Asian Journal of Chemistry Vol. 20, No. 4 (2008), 2891-2902

Extraction of Anthocyanin Pigments from Red Onion (*Alliumcepa* L.) and Dyeing Woolen Fabrics

GÜLSAH GÜMRÜKÇÜ*, MAHMURE ÜSTÜN ÖZGÜR and CENKKUT GÜLTEKIN†
Department of Chemistry, Faculty of Art and Science
Yildiz Technical University, Davutpasa, 34210, Istanbul, Turkey
E-mail: gumrukcugulsah@hotmail.com; mozgur@yildiz.edu.tr

Natural colours have attracted the attention of the entire world because of their non-hazardous nature. In present study, woolen fabrics were dyed with natural dyes derived from red-onion (*Alliumcepa* L.) using various mordants by open bath dyeing technique. Natural dye (anthocyanins) was extracted from red-onion skins with acetic acid:ethanol:water (1:80:19, v/v/v) mixture solution. The amount of total anthocyanins was determined by using the derivative spectrophotometric method and found to be 13.5 mg/100 g for fresh onion skin and 5.2 g/100 g for dry onion skin. Dyeing processes were carried out according to pre-, together- and last-mordanting methods by using buffer solutions at the pH = 2-8 interval and for 1 h at 98-100 ºC. Some metal salts such as $Al(OH)_3$, $Cu(NO_3)_2$, $Fe(NO_3)_2$, $Zn(NO_3)_2$, $NiCl_2$, $SnCl_2$, $Pb(CH_3COOH)_2$ were used as mordantation agents. In addition, various studies were carried out on the effect of mordant quantity and kind of mordant salt in dyeing. The colour changes were evaluated instrumentally with a colour difference meter. Colour differences in CIE L*a*b* units and gray scale classifications were reported. Dyeing conditions and other characteristics showed that mordant was more important than dye in predicting lightfastness of coloured textiles and good lightfastness which was between 2 and 4 values were obtained.

Key Words: Anthocyanins, Red onion, *Alliumcepa* L., Woolen fabrics, Mordants.

INTRODUCTION

The contemporary textile processing industry is getting more and more inquiries regarding 'dyeing with natural dyes' and therefore, the subject of natural colours has assumed a great significance. An exhaustive review on the subject on natural dyes in textile applications has been published by Taylor[1]. An increasing realization, that the intermediates and chemicals

†Department of Textile Studies, Faculty of Technical Education, Marmara University, Goztepe, 34722, Istanbul, Turkey.

used in synthetic dyes are toxic and hazardous to human health as well as to the environment, has led to revival of interest in the non-toxic eco-friendly colouring materials. The use of natural dyes can be one of the substitute alternatives for many hazardous synthetic dyes. Serious efforts are now being made to boost the use of natural dyes and to identify more raw materials and to standardize the recipes for their use.

Nowadays, the natural dyes are produced in Asian countries such as Turkey, Iran, India, Azerbaijani and being used in most countries of the world[2].

There are many industrial plants which contain natural dyes in Turkey[3]. Red-onion (*Allium cepa* L.) is one of them. The outermost dry papery skin of red-onion contains anthocyanins. The natural pigments, anthocyanins are available from a number of fruits and vegetables. The depth of colour in fruit depends on the quantity of anthocyanin present. The anthocyanins are water-soluble and are easily extracted into weakly acidic solutions. Their colourant performance can be modified by the presence of metals, by pH and by interaction with colourless flavonoids[4]. Anthocyanidins, which are in plant tissue, show different properties with the number of -OH group which are in 2-phenyl group (Fig. 1).

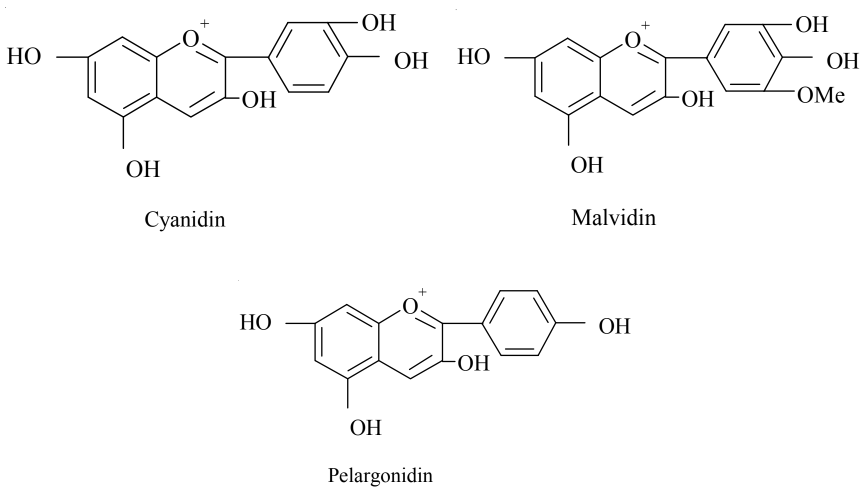


Fig. 1. Main anthocyanins in the red-onion skins were pelargonidin, malvidin and cyanidin[4-6].

The four novel cyanidin have been isolated in minor amounts from pigmented scales of red-onion, in addition to six known anthocyanins by several workers[7,8].

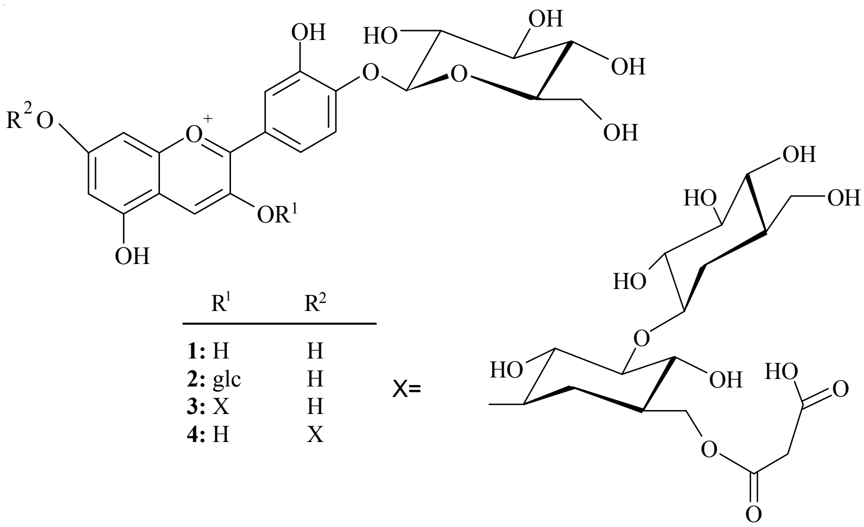


Fig. 2. Molecular structure of the new cyanidins isolated from pigmented scales of red onion

The literature survey indicates that there is no work reported in the field of dyeing wool fabrics with red-onion skins.

Önal[5] has dyed wool, feathered-leather and cotton with dyestuff extracted from yellow onion and some mordant agents (various salts, acid-base and a new mordant mixture. Another study was given by Lokhande *et al*[7]. In their study, nylon fabric was dyed with natural dye derived from yellow onion (*Allium cepa* L.) by using various mordants (alum, copper sulfate, ferrous sulfate, stannous chloride, tannic acid, harda powder and aluminium sulfate) by two different techniques (*viz.*, open bath and HTHP dyeing methods). They were obtained between 2-4 values for lightfastness in gray scale[8]. In other study, on this subject, anthocyanin was obtained from cultured Euphorbiamilli cells and used for dyeing silk, wool and cotton at low pH. Through the application of different salts as post-mordants, red silk cloth has been turned violet, red-violet, orange, yellow, green-yellow and green. 500 Silk cloth samples have been dyed by Yamamato and 25 of them have been an acceptable level of lightfastness[9].

The present paper is an effort for determining the dyeing capacity of anthocyanins for woolen fabrics from the point of view of their lightfastness. In order to investigate the most proper mordant and pH value in terms of the light-fastness in dyeing the wool samples by anthocyanins some selected metal salts such as $Al(OH)_3$, $Cu(NO_3)_2$, $Fe(NO_3)_2$, $Zn(NO_3)_2$, $NiCl_2$, $SnCl_2$, $Pb(CH_3COOH)_2$ were used as mordant agents at different pH (pH = 2, 4, 6, 8) values. Dyeing procedures were carried out at different pH values by three types of mordanting methods; pre-, together- and last-mordanting. 90 woolen fabrics were dyed.

EXPERIMENTAL

Spectrophotometer (Philips PU 8700 UV-VIS), cuvette (Hellma, 100-QS), mechanic blender (Bosch 1210, 500W, 27000, 1/min). Dyeing was carried out 1994 Roaches dyeing machine, 4-dye compertment each with 4-dye cans each. 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.

The source of natural dye was from onion. The onions were purchased from the local market. Before the experiment the outer skin were dried in shade and than cut very tiny pieces. A 100 % wool woven fabric, medium weight, scoured and bleached was used for dyeing. It was obtained from YUNSAN A.S., Istanbul, Turkey. The following mordants were used for mordanting $AlCl_3.6H_2O$, $Al(NO_3)_3.9H_2O$, $Al_2(SO_4)_3.16H_2O$, $KAlSO_4.12H_2O$, $Al(OH)_3$, $Cu(NO_3)_2.3H_2O$, $Cu(NO_3)_2.6H_2O$, $Pb(CH_3COOH)_2.3H_2O$, $Fe(NO_3)_2.9H_2O$, $Zn(NO_3)_2.6H_2O$, $NiCl_2.6H_2O$, $MgCl_3.6H_2O$, $SnCl_2.2H_2O$. Acetate and phosphate buffer solutions were used for adjusting the acidic and alkaline pH respectively.

Extraction solution: The mixture of 800 mL ethanol and 10 mL acetic acid was completed with distilled water to 1 L and used for the extraction anthocyanins from the red-onion skins.

Extraction of dyestuff from the red-onion skin: Dried and cut very tiny pieces of the red-onion skin (10 g) was mixtured with 500 mL extraction solution and heated at 40-50 ºC for extraction of anthocyanins from *Allium cepa* L. The heating continued till the total dyestuff in the skin of the onion passed the extraction solution. This mixture homogenized by using a mechanic blender for 20 min. Then, the suspension was transferred into 1 L volumetric flask by using coarse filter paper and diluted to an appropriate volume with distilled water and the dark red extract was used as dye-solution. This solution has mainly cyanidin, malvidin and pelargonidin, which are known earlier[4-6]. First derivative spectrophotometric method was utilized to determine the total dyestuff in the skin of the onion[10].

Effect of amount of mordant on dyeing of woolen fabrics: To research how the amount of mordant affected to dyeing of woolen fabrics; each of the white woolen fabrics (1 g) was treated with 0.1-2.5 g $Cu(NO_3)_2$ as a mordant salt by using together mordanting method at pH = 4 (this pH and mordanting method was chosen because of obtained darker shades than the others). Tones of the colours were evaluated according to the quantities of the mordant salt.

Effect of the kind of mordant on dyeing of woolen fabrics: This study was carried out to determine the effect of different salts of the same mordant on dyeing woolen fabrics. Each of the white woolen fabrics (1 g) was treated with required amount of mordant (on the weight of fabric basis) $AlCl_3.6H_2O$, $Al(NO_3)_3.9H_2O$, $Al_2(SO_4)_3.16H_2O$ and $KAlSO_4.12H_2O$. Dyeing of woolen fabrics was carried out by using together mordanting method at pH = 4. The colour differences of dyed woolen fabrics were determined according to without mordant composite fabrics.

Dyeing of woolen fabrics: Dyeing of woolen fabrics was carried out using the three types of mordanting methods: Pre-, together- and last-mordanting. The methods were carried out at pH: 2, 4, 6 and 8 for each mordant. Material-to-liguor-ratio (M.L.R.) of 1/250 was mentained for dyeing. The intensity of the colour was selected 2 %.

Pre-mordanting: Each of woolen fabrics (1 g) was placed into 250 mL of mordant solution in room temperature (25 ºC). The temperature of the bath was raised to boil and mordanting was continued for 1 h, at boil (98 ºC). After cooling the fabric was removed, squeezed and placed in 250 mL dye bath (dye solution + buffer solution). The temperature of the bath was raised to boil and dyeing was continued for another 1 h at the boil. It was allowed to cool. The dyed woolen fabric was rinsed, washed with hot and cold distilled water and dried.

Together-mordanting: Required amount of mordant (on the weight of fabric basis), 250 mL dye-bath (dye solution + buffer solution) and 1 g of woolen fabrics were placed into 300 mL dye-pots at room temperature. The temperature of the bath was raised to boil and dyeing was continued for 1 h at boil. After cooling, the fabrics were removed, squeezed and washed with hot and cold water. Then, they were dried.

Post-mordanting: 1 g of woolen fabric was placed into 250 mL of dye-bath at room temperature. The temperature of the bath was raised to boil and dyeing was continued for 1 h at boil. After cooling the fabric, squeezed and washed. Then this was put in 250 mL buffer solution consisting of required amount of mordant at room temperature. The temperature of the bath was raised to boil and mordanting was continued for 1 h at boil. Finally, the fabric was squeezed, washed and dried.

RESULTS AND DISCUSSION

Anthocyanins were extracted from red-onion skins, with acetic acid: ethanol:water (1:80:19, v/v/v) mixture solution. First derivative spectrophotometric method was utilized to determined total dyestuff in the skin of the onion[10]. In this study 90 woolen fabrics were dyed with the pre-, together- and last-mordanting methods at the pH = 2-8 interval. The effect of the quantity of mordant was carried out. Most suitable mordant quantity was determined as 1 g. Thus, in present studies, 1 g mordant salts was used. When we used different salt of Al^{3+} ions such as $Al(OH)_3$, $AlCl_3$, $Al(NO_3)_2$, $KAlSO_4$ and $Al_2(SO_4)_3$ as a mordant, it was obtained darker and bright colour tones with $Al(OH)_3$. Woolen fabrics were not dyed using any mordant. When mordant was used various colour tones except for red were obtained. We used more than ten chemical substances (mordant) to bind dye to woolen fabric to maintain strongness and brightness of the colours and to obtain various colours.

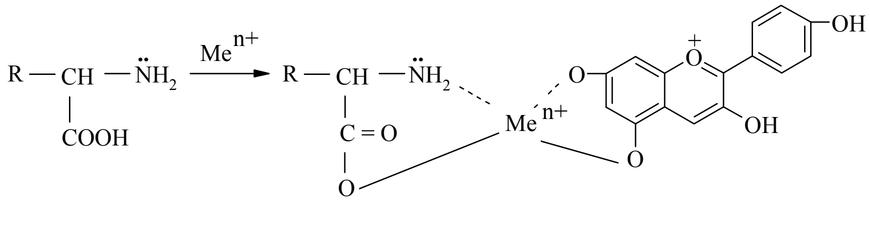
Molecules of wool consist of amino acid units. Proteins are formed from amino acids which contain free amino and carboxyl groups. Therefore, wool can be considered as an amphoteric compound[11]. During the dyeing of the wool, a hydrogen bond occurs between the dyestuff and the amino groups of the wool (Fig. 3)[5,12].

\+ ....- Y: Wool Molecule
Y - NH OO - Bo BoOO: Dyestuff

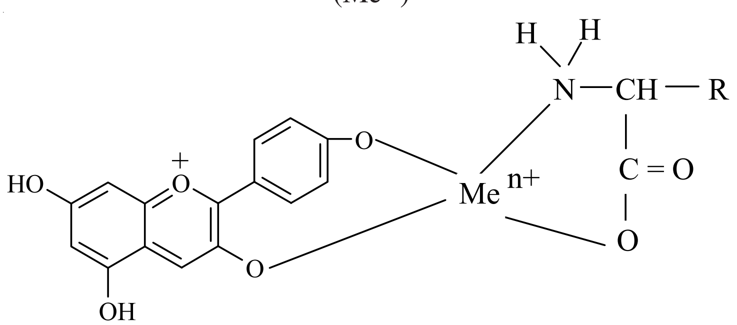
Fig. 3. The dyestuff and the amino groups of the wool

Mechanism of pre-mordantation (1), together mordantation (2) and last mordantation (3) can be considered as given in Fig. 4[12].

Wool --------- Mordant-------- Dyestuff (1)
(Me^{n+})



Dyestuff --------- Mordant --------- Wool (2)
(Me^{n+})



Wool --------- Dyestuff --------- Mordant (3)
(Me^{n+})

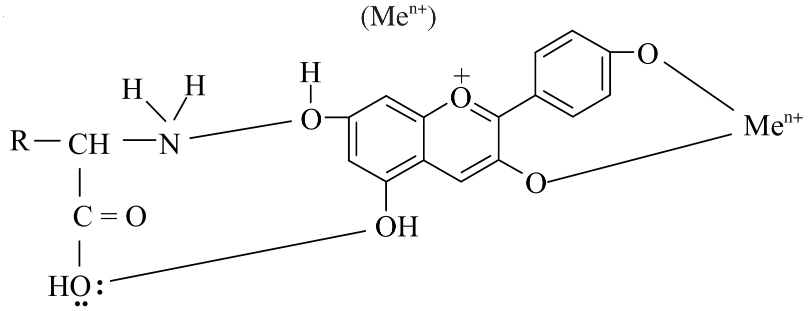


Fig. 4. Mechanism of pre-mordantation (1), together mordantation (2) and last mordantation (3)

Vegetative dyestuff must have oxochrome groups in order to obtain better 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[5,12].

Table-1 described that the effect of mordants on CIE L*a*b* values and light fastness properties for dyeing of woolen fabrics with red onion in open bath. When the colours were compared at pH= 2-8 interval, it was observed that pale colours at pH = 2 and 8. The dyestuff 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) conditions. The colour differences of dyed woolen fabrics were determined without mordant dyed woolen fabrics.

From Table-1, it can be noted that mordanting with Fe^{2+} in open bath dyeing gave maximum total colour differences (DE* = 41, 48, 35, 74, 47, 46; pre-, together- and last- mordanting, respectively) as compared to the control, which is mainly attributed to the lover values of L*, which is followed by Pb^{2+} (DE* = 22, 13, 35, 26, 41, 08) and Cu^{2+} (DE* = 25, 73, 28, 93, 27, 79). The rest of the mordants gave nearly the same values of DE*. The C* represents Chroma and indicates the saturation value of the colour and h* represents the hue angle (hue angles for red, yellow, green and blue are 30, 90, 180 and 270, respectively). From Table-1, it can be noted that mordanting Cu^{2+} and Pb^{2+} gave a maximum total colour difference when last-mordanting method was used. Al^{3+}, Co^{2+} and Fe^{2+} gave a maximum value when pre- and last-mordanting methods were used. The other mordants gave highest values of DE* when pre-mordanting method was used. At pH = 6 (Table-1), all the mordants gave the highest values of DE* when together-mordanting method was used, except Al^{3+} salt. It gave a maximum value of DE*, dyeing with pre-mordanting method. When together-mordanting was used Cu^{2+} and Pb^{2+} gave a maximum value of total colour difference

TABLE-1
EFFECT OF MORDANTS ON CIE L*a*b* VALUES AND LIGHTFASTNESS PROPERTIES FOR DYEING OF WOOL WITH RED ONION IN OPEN BATH

	Mordants	DE*	L*	a*	b*	C*	h*	LF
Pre-mordanting pH = 2	Co^{2+}	19.135	67.44	6.13	21.69	72.98	34.76	3
	Cu^{2+}	25.732	65.05	6.98	20.89	71.23	36.92	3
	Fe^{2+}	41.478	57.27	10.12	21.12	25.23	65.31	3
	Ni^{2+}	22.130	69.15	9.53	18.75	23.70	66.81	3
	Sn^{2+}	38.226	69.94	-3.46	25.93	20.42	77.39	2
	Al^{3+}	20.798	70.15	8.52	18.94	20.77	65.77	3
	Cd^{2+}	18.950	70.32	8.54	18.96	20.45	65.24	3
	Mg^{2+}	17.432	69.25	9.47	18.69	23.78	66.80	3
	Zn^{2+}	18.579	73.53	8.56	19.30	20.82	67.11	3
	Pb^{2+}	22.136	59.92	5.69	14.58	19.73	41.12	3
Together-mordanting pH = 2	Co^{2+}	34.971	60.12	9.97	22.34	25.46	59.87	3
	Cu^{2+}	28.934	63.10	-3.67	25.17	26.23	83.51	3
	Fe^{2+}	35.746	58.97	9.78	20.15	24.23	63.27	3
	Ni^{2+}	27.331	64.09	13.53	12.16	27.81	78.31	2
	Sn^{2+}	18.769	68.05	6.95	17.67	71.35	35.86	3
	Al^{3+}	30.227	59.02	4.25	15.29	13.31	67.38	1
	Cd^{2+}	29.631	64.45	17.53	12.14	25.82	79.51	2
	Mg^{2+}	26.869	65.09	14.53	13.27	25.81	78.31	2
	Zn^{2+}	20.602	71.36	6.76	17.18	20.14	56.30	2
	Pb^{2+}	35.265	52.04	6.96	7.06	11.82	46.33	2
Last mordanting pH = 2	Co^{2+}	18.558	67.05	6.56	21.67	70.35	35.76	4
	Cu^{2+}	27.792	61.92	4.69	18.58	19.73	41.12	3
	Fe^{2+}	47.467	57.97	9.95	19.86	21.46	69.34	4
	Ni^{2+}	16.900	70.15	8.52	18.94	20.77	65.77	3
	Sn^{2+}	22.164	71.83	4.31	26.03	26.38	80.60	3
	Al^{3+}	19.522	72.41	6.78	17.42	19.78	70.87	3
	Cd^{2+}	20.454	73.23	6.70	18.71	19.88	70.29	3
	Mg^{2+}	19.412	73.13	8.43	19.03	20.82	66.10	3
	Zn^{2+}	21.433	71.95	6.86	17.22	19.95	55.39	3
	Pb^{2+}	41.081	54.63	10.10	18.21	20.82	60.98	3
Pre-mordanting pH = 4	Co^{2+}	42.213	58.27	9.98	22.15	27.23	67.31	3
	Cu^{2+}	43.368	54.28	-15.31	42.62	50.89	77.16	3
	Fe^{2+}	50.722	39.23	6.15	18.81	22.75	82.08	3-4
	Ni^{2+}	43.954	60.67	8.80	10.25	15.69	49.29	3
	Sn^{2+}	57.018	48.07	-5.74	27.60	26.83	77.36	2
	Al^{3+}	42.404	55.28	-11.31	45.62	50.89	77.16	3
	Cd^{2+}	45.063	47.16	15.79	16.83	32.74	53.30	3
	Mg^{2+}	41.695	49.14	13.32	17.79	35.72	56.31	3
	Zn^{2+}	40.713	50.24	15.26	19.34	24.84	54.96	3
	Pb^{2+}	33.804	47.16	15.79	16.83	32.74	53.30	3

	Mordants	DE*	L*	a*	b*	C*	h*	LF
Together-mordanting pH = 4	Co^{2+}	35.762	60.77	7.34	7.96	10.82	47.33	3
	Cu^{2+}	34.363	52.13	-21.34	30.12	49.58	81.03	4
	Fe^{2+}	36.772	57.59	3.61	15.18	17.70	73.58	3
	Ni^{2+}	30.117	66.01	6.94	15.33	16.83	61.64	3
	Sn^{2+}	21.416	83.09	4.47	22.02	22.47	78.51	3
	Al^{3+}	22.370	72.10	-0.67	21.17	25.23	56.51	3
	Cd^{2+}	38.821	68.02	6.01	14.03	17.80	62.74	3
	Mg^{2+}	32.966	58.53	12.61	19.60	23.31	57.24	3
	Zn^{2+}	11.840	65.67	7.80	11.25	13.69	55.29	3
	Pb^{2+}	33.804	68.43	6.13	14.17	18.85	63.75	3
Last mordanting pH = 4	Co^{2+}	40.429	57.97	10.78	20.11	24.23	69.27	2-3
	Cu^{2+}	49.438	38.45	6.17	18.75	21.75	79.08	4
	Fe^{2+}	49.686	51.62	11.13	16.76	21.82	69.98	4
	Ni^{2+}	40.062	52.13	10.25	18.05	26.23	51.27	3
	Sn^{2+}	43.686	49.67	-4.74	28.98	29.83	79.45	3
	Al^{3+}	42.699	49.67	1.74	22.98	29.65	68.45	3
	Cd^{2+}	12.653	60.91	5.68	9.53	11.10	59.20	1
	Mg^{2+}	27.256	45.59	14.28	17.13	31.02	57.51	3
	Zn^{2+}	11.312	48.21	14.51	22.03	26.38	56.62	2
	Pb^{2+}	49.519	51.96	8.63	15.18	17.86	61.25	3
Pre-mordanting pH = 6	Co^{2+}	4.387	54.54	9.65	19.43	21.70	63.59	3
	Cu^{2+}	8.162	53.30	5.55	23.26	23.92	76.58	3
	Fe^{2+}	70155	66.14	9.91	17.85	20.41	60.97	3
	Ni^{2+}	4.669	56.76	8.78	22.42	24.08	68.61	3
	Sn^{2+}	11.266	51.44	5.03	25.85	26.33	78.99	3
	Al^{3+}	30.21	56.95	12.83	20.06	23.81	57.39	3
	Cd^{2+}	7.647	55.05	14.64	20.54	25.23	54.52	3
	Mg^{2+}	3.405	59.29	11.76	19.50	22.77	58.89	3
	Zn^{2+}	6.344	57.10	14.40	19.74	24.43	53.88	3
	Pb^{2+}	4.767	60.99	12.83	19.37	23.23	56.50	3
Together-mordanting pH = 6	Co^{2+}	36.985	60.72	5.13	18.05	20.73	41.54	3
	Cu^{2+}	39.030	49.85	1.65	22.85	29.14	68.54	3
	Fe^{2+}	26.121	63.09	13.63	12.12	27.71	78.36	3
	Ni^{2+}	37.026	51.64	14.06	19.45	27.84	53.96	3
	Sn^{2+}	34.592	57.40	4.70	19.15	20.79	71.23	3
	Al^{3+}	23.610	63.32	8.27	21.94	26.73	60.17	3
	Cd^{2+}	22.664	52.66	14.26	19.18	27.54	53.15	3
	Mg^{2+}	38.416	52.67	14.36	19.28	27.55	53.36	3
	Zn^{2+}	36.360	62.45	18.53	15.14	25.82	79.51	3
	Pb^{2+}	39.307	62.63	17.24	15.96	25.33	78.61	3

	Mordants	DE*	L*	a*	b*	C*	h*	LF
Last mordanting pH = 6	Co^{2+}	28.589	66.73	4.64	13.84	14.60	71.48	3
	Cu^{2+}	33.715	48.12	1.35	21.97	25.31	65.32	4
	Fe^{2+}	35.578	59.16	9.99	20.11	24.06	63.18	4
	Ni^{2+}	32.724	62.19	13.45	12.03	27.79	78.26	3
	Sn^{2+}	27.959	65.01	6.85	14.28	72.32	36.89	3
	Al^{3+}	23.615	73.32	6.71	18.56	19.75	70.32	3
	Cd^{2+}	12.992	69.83	1.83	13.95	14.07	82.54	3
	Mg^{2+}	30.131	53.04	7.96	5.06	12.82	49.33	3
	Zn^{2+}	11.300	64.05	5.85	8.60	10.40	55.79	3
	Pb^{2+}	29.175	56.95	12.83	20.06	23.81	57.39	3
Pre-mordanting pH = 8	Co^{2+}	18.35	58.22	5.41	14.91	15.86	70.04	3
	Cu^{2+}	17.155	62.15	1.56	19.40	19.46	85.39	3
	Fe^{2+}	8.117	68.07	7.50	11.12	13.42	56.00	3
	Ni^{2+}	12.117	66.12	4.25	17.49	18.00	76.33	3
	Sn^{2+}	46.325	72.15	7.52	19.24	21.57	64.72	3
	Al^{3+}	15.809	62.56	9.78	19.45	21.77	63.31	3
	Cd^{2+}	16.257	67.14	4.70	24.85	25.29	79.30	3
	Mg^{2+}	8.785	68.56	6.25	15.82	17.01	68.43	3
	Zn^{2+}	8.815	69.73	6.68	17.61	18.83	69.22	3
	Pb^{2+}	7.945	69.50	6.30	15.75	16.96	68.21	3
Together-mordanting pH = 8	Co^{2+}	33.325	65.72	4.65	13.86	14.61	71.49	3
	Cu^{2+}	35.058	59.85	-3.16	22.33	22.85	80.23	4
	Fe^{2+}	13.972	68.43	6.16	21.29	72.58	35.72	4
	Ni^{2+}	21.821	61.92	4.69	18.58	19.73	41.12	3
	Sn^{2+}	39.424	59.28	5.31	42.68	51.80	79.15	2
	Al^{3+}	23.880	63.69	8.58	20.05	20.51	62.01	3
	Cd^{2+}	28.325	65.75	4.86	21.23	21.78	77.11	3
	Mg^{2+}	23.336	64.89	4.65	22.46	19.16	37.26	3
	Zn^{2+}	28.133	59.92	5.69	14.58	19.73	41.12	3
	Pb^{2+}	18.200	68.91	6.25	15.32	17.01	59.01	3
Last mordanting pH = 8	Co^{2+}	23.466	60.78	7.25	7.56	10.63	47.32	3
	Cu^{2+}	23.848	58.39	5.37	14.56	14.65	70.33	3
	Fe^{2+}	20.419	69.17	9.52	18.76	23.72	66.51	3
	Ni^{2+}	22.335	63.25	4.23	17.56	15.12	39.79	3
	Sn^{2+}	18.885	73.23	6.70	18.71	19.88	70.29	3
	Al^{3+}	19.627	68.15	7.52	19.54	20.37	65.47	3
	Cd^{2+}	23.520	64.15	3.92	23.56	16.13	38.76	3
	Mg^{2+}	24.491	65.43	6.13	13.17	18.85	63.75	3
	Zn^{2+}	23.101	68.25	6.32	15.41	17.91	68.19	3
	Pb^{2+}	22.660	68.05	6.95	17.67	71.35	35.86	3

(39, 03, 39 and 30, respectively). At pH = 8 (Table-1), most of the mordant gave higher DE* values dyeing together- mordanting method. Pale of colour-tones were obtained at this pH, except Sn^{2+} salt. Sn^{2+} salt gave good greenish-brown shades at this pH, but its light fastness is not good.

The dyed woolen samples were given in Table-2. From the dyeing woolen fabrics 90 different colours or colour tones were obtained. When the comparison was made among pH values 2, 4, 6 and 8, it was observed that Cd^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} gave nearly the same colour tones by all mordanting methods. Sn^{2+} gave greenish brown shades at pH = 8 by the together mordantation method.

TABLE-2
WOOLLEN FABRICS DYED BY USING VARIOUS MORDANTS ACCORDING TO METHODS OF PRE- TOGETHER- AND LAST-MORDANTATION

Mordant Salt and Mordantation Methods		pH=2 KCl HCl Buffer	pH=4 CH_3COOH CH_3COONa Buffer	pH=6 KH_2PO_4 NaOH Buffer	pH=8 KH_2PO_4 NaOH Buffer
Co^{2+}	Pre				
	Together				
	Last				
Cu^{2+}	Pre				
	Together				
	Last				
Fe^{2+}	Pre				
	Together				
	Last				
Ni^{2+}	Pre				
	Together				
	Last				
Sn^{2+}	Pre				
	Together				
	Last				

Mordant Salt and Mordantation Methods		pH=2 KCl HCl Buffer	pH=4 CH_3COOH CH_3COONa Buffer	pH=6 KH_2PO_4 NaOH Buffer	pH=8 KH_2PO_4 NaOH Buffer
Al^{3+}	Pre				
	Together				
	Last				
Cd^{2+}	Pre				
	Together				
	Last				
Mg^{2+}	Pre				
	Together				
	Last				
Zn^{2+}	Pre				
	Together				
	Last				
Pb^{2+}	Pre				
	Together				
	Last				

The effect of mordants of Co^{2+}, Cu^{2+}, Fe^{2+} and Ni^{2+}, on colour tones of wool dyed was better by all dyeing techniques, although it was observed that the colours were light pastel at pH = 2 and 8. When the wool fabrics dyed at pH = 4 and 6 were examined, it was observed that the brightest colours and more tones of colours were obtained. Cu^{2+} gave a green shade, while Fe^{2+} produced brown shade. It was also obtained brown and earth coloured wool fabrics with the effect of Pb^{2+} mordant.

We can use Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Sn^{2+} salts for obtaining good fastness colours. Consequently bright and desired colours were obtained. When all the samples were subjected to light, it was observed that the samples mordanted with Cu^{2+}, Co^{2+} and Fe^{2+} ions showed good light fastness rating (4) while the rest of the mordant studied gave a fair light fastness (2,3).

Conclusion

This method can be applied in textile industry, in weaving of the carpets and kilims. Furthermore investigations are under progress.

ACKNOWLEDGEMENTS

The authors express their thanks to Department of Textile Studies, Faculty of Technical Education, Marmara University for providing the opportunity to make analyses.

REFERENCES

1. G.W. Taylor, *Rev. Progr. Color.*, **16**, 53 (1986).
2. J.P. Haluk, B. Churrier and M. Nargues, *Holz Forschum*, **46**, 87 (1992).
3. N. Tanker, M. Koyuncu, M. Coskun and A. Güvenç, *Turk. J. Med. Sci.*, **26**, 289 (1996).
4. A. Frankly, Food and Chemistry, Mc Graw Hill Book Camp., USA, edn. 2 (1983).
5. A. Önal, *Turk. J. Chem.*, **20**, 194 (1996).
6. N. Terahara, M. Yamaguchi AND T. Honda, *Biosci. Biotechnol. Biochem.*, **58**, 1324 (1994).
7. H.T. Lokhande and V.A. Dorugade, American Dyestuff Reporter, pp. 29-32 (1999).
8. T. Fossen, R. Slimestad and M.O.M. Andersen, *Phytochemistry*, **64**, 1367 (2003).
9. Y. Yamamoto, *Tehno-Cosmos*, **5**, 19 (1994).
10. G. Gümrükçü, Dyeing Wool Fabric With Natural Pigment Anthocyanin Produced From The Alliumcepa L. Skin, Master Thesis, Yildiz Technical University, Istanbul, Turkey (2003).
11. I. Baser, Tekstil Teknolojisi, Marmara Universitesi Yayinlari, 634-13, Istanbul, Turkey (1998).
12. A. Önal and M. Kepez, *Bull. Pure Appl. Sci.*, **17**, 43 (1998).

(*Received*: 25 June 2007; *Accepted*: 11 January 2008) AJC-6194