PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 12 (2019), 219-230

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Effect of Acids and Different Mordanting Procedures on Color Characteristics of Dyed Wool Fibers Using Eggplant Peel (Solanum melongena L.)

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ARTICLE INFO

Article history:
Received: 10 Jan 2019
Final Revised: 2 Mar 2019
Accepted: 4 Mar 2019
Available online: 25 Jun 2019

Keywords:
Color measurement
Dye characterization
Mordanting process
Natural dyeing.

ABSTRACT

The dyeing of woolen yarn with eggplant peel, a natural colorant, has been studied. The main coloring component in this natural colorant is anthocyanin, which is an interesting class of dyes in the blue and red area. Eight mordants including alum, copper sulfate, ferrous sulfate, potash alum, nickel chloride, zinc sulfate, tin chloride, and potassium dichromate were used for mordanting the fibers. Four different mordanting procedures, pre-mordanting, simultaneous mordanting, a combination of pre and simultaneous mordanting and post-mordanting were used for study the effect of the mordanting procedure on color properties. Various acids such as acetic, chloric, citric, formic, lactic, nitric, oxalic, sulfuric, and tartaric were used to investigate the role of acids in dyeing. Different shades of greenish yellow to semi-blue were obtained from the dye extracted from eggplant peel. Tin chloride as a mordant produced the noticeable semi-blue color. The chromaticity values showed that sulfuric acid resulted in better navy blue hue compared to other acids for mordanted woolen yarn with tin chloride. The combination of pre and the simultaneous (or meta) mordanting procedure was found to be the efficient route for dyeing wool yarn with eggplant peel. Prog. Color Colorants Coat. 12 (2019), 219-230© Institute for Color Science and Technology.

1. Introduction

Natural dyes are found in natural sources such as plants, animal, and fungi. In the last decade, a revival interest in the use of natural dyes in textile dyeing has been growing due to renewable and biodegradability of these dyes as well as the environmental standards imposed by many countries [1]. There are several types of research concerning the extraction of dyes from different plants parts such as saffron [2], madder [3], marigold flower [4], tea polyphenol [5] using various methods such as boiling, microwave [6, 7], ultrasonic [8, 9], etc. The studies showed that there are various natural dyes, which contain chromophores with a variety of chemical structures. Based on chemical structures, natural dyes are classified to indigoid dyes, anthraquinone dyes, anthocyanidins, flavones, and carotenoids. However, the natural hue and color of dyes can be changed by using mordants. Unlike the large value of yellow and brown, the sources of red and blue color are limited [10]. The red can be produced from madder, cochineal, and brazilwood. Indigo and logwood are the oldest natural dyestuffs that provide blue dye [11]. On the literature survey, it is found that dyeing textiles with new natural blue dyes can be

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interesting research.

Generally, enormous amounts of the vegetable materials are un-utilized and dispose of daily that can be used for extraction of natural colorants for textile dyeing. One of these materials is an eggplant. The eggplant is a popular vegetable crop grown in the subtropics and tropics and is originated in Asia. Eggplant is a member of the family *Solanaceae* and Genus *Solanum* [12]. The major group of water-soluble colorant in the peel of the eggplant is Anthocyanin. Anthocyanin colorants are categorized as phenolic compounds named flavonoids [13, 14] (Figure 1) and handle the blue, purple, red and orange color of vegetables and fruits. The pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin are the typical structures of anthocyanins (Figure 2). The color type of anthocyanins is related to hydroxyl and methoxyl group numbers. Anthocyanin provides bluish shade when the hydroxyl groups of its structure increased and provide reddish shade when the methoxyl groups increased [15-17].

Researchers found that nasunin and delphinidin-3-rutioside were the major anthocyanins of eggplant peel [21, 22]. The color and stability of anthocyanin depend on the variations in the treatment conditions such as temperature and pH [23]. Figure 3 illustrates the structural transformation of anthocyanin according to pH. The hydroxyl group of C-3, which is frequently glycosylated, shifts the color of anthocyanin from yellow-orange to red [24]. Anthocyanin is orange or red at a pH about 3 or lower because of the presence of eight conjugated double bonds carrying a positive charge. Increasing pH resulted in colorless carbonyl pseudo-base that can undergo ring opening to a low chalcone. At a pH of 6-7, the blue resonance-stabilized quinonoid anions are formed [20, 25, 26].

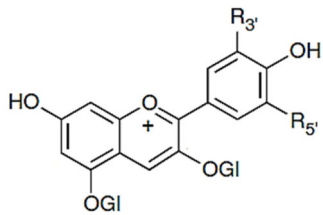

Figure 1: The molecular structure of anthocyanin; OGl=glycoside.

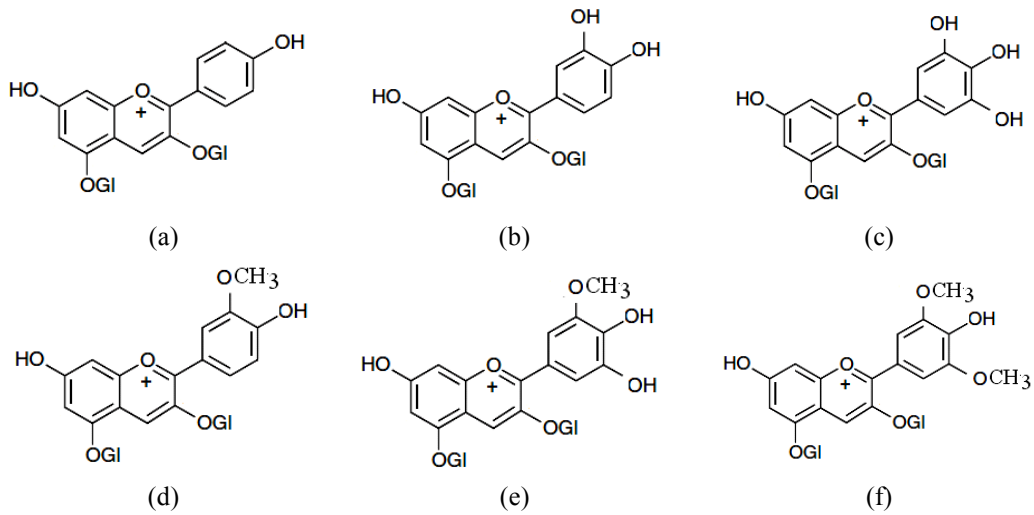

Figure 2: The common structures of anthocyanins, (a) pelargonidin (orange color), (b) cyaniding (orange-red color), (c) delphinidin (bluish- red color), (d) paeonidin (orange-red color), (e) petunidin (bluish- red color), and (f) malvidin (bluish-red color) [18-20].

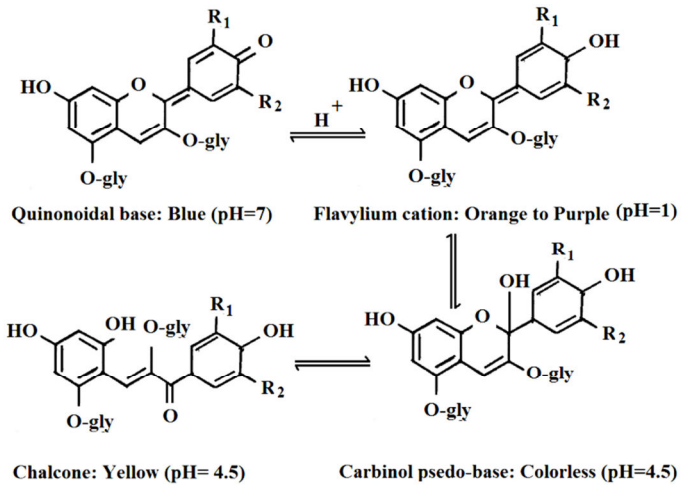

Figure 3: The change of color of anthocyanins against the pH [27].

Anthocyanin is reactive towards oxygen radicals because of natural electron deficiency. This antioxidative property allows chelation of metal ions [23]. In fact, the electron donor functional groups (OH and C=O) of the anthocyanin molecule make a complex form with metal ions. This complex formation can be suitable for dyeing of woolen samples, which along with the functional group of the wool (NH_2 and COOH) provide a bridge between the dye and the woolen samples. Figure 4 shows the complex formation between dye, metal ion (i.e., Fe^{2+}), and wool strucutre. The studies focused on the color stability in plants reported that the blue colors obtained by such as Al, Fe, Cu, Sn, Mg and Mo [28-30]. The study shows that there is a high level of interest in the investigation of dyeing of textile materials by using complex of anthocyanin and metal salts to obtain blue color. From the literature survey, Parvinzadeh studied the eggplant peel for dyeing wool fibers [31] and used pre-mordanting method for dyeing wool fibers with 50% (o.w.f) eggplant peel powder and found that all of the mordants improved the fastness of fibers. However, the effect of dye concentration, type of acid, mordanting methods, etc had not been investigated. Abdeldaiem also found that the eggplant peel has a red pigment which is suitable as a natural food colorant [32]. Vankar and Shukla studied dyeing of silk and cotton fabrics with the anthocyanin extracted from Hibiscus flowers [33]. The fabric treated with 2% different metal salts (pre-mordanting method) such as Sn, Al, Cr, and Cu, then dyed with anthocyanin extract for about 2hrs at 35°C. The results show that different metal salts caused various hue color from dark pink to purple. Tin metal salts show the best value of K/S for dyed cotton and silk fabrics. Wang et al. extracted anthocyanins dyes from liriope platyphylla fruits and studied the color values of dyed silk fabrics [34]. They found that treated fabrics with stannous chloride in the mordanting procedure (premordanting, metamordanting, and postmordanting) improve the dye depth and fastness and show that the color of the dyed fabrics was red-purple, blue, green and so forth according to the pH of dyeing solutions. Haddar et al. using red cabbage as an anthocyanin source for dyeing protein fibers [35]. They found that the purple to pink and blue shade could be obtained from red cabbage extract. The high color yield (K/S) of dyed protein fibers obtained at pH 2 medium. In addition, the high color yield (K/S) of pre-mordanting, meta-mordanting, and post-mordanting was obtained with using tannic acid, alum, and stannous chloride, respectively. Tidder et al. extracted anthocyanin colorants from the waste peel of blackcurrants for dyeing protein fibers [36]. They showed that the color of wool fibers were purples and blues when used aluminum sulfate as mordant at pH lower than 7 and higher than 9, respectively.

The objective of this study is comprehensive to investigate the extracting natural dye from the eggplant peel (dark purple colored, moderate size) by aqueous extraction method. Since the wool fibers are the primary fibers used in carpet, especially handmade carpet, dyeing of wool fibers with eggplant peel was investigated. Critical process parameters, the concentration of eggplant peel, type and concentration of metal salts and acids, and mordanting procedure affecting the color characteristics of dyed wool fibers are studied.

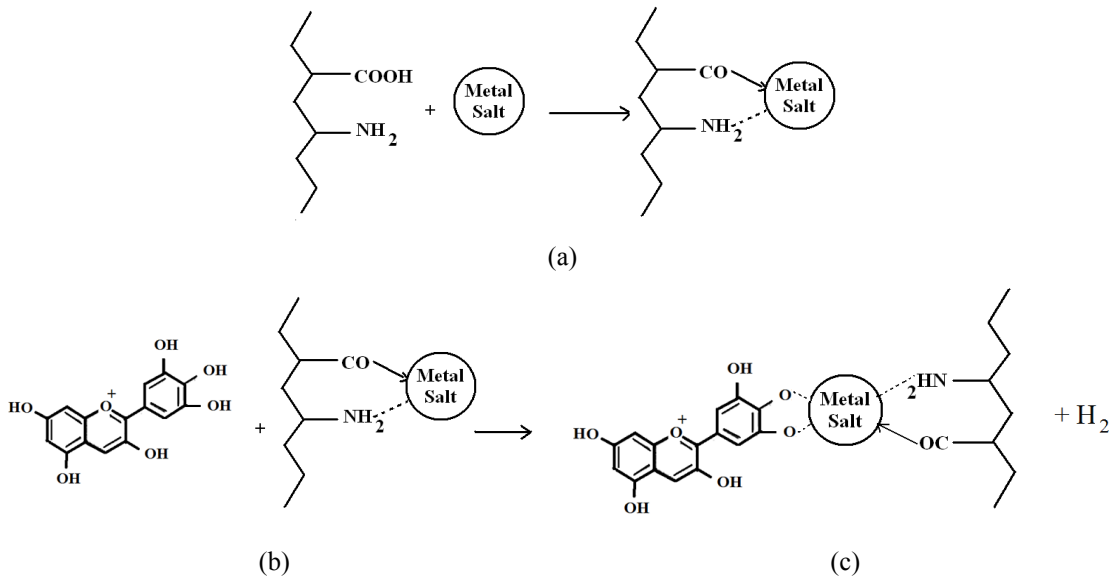

Figure 4: (a) Complex formation between the functional groups of the wool yarn and the metal ions in premordanting route and (b) adding the dye to the mordanted wool and the complex formation between the dye and the mordanted wool.

2. Experimental

2.1. Materials

The wool yarn of 430/2 tex and 144 twists/m prepared from purchased from the market used in this study. The peel of the eggplant was dried, powdered and used for dyeing. Analytical reagents grade of metallic salt, such as aluminum sulfate ($Al_2(SO_4)_3$), potassium aluminium sulfate (alum) ($KAl(SO_4)_2.12H_2O$), stannous chloride ($SnCl_2.2H_2O$), Nickel Chloride ($NiCl_2$), potassium dichromate ($K_2Cr_2O_7$), copper sulfate ($CuSO_4$), zinc sulfate ($ZnSO_4$), and ferrous sulfate ($FeSO_4$) were used. Since the color and stability of anthocyanin, the colorant of eggplant peel, depends on the variations of pH treatment, various acids were used. Acetic, chloric, citric, formic, lactic, oxalic, sulfuric, nitric, and tartaric acid were purchased from Merck, Germany. The wool fibers were first washed with a solution containing 2 gL^{-1} non-ionic detergent and 0.5 gL^{-1} sodium carbonate at 40°C for 30 minutes to remove waxes and impurities materials.

2.2. Dyeing and Mordanting

The yarns were mordanted by four mordanting methods such as pre-mordanting, simultaneous mordanting, post-mordaning, and pre-simultaneous-mordanting. The pre-mordanting experiment was performed using the material to liquor ratio (M:L) of 1:40 at pH=4~5 (Table 1). Mordanting bath temperature was raised to a boil during 20 minutes and kept at that level for 1 hour. After application of mordants, the samples were washed carefully and soaked in a dye bath using 5-100% o.w.f (on the weight of fiber/yarn) eggplant concentration, M:L of 1:40, and boil temperature for 1 h. In combination pre- and simultaneous mordanting procedure, the woolen yarns were mordanted in the mordanting bath, and then kept in this bath without a wash, added the dye and dyed in the same bath. In the simultaneous mordanting method, the woolen yarns were dyed with dye and mordants simultaneously. In the post-mordanting procedure, woolen yarns were dyed with aqueous dye solution, then taken out, squeezed and treated with a solution of mordants.

2.3. Chemical Structure Determination

Woolen yarns, eggplant peel, and dyed yarns were made into a pellet with KBr powder and analyzed by Fourier transform infrared spectroscopy (Bomem-MB 100, Canada). Four scans for each sample were taken with a resolution of 8 cm^{-1} with a range of 4000-400 cm^{-1}.

Table 1: Experimental conditions of dyeing and mordanting of woolen yarn.

	Dye Conc. (% o.w.f)	Mordant		Method of Mordanting	Acid	
		Type	Conc. (%)		Type	Conc. (%)
1	5-100	$KAl(SO_4)_2$	3	Pre mordanting	Acetic	1
2	100	Al, Cu, Fe, KAl, Cr, Ni, Sn, Zn	3	Pre mordanting	Acetic	1
3	100	$SnCl_2$	3	Pre-mordanting, Sim-mordanting, Pre-Sim-mordanting, Post-mordanting	Acetic	1
4	100	$SnCl_2$	3	Pre- Sim-mordanting,	Acetic, Citric, Chloric, Formic, Lactic, Nitric, Oxalic, Sulfuric, Tartaric	1-3

2.4. Color Measurements

The spectral reflectance of the dyed fibers was measured using a Tex flash spectrophotometer (Data color corp.). Three measurements were made on each of the four samples. The *CIELAB* values (*L*, a*, b**, C*, h°) were also recorded for all dyed samples along with the controlled sample. The color differences (ΔE) between a sample color ($L_2a_2b_2$) and a reference color ($L_1a_1b_1$) were measured.

2.5. Fastness Properties

Dyed woolen yarns were tested for washing and light fastness according to the ISO 105-C10 and AATCC Test Method 16-2004, respectively. In washing fastness route, the yarns were treated in a solution containing 5 gL^{-1} soap solutions for 45 min at 50 °C using the liquor to material ratio 50:1. The standard grayscale (rating from 1 (poor) to 5 (excellent)) was used to determine the change in color of the dyed woolen yarns. The standard blue scale (rating from 1 (poor) to 8 (excellent)) was used to measure the light fastness of the samples after exposure to artificial illumination with Xenon arc light source. The temperature of the black body was 65 °C with a relative humidity of the air as 40% and the daylight filter, a wavelength of 420 nm at 5 hours.

3. Results and Discussion

3.1. Chemical Structure

The Wool fiber consists of free amino and carboxyl groups at the end of the chain and intermediate amide linkage. In FT-IR spectrum of wool fibers, the absorption peak at 1200-1300 cm^{-1} refers to free amide III band results from coupled C-N stretching and N-H bending motions, the peak at 1600-1700 cm^{-1} is due to amide I band and mainly to C=O, the peaks in the range of 3200-3500 cm^{-1} are refers to N-H and O-H valence vibrations [37]. Figure 5 shows distinct peaks of eggplant peel at 624 cm^{-1} (CH=CH stretching vibration), 1067 cm^{-1} (C-O stretching), 1257, 1330, 1423 cm^{-1} (CH_2 scissors vibration), 1639 cm^{-1} (C=C stretch), 1747 cm^{-1} (C=O stretching), 2927 cm^{-1} (CH asymmetric stretch), and 3417 cm^{-1} (-OH stretching) [38]. According to Figure 4, the fixation of anthocyanin exist in eggplant peel on wool fiber is due to bond formation between hydroxyl and carboxyl groups of dye-mordant-amine and carboxyl groups of wool fiber. Figure 5 confirmed this mechanism of fixation. The absorbance band at 1747 cm^{-1} and 3400 cm^{-1} for carboxyl and hydroxyl in eggplant peel are reducing in intensity.

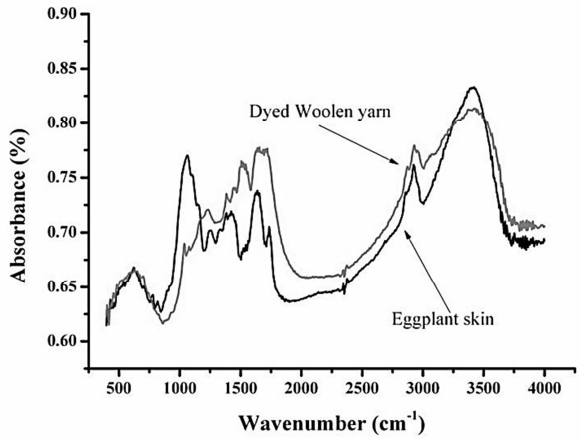

Figure 5: FT-IR spectra of eggplant peel and dyed woolen yarn.

3.2. Dye Concentration

Various dye concentrations ranging from 5% to 100% (o.w.f) were used to study the dyeability woolen yarns with eggplant peel. The data of *CIELAB* were shown in Table 2. The location of color in the *CIELAB* color space is distinct in a three-dimensional Cartesian coordinate system. The lightness value (L^*) shows the light or dark degree of color. The a^* and b^* values display the positions along the red-green and yellow-blue axes, respectively. The results indicate that a^* and b^* become more negative with an increase in dye concentration. This means that the woolen samples shift from red to green and from yellow to blue with dye concentration. The value of lightness (L^*) decreases with dye concentrations as the dye absorption increased. The results show that the hue angle (h°) increased with dye concentration, which is between 90° and 180° for dye concentration lower than 75% (o.w.f) and is between 180° and 270° for dye concentration higher than 75% (o.w.f). The latter range illustrates the greenish blue and greenish navy blue shades.

The difference between the two colors is a metric of interest in color science called ΔE^*_{ab} or ΔE. The color difference (ΔE) was calculated between the undyed samples and the dyed samples. The results show that the color differences increased with dye concentration. For example, the color difference increased from 6.13 (sample dyed with 5%) to 33.52 (sample dyed with 100%) (Table 2).

The color difference between the dyed samples with higher and lower dye concentration was also investigated. The results are indicated in Figure 6. It founds that the changes in dyed samples color depended on dye concentration and could become noticeable (ΔE > 4) after 5% of dye concentration (Table 2). It can be seen from Figure 6 that the largest differences between any pair of dyed samples are 14. This indicates that variation when comparing the color difference between the dyed samples.

Table 2: Effect of dye concentration on *CIE lab* data of dyed wool yarns, pre-mordanting with $KAl(SO_4)_2$ of 10% (o.w.f).

Dye cons. (%)	L*	a*	b*	C*	h°	ΔE	Hue observation
Raw Wool	77.27	2.69	18.42	18.62	81.71	-	Yellow
5.0	81.63	-1.02	16.21	16.24	93.60	6.13	Yellowish greens
10	77.45	-2.35	14.32	14.44	99.31	6.49	Yellowish greens
25	71.35	-3.51	8.56	12.19	112.29	13.07	Olive greens
50	61.92	-5.53	1.56	5.75	164.22	24.23	Greenish yellows
75	58.32	-6.41	-0.96	6.48	188.47	27.25	Greenish blue
100	52.89	-7.25	-2.32	7.61	197.74	33.52	Turquoise blue

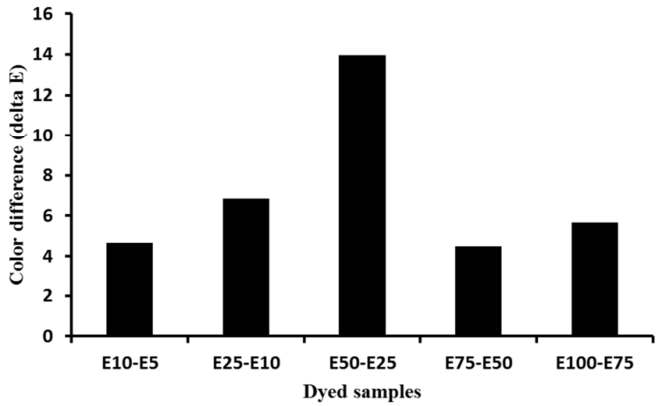

Figure 6: The color differences between the dyed samples.

3.3. Kind of Mordant

Generally, tannic acid, metallic or oil mordants by using the chemical reaction between the dye and the fiber bound the natural dyes to the fibers. In this study, various metal salts were used to investigate the effect of type of these materials on color characteristics of dyed woolen yarns with eggplant peel. It is well known that the high concentration (e.g. 10%) of metal salts such as copper sulfate, ferrous sulfate, and dichromate was not proposed for mordanting woolen fibers. So, the same concentration of different mordants (at 3% (o.w.f)) was used. Since the metal salts affect the electron distribution and density within the dye, the color of the dyed woolen yarns tends to change. Table 2 shows the chromaticity values obtained from a measurement based on the *CIE* system. Various kinds of shades, like yellow to green to blue, can be achieved by the application of different mordants. Based on the h° value, colored woolen yarn became bluish, when tin chloride was used as the mordanting agent. It can be clearly seen from Table 3 that the yellowish brown color was obtained with dichromate, nickel, and zinc. However, the aluminum and the alum result in a greenish blue and greenish yellow color, respectively. Wool yarn, when mordanted with aluminum, ferrous, and alum, produced the lower depth of shade, whereas stannous, copper, and dichromate produced the highest depth. Figure 7 shows the spectral curves of dyed woolen yarns. As can be seen, the reflectance curves of stannous mordant represented the reflectance function of a blue dye. This finding is confirmed by Vankar *et al*. and Wang *et al.* study. They showed that the solution of red flavylium cation as one of the anthocyanin forms in acidic aqueous solution becomes violet complex when reacted with Sn^{2+} as a chelating agent. As the access to blue color is the aim of this research, the different mordanting methods are focused on stannous mordant.

Table 3: *CIE lab* data of dyed wool yarns with 50% (o.w.f) of dye and pre-mordanting using 3% (o.w.f) of mordant.

Mordant	L*	a*	b*	C*	h°	Hue observation
$Al_2(SO_4)_3$	64.04	-5.83	0.37	5.85	176.39	Blue Green
$CuSO_4$	57.30	-5.21	12.59	13.63	112.49	Green Yellow
$FeSO_4$	44.17	-4.78	-0.79	4.84	189.38	Green Blue
$KAl(SO_4)_2$	61.92	-5.53	1.56	5.75	164.22	Green
$K_2Cr_2O_7$	61.63	4.28	17.92	18.42	76.57	Orange Yellow
$NiCl_2$	67.29	1.78	9.02	9.19	78.84	Orange Yellow
$SnCl_2$	39.22	-9.92	-11.17	14.93	228.39	Turquoise Blue
$ZnSO_4$	66.70	1.89	9.62	9.80	78.88	Orange Yellow

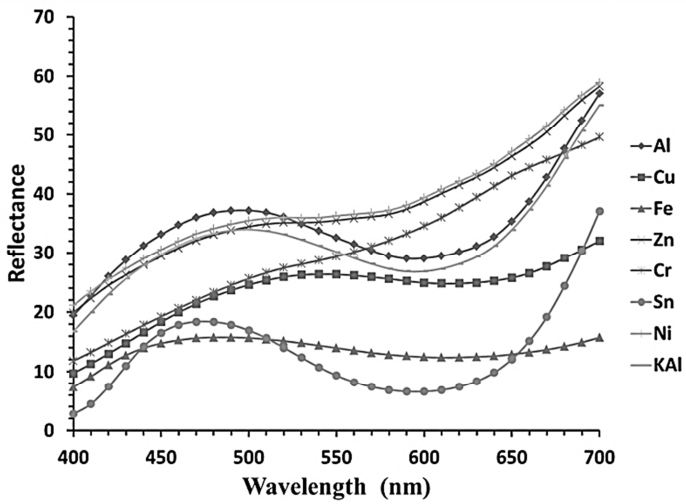

Figure 7: Reflectance curves of dyed woolen yarn with eggplant peel (50% (o.w.f)) using various mordants (3% (o.w.f)).

3.4. Mordanting Procedure

The obtained data, Table 4, showed that the post-mordanting route produced greenish yellow, whereas, the other mordanting procedures produced blue hue in the case of $SnCl_2$ mordant. It seems that part of the dye in post-mordanting method removed from the fabric and reduced the dye concentration on fabric. This finding is consistent with Wang *et al.* study, which found that the part of dye not absorbed to the fabric and remained in the dyeing bath in the post-mordanting procedure. The results show that the dyed fabric with lower dye concentration resulting in reddish yellow color.

As the three methods (pre, pre-sim, and sim) producing a blue hue, so, the color differences were measured for these methods. With respect to the color difference (ΔE, there is the difference between pre, simultaneous, and the combination of pre and simultaneous mordanting methods (Figure 8), which provided blue hue. In the combination of pre- and simultaneous mordanting method lowest *L** and highest C* values were obtained. In another words, this mordanting route show lower values of lightness and higher shades. From an economic standpoint, a combination of pre and the simultaneous mordanting procedure is better method due to eliminate the washing step of after mordanting route, the treatment the mordanting and dyeing in one bath, and time saving due to remove of water and bath change.

Table 4: *CIE lab* data of dyed wool fibers with 100% (o.w.f) of dye and 3% (o.w.f) of $SnCl_2$ with different mordanting procedure.

Code	Procedure	L*	a*	b*	C*	h°	Hue observation
P	Pre-mordanting	45.49	-10.92	-6.74	12.83	211.68	Green Blue
S	Sim-mordanting	46.57	-9.25	-12.20	15.31	232.83	Blue
PS	Pre- Sim-mordanting	41.01	-10.17	-11.87	15.63	229.42	Blue
Po	Post-mordanting	70.13	-3.02	11.82	12.20	104.33	Green Yellow

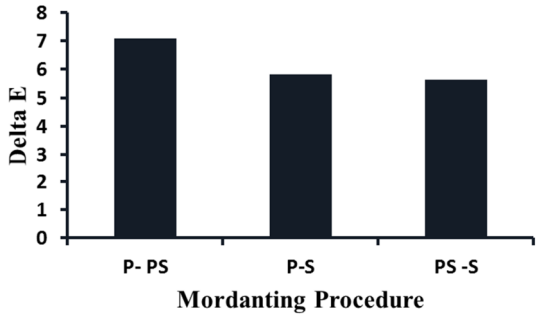

Figure 8: The color difference between pre- and pre- simultaneous -mordanting (P-PS), pre- and simultaneous mordanting (P-S), and pre- simultaneous and simultaneous mordanting (PS-S).

3.5. Type and Concentration of Acids

The chromaticity values of dyed woolen yarns in different acidic conditions are shown in Table 5. In this experiment, the pre-simultaneous mordanting procedure and $SnCl_2$ as better method and mordant, respectively, resulted in this study were used. The results show that all of the acids led to blue color (hue angle between 226° to 265°). Sulfuric acid resulted in navy blue in the concentration of 3% and 5% (v/v). The pH of the dye bath was measured and with respect to type and concentration of acids was between 2 and 4. According to Horbowicz et al. finding [17], the quinoidal blue species dominate at pH values between 2 and 4. Therefore, it is reliable to get blue color in these acidic conditions. The experimental data show that the increase in the concentration of acetic, formic, lactic, nitric, and tartaric acid does not have a meaningful effect on color difference (ΔE) values.

Table 5: Effect of acid solutions on *CIE lab* data of dyed wool fibers, the parameter process: a combination of pre and simultaneous mordanting method, using 100% (o.w.f) of dye and 3% (o.w.f) of $SnCl_2$.

Acid	Cons. (%)	L*	a*	b*	C*	h°	ΔE
Acetic	1	34.55	-10.11	-13.14	16.58	232.44	-
	3	30.83	-10.09	-13.04	16.49	232.25	3.72
	5	33.31	-9.32	13.80	16.66	235.97	2.70
Citric	1	34.68	-9.63	-13.24	16.37	233.97	-
	3	38.76	-10.27	-14.45	17.73	234.59	4.30
	5	39.42	-7.31	-14.99	16.68	243.99	3.08
Chloric	1	34.33	-10.00	-12.85	16.28	232.09	-
	3	31.57	-8.92	-14.36	16.91	238.17	3.32
	5	36.95	-8.62	-13.48	16.00	237.41	5.46
Formic	1	32.92	-10.28	-13.52	16.97	232.74	-
	3	33.79	-9.62	-13.44	16.53	234.41	1.09
	5	32.63	-9.38	-13.88	16.75	235.95	1.26
Lactic	1	33.99	-10.62	-11.36	15.56	226.92	-
	3	32.96	-10.35	-13.03	16.64	231.53	1.98
	5	34.48	-10.85	-11.27	15.64	226.08	2.37

Table 5: Continue.

Acid	Cons. (%)	L*	a*	b*	C*	h°	ΔE
Nitric	1	34.66	-10.43	-13.49	17.05	232.29	-
	3	34.27	-9.04	-14.92	17.45	238.78	2.03
	5	35.14	-8.70	-15.51	17.78	240.72	1.10
Oxalic	1	37.86	-10.44	-11.98	15.89	228.93	-
	3	39.59	-7.12	-14.29	15.96	243.51	4.39
	5	36.20	-9.50	-13.50	16.51	234.87	4.21
Sulfuric	1	32.81	-9.15	-13.85	16.60	236.56	-
	3	43.90	-3.86	-16.97	17.40	257.18	12.67
	5	47.33	-1.38	-15.11	15.17	264.76	4.62
Tartaric	1	31.91	-9.64	-13.63	16.69	234.73	-
	3	34.71	-9.58	-15.00	17.80	237.43	3.11
	5	35.50	-8.92	-16.87	19.08	242.14	2.13

3.6. Color Fastness

The color fastness results of dyed woolen yarn are shown in Table 6. The use of a mordant in dyeing results in excellent color fastness. The mechanism of complex formation of dye and the mordant protects the chromophore from photolytic degradation and results in high lightfastness. The results show that all of the mordants improved the washing fastness. The effect of the mordanting procedure on colorfastness of dyed woolen fibers with $SnCl_2$ mordant was shown in Table 7. The experimental data indicated that the pre-mordanting and combination of pre and simultaneous mordanting employing stannous improved the wash and light fastness.

Table 6: Colorfastness of dyed woolen yarn with eggplant peel (50% o.w.f) with different mordants (3% o.w.f).

Fastness	Raw	$Al_2(SO_4)_3$	$CuSO_4$	$FeSO_4$	KAl	$K_2Cr_2O_7$	$NiCl_2$	$SnCl_2$	$ZnSO_4$
Washing fastness	2-3	3-4	4	4	3-4	4	3-4	3-4	3-4
Light fastness	4	5	5-6	6	4-5	5	5	6	5-6

Table 7: Colorfastness of dyed woolen yarn with eggplant peel (50% o.w.f) with the different mordanting procedure. Stannous chloride at 3% o.w.f was used.

Fastness	Un-mordanting	Pre-mordanting	Simultaneous	Pre-Sim-mordanting	Post-mordanting
Washing fastness	2	4	3	3-4	4
Light fastness	2	5	5	6	5

4. Conclusion

In this research, eggplant peel has been introduced as a natural colorant for dyeing wool samples. Eight mordants and nine acids were used for dyeing wool yarn by different mordanting procedures. The chemical structure of eggplant peel was determined using Fourier transform infrared (FT-IR) spectroscopy. Colorimetric properties of the dyed woolen yarn such as lightness (L^*), redness-yellowness (a^*), blueness-greenness (b^*), chroma (c*), hue (h°), color difference and spectral reflectance, as well as fastness properties, were determined. The FT-IR spectrum confirmed the fixation mechanism of hydroxyl and carboxyl groups of anthocyanin exist in eggplant peel - mordant- amine and carboxyl groups of wool fiber. The results showed that the hue angle of dyed wool increased with dye concentration, which illustrates the greenish blue and semi- navy blue shades. The chromaticity values showed that eggplant peel has polygenetic properties, which various kinds of shades like yellow to green to blue were obtained by the application of different mordants. It was found out that semi- blue color could be obtained with eggplant peel in the presence of stannous chloride, alum, potash alum, and ferrous sulfate. Navy blue color can be obtained with tin salts in presence of sulfuric acid. When a combination of pre and the simultaneous mordanting procedure was used, the high chromaticity values and fastness properties were suitable for the end use of woolen yarn. The pre-mordanting and combination of pre and simultaneous mordanting employing stannous improved the wash and light fastness.

5. References

1. A. K. Samanta, P. Agrawal, Application of Natural Dyes on Textiles, *Indian J. Fiber Text.* Res., 34(2009), 384- 399.
2. Sh. Adeel, M. Salman, Sh. A. Bukhari, Kh. Karrem, F. U. Rehman, A. Hassan, M. Zuber, Eco-friendly food products as source of natural colorant for wool yarn dyeing, *J. Nat. Fibers*, 21(2018), 1-15.
3. A. Jahangiri, S. M. Ghoreishian, A. Akbari, M. Norouzi, M. Ghasemi, M. Ghoreishian, E. Shafiabadi, Natural dyeing of wool by madder (rubia tinctorum L.) root extract using tannin based biomordants: colorimetric, fastness and tensile assay, *Fibers. Polym.*, 19(2018), 2139-2148.
4. Sh. Adeel, T. Gulzar, M. Azeem, F. U. Rehman, M. Saeed, I. Hanif, N. Iqbal, Apparaisal of marigold flower based leutin as natural colorant for textile dyeing under the influence of gamma radiations, *Radiat. Phys. Chem.*, 130 (2017), 35-39.
5. F. Wang, J. Gong, Y. Ren, J. Zh, Eco-dyeing with biocolourant based on natural compounds, *R. Soc. Open Sci.*, 5(2018), 1-11.
6. Sh. Adeel, M. Zuber, F. U Rehman, K. Mahmood Zia, Microwave-assisted extraction and dyeing chemical and bio-mrdanted cotton fabric using harmal seeds as a source of natural dye, *Env. Sci. Poll. Res.*, 25(2018), 11100-11110.
7. M. D. Teli, J. Sheikh, P. Jagtap, Microwave assisted extraction of natural dyes and natural mordants vis a vis dyeing, *Asian Dyer*, 10 (2018), 32-38.
8. Sh. Adeel, F. Z. Rehman, M. U. Iqbal, N. Habib, Sh. Kiran, M. Zuber, Kh. Mahmood Zia, A. Hameed, Ultrasonic assisted sustainable dyeing of mordanted silk fabric using arjun (Terminalia arjuna) bark extracts, *Env. Prog. Sut. Ene.,* 21(2018), 26-32.
9. H. Almahy, H. H. Abel-Razik, Y. El. Badry, E. M. Ibrahim, Ultrasonic extraction anthocyanins as natural dyes from hibiscus sabdariffa (karkade) and its application on dyeing foodstuff and beverage in kingdom saudi arabia, *American. J. Biolog. Pharm. Res*., 2(2015), 168-174.
10. P. S. Vankar, D. Shukla, Natural dyeing with anthocyanins from hibiscus rosa sinensis flowers, *J. Appl. Polym. Sci.,* 122(2011), 3361-3368.
11. A. Manhita, T. Ferreira, A. Candeias, C. B. Dias, Extracting natural dyes from wool-an evaluation of extraction methods, *Anal. Bioanal.Chem.,* 400(2011), 1501-1514.
12. E. Sadilova, F. C. Stintzing, R. Carle, Anthocyanins, Colour and Antioxidant Properties of eggplant (solanum melongena l.) and violet paper (capsicum annuum l.) peel extracts, *Z. Naturforsch,* 61(2006), 527- 535.
13. Z. Bahreini, V. Heydari, B. Vahidi, M. Asadi, Extraction, identification and thermal stability of anthocyanins from eggplant peel as a natural colorant, *Prog. Color Colorants Coat.,* 8(2015), 59- 67.
14. H. Y. Huang, C. K.chang, T. K. Tso, J. J. Huang, W. W. Chang., Y. C. Tsai, Antioxidant activities of various fruits and vegetables produced in taiwan, *Int. J. Food sci. Nutr.,* 55(2004), 423-429.
15. F. Delgado-vargas, O. Paredes-lópez, Anthocyanins and betalains. in natural colorants for food and nutraceutical uses, *Crc Press, Boca Raton.*, 17(2003), 167- 219.

16. F. J. Heredia, E. M. Francia-aricha, J. C. Rivas-Gonzalo, I. M. Vicario., C. Santos Buelga, Chromatic characterization of anthocyanins from red grapes. I. pH effect, *Food Chem.,* 63(1998), 491-498.
17. M. Horbowicz, R. Kosson, A. Grzesiuk., H. Dębski, Anthocyanins of fruits and vegetables-their occurrence: analysis and role in human nutrition, *Veg. Crops res. Bull.,* 68(2008), 5-22.
18. T. Bechtold, handbook of Natural Colorants. In: Bechtold, T. & Mussak, R. (eds.). Leopold-Franzens University, Austria: John Wiley & Sons. Ltd, (2009), 136.
19. A. Castañeda-ovando, M. L. Pacheco-hernández, M. E. Páez-hernández, J. A. Rodríguez, C. Galán-vidal, Chemical studies of anthocyanins: a review, *Food Chem.,* 113(2009), 859-871.
20. P. Jing, Purple corn anthocyanins: chemical structure, chemopreventive activity, and structure/function relationships, U.S.A: The Ohio State University, (2006), 5-90.
21. N. Matsuzoe, M. Yamaguchi, S. Kawanobu, Y. Watanable, H. Highashi., Y. Sakata, Effect of dark treatment of the eggplant on fruit peel color and its anthocyanin component, *J. Jpn. Soc. Hortic. Sci.,* 68(1999), 138-145.
22. X. Wu, R. L. Prior, Identification and characterization of anthocyanin by high-performance liquid chromatography electrospray in common foods in the united states, *J. Agric. Food Chem.,* 53(2005), 3101-3113.
23. C. R. Welch, Q. Wu, J. E. Simon, Recent advances in anthocyanin analysis and characterization, *Curr. Anal. Chem.,* 4(2008), 75-101.
24. J. Ahmed, U. S. Shivhare., G. S. V. Raghavan, Thermal degradation kinetics of anthocyanin and visual color of plum puree, *Eur. Food res. Technol.,* 218(2004), 525- 528.
25. R. Brouillard, The flavonoids, advance in research since 1980, In: Harborne, J. B. (ed.). London: Chapman and Hall, (1998), 525.
26. R. E. wrolstad, Anthocyanin pigments—bioactivity and coloring properties, *J. Food sci.,* 69(2004), c419-c425.
27. M. G. Miguel, Anthocyanins: antioxidant and /or anti-inflammatory activities, *J. Appl. Pharm. Sci.,* 01(2011), 7-15.
28. K. L. Hale, S. P. McGrath, E. Lombi, S. M. Stack, N. Terry, I. J. Pickering, Molybdenum sequestration in brassica species. a role for anthocyanins?, *Plant Physiol.,* 126(2011), 1391- 1402.
29. M. C. Moncada, S. Moura, M. J. Melo, A. Roque, C. Lodeiro., F. Pina, Complexation of aluminum(iii) by anthocyanins and synthetic; flavylium salts: a source for blue and purple color, *Inorg. Chimica Acta,* 356(2003), 51- 61.
30. M. S. Starr, F. J. Francis, Effect of metallic ions on color and pigment content of cranberry juice cocktail, *J. Food Sci.,* 38(1973), 1043- 1046.
31. M. Parvinzadeh, An environmental method for dyeing rug pile using fruit waste colorants, *Res. J. Chem. Environ.,* 13(2009), 49- 53.
32. M. H. Abdeldaiem, Use of red pigment extracted from eggplant (Solanum melongena L.) peels as natural antioxidant and colorant, *J. Nuclear Technol. Appl. Sci.*, 1(2013), 7-20.
33. P. S.Vankar, D. Shukla, Natural dyeing with anthocyanins from hibiscus rosa sinensis flowers, *J. Appl. Polym. Sci.,* 122(2011), 3361-3368.
34. H. Wang, P. Li., W. Zhou, Dyeing of silk with anthocyanins dyes extracts from liriope platyphylla fruits, *J. Text.*, (2014), 1-9.
35. W. Haddar, M. B. Ticha., N. Meksi., A. Guesmi, Application of anthocyanins as natural dye extracted from brassica oleracea l. var. capitata f. rubra: dyeing studies of wool and silk fibers, *Nat. Prod. Res.*, 32(2018), 141-148.
36. A.Tidder, M. Benohoud, C. M. Rayner, R. S. Blackburn, Extraction of anthocyanins from blackcurrant (Ribes nigrum L.) fruit waste and application as renewable textile dyes. In: *91st Textile Institute World Conference Book of Abstracts*. TIWC 2018: 91st, Textile Institute World Conference, 23-26 Jul 2018, Leeds, UK. Textile Institute,18-19.
37. E. Bendit, Infrared absorption spectrum of keratin. I. spectra of α and β and supercontracted keratin, *Biopolymers*, (1996), 539-559.
38. S. M. Mortazavi, M. Kamali Moghaddam, S. Safi, R. Salehi, Saffron Petals, A By-Product For Dyeing of Wool Fibers. *Prog. Color Colorants Coat.,* 5(2012), 75- 84.

How to cite this article:
M. Kamali Moghaddam, M. Ghanbari Adivi, M. Tehrani Dehkordi, Effect of Acids and Different Mordanting Procedures on Color Characteristics of Dyed Wool Fibers Using Eggplant Peel (Solanum melongena L.). Prog. Color Colorants Coat., 12 (2019), 219-230.