(CH_3COO)_2·3H_2O$										
Method 1	66.81	5.99	37.76	38.23	80.99	36.25	36.38	15.53	0.4112	0.4126
Method 2	58.38	8.89	40.67	41.63	77.67	27.13	26.36	9.01	0.4341	0.4218
Method 3	68.06	5	29.03	29.46	80.22	37.59	38.05	20.88	0.3894	0.3942
Method 4	54.08	9.03	39.5	40.52	77.13	22.84	22.05	7.22	0.4383	0.4232
Method 5	62.89	8.22	39.73	40.57	78.3	32.04	31.46	11.98	0.4245	0.4168
Method 6	69.93	3.66	24.81	25.08	81.62	39.69	40.65	25.18	0.3762	0.3852
$Cu(CH_3COO)_2·H_2O$										
Method 1	52.92	3.68	25.9	26.16	81.9	20.64	20.98	10.77	0.394	0.4005
Method 2	39.84	4.51	22.47	22.92	22.92	78.65	11.18	11.15	0.4032	0.4023
Method 3	42.17	3.14	22.13	22.35	81.93	12.41	12.61	6.41	0.3949	0.4013
Method 4	36.65	6.21	22.53	23.37	74.58	9.61	9.35	4.26	0.4139	0.4025
Method 5	41.79	6.57	25.93	26.75	75.79	12.67	12.36	5.37	0.4168	0.4066
Method 6	49.78	2.51	24.32	24.45	84.1	17.76	18.24	9.49	0.3904	0.401
$FeCl_3$										
Method 1	39.62	2.52	6.46	6.93	68.66	10.78	11.02	9.6	0.3434	0.351
Method 2	32.75	0.89	5.16	5.23	80.17	7.13	7.42	6.59	0.3372	0.3511
Method 3	28.32	2.11	-1.82	2.79	319.17	5.46	5.58	6.42	0.3129	0.3193
Method 4	40.44	4.73	13.98	14.76	71.3	11.57	11.52	7.76	0.375	0.3733
Method 5	36.56	2.33	6.62	7.02	70.62	9.09	9.3	7.995	0.3452	0.3531
Method 6	43.88	3.55	8.84	9.53	68.14	13.58	13.75	11.28	0.3517	0.3561
Ag_2SO_4										
Method 1	32.36	6.88	13.26	14.94	62.57	7.57	7.25	4.62	0.3895	0.3727
Method 2	26.39	8.98	11.13	14.3	51.11	5.34	4.88	3.19	0.3983	0.3638
Method 3	30.28	7.04	9.39	11.73	53.13	6.68	6.35	4.68	0.3772	0.3585
Method 4	24.5	6.39	5.54	8.46	40.94	4.5	4.26	3.56	0.365	0.3456
Method 5	30.08	3.91	6.4	7.5	58.59	6.3	6.27	5.23	0.354	0.3522
Method 6	30.64	7.11	10.68	12.83	56.35	6.84	6.5	4.55	0.3823	0.3633

$KAl(SO_4)_2 \cdot 12H_2O$										
Method 1	78.9	2.35	29.06	29.15	85.38	52.82	54.76	32.69	0.3767	0.3904
Method 2	69.33	1.87	30.75	30.8	36.53	38.31	39.8	21.14	0.386	0.401
Method 3	74.79	3.96	21.96	22.31	79.79	46.84	47.94	32.69	0.3675	0.3761
Method 4	62.63	4.56	34.47	34.77	82.47	30.74	31.15	13.87	0.4058	0.4112
Method 5	69.16	5.2	31.71	32.14	80.69	39.13	39.56	20.46	0.3946	0.399
Method 6	71.93	2.88	36.35	36.46	85.48	42.25	43.56	20.54	0.3972	0.4096

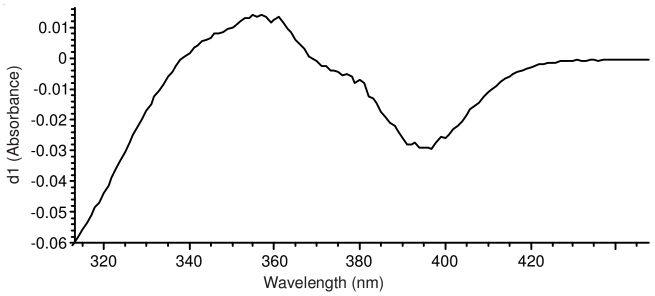


Fig. 7. 1st derivative spectrum of the *Punica granatum* L. rind extract

for the purpose of enabling the dyestuff to get attached to the wool and preventing it from being dissolved. Different colours were obtained as the dyeing method changed. It was observed that the colours that were formed as a result of the dyeings performed with the mordant salts of $Al(NO_3)_3 \cdot 9H_2O$, $CdCl_2 \cdot H_2O$, $MgCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ varied between grey, greyish dark blue, light yellow, khaki green, earth colour and light brown and that colour tones were very close to each other. The colours, which were formed as a result of the dyeings performed with the mordant salts of $Cu(CH_3COO)_2 \cdot H_2O$, K_2CrO_4 and $K_2Cr_2O_7$, were observed to be grey, khaki green, dark green. On the other hand, the colours, which were formed as a result of the dyeings performed with the mordant salts of $FeCl_3$ and Ag_2SO_4, were observed to vary between grey and greyish dark blue.

The constitution of colour change together with changing the transition metal salts used as mordant could be explained by; the transition element cation, the difference of the light absorption on the complexes constituted by the free aminoacid molecules in the dyestuff and wool and the theorem of ligand field splitting. Since the splitting energies are different for each cation, the constituted colours are different as well. The colour change that occurs as a result of the pH change, on the other hand, is explained by the change that occurs on the wave length of the light absorption that emerges together with the deactivation of the auxochrome groups.

Determining the colour codes of the mordanting wool fabric partrides (Table-1), their colour differences with the wool fabric partride, which was only in contact with the dyestuff without mordanting, were measured.

The results obtained through performing light fastness[19] and rubbing fastness[20] tests on the dyed wool fabric samples were assessed in accordance with the blue and grey scale for the light fastness and with the grey scale for the rubbing fastness test (Table-2). Accordingly, the test results of the light fastness were found to be rarely 3, averagely between 4-6 and 7-8 in some dyeings. It was determined that the results of the rubbing fastness are between 4-5 for all of the mordant salts, except for the mordant salts of $FeCl_3$ and Ag_2SO_4 and this result is very good; they are approximately between 2-3 for the mordant salts of $FeCl_3$ and Ag_2SO_4 and this result is normal. The fact that these results are considerably high values for natural dyeing is important in terms of dyeing quality.

For the purpose of determining the colour densities of the dyed wool fabric partrides, their K/S values were measured. Since the quercetin solution in the methanol gave maximum absorption at 360 nm, the whole K/S chart was drawn by taking the K/S values at 360 nm.

Examining the acquired K/S values of the used mordants and applied methods (Table-3), the appropriate method was determined for the mordant used during the dyeing processes at pH: 4. The results were given in Table-4.

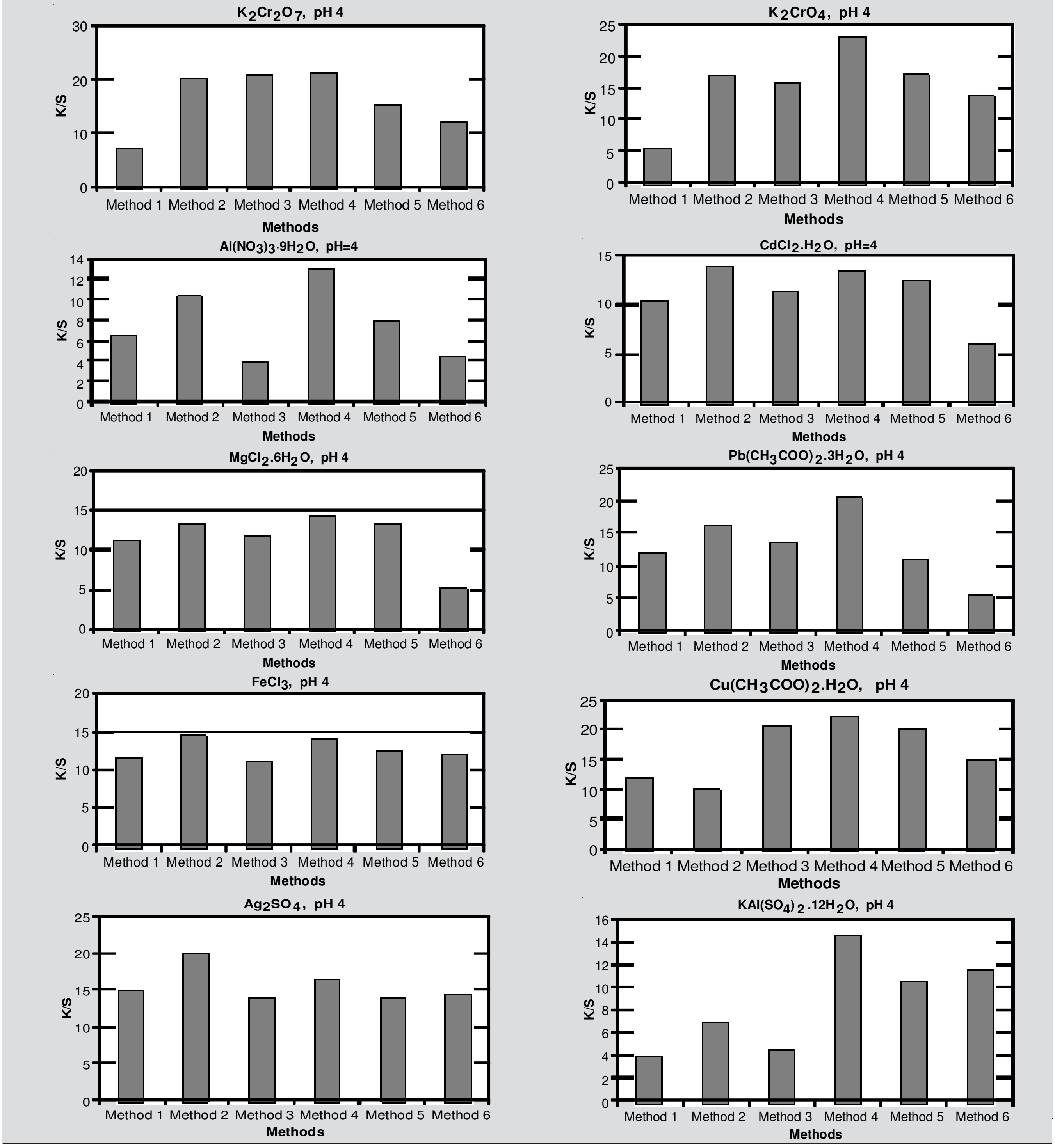
As is seen in the table, to sum up the methods to be used in pH: 4 shortly; it was seen that the 5th method was more suitable for $K_2Cr_2O_7$, 2nd method was more suitable for Ag_2SO_4 and 4th method was more suitable for the rest of the mordants, thereby darker colours were obtained during the dyeing processes performed with these methods.

In the study that was performed for the purpose of researching the effect of the quantity of mordant salt on the dyeing process, it was determined that 1 g of mordant salt was sufficient for 5 g of wool fabric and colour intensity of 2 % and there was no difference in the colour tone after 1 g of

TABLE-2
RUBBING AND LIGHT FASTNESS TEST RESULTS OF THE DYED WOOL FABRIC SAMPLES

Mordant salts	Rub fastnesses pH = 4												Light fastnesses pH =4					
	1.Method		2.Method		3.Method		4.Method		5.Method		6.Method		1. Method	2. Method	3. Method	4. Method	5. Method	6. Method
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet						
$K_2Cr_2O_7$	5	4-5	4-5	4	4-5	4	4-5	4	5	4-5	5	4-5	3	3	3	3	3-4	4-5
K_2CrO_4	4-5	4-5	5	4-5	4-5	4	4	3-4	4	3-4	4-5	4	3-4	3	3	3-4	3-4	4-5
Al^{+3}	4-5	4	4-5	4	5	4	4-5	4	4-5	4	4-5	4-5	3-4	3-4	4	2-3	3-4	3-4
Cd^{+2}	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4-5	4	4	4	4	5	5	6-7
Mg^{+2}	4-5	4	4-5	4	4-5	4	5	4-5	5	4-5	5	4-5	5	5	5	5	6	7
Pb^{+2}	4	3-4	4-5	4	4-5	4	4-5	4	3	2-3	4-5	4	5	5-4	4	4-3	7	7
Cu^{+2}	4	3-4	3	2-3	4	3-4	5-4	4	4	3-4	4	3-4	5	5	5	7-8	7-8	7-8
Fe^{+3}	3-4	3	4	3-4	2-3	2	3-4	3	2-3	2	3-4	3	3	3	3	4	3-4	3-4
Ag^{+1}	2	1-2	3	2-3	2	1	3	2	2-3	2	2-3	2	3-4	3-4	4-5	4	4	4-5
KAl Alum	4-5	4	4-5	4-5	4	4	4	3-4	4	3-4	4-5	4	3	3	3	3	2-3	2-3

TABLE-3
K/S VALUES OF DIFFERENT MORDANT SALTS AND THE METHODS BEING USED



mordant and light fastness values dropped to the values of 2-3 for 2.5 g. Considering the test results of light fastness, it was determined that the highest light fastness values (7-8) are observed during the dyeings in which 0.05-0.3 g of mordant salt is used and that light fastness decreases as the mordant quantity is increased. Considering the test results of rub fastness, it was determined that rub fastness does not change as the quantity of mordant salt increases and is between *ca.* 4-5 (Table-5). Considering the K/S values, it was seen that almost the same colours were obtained after 0.5 g of mordant salt. It could be said that a healthier dyeing could be performed through taking 0.5 g of mordant salt (Fig. 8).

In the study that was performed for the purpose of researching the effect of the tannic acid quantity on dyeing, the tannic acid quantity to be used in dyeing processes was determined as 0.2 g, since the increase in the tannic acid quantity was observed to be non-effective upon dyeing. Considering the light fastnesses, all of them were observed to be *ca.* 3-4. Considering the rub fastnesses, on the other hand, it was determined that the values were 4-5 and this result was pretty

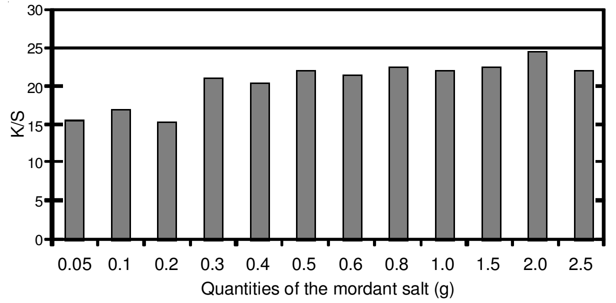


Fig. 8. Column chart for K/S values of the wool fabric partrides dyed with the varying quantities of the mordant salt ($K_2Cr_2O_7$)

TABLE-4
pH: METHOD ASSESSMENT IN THE ENVIRONMENT OF 4 BUFFER SOLUTIONS ACCORDING TO THE RESULTS OF K/S

Mordant	pH	Method
$K_2Cr_2O_7$	4	5
K_2CrO_4	4	4
$Al(NO_3)_3\cdot 9H_2O$	4	4
$CdCl_2\cdot H_2O$	4	2 and 4
$MgCl_2\cdot 6H_2O$	4	4
$Pb(CH_3COO)_2\cdot 3H_2O$	4	4
$FeCl_3\cdot 6H_2O$	4	2 and 4
$Cu(CH_3COO)_2\cdot H_2O$	4	4
Ag_2SO_4	4	2
$KAl(SO_4)_2\cdot 12H_2O$	4	4

good (Table-6). Considering the K/S values, it was observed that a darker colour dyeing was observed with 0.2 g of tannic acid (Fig. 9). Considering the fact that tannic acid is also effective in terms of health, it was determined that the dyeing with 0.2 g of tannic acid would be much better.

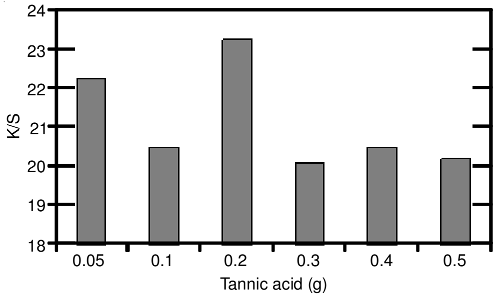


Fig. 9. Column chart for K/S values of the wool fabric partrides dyed with different tannic acid quantities

Considering the values of the dyeings performed at pH: 4 with the mordant salts of $KAl(SO_4)_2\cdot 12H_2O^1$, $AlCl_3\cdot 6H_2O^2$, $Al(OH)_3{}^3$, $Al_2(SO_4)_3\cdot 18H_2O^4$ and $Al(NO_3)_3\cdot 9H_2O^5$ according to the 2nd method for the purpose of examining the effect of different salts of the metal ion used as mordant on the dyeing; it was observed that the use of the different salts of the metal ion does not immensely affect the dyeing and a darker colour dyeing could be obtained by means of $Al(OH)_3$ (Fig. 10). In the dyeing processes performed at pH: 4 with the 4th method by using different mordant salts, the darkest colour was obtained during the dyeing performed with the mordant salt of K_2CrO_4 (Fig. 11).

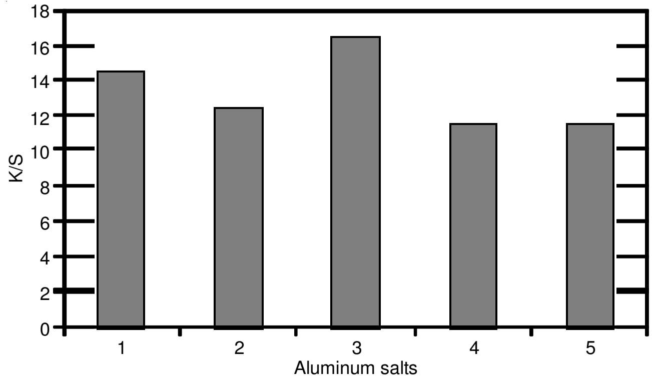


Fig. 10. Column chart for K/S values of the wool fabric partrides dyed by using different Aluminum salts as the mordant salt

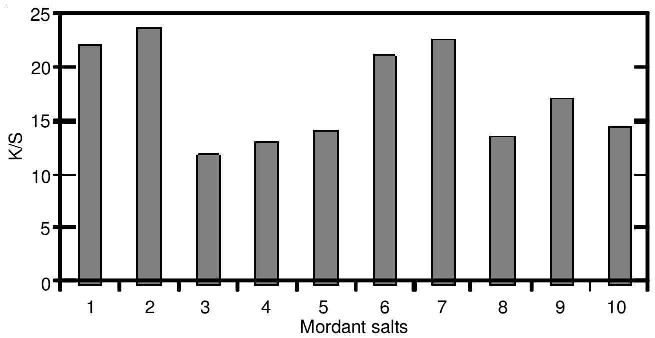


Fig. 11. Column chart for K/S values of the wool fabric partrides dyed with different mordant salts 1-$K_2Cr_2O_7$, 2-K_2CrO_4, 3-$Al(NO_3)_3\cdot 9H_2O$, 4-$CdCl_2\cdot H_2O$, 5-$MgCl_2\cdot 6H_2O$, 6-$Pb(CH_3COO)_2\cdot 3H_2O$, 7-$Cu(CH_3COO)_2\cdot H_2O$, 8-$FeCl_3$, 9-Ag_2SO_4, 10-$KAl(SO_4)_2\cdot 12H_2O$

TABLE-5
COLOR MEASUREMENT RESULTS, LIGHT AND RUB FASTNESSES OF THE WOOL FABRIC PARTRIDES DYED WITH THE VARYING QUANTITIES OF THE MORDANT SALT ($K_2Cr_2O_7$)

$K_2Cr_2O_7$ mordant quantity (g)	Color differences						Light fastnesses	Rub fastnesses	
	DE*	DL*	Da*	Db*	DC*	DH*		Dry	Wet
0.05	3.796	-3.478	-0.07	1.519	1.488	0.311	7	4-5	4-5
0.10	11.347	-10.88	1.713	2.730	2.996	-1.189	7	4-5	4-5
0.20	6.948	-6.564	0.559	2.209	2.271	-0.183	8	4-5	4-5
0.30	17.902	-17.46	3.591	-1.652	-0.812	-3.868	7	4-5	4-5
0.40	19.00	-18.62	3.441	-1.990	1.179	-3.796	5	4-5	4-5
0.50	19.521	-19.11	3.206	-2.381	-1.620	-3.651	4	4-5	4-5
0.60	20.728	-20.21	3.338	-3.162	-2.332	-3.963	4	4-5	4
0.80	21.460	-20.99	3.332	-2.984	-2.163	-3.915	4	4-5	4
1.00	20.619	-20.19	3.258	-2.557	-1.774	-3.742	5-4	5	4-5
1.50	22.872	-22.31	3.641	-3.466	-2.534	-4.341	3-4	4-5	4
2.00	23.681	-23.14	3.378	-3.736	-2.870	-4.139	2-3	4-5	4
2.50	23.597	-22.91	2.670	-5.007	-4.291	-3.713	2-3	4-5	4

TABLE-6
COLOR CODES, LIGHT AND RUB FASTNESSES OF THE WOOL FABRIC PARTRIDES DYED WITH TANNIC ACID IN DIFFERENT QUANTITIES

$K_2Cr_2O_7$ tannic acid quantity (g)	Color differences						Light fastnesses	Rub fastnesses	
	DE*	DL*	Da*	Db*	DC*	DH*		Dry	Wet
0.05	21.969	-21.33	2.545	-4.611	-3.945	-3.489	3	4-5	4
0.1	20.255	-19.73	2.700	-3.702	-3.029	-3.438	3	4-5	4
0.2	20.657	-20.16	3.001	-3.358	-2.615	-3.667	3-4	4-5	4
0.3	18.548	-18.12	3.620	-1.664	-0.816	-3.899	3-4	4-5	4
0.4	18.909	-18.46	3.464	-2.222	-1.395	-3.872	4	4-5	4
0.5	18.577	-18.11	3.806	-1.642	-0.741	-4.078	4	4-5	4

When dyeings without mordants were performed by using the *Punica granatum* L. rind extract as a dyestuff on four different fabric and fiber types (100 % flax, 100 % cotton, 100 % soy fiber and 100 % angora wool) in an attempt to research on what sort of fabrics and fibers the natural dyeing could be performed outside of wool fabrics, it was seen that natural dyeing could not be performed on 100 % flax and 100 % cotton. It was also observed that soy fiber and especially angora wool could be dyed very well with natural dyes.

Conclusion

In recent years, ecological balance, biological decomposition and better adaptation of natural dyes with the environment have increased the importance of natural dyes. Turkey has a considerably old historical tradition in terms of natural dyeing and a rich potential in terms of the plants used in natural dyeing. This richness can not be reflected on the number of plant species used in dyeing today. Together with the determination of the economically significant dye plants and production of these plants in certain standards, agricultural field of activity will become current again and additionally, raw materials will be provided for the dyeing of local handicrafts and especially carpets and rugs which have a high export value. This condition will enable the progress of tourism and a better income for the producer.

Punica granatum L. is one of the dye plant species that is cultivated today and totally 60 dyeings were performed during the study, which was carried out with this plant through using different dyeing methods and mordants. A spectrum of colours consisting khaki green, grey, yellow and brown tones was obtained. In the study, it was observed that light fastness values (3-8) vary between rub fastnesses (wet (2-4) and dry (3-5)). These obtained fastness values are at medium and fine level, in general.

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