Effectual Parameters in Natural Dyeing: Dyeing of Woolen Yarns by Madder

Zahra Ahmadi and Narges Shayegh Broujeni

Abstract— **According to the literature, it is possible to replace synthetic dyes with more echo-friendly natural dyes. One of the popular natural dyes in Iran is madder. This paper reports the effect of age and type of madder in natural dyeing process for better color behavior prediction. Effects of 4 different types of madder along with the role of the concentration and pH of dye bath are investigated. The amount of dye absorption is also evaluated by calculation of K/S value in the wavelength of minimum reflection. Samples are treated by using the classical aftertreatment process for natural dyes and the effect of aftertreatment on light and washing fastnesses of samples are reported. The CIELAB colorimetric specifications of samples are measured under D65 illuminant and 1964 standard observer. The light and washing fastnesses of dyed samples are also reported. Finally, the chemical structures of employed madders are studied by FTIR technique.**

Key words: Madder, natural dyeing, wool, age.

I. INTRODUCTION

NOWADAYS, the sustainable uses of natural resources are on the rise. In this aspect, the use of natural dyes for textile coloration has re-grown due to recently discovered deodorizing, antimicrobial, antifeedant and UV protective properties [1], in addition to the elegant shades on different types of hand woven carpet. This group of dyestuffs contains different natural coloring matters that are neither carcinogenic nor hazardous to environment. Besides, the colors are soothing to eyes, earthly, warm and highly appealing.

The natural dyes and their dyeing process are as old as textile fibers. Nature has always been attractive issue for Man and discovering of natural dyes and the art of natural dyeing goes back to prehistory [1, 2].

Nearly, all parts of the plants like root, bark, leaf, fruit, wood, seed and flower contains coloring materials and could be considered as natural dyes. It is interesting to note that over 2000 pigments are synthesized by various parts of plants, of which about 150 have been commercially exploited. While plants exhibit a wide range of colors, not all of these pigments can be used as dyes, due to the fastness properties.

The content and the amount of the coloring materials in plants greatly varies with the harvest season as well as the age of the plants [3]. Madder is the one of the important natural dye that is widely used for dyeing of woolen yarns used in handmade Persian carpets. It is classified on the bases of the planting season and the age of madder [7]. Different types of coloring compound, i.e. alizarin, rubiyadin, purpurin, have been found in madder. Figure 1 shows the chemical structure of most important madder [6, 8]. The colorimetric specifications of natural dyes along with the optimization of coloration process and the fastness properties of natural dyes has been the subject of several research work and the issue is still an active study area. However, the application and characterization of madder have not been deeply reported. For instance, there is a lack of intensive study on the selection of characterized plant raw materials, optimal dyeing procedures, predictable shade of dyeing as well as the fastness properties of products. In the dyeing of woolen yarns by madder, the employed mordant and the type of application are very important. Mordants have significant impact on the fastness properties of dyed fibers and also improve the dye uptake. Madder is a natural mordant dye and requires the inclusion of one or more metallic salts of aluminums, iron, zinc, copper and similar metals for ensuring reasonable fastness of color to light and wet processing. Such metallic salts aggregate with the dyestuff and improve the fastness properties. The original colors of madder are found by using alum as mordant.

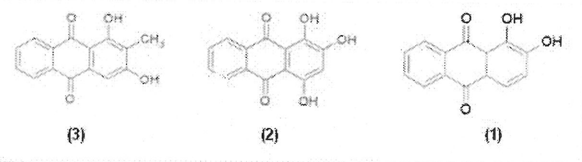

Fig. 1. Chemical structure of madder constitution [6].

In this paper, attempt has been made to make an in depth scientific study on dyeing of woolen yarns with madder. In fact, the effect of variations among different crops of the same plant, reproducibility of dyeing, the proportions of the plant's structural components according to the harvest region have been reported. Besides, the influences of some dyeing parameters such as dyeing temperature, dyebath pH, mordant and dye concentrations and the water contaminants are also investigated.

II. EXPERIMENTAL

A. *Materials*

Wool yarn (2/6 Nm) and 4 kinds of madder with different ages and production regions (Bafgh, Naeen,

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Ardakan madder from central part of Iran and Momtaz madder, mixture of Ardakan and Bafgh peeled madder root) were used for dyeing process. The laboratory grade of the metallic salt mordant (Kal$(SO)_4$.12 H2O), acetic acid, oxalic acid, ammonia were also used as chemicals. All chemicals were supplied by Merck.

B. Preparation of Raw Materials

The root of madder was cleaned with water by brushing to remove the soil and other impurities. They were then dried at room temperature and ground into powder by using a grinder. The powder of madder was soaked in water and boiled for one hour to increase its dyeing efficiency. Finally, the aqueous extract of madder (30, 50, 70 % on weight of fiber, owf) were used for dyeing.

C. Mordanting and Dyeing Procedure

Woolen yarns were scoured in mild aqueous washing bath comprises water containing common nonionic detergent for 10 minutes at 40°C prior to mordanting and dyeing. The scoured yarns were then mordanted by pre-mordanting method using potash alum (4% owf). Mordants were firstly dissolved in water in separate baths, and the mordanting process was done in a bath with liquor to good ration (L: G) of 40:1 and 3% owf of oxalic acid was added to mordanting bath. The temperature of mordant baths was gradually raised till simmering point (89-91° C) and the treatment continued for 1 h under constant stirring. Mordanted woolen yarns were then used for next dyeing process, directly.

Dyeing experiments were performed using L:G of 40:1 in new baths with manual agitation at different acidic pHs (3 and 4.5) provided by oxalic and acetic acids while 3% owf dye was used. Table I shows the specifications of employed madders and the pH of desired baths. Dyeing curve is demonstrated in Figure 2. As the figure shows, the dye bath temperature was raised from 40°C to simmering point (89-91°C) within 20-30 minutes and maintained at this level for 1 hour before washing.

TABLE I
SAMPLE SPECIFICATIONS

Sample code	Kind of madder	Sample code	Kind of madder
Y	Ardakan,70%, AA*	O	Naein, 30%, AA*
K	Momtaz, 70%, AA*	S	Bafgh, 30%, AA*
Q	Naein, 70%, AA*	I	Momtaz, 30%, AA*
U	Bafgh, 70%, AA*	W	Ardakan, 30%, AA*
R	Naein, 70%, OA$^◆$	X	Ardakan, 30%, OA$^◆$
Z	Ardakan,70%, OA$^◆$	T	Bafgh, 30%, OA$^◆$
V	Bafgh, 70%, OA$^◆$	P	Naein, 30%, OA$^◆$
L	Momtaz,70%, OA$^◆$	J	Momtaz, 30%, OA$^◆$
B	Momtaz,50%, OA$^◆$	E	Momtaz, 50%, AA*

*: Acetic Acid
◆: Oxalic Acid

Several dyeing baths containing water with different contaminants were prepared to investigate the effect of water quality on dyeing results. The employed materials for preparation of water with different type of impurities are illustrated in Table II.

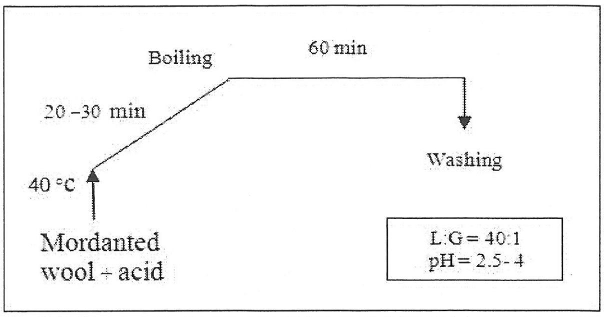

Fig. 2. Dying curve.

TABLE II
DETAILS OF PRODUCED HARD WATERS

Sample #	Type of contaminate in hard water
1	Portland Cement
2	$CaCO_3$
3	Na_2CO_3
4	NaCl (Salty water)

Based on traditional dyeing procedures with natural dyes, in this study some of the most popular aftertreatment techniques were carried out on woolen dyed yarns. For instance, the dyed yarns were immersed in the solution of dyeing bath waste water for 24 hours. Besides in another aftertreatment method, the dyed materials were dipped in the ammonia solution for 5 minutes while in the third aftertreatment procedure, the dyed samples were left in the yoghourt solution for 2 hours. The aftertreated samples were removed from the bathes and rinsed thoroughly in soft water and finally dried in the room temperature. The specification of aftertreatment processes is shown in the Table III.

TABLE III
DETAILS OF EMPLOYED AFTER TREATMENT METHODS

sample #	Aftertreatment method
5	2 hours in yoghourt solution after dyeing
6	5 min. in 3% ammonia solution
7	24 hours in dyeing waste water

D. Techniques

1) Color Measurements

The reflectance spectra of samples were measured by an abridge spectrophotometer named Color-Eye 3100A from Gretag Macbeth. The CIELAB color specifications were then computed under D65 illuminant and 1964 standard observer. The dye absorption and the color strength of samples were also evaluated through $\left(K/S\right)_{\lambda}$ values obtained by Eq. (1) 1 in the wavelength of minimum reflectance of samples [4].

$$\left(\frac{K}{S}\right)_{\lambda} = \frac{(1-R_{\lambda})^2}{2R_{\lambda}}, \qquad (1)$$

where, R_{λ} is the fraction of the reflectance of sample. The color specifications of samples and the $\left(K/S\right)_{\lambda}$ values in the desired wavelength are demonstrated in Tables IV and V.

2) Light fastness

The light fastness of samples was carried out according to the standard PN-ISO 105-B02:1997 using Xenotest 150S manufactured by Atlas Material Testing Technology. The naturally dyed samples were exposed to simulated sunlight for desired period of time and then were evaluated by comparison to standard blue scale.

3) Color fastness to washing

The color alteration and the staining of samples during the washing process were assessed by implementation of standard PN-ISO 105-C06:1996 method.

4) FTIR Spectrophotometry

The FTIR spectroscopy was used for characterization of 4 different types of employed Madders. A Nicollet Nexus FTIR spectrophotometer with a Germanium crystal was used to record the spectra of samples between 400 and 4000 cm^{-1} in a absorption mode. The nominal resolution of the spectrometer was 4 cm^{-1}. All samples were prepared in the same weight of madder and KBr.

III. RESULTS AND DISCUSSIONS

According to Table IV, samples that were dyed with lower concentrations of dye show higher L* and lower C* values that identified by lighter and less saturated appearances in comparison to those dyed with higher dye concentrations. According to Fick's law, the driving force for dye transport toward the fiber surface increases with the concentration gradient of dye in two phases, i.e. dye concentrations in solution and fiber phases. Consequently, samples that were dyed with higher concentrations of Madder were appeared deeper.

Table IV also shows the color strength of samples in terms of K/S values for all dyed woolen yarn specimens. No particular trends are evident between the color strength of samples and the type and age of employed madders. Results of Table IV show that the minimum yellowness was achieved on samples dyed with 30% of dyestuff in acetic acid baths.

The higher K/S values of samples that were dyed in oxalic acid baths indicate to color intensity of these samples. The pH values of dyeing baths varied between 3 to 5. The effect of pH variations on the color yield and the CIELAB coordinates are also reported in Table IV. The table reveals that the color yield, i.e. K/S value, increased with decreasing of pH of the dyeing baths. Obviously, the L* values are smaller for such samples. The a* and b* values apparently changed by madder type as well as the pH of dyeing baths. The highest K/S value was obtained at pH 3 for momtaz madder. The effect of dyebath pH can originate from changes in dye and fiber structures. The changes could be explained by the important attraction between both the protonated terminal amino groups of wool and the anthraquinone molecular structure which benefit from high electronic density. However, the dyeability decreased with increasing the pH of the dyeing baths due to the decreasing of numbers of protonated terminal amino groups of wool fibers that leads to decreasing of dye attraction by woolen fiber. In fact, the carboxyl groups in dye structure would ionically interact with the protonated terminal amino groups of wool fibers at acidic pH by an ion exchange reaction. The complex structure of anion group of dye could be bonded with fiber and a kind of interactions take place with ionic forces. Clearly such type of ionic attraction would increase the dyeability of the fiber.

However in pH>4 (the isoelectric point of wool is about 4.8), the ionic interaction between the anion of dye and wool fibers decreases due to decreasing the number of protonated terminal amino groups of wool fibers that leads to lower dyeability [7]. At pH 4, the numbers of the protonated terminal amino groups of wool fibers become constant and no additional dye could be adsorbed and consequently the maximum color strength was obtained at this pH value. At pH<4, the result can be attributed to the losses of indicaxanthin stability at low pH.

The effect of liquor to ratio (L:G) on color strength is shown in Table V. It is clear that color strength increases with increase of L:G. Lower relative color strength value at low L:G may be explained by the overcrowding of dye molecules at lower L:G resulting in reduced dye exhaustion on the woolen yarn.

The effect of dyeing temperature on color strength is demonstrated in Table V, too. As can be observed, the color strength increases with the increase of dyeing temperature. This increment in dye uptake can be related to better dye exhaustion at higher temperatures.

Fastness properties of samples are given in Table VI. All samples exhibited good light and wash fastnesses. The dyestuff concentration and the kind of madder do not have any effect on the light and wash fastness values. Results indicate that the oxalic acid caused better light fastness and the increase of dye concentration led to decrease in washing fastness of samples.

Table VII shows the colorimetric and the K/S specifications of aftertreated samples. As the table shows, the L* and K/S values increased for treated samples in compare to untreated ones. Tables VII and VIII show that the aftertreatment and increasing the water hardness led to some variations in the colorimetric specifications of samples. While dyeing of samples in hard water, e.g. sample #1, decreased the quality of woolen yarn, the color strength of samples increased in salty water. As Samples #5 and #6 show, when samples were left in dyeing waste water for 24 hours, the lightness increased. Aftertreatment by yoghurt solution caused to improvements in both light and washing fastnesses. Besides, aftertreatment in alkaline solution caused to increase of fastnesses whereas the treatment in dyeing waste water led to decrease of fastness. This sample, i.e. sample treated in alkaline solution, is

TABLE IV
COLOR DEVELOPED AND DYE ABSORPTION ON WOOL YARNS

Sample	Acid type	Dye conc.%	Color specifications					K/S	λ_{max}, nm	R (%)
			L*	C*	h°	a*	b*			
Y	acetic	70	33.136	42.384	32.249	35.846	22.616	16.71	490	2.830
K	acetic	70	32.710	44.543	37.508	35.335	27.121	17.82	500	2.660
Q	acetic	70	34.924	45.388	37.112	36.195	27.386	21.68	490	2.206
U	acetic	70	36.090	45.699	37.539	36.236	27.844	18.21	500	2.605
R	oxalic	70	28.258	36.829	35.155	30.111	21.205	23.85	500	2.013
Z	oxalic	70	27.873	37.199	34.272	30.740	20.948	25.29	500	1.900
V	oxalic	70	31.423	42.160	36.324	33.967	24.973	23.10	500	2.080
L	oxalic	70	37.621	43.543	40.075	33.319	28.033	24.69	500	1.950
E	acetic	50	33.000	42.200	36.400	25.100	20.300	20.50	500	2.300
O	acetic	30	38.957	43.175	34.945	35.391	24.730	11.81	500	3.910
S	acetic	30	41.686	43.853	34.403	36.183	24.777	09.91	500	4.590
I	acetic	30	37.408	40.755	28.041	35.971	19.159	11.66	510	3.960
W	acetic	30	40.038	44.053	36.191	35.553	26.012	11.44	500	4.025
X	oxalic	30	39.277	46.273	39.935	35.481	29.704	14.66	500	3.200
T	oxalic	30	41.111	44.453	39.997	34.055	28.572	11.80	500	3.920
P	oxalic	30	31.717	44.981	35.516	36.613	26.131	14.93	490	3.140
J	oxalic	30	39.912	52.238	35.013	42.784	29.972	16.81	500	2.800
B	oxalic	50	32.700	42.300	38.200	33.500	26.600	23.60	500	2.500

TABLE V
COLOR DEVELOPED AND DYE ABSORPTION VALUES ON WOOL YARNS DYED BY MADDER IN DIFFERENT TEMPERATURE AND L:G

Sample	Temp	L:G	CIEL*a*b* System					K/S	λ_{max}, nm	R (%)
			L*	C*	h°	a*	b*			
A	boiling	30:1	32.9	43.0	38.1	34.7	26.0	24.0	500	2.5
B	boiling	40:1	32.7	42.3	38.2	33.5	26.6	23.6	500	2.5
C	boiling	50:1	32.2	42.6	37.4	33.8	25.9	23.3	500	2.0
D	70°c	50:1	37.7	44.5	33.8	30.0	32.0	18.7	490	2.5

TABLE VI
COLOR FASTNESS RESULTS OF DYED SAMPLES

sample	Dyeing Acid	Dye Conc.%	Light Fastness	Washing Fastness		
				Cotton	Wool	Dye exchange
Y	acetic	70	>5	5	5	4
K	acetic	70	3	5	5	4.5
Q	acetic	70	>5	4	5	4
U	acetic	70	>5	4	4	3
L	oxalic	70	6	5	5	3
R	oxalic	70	3	5	5	3
Z	oxalic	70	>5	5	5	3
V	oxalic	70	6	4	4	3
O	acetic	30	>5	5	5	3
S	acetic	30	>5	5	5	4.5
I	acetic	30	3	5	5	4.5
W	acetic	30	>5	5	5	4.5
X	oxalic	30	6	5	5	4
P	oxalic	30	3	5	5	3-4
J	oxalic	30	6	5	5	4
T	oxalic	30	6	5	5	3

more reddish than all others.

After treatment by ammonia and yoghurt decreased the extent of staining on the adjacent cotton fabric and the aftertreatment effectively reduced the staining of dyed samples. As the table show, the color strength of this sample is also high. The employed aftertreatment techniques did not or slightly affect the light fastness of samples except for those retreated with waste water.

It can be concluded that the treating of sample in dyeing waste water for a long period of time does not improve the dyeing efficiency in the both hue and fastness parameters while it is a very common process in the traditional dyeing procedure.

As Figure 3 shows, all four types of madders exhibit same FTIR Spectra and the peaks appear identical positions. Besides, a negligible difference in absorption intensity of sample K is evident around 1700 Cm^{-1} wave number that could be related to carbonyl groups. However, further study is required for comprehensive chemical characterization of different type of madders.

TABLE VII
COLOR DEVELOPED AND DYE ABSORPTION VALUES ON WOOL YARNS DYED BY MADDER AFTER TREATMENT

Sample	Acid type	Dye conc.%	CIEL*a*b* System					K/S	λ_{max}, nm	R (%)
			L*	C*	h°	a*	b*			
0	oxalic	70	33.14	42.384	32.249	35.846	22.616	16.71	490	2.83
1	oxalic	70	46.95	29.974	43.352	21.796	20.577	-	-	-
2	oxalic	70	41.73	37.982	29.562	33.037	18.739	08.30	510	5.40
3	oxalic	70	37.70	50.294	38.980	39.097	31.637	18.05	490	2.63
4	oxalic	70	33.85	46.392	36.850	37.123	27.822	21.46	500	2.23
5	oxalic	70	33.70	42.439	37.924	33.477	26.083	19.69	500	2.42
6	oxalic	70	29.75	37.049	32.164	31.363	19.723	22.59	500	2.12
7	oxalic	70	35.40	47.100	40.200	35.900	30.400	19.80	480	2.30

TABLE VIII
COLOR FASTNESS RESULTS OF AFTER TREATED SAMPLES

After treatment method	Light fastness	Washing fastness		
		Staining on wool	Staining on cotton	Color change
7	>5	5	5	4/5
8	>5	5	5	4/5
9	3	4	5	2

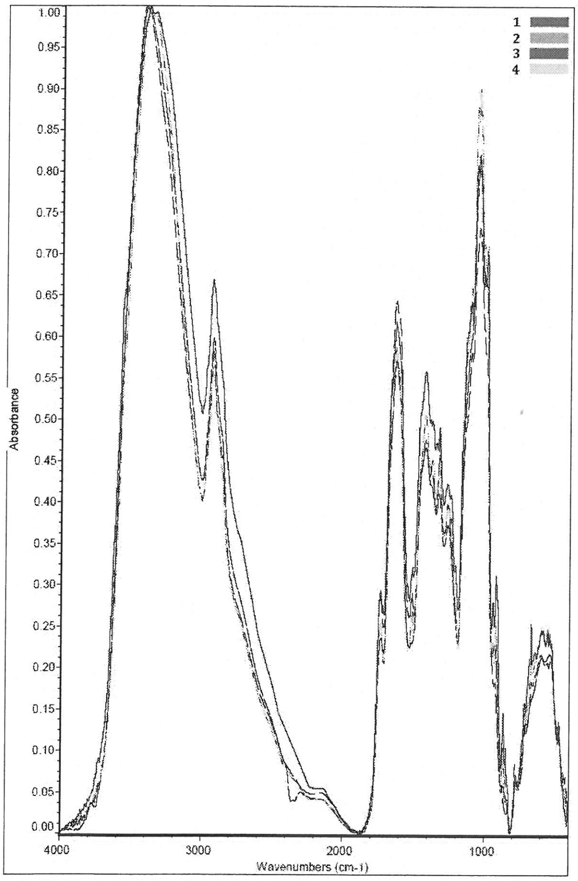

Fig. 3. FTIR spectra of 4 kind of madder: 1-Bafgh, 2- Momtaz, 3-Ardakan and 4- Naeen.

IV. CONCLUSION

In this paper, the role of dye bath conditions and aftertreatment process is investigated for woolen yarn samples which have been dyed with four different types of madder. It was shown that the dye bath pH, L/G and water hardness affect on the dyeing of wool samples with madderes and the color strengths of different samples were quantitatively investigated.

The effects of different aftertreatment processes were also investigated and it was shown that such process could improve the sample fastnesses and the colorimetric specifications of dyed samples consequently changed by aftertreatment procedures. However, the economical parameters should be taken into account for selecting the best effective aftertreatment procedure.

Some differences between the dyeing qualities of different types of madder were also investigated. In fact, some dyeing advantages were found for specific types of madders, e.g. Ardakan and Momta while, the growing place and the age of herbs played important roles in dyeing efficiencies.

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