

## Effect of Tannic Acid and Metal Salts on Dyeing of Woolen Fabrics with Red Onion (*Alliumcepa L.*)

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(Received: 22 February 2010;

Accepted: 27 November 2010)

AJC-9337

A natural dye (anthocyanins) was extracted from red onion (*Alliumcepa L.*) using different buffers as extractant at 25 °C for 20 min. The amount of total anthocyanins was determined by using the derivative spectrophotometric method. The dyeing behavior of these colour components on wool has also been evaluated. Dyeing processes were carried out using the mordant mixtures (tannic acid + metal salts) according to pre- and post-mordanting methods by using buffer solutions at pH 2-8 for 1 h at 98-100 °C with open bath dyeing technique. Colour differences in CIE L\*a\*b\* unit and gray scale classifications are reported. Dyeing conditions and other characteristics show that the mordant mixture is more beneficial than dye as it shows good light fastness and antibacterial property. The dye obtained from the red onion may be alternative source to synthetic dyes for the dyeing of wool.

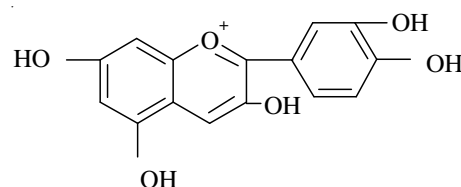
**Key Words:** *Alliumcepa L.*, Natural dyes, Anthocyanins, Tannic acid, Mordants, Woolen fabrics.

### INTRODUCTION

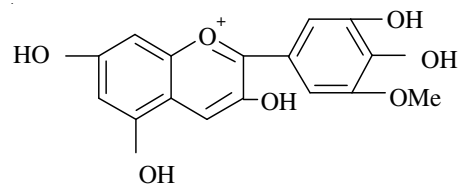
Natural dyes have attracted the attention of entire world because of their non-hazardous nature. The study of natural colourants is an extensive and active area of investigation due to the growing interest of substituting synthetic colourants with toxic effects in humans<sup>1</sup>. In Turkey, there are approximately, 150 spices of plants used in natural dye production<sup>2</sup>. Red onion (*Alliumcepa L.*) is one of the natural product whose the outermost dry papery skins is the best source of the red colour due to the presence of anthocyanins. Anthocyanins are natural colourants which have raised a growing interest due to their extensive range of colours, innocuous and beneficial health effects.

Anthocyanins, present in plant tissue, show different properties based on the number and position of -OH group which are in 2-phenyl group. Up to now there are reports of more than 500 different anthocyanins and 23 anthocyanidins of which only six are the most common in vascular plants, pelargonidin, peonidin, cyanidin, malvidin, petunidin and delphinidin<sup>3,4</sup>. The main anthocyanins in the red-onion skins are pelargonidin, malvidin and cyanidin<sup>5-7</sup>.

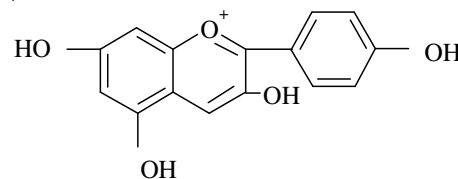
Natural dyes are substantive, requiring a mordant to fix on to the fabric and prevent the colour from either fading with exposure to light or washing out. Mordants bind the natural dyes to the fabric. They also play a large role in making the resulting shade faster to light and washing. The shade will vary depending on the mordant used.



Cyanidin



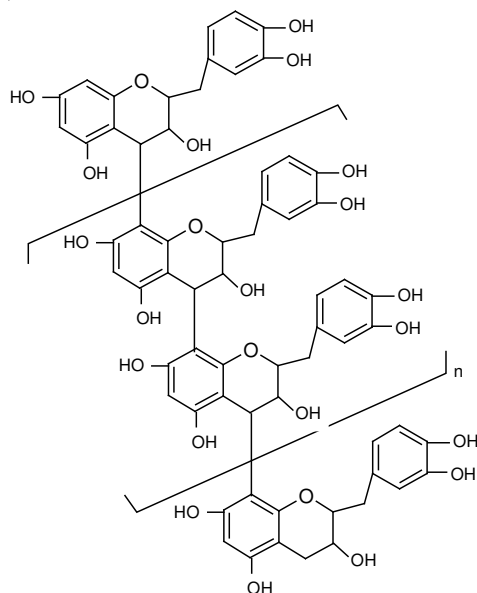
Malvidin



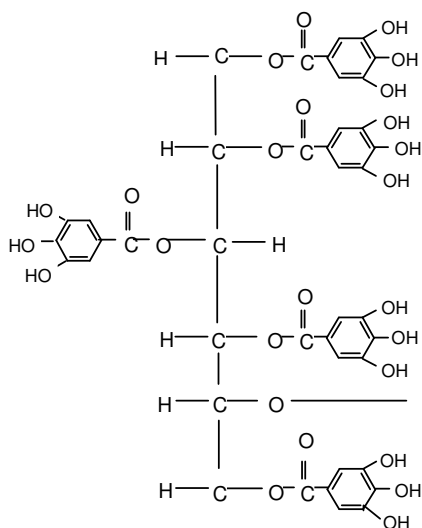
Pelargonidin

Mordants can be obtained from plants, such as oxalic acid which is found in rhubarb leaves, alum which comes from clubmoss and tannin from oak galls and sumac leaves. Tannins

are natural dyes and natural mordants. They are found in the leaves, fruits, barks, roots and wood of trees<sup>8</sup>. They can be divided into two groups condensed tannins (derives from flavanols) and hydrolyzable tannins (esters of a sugar, usually glucose)<sup>9,10</sup>. The molecular structures of these compounds are given below:



Condensed tannins



Hydrolyzable tannins

Their multiple phenolic hydroxyl groups lead to formation of complexes with proteins<sup>11-13</sup> with metal ions<sup>14-16</sup> and with other macromolecules like polysaccharides. Tannins are used in tanning animal skins to make leather and it has got some characteristics such as antibacterial and antibiotics properties. It is also used in manufacturing ink and in medicine as a very strong astringent and for treatment of burns, besides as an additive mordant with other mordants in dyeing<sup>10</sup>.

The literature survey indicates that antimicrobial, antibacterial, antiallergic fabrics with good fastness were manufactured when the fabrics (wool, silk or cotton) treated with tannic acid solution<sup>8-10</sup>. Another two studies in this subject indicated that the carpets had been chemically treated with

tannic acid solution for reducing mite and other allergen levels in carpets<sup>11-17</sup>. Tannic acid, a protein denaturing agent has been reported to reduce allergen levels in house dust and is marketed for that purpose as 1 and 3 % solutions<sup>17</sup>. Recent investigations with tannic acid have shown when tannic acid is used as a mordant the dye ties up to the fiber better and so the quality of the dyeing increases<sup>18</sup>.

The literature survey indicates that there is no work reported in the field of dyeing wool fabrics with anthocyanins and mordant combinations (tannic acid + metal salts). So the present paper is an effort for determining the dyeing properties of anthocyanins and tannic acid + metal salts mixtures for wool, from the point of view of their fastness. Important aspects presented in this paper consider various stages of material processing: (a) Extraction of natural dye and quantification of extracted dye; (b) application in wool dyeing; (c) measurement of colour depth and shade on woolen fabrics; and (d) determination of light fastness properties as key properties for technical and commercial success.

In this study, to obtain better light fastness and antibacterial-antiallergic wool samples we also studied that the effects of tannic acid-metal salt mixtures for dyeing woolen fabrics. In order to investigate the most proper mordant mixture and pH in terms of the light fastness in dyeing woolen fabrics by anthocyanins, some selected metal salts and tannic acid were used as mordant agents at pH 2-8 by two types of mordanting methods *i.e.*, pre- and post-mordanting.

## EXPERIMENTAL

The source of natural dyes was from red onions. The red onions were purchased from the local market. The dye obtained from *Alliumcepa* L. has good colouring capacity. Before the experiment the outer skin were dried in shade and then cut very tiny pieces. It is thermostable, thus is also suitable for conventional dyeing where the bath temperature ranges from 60-98 °C.

100 % wool fabric, medium weight, obtained from Yunsan A.S., Istanbul/Turkey was scoured before use by treatment with a solution containing 0.5 g/L of sodium carbonate and 2 g/L of non-ionic detergent (Labolene) at 40-45 °C for 0.5 h, keeping the material to liquor ratio at 1:50. The scoured material was thoroughly washed with tap water and dried at room temperature. The scoured material was soaked in distilled water for 0.5 h prior to dyeing or mordanting.

Mordants such as  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  and tannic acid were used. Mordants, tannic acid and other chemicals were supplied by E. Merck, Darmstadt. Distilled water was used in extraction and for preparation of all chemical solutions; de-ionized water was used for dyeing processes.

### Methods

**Preparation of stock and standard solutions:** Acetate and phosphate buffer solutions were used for extraction of anthocyanins from the red-onion skins and to prepare stock and standard solutions at various pH values. Acetate (pH = 2; 4) and phosphate (pH = 6; 8) buffer solutions were used for adjusting the acidic and alkaline pH, respectively.

Stock solutions of anthocyanins were prepared with buffer solutions at pH 2-8 to construct of standard curves. Therefore, 0.1 g pure anthocyanins were weighted and the volume was diluted to 50 mL with desired pH (2 and 4) buffer solutions. 0.2 g pure anthocyanins were weighted and the volume was completed to 50 mL with desired pH (6 and 8) buffer solutions. These solutions were diluted to obtain standard solutions (200-1000  $\mu\text{g mL}^{-1}$  concentration range for pH = 2 and 4, 400-2000  $\mu\text{g mL}^{-1}$  concentration range for pH = 6 and 8) for the preparation of calibration curves. These solutions were freshly prepared every day.

**Calibration graphs:** Absorption and the first derivative absorption spectra of anthocyanins standard solutions were recorded between 450-700 nm (Philips PU 8700 UV-vis, spectrophotometer; Hellma, 100-QS, cuvette). In these spectra, the peak-to-peak amplitudes of 498 and 551 nm for pH = 2; 500-561 nm for pH = 4; 518-645 nm for pH = 6 and 551-645 nm for pH = 8 were used for the establishment of the calibration graphs for red onion. The regression equation of the calibration graphs were calculated by the method of least squares.

**Extraction of anthocyanins from *Alliumcepa* L.:** The outermost dry papery skin of onion (10 g) or wet skin onion (50 g) was removed and cut into small pieces, then stirred with 250 mL of buffer solution at desired pH by using mechanic blender (Bosch 1210, 500W, 27000, 1/min) for about 20 min at room temperature so that the mixture was homogenized to extract the anthocyanins from the *Alliumcepa* L. skin. The onion stem pieces were squeezed to get the colourless extract. Then, the suspension was transferred into 1 L volumetric flask by using filter paper and diluted to an appropriate volume with desired pH solution and the dark red extract was used as a dye-bath for the dyeing of woolen fabric and quantitative analysis for anthocyanins. This solution has mainly cyanidin and malvidin<sup>19</sup>. First derivative spectrophotometric method was utilized to determine the total dyestuff in the skin of the red onion.

**Sample analysis:** The first derivative spectrum of sample solution was recorded against the desired pH solution. The peak to peak amplitudes which were given in calibration graphs section measured from these spectra. The concentration of anthocyanins in the sample solutions was deduced by means of the regression equations of the related calibration graphs.

**Dyeing procedure of woolen fabrics:** Dyeing was carried out 1994 Roaches dyeing machine, 4-dye compartment each with 4-dye cans each. Accurately weighted wool sample was treated with different metal salts and tannic acid. The woolen fabrics were dyed with the extract, keeping material to liquor ratio (MLR) as 1:250. The intensity of the colour was selected 2 %. From initial experiments, it was observed that the pre- and post-mordanting technique imparted better fastness properties to the fabrics compared to simultaneous mordanting technique. Therefore, the dyeing procedures of woolen fabrics were carried out by using the two types of mordanting methods given below. pH was selected as 2-8. From the preliminary experiment, it was found that the optimum dyeing time and temperature were 1 h and 98-100 °C, respectively. The dyed material was washed with cold water and dried at room temperature; it was then dipped in brine for dye fixing.

**Mordanting:** Vegetable dyes require chemical in the form of metal salts to produce an affinity between the woolen fabric and the dye, these chemicals are known as mordants. Accurately weighted wool sample was treated with different metal salts and tannic acid, for pre-mordanting with mordant mixtures (tannic acid + metal salts) was carried out before dyeing and for the post-mordanting method after dyeing. The wetted sample was introduced into the mordant mixture solution and then it was brought to heating. The temperature of the bath was raised to boil and mordanting was continued for 1 h, at boiling temperature. After cooling, it was washed and placed in a 250 mL dye-bath. It was heated for 1 h at 98-100 °C and then allowed to cool and then unfixed dyestuff was removed by rinsing three times with distilled cold water and dried. This method was carried out at pH: 2, 4, 6 and 8 for each mordants. The colour differences of dyed woolen fabrics were determined against dyed woolen fabrics without tannic acid and metal salt.

**Colour measurement:** The CIE  $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$  and  $h$  colour co-ordinates were measured from the reflectance values at the appropriate  $\lambda_{\text{max}}$  for each dyeing using a Datacolor Spectroflash 600 PLUS spectrophotometer under illuminant D65, using a 100 standard observer with UV component included and specular component excluded, in Marmara University, Faculty of Technical Education and Department of Textile Studies.

The colours are given in CIE-Lab coordinates, L corresponding to brightness (100 = white, 0 = black), a to the red-green coordinate (positive sign = red, negative sign = green) and b to the yellow-blue coordinate (positive sign = yellow, negative sign = blue)<sup>20</sup>.

**Fastness testing:** Light fastness was evaluated by standard test methods with light fastness, James H. Heal Co. Ltd. Colourfastness test to light was carried out in a Fad-O-meter and the fastness ratings were given in grey-scales<sup>21</sup>.

**Hunter coordinates:** The hunter coordinates L, a and b of the samples dyed and mordanted with 1 % solution of each mordants were calculated from the tristimulus values x, y, z using the following equations<sup>22</sup> and were converted to CIELab (L, a, b) co-ordinates.

$$L = 10y^{1/2}$$

$$a = 17.5(1.02x - y)/y^{1/2}$$

$$b = 7(y - 0.84z)/y^{1/2}$$

CIE (Commission Internationale de l'Eclairage or International Commission on Illumination)  $L^*$ ,  $a^*$ ,  $b^*$  are CIE 1976 psychromic (or metric) lightness, redness (or greenness) and yellowness (or blueness), respectively<sup>23</sup>. The higher values of a and b indicate brightness, which is more due to redness and yellowness, respectively and the negative values indicate greenness and blueness, which are more towards the dull side. The lower the value of L, the greater is the depth<sup>19</sup>.

## RESULTS AND DISCUSSION

The natural dye (anthocyanins) was extracted with buffer solutions (pH 2, 4, 6 and 8) from outermost dry papery skin of red onion. The natural dye obtained from *Allium cepa* L. was used for dyeing of woolen fabric with mordant combinations. The visible spectrum of anthocyanins shows one major peak

at  $\lambda_{\text{max}} = 518 \text{ nm}$  in visible region and slight changes in different pH as shown in Fig. 1a. At pH 2, 4, 6 and 8, the  $\lambda_{\text{max}}$  are at 517.0, 524.0, 565.0 and 592.0 nm, respectively. Also Fig. 1b shows first derivative spectra of the absorption spectra given in Fig. 1a.

A spectrophotometric method cannot be used directly for the determination of anthocyanins; in fruits and vegetables owing to the matrix effect of UV-vis absorbing substances in sample matrix<sup>24</sup>. To overcome this difficulty, some tedious background correction techniques have been used<sup>25-27</sup>. In contrast, the derivatization of the absorption spectrum and measurement of the distance between neighboring extremum values allow the elimination of matrix effects, because the valuable background absorptions overlapping the analyte peaks are smoother in derivative spectra.

Concentrations of 200-1000  $\mu\text{g mL}^{-1}$  (for pH 2 and 4) and 400-2000  $\mu\text{g mL}^{-1}$  (for pH 6 and 8) anthocyanins were prepared and their first derivative absorbance of peak to peak values measured at 498-551 nm for pH 2, 500-561 nm for pH 4, 518-645 nm for pH 6 and 551-645 nm for pH 8. Table-1 shows the calibration equations and regression coefficients obtained from the first derivative spectra.

TABLE-1 CALIBRATION EQUATIONS OF ANTHOCYANINS			
Equation	Regression coefficient	Concentration range ( $\mu\text{g mL}^{-1}$ )	pH Values
$^1D_{498-551} = 3.05 \cdot 10^{-4} C_A + 0.0040$	$r = 0.9994$	200-1000	2
$^1D_{498-551} = 3.05 \cdot 10^{-4} C_A + 0.0040$	$r = 0.9994$	200-1000	4
$^1D_{518-645} = 6.75 \cdot 10^{-5} C_A + 0.0016$	$r = 0.9997$	400-2000	6
$^1D_{551-645} = 7.90 \cdot 10^{-5} C_A + 0.0030$	$r = 0.9997$	400-2000	8

$C_A$  = Anthocyanins concentration ( $\mu\text{g mL}^{-1}$ ). \*Five separate workups were performed and the mean calculated.

When the spectrophotometric method was applied to the determination of total anthocyanins in skin of onion higher values were found due to the turbidity. This makes the derivative method particularly useful for quantitative determination in the presence of turbidity or when the background absorbance is higher not very well detailed. The first derivative method was applied to overcome this difficulty. The total anthocyanins were found to be 13.5 mg/100 g for fresh onion skin and 5.2 mg/100g for dry red onion skins.

The dye exhaustion, fixation and levelness of dyeing depend on several factors such as the properties of fibres, the molecular structure of dyes, the medium of the dye bath<sup>28</sup> and the mordanting. The dye is fixed in the wool with mordant agents to improve the fastness of the dye against water, light and perspiration.

Molecules of wool consist of amino acids units. Proteins are formed from amino acids which contain free amino and carboxyl groups. Therefore, wool can be considered as an amphoteric compound. During the dyeing of wool, inter molecular hydrogen bonding and coordinative bonding occur between the dyestuff and amino acid groups of the wool as shown in Fig. 2<sup>29,30</sup>.

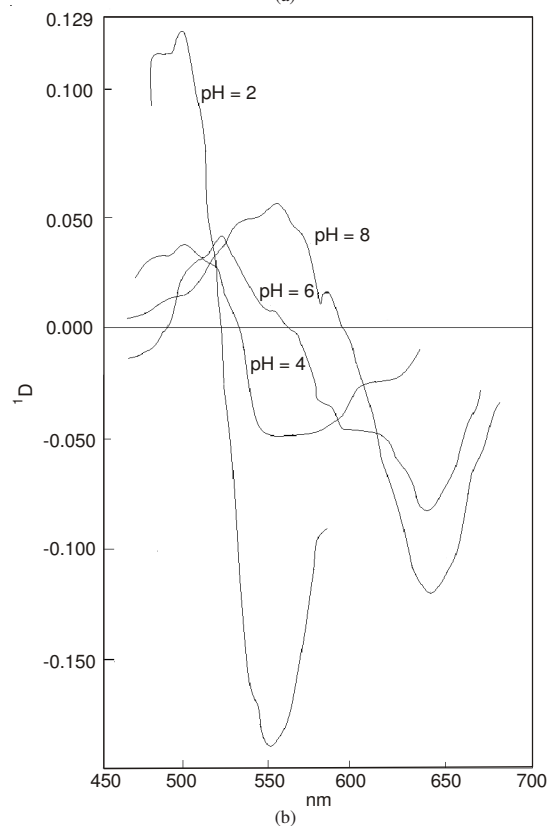
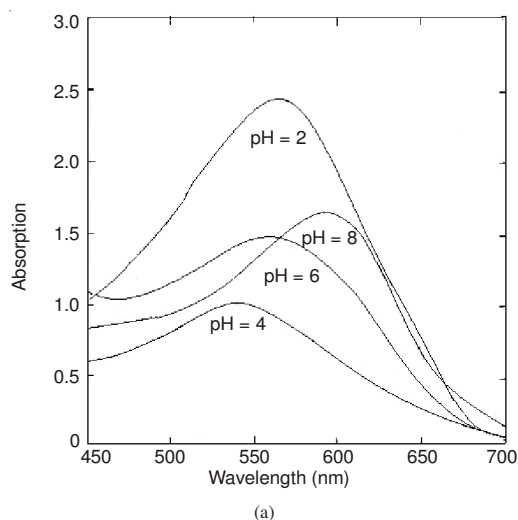


Fig. 1. (a) Visible absorption, (b) First derivative spectra of anthocyanins solution at different pH

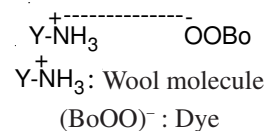


Fig. 2. Bonding between the dyestuff and amino acid groups of the wool

The dyeing mechanisms of wool with anthocyanins by pre-mordanting (1) and post-mordanting (2) can be considered as Fig. 3<sup>31</sup>.

Vegetative dye must have oxochrome groups in order to obtain good results in dyeing. Pelargonidin has four, cyanidin has five and malvidin has six oxochrome groups. These groups cause stable complex compounds to the woolen fabrics. These are inner complex<sup>6,32</sup>.



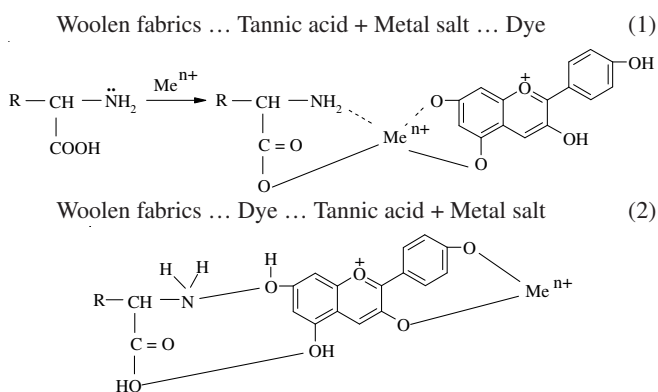


Fig. 3. Mechanism of pre-mordanting (1) and post-mordanting (2)

From the preliminary experiment, it was found that the optimum dyeing time and temperature were 1 h and 98-100 °C to give the highest K/S values for woolen fabrics. Therefore, the woolen fabrics and pre-treated woolen fabrics, with mordant mixture, were dyed with *Alliumcepa* L. extract solution at 98-100 °C for 1 h and different pH values. Different metal salts were used with tannic acid in 2-4 % keeping in mind the toxicity factor of some metal salts particularly copper, chromium and lead.

From initial experiments, it was also observed that pre- and post-mordanting techniques imparted better fastness properties for the woolen fabrics. Therefore, by adopting the pre- and post-mordanting techniques the dyed and un-dyed fabrics were mordanted with mordant mixtures (tannic acid + metal salt) given at Table-2.

The dyeing processes of the woolen fabrics with *Alliumcepa* L. dye were carried out by using some selected transition metal salts as mordant agents and tannic acid as second mordant agent at various pH values by pre- and post-mordanting methods. 88 woolen fabrics were dyed at pH 2, 4, 6 and 8. From the dyeing woolen fabrics 88 different colours or colour tones were obtained. When the comparison was made among the pH values, it was observed that  $Pb^{2+}$ ,  $Al^{3+}$ ,  $Sn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  gave nearly the same colour tones by all mordanting methods. The dyed woolen samples were given in Table-2, which shows woolen fabrics dyed by using mordant mixture (tannic acid + metal salts) according to methods of pre- and last-mordantation.

For an application in a textile dyeing procedure bright and intensive colours with good fastness properties have to be identified. To estimate the potential of dye extracted from red onion the application in a standardized dyeing procedure was tested. The technical potential of extracted material with regard to colour strength and light fastness properties of dyeing was checked. In Table-3 the results of the dyeing experiments are presented in the form of CIE-Lab coordinates, colour codes and light fastness properties. In many cases light fastness of natural dyeing is strongly influenced by the type of mordant used.

From the results shown in Table-3, significant improvement of light fastness is found for all of the metal salts and tannic acid.

It was observed that the colour quality of treated woolen fabrics, with tannic acid as second mordant, were higher than those of un-mordanted fabrics with tannic acid. Light fastness

was identified to be the major hint for a general introduction of tested natural dye (anthocyanins). A light fastness of at least 2-3 was set as a lower limit for positive selection. All the types of mordanting with various metal salts in presence of tannic acid showed a strong improvement at values of light fastness (from 4-8) while the mordants in absence of tannic acid had lower values (2-4) on light fastness<sup>32</sup>. The increase in the light fastness after mordanting in presence of tannic acid with metal ions may be due to the easier formation of the dye-metal-fiber bond<sup>33</sup>. Table-3 also describes that the effect of mordant mixtures on CIE  $L^*a^*b^*$  values for dyeing of woolen fabrics with red onion skins in open bath in the presence of varying the kind of mordant mixture, the colour of dyed wool fabrics changed from beige to black and from yellow to brown. When the colours were compared at pH = 2-8, it was observed that pale colours at pH = 2 and 8. The dye showed a higher dye uptake under weak acidic conditions (pH = 4 and 6) as compared to the alkaline (pH = 8) and strong acidic (pH = 2). This result showed that the chemical bond or bonds do not occur between dye and glucoside units at these pH values.

All the colour coordinates (except a few value of  $a^*$  and  $b^*$ ) were positive with respect to brightness ( $L^*$ ), red-green ( $a^*$ ) and yellow-blue ( $b^*$ ) and therefore all of them lie in the yellow-red quadrant of the colour space diagram (Table-3). Also it can be observed that mordant mixtures which show higher value of  $L^*$  show lighter shades while lower  $L^*$  values signify deeper shades for woolen fabrics. Similarly, negative  $a^*$  and negative  $b^*$  represent green and blue, respectively.

As shown in Table-2, varied hues of colour were obtained from pre- and post-mordanted woolen fabrics with  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Sn^{2+}$ ,  $Al^{3+}$ ,  $Cd^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$ . The variation in colour due to the use of different mordant is a well-known phenomenon<sup>5</sup>. The best colours were obtained in the presence of tannic acid with metal salts;  $Pb^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$  and  $Cu^{2+}$  at pH 2, all kinds of the mordant salts at pH 4,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$  and  $Mg^{2+}$  at pH 6 and pH 8, respectively. From the above findings, it was concluded that the apparent colours depended on the kind of mordant mixtures used in this study. The different mordant mixtures not only cause difference in hue colour but also changes in  $L^*$  values and brightness index values.

From Table-3 it can be noted that the woolen fabrics dyed pre- and post-mordanting at all pH values with  $Cu^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  showed the low  $L^*$  values indicating deeper shades obtained on mordanting with these metal salts, compared to that obtained with others with high  $L^*$  values. Thus, for all the pH,  $Cu^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  may effectively be used as mordant salts. Also, the woolen fabrics dyed pre- and post mordanted with  $Ni^{2+}$  and post mordanted with  $Pb^{2+}$  at pH = 4 and pH = 6 indicated low  $L^*$  values and deeper shades. From Table-3 it can also be seen that the woolen fabric post-mordanted with  $Cu^{2+}$  and tannic acid at pH = 4 showed the lowest  $L^*$  values indicating deeper shades obtained on mordanting with these metal salt compared to that obtained with the same mordant agents at pH = 2, 6 and 8 with higher  $L^*$  values. Also post-mordanting with  $Fe^{2+}$  and tannic acid at pH = 6 gave a maximum total colour difference ( $DE^* = 39.85$ ) as compared to the control, which is mainly attributed to the lower values of  $L^*$ , which is followed by  $Cu^{2+}$  and tannic acid at pH = 4 ( $DE^* = 29.72$ ). Post-mordanting with  $Fe^{2+}$  produced a very dark shade at pH = 6, while gave a

TABLE-2  
WOOLEN FABRICS DYED BY USING MORDANT MIXTURES (TANNIC ACID + METAL SALT)  
ACCORDING TO METHODS OF PRE- AND POST-MORDANTING

Tannic acid + metal salts and mordantation methods		pH = 2	pH = 4	pH = 6	pH = 8
		KCl, HCl, Buffer	CH <sub>3</sub> COOH, CH <sub>3</sub> COONa, Buffer	KH <sub>2</sub> PO <sub>4</sub> , NaOH, Buffer	KH <sub>2</sub> PO <sub>4</sub> , NaOH, Buffer
Co <sup>2+</sup>	Pre				
	Post				
Cu <sup>2+</sup>	Pre				
	Post				
Fe <sup>2+</sup>	Pre				
	Post				
Fe <sup>3+</sup>	Pre				
	Post				
Ni <sup>2+</sup>	Pre				
	Post				
Sn <sup>2+</sup>	Pre				
	Post				
Al <sup>3+</sup>	Pre				
	Post				
Cd <sup>2+</sup>	Pre				
	Post				
Mg <sup>2+</sup>	Pre				
	Post				
Zn <sup>2+</sup>	Pre				
	Post				
Pb <sup>2+</sup>	Pre				
	Post				

very pale colour at pH = 2. The rest of mordant mixtures gave nearly the same DE\* values.

### Conclusion

It may be concluded that the colour component isolated from the outer skin of red onion contained mainly anthocyanins.

The purpose of this study was extraction of anthocyanins from red onion skins and to investigate dyeing and lightfastness properties of woolen fabrics. In dyeing of woolen fabrics better fastness values were obtained from using of tannic acid together with various metal salts used as a mordant when compared to

TABLE-3  
EFFECT OF MORDANT MIXTURES ON CIE L\*a\*b\* VALUES AND LIGHT FASTNESS  
PROPERTIES FOR DYEING OF WOOLEN FABRICS WITH RED ONION IN OPEN BATH

	Mordants	DE*	L*	a*	b*	C*	h*	LF
Pre-mordanting pH = 2	Co <sup>2+</sup>	15.63	65.98	06.30	20.57	21.51	72.98	4
	Cu <sup>2+</sup>	13.87	56.22	05.10	21.37	21.97	76.58	8
	Fe <sup>2+</sup>	21.90	52.39	04.19	02.84	05.06	34.15	7-8
	Fe <sup>3+</sup>	15.77	49.86	04.59	16.81	17.43	74.73	7-8
	Ni <sup>2+</sup>	19.42	70.77	05.38	19.47	20.20	74.57	5
	Sn <sup>2+</sup>	18.26	73.28	05.34	22.03	21.32	74.75	8
	Al <sup>3+</sup>	21.00	72.73	05.39	21.08	21.76	75.65	7
	Cd <sup>2+</sup>	20.23	71.32	04.95	23.14	21.15	74.58	6-7
	Mg <sup>2+</sup>	18.24	70.45	04.48	23.03	20.64	73.26	8
	Zn <sup>2+</sup>	16.25	73.25	05.64	22.36	24.36	75.64	7
Pb <sup>2+</sup>	13.25	69.56	05.98	21.36	23.65	74.81	8	
Post-mordanting pH = 2	Co <sup>2+</sup>	18.19	69.39	05.87	20.73	21.55	74.19	4
	Cu <sup>2+</sup>	13.95	52.43	05.97	22.52	23.30	75.14	8
	Fe <sup>2+</sup>	19.60	51.92	02.84	08.18	08.66	70.84	8
	Fe <sup>3+</sup>	28.04	30.49	08.77	20.43	22.24	66.78	8
	Ni <sup>2+</sup>	19.33	71.20	05.98	19.45	20.35	72.91	4-5
	Sn <sup>2+</sup>	22.16	75.09	04.47	22.02	22.47	78.51	8
	Al <sup>3+</sup>	17.62	68.15	06.03	22.90	23.68	75.26	8
	Cd <sup>2+</sup>	15.99	66.82	06.61	21.22	22.22	72.70	6
	Mg <sup>2+</sup>	20.16	71.96	05.78	21.00	21.78	74.62	8
	Zn <sup>2+</sup>	18.80	70.26	05.72	18.64	19.50	72.95	7
Pb <sup>2+</sup>	15.68	59.94	-03.86	22.46	22.78	80.24	8	
Pre-mordanting pH = 4	Co <sup>2+</sup>	09.26	50.63	10.10	18.21	20.82	60.98	4
	Cu <sup>2+</sup>	21.58	38.95	-06.01	19.75	20.65	73.08	7-8
	Fe <sup>2+</sup>	20.35	48.65	02.02	12.32	16.32	69.28	6
	Fe <sup>3+</sup>	27.51	33.94	04.82	12.54	13.44	68.97	8
	Ni <sup>2+</sup>	05.63	53.86	11.71	18.68	22.05	57.91	4
	Sn <sup>2+</sup>	30.72	55.28	-11.31	49.62	50.89	77.16	7
	Al <sup>3+</sup>	17.48	62.10	-01.67	27.17	27.23	93.51	8
	Cd <sup>2+</sup>	12.04	47.16	14.79	19.83	24.74	53.30	7
	Mg <sup>2+</sup>	08.94	50.24	14.26	20.34	24.84	54.96	8
	Zn <sup>2+</sup>	09.43	51.93	08.61	15.78	17.97	61.37	8
Pb <sup>2+</sup>	13.58	46.24	11.05	15.85	19.32	55.12	5	
Post-mordanting pH = 4	Co <sup>2+</sup>	07.48	57.81	07.05	15.90	17.40	66.09	5
	Cu <sup>2+</sup>	29.72	35.11	-05.17	15.12	15.98	71.13	8
	Fe <sup>2+</sup>	21.56	39.62	07.69	16.23	19.26	64.31	7-8
	Fe <sup>3+</sup>	20.25	38.50	08.07	16.37	18.25	63.75	7
	Ni <sup>2+</sup>	06.82	55.18	08.79	16.49	18.69	61.95	6
	Sn <sup>2+</sup>	08.88	63.23	07.61	24.15	25.33	72.51	8
	Al <sup>3+</sup>	11.91	66.72	04.50	18.19	18.73	76.11	6
	Cd <sup>2+</sup>	06.05	53.61	11.56	17.88	21.29	57.12	7
	Mg <sup>2+</sup>	07.21	58.42	07.67	15.22	17.04	63.26	8
	Zn <sup>2+</sup>	11.21	49.13	08.80	17.71	19.78	63.57	8
Pb <sup>2+</sup>	16.35	46.07	-05.74	25.60	26.83	77.36	8	
Pre-mordanting pH = 6	Co <sup>2+</sup>	03.99	56.39	05.70	18.95	19.79	73.25	6
	Cu <sup>2+</sup>	12.49	49.72	-06.32	20.03	20.26	76.25	8
	Fe <sup>2+</sup>	30.32	30.93	05.56	-00.170	05.56	01.77	4
	Fe <sup>3+</sup>	10.97	51.59	03.59	12.18	12.70	73.58	6
	Ni <sup>2+</sup>	07.04	53.34	05.39	20.87	21.55	75.52	7
	Sn <sup>2+</sup>	14.42	70.90	04.55	25.75	26.15	79.98	7-8
	Al <sup>3+</sup>	11.74	70.00	04.45	16.58	17.16	74.97	8
	Cd <sup>2+</sup>	02.91	60.49	06.32	19.72	20.71	72.24	5-6
	Mg <sup>2+</sup>	01.89	57.71	08.40	17.18	19.13	63.96	7
	Zn <sup>2+</sup>	05.60	63.97	05.72	18.38	19.25	72.71	6-7
Pb <sup>2+</sup>	09.68	66.73	04.64	13.84	14.60	71.48	6	
Post-mordanting pH = 6	Co <sup>2+</sup>	05.78	54.29	07.44	15.48	17.17	64.34	6
	Cu <sup>2+</sup>	10.94	49.17	04.42	16.58	17.16	75.07	8
	Fe <sup>2+</sup>	39.85	24.84	01.62	-00.67	01.76	34.53	6
	Fe <sup>3+</sup>	05.49	31.56	07.49	21.34	25.48	65.12	7
	Ni <sup>2+</sup>	08.07	51.85	-05.34	17.07	17.89	72.62	5
	Sn <sup>2+</sup>	05.23	63.39	10.71	20.55	23.17	62.46	8
	Al <sup>3+</sup>	03.54	56.34	09.94	20.06	22.39	63.64	7
	Cd <sup>2+</sup>	04.72	57.01	06.87	14.55	16.09	64.47	5
	Mg <sup>2+</sup>	11.34	49.45	08.03	16.55	14.90	57.39	7-8
	Zn <sup>2+</sup>	03.49	60.85	07.58	15.53	17.58	63.99	6
Pb <sup>2+</sup>	08.26	52.86	08.90	13.05	15.80	55.69	6	

Pre-Mordanting pH=8	Co <sup>2+</sup>	30.24	47.11	-07.40	20.05	21.37	69.73	5
	Cu <sup>2+</sup>	35.87	42.15	-04.60	22.63	23.09	78.52	7-8
	Fe <sup>2+</sup>	26.97	51.24	02.32	02.91	03.72	51.49	4
	Fe <sup>3+</sup>	20.04	56.76	02.72	11.50	11.81	76.69	4
	Ni <sup>2+</sup>	28.82	48.97	07.07	21.22	22.37	71.57	6
	Sn <sup>2+</sup>	09.60	67.46	04.83	14.48	15.27	71.55	8
	Al <sup>3+</sup>	12.80	66.94	04.46	19.93	20.42	77.39	7
	Cd <sup>2+</sup>	21.22	63.21	06.24	28.41	29.09	77.61	7
	Mg <sup>2+</sup>	19.88	57.27	08.12	17.12	19.23	62.31	7
	Zn <sup>2+</sup>	16.58	62.41	07.00	20.91	22.05	71.49	6
Pb <sup>2+</sup>	21.88	54.72	03.42	11.94	12.43	74.00	7	
Post-mordanting pH = 8	Co <sup>2+</sup>	17.39	59.24	05.30	14.87	15.79	70.37	4
	Cu <sup>2+</sup>	24.97	52.23	05.37	18.39	19.16	73.74	8
	Fe <sup>2+</sup>	26.97	41.50	02.26	02.20	03.15	44.21	5
	Fe <sup>3+</sup>	12.88	65.79	05.34	18.92	19.66	74.24	4
	Ni <sup>2+</sup>	19.72	56.83	05.34	14.75	15.69	70.11	6
	Sn <sup>2+</sup>	13.48	63.06	06.49	14.54	15.93	65.94	7
	Al <sup>3+</sup>	10.82	62.56	09.78	19.45	21.77	63.31	7
	Cd <sup>2+</sup>	17.74	60.05	05.06	18.57	19.25	74.77	7
	Mg <sup>2+</sup>	18.38	57.99	05.76	12.66	13.91	65.53	7-8
	Zn <sup>2+</sup>	15.89	60.73	07.48	15.40	17.12	64.10	5-6
Pb <sup>2+</sup>	15.38	61.02	05.12	12.29	13.31	67.38	6	

L\* = Lightness; a\* = red-green; b\* = yellow-blue, Control: Dyed shades without mordanting, LF: Light fastness (fastness to light: 1 = poor, 8 = excellent).

the dyeing with *Alliumcepa* L. alone. The shade and the light fastness of the natural dye containing anthocyanin component is depended on the type of mordant. As can be seen in the experiments with different metal salts and tannic acid, the fastness to light of the dyeing is strongly influenced by the type of mordant mixtures. The best mordants found to be Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O for improving the colour tone of woolen fabrics in the presence of tannic acid. Mordanting with Fe<sup>2+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> gave dull shades, while the rest of the mordants gave brighter shades.

The presented results prove the possibility of using red onion skins as source for natural dyeing of woolen fabrics. The use of natural dyes can be one of the substitute alternatives for many hazardous synthetic dyes. Red onion skins are not used for any purpose. If they are used to obtain dye, it would probably be an important raw material in terms of commercial use. Generally, different colours and colour tones and excellent light fastness dyeing were obtained with anthocyanins. The dyes obtained from the native plants may be alternative sources to synthetic dyes for the dyeing of wool. Preparation of dry powder is in progress so that this can be a cheap source of natural dye having good shelf life.

#### ACKNOWLEDGEMENTS

The authors thanks Marmara University, Faculty of Technical Education and Department of Textile Studies for conducting the analyses.

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