Traditional Dyeing of Silk with Natural Dyes by Eco-Friendly Method

Samera Salimpour Abkenar

***Abstract*—**In traditional dyeing of natural fibers with natural dyes, metal salts are commonly used to increase color stability. This method always carries the risk of environmental pollution (contamination of arable soils and fresh groundwater) due to the release of dyeing effluents containing large amounts of metal. Therefore, researchers are always looking for new methods to obtain a green dyeing system. In this research, the use of the enzymatic dyeing method to prevent environmental pollution with metals and reduce production costs has been proposed. After degumming and bleaching, raw silk fabrics were dyed with natural dyes (Madder and Sumac) by three methods (pre-mordanting with a metal salt, one-step enzymatic dyeing, and two-step enzymatic dyeing). Results show that silk dyed with natural dyes by the enzymatic method has higher color strength and colorfastness than the pretreated with a metal salt. Also, the amount of remained dyes in the dyeing wastewater is significantly reduced by the enzymatic method. It is found that the enzymatic dyeing method leads to improvement of dye absorption, color strength, soft hand, no change in color shade, low production costs (due to low dyeing temperature), and a significant reduction in environmental pollution.

***Keywords*—**Eco-friendly, natural dyes, silk, traditional dyeing.

I. Introduction

NATURAL dyes or colorants are widely considered to dyeing of natural fibers (cotton, wool, and silk) due to their non-toxic, non-carcinogenic, eco-friendly, and biodegradable properties [1]. Nevertheless, natural dyes have limitations such as the difficulty of color matching, color reproduction, low color absorption rate … [2]. In addition, natural dyes do not have a good affinity for adsorption onto the fibers, thus in most cases, their fastness properties are poor. To improve these properties, traditional dyers generally use the metal mordanting methods (with metal salts) together with increasing dyes concentration, which leads to environmental pollution and is not economically viable. According to previous research [3]-[5], in order to increase the colorfastness of naturally dyed fibers, the application of compounds such as metal salts, tannic acid, syntan, polyvinyl alcohol, glucose ... have been suggested. By using natural mordant (such as tannins) or synthetic mordant (such as syntan) to increase the dye absorption and colorfastness properties, there is also a significant color change. They make a protective layer (or shell) on the natural dyed sample, which leads to preventing the dye removal or migration against washing, light, and abrasion factors. This layer causes yellowing on the sample and occasionally reduction of light fastness [6], [7]. Accordingly, it was decided to use the eco-friendly method for traditional dyeing of silk with natural dyes, without any negative effects on silk, natural dyes, human health, and especially the environment. Therefore, in this study, the possibility of using enzymes in the traditional dyeing of silk fabric with natural dyes was evaluated.

Enzymes are protein-chemical biocatalysts, which can facilitate the acceleration of reactions. It is found that these compounds change physically during the reaction but return to their initial form at the end of the reaction. Firstly, the substrate molecules (in this study: silk) are placed near the active site of the enzyme. Then, the enzyme is exposed in its most suitable position to bind to the substrate and perform catalyst by changing the spatial arrangement. The performance of enzymes can be affected by some factors (such as temperature, concentration enzyme, substrate concentration ...). Therefore, the main point in enzymatic dyeing is to control the dyeing conditions (temperature, time, natural dye concentration, and enzyme concentration), which can have negative effects on the activity of the used enzymes. Since natural dyes *Madder* and *Sumac* are widely used in traditional Iranian dyeing, these two natural dyes were also used in this study.

In this work, silk samples were pre-treated with aluminum salt, α-amylase enzyme (one- and two-step methods), and then were dyed with natural dyes. Finally, the color strength and color fastness of the samples were evaluated and compared.

II. Experimental Procedure

A. Materials

Raw silk fabric (50 g/m^2) was prepared from the Guilan silk factory. α-amylase from Sigma Aldrich and other chemicals (aluminum salt, sodium dithionite, and acetic acid) were obtained from Merck.

B. Degumming and bleaching

Degumming and bleaching processes were performed according to Fig. 1. Afterwards, the samples were rinsed thoroughly in distilled water and dried at room temperature [8].

C. Extraction of Natural Dyes

It is worth noting that sumac (*Rhus coriaria*) *and* madder (*Rubia tinctorum*) are rich sources of hydrolyzable-tannin and alizarin, respectively (Fig. 1). Dye extraction was carried out using 1-10 g of the powders in 1000 ml distilled water at pH 4-5 (acetic acid) for 1 h at 95 ºC [9]. In each process of extraction, after cooling, the obtained mixture was accurately filtered using

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a vacuum pump. The absorption spectrum of the natural dyes was measured by ultraviolet-visible (UV-VIS) spectrophotometer (Jenway 6105/USA) in interval wavelengths ranging from 400 to 700 nm.

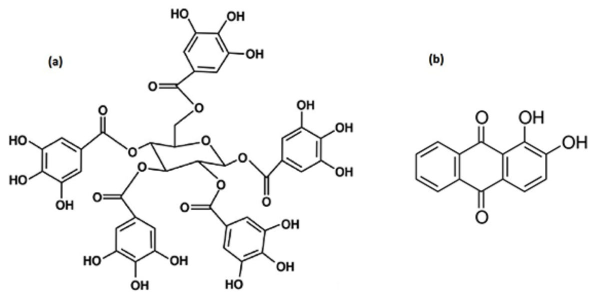


Fig. 1 Chemical structure: (a) Hydrolysable-tannin (b) Alizarin

D. Pre-Mordanting and Dyeing

Pre-mordanting and dyeing of silk fabrics (1 g) were carried out using Hanau-Linitest laboratory-scale dyeing machine in exhaust method with the extracted dyes according to standard dyeing conditions recommended for silk sample (Fig. 2) [10], [11]. Then, all the silk samples were rinsed thoroughly in distilled water and finally dried at room temperature.

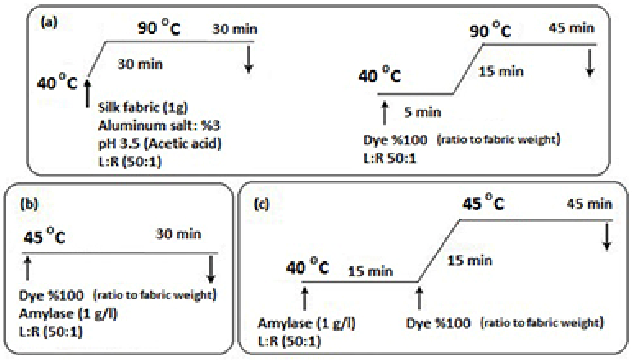


Fig. 2 Pre-mordanting and dyeing of silk (a) Classic (b) One-step process (c) two-step process

E. Color Measurements

After the dyeing process, the color strength (*K/S*) of the samples was measured according to the well-known Kubelka-Munk equation [12]:

$$K/S = [(1- R)^2 / 2R] \quad (1)$$

where *K* is the light absorption coefficient, *S* is the scattering coefficient, and R is the reflectance at the maximum wavelength. Two optical coefficients, *K* and *S*, are introduced to denote the amount of absorption and direction changing scattering, respectively. The scattering and absorption are both proportional to the intensities and to the thickness of the sample. A Gretag Macbeth Color-Eye 7000A reflectance spectrophotometer was used to measure the reflectance of the samples.

F. Color Fastness

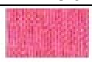
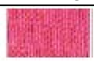
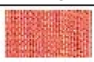
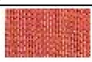
The silk samples were tested according to the standard method of wash test: ISO 105-C06: 1994. In order to assess staining, James Heal Multi Fibers were stitched to the dyed samples prior to testing. The ISO 105-C06: 1994 tests were carried out using Atlas Launder-Ometer M228AA, and then the washed samples were dried at the temperature room. The colorfastness to light was determined with ISO 105-B02: 1994, using an air-cooled xenon arc lamp (with max 2800 Watt) for a period of 24 h. In the case of wash fastness, the degree of color change and staining was assessed by a James Heal greyscale (1-5) and according to ISO 105-A05: 1996 (E) and ISO105-A04: 1989 (E), respectively. The light fastness values of the samples were also evaluated by blue wool standards (1-8). In addition, colorfastness to rubbing was examined with ISO 105-X16: 2016, using Crock meter instrument.

III. Results and Discussion

Poor color stability and low affinity to penetrate fibers are important limitations of natural dyes. Accordingly, the mordants are used, which can create a strong bond between the dye and the fiber and also increase affinity to penetrate fibers [13].

Table I presents the color measurements of the silk samples dyed by different methods. The results show that the color strength (*K/S*) of the samples treated with metal mordant has increased compared to the untreated sample. Metal mordant has a dye-stabilizing role in the classic dyeing of silk samples. This mordant increases the dye absorption and affinity by creating scratches on the fibers. After the adsorption process, it prevents dye migration by forming a complex between the fiber and the dye [9]. On the other hand, Table I shows that the color strength of silk samples dyed with both natural dyes by one-step and two-step enzymatic dyeing methods is higher than that in the traditional dyeing method. This result can be attributed to the stabilizing role of enzymes in the silk sample. Although the chemical structure of enzymes is not well distinct; however, due to their protein nature, it is possible to establish a linkage between the amino acids of the α-amylase enzyme and the protein structure of silk through hydrogen bonds, bipolar-bipolar interactions, and electrostatic forces [5]. Amylase enzyme is able to partially damage silk protein structure (low temperature and neutral pH) and accordingly, this weight loss can cause the mobility of molecular chains of silk. This leads to better penetrate the dye molecules into the crystalline and regular structure of the silk fiber (the dye affinity parameter). On the other hand, after the adsorption process, the enzyme forms an enzyme-dye complex with the dye molecules, which as a physical barrier prevents the dye migration or removal of the silk fibers. It is worth mentioning that the pre-treatment with enzyme causes a soft handle, transparency, and no change shade compared with the pre-treated with a metal salt. Also, the amount of adsorbed dye (for Madder and Sumac) in the two steps enzymatic dyeing method is higher than in the one-step method. This result is probably to be related to (i) competition between the dye molecule and enzyme for access to adsorption sites of silk, and (ii) the possibility of complex formation between enzyme and dye in dyeing bath in one-step enzymatic dyeing method [14]. It seems that in the two-step method, the amylase enzyme has enough time to be absorbed by the sites of the silk. Therefore, when the dye molecules absorbed by these sites, a larger enzyme-dye complex with less solubility can be formed, which prevents dye migration or dye removal. In addition, Table I shows that the color strength of the Sumac is higher than that of the Madder. This result can be due to the abundance of tannin compounds in the sumac plant, which acts as a natural mordant. Then, together with the amylase enzyme it can increase the dye absorption from the dye bath. Therefore, it seems that the adsorption rate of natural dyes by the enzymatic dyeing method (one-step or two-step) extremely depends on the chemical structure of the used dye.

TABLE I
COLOR MEASUREMENT DATA

	Pre-mordanting and Dyeing	Dyed silk	Remaining dye Conc.(g/50ml)**
Sumac	Control	 L^*=54.6 a^*=34.4 b^*=7.9 K/S= 2.9	0.325
	Aluminum salt	 L^*=48.5 a^*=38.4 b^*=7.2 K/S= 3.5	0.184
	One-step method	 L^*=42.4 a^*=46.5 b^*=5.3 K/S= 4.3	0.132
	Two-step method	 L^*=40.2 a^*=48.9 b^*=4.9 K/S= 5.1	0.0634
Madder	Control	 L^*=41.9 a^*=29.2 b^*=30.4 K/S= 2.3	0.367
	Aluminum salt	 L^*=38.7 a^*=32.3 b^*=30.4 K/S= 3.1	0.201
	One-step method	 L^*=37.6 a^*=28.3 b^*=27.5 K/S= 3.6	0.142
	Two-step method	 L^*=35.8 a^*=28.9 b^*=25.5 K/S= 4.7	0.0877

K/S: Color strength; $L^*a^*b^*$: Color coordinates: L^* indicates lightness ($0 < L^* < 100$); a^* and b^* are color directions: $+a^*$ is the red axis, $-a^*$ is the green axis, $+b^*$ is the yellow axis and $-b^*$ is the blue axis. Also, five measurements were recorded for all the dyed silk samples.
** Initial dye concentration is 1 g/50 ml.

According to Table II, it is clear that the pretreatments improve the color fastness of silk samples compared to control silk. On the other hand, the silk samples pretreated with amylase enzyme in one and two-step methods have higher colorfastness than samples treated with a metal salt. These results indicate that the enzyme amylase has a more stabilizing role than metal salt, and thus can prevent dye migration or dye removal from silk samples. Also, the color fastness of the silk dyed with sumac is higher than that of the silk dyed with Madder. This can be due to the abundance of tannin compounds (a natural mordant) in the chemical structure of the sumac plant. Also, the silk dyed with two-step enzymatic dyeing dyed has the highest dye stability against washing, light and abrasion. These results can be attributed to the formation of a larger enzyme-dye complex compared to the metal-dye complex.

TABLE II
RESULT OF COLOR FASTNESS

	Pre-mordanting and Dyeing	WF(CC)[1]	WF (CS)[2]		LF[3]	RF[4]
			Silk	Cotton		
Sumac	Control	2-3	3-4	2-3	3-4	2-3
	Aluminum salt	3-4	4-5	3-4	4-5	3-4
	One-step method	4-5	4-5	4-5	5-6	4
	Two-step method	4.5-5	5	5	6-7	5
Madder	Control	2-3	2-3	2-3	2-3	2-3
	Aluminum salt	3-4	3-4	3-4	4-5	3-4
	One-step method	3.5-4	4-5	4	5	4-5
	Two-step method	4-5	4-5	4-5	5-6	4-5

[1] WF (CC): Wash fastness (Color Change); [2]WF (CS): Wash fastness (Color Staining); [3]LF: Light Fastness; [4]RF: Rubbing Fastness.

IV. CONCLUSION

In this research, the natural dyes (sumac and madder), which are commonly used in traditional dyeing of natural fibers, have been used in silk dyeing with an environmentally friendly method. This eco-friendly method is the traditional silk dyeing using enzyme mordant. In this method, the traditional dyeing of silk can be carried out at low temperatures (40-45 °C) and with reduced energy and costs. In addition, the application of biodegradable enzyme mordant (with low concentration) instead of the common metal mordant in traditional dyeing reduces the amount of dye wastewater pollution. The results indicate that the enzyme (a bio-mordant) can be significantly improved the dyeing parameters such as the dye exhaustion from the dye bath, the dye affinity to fiber, the color strength (K/S), and the color fastness.

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