

## Pistachio Hulls, A New Source of Fruit Waste for Wool Dyeing

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### Abstract

Natural dyes have been employed in dyeing Persian carpet piles for many years. In this study, the dried pistachio hulls were powdered and used for dyeing wool yarns. The Iranian wool yarn was first scoured with nonionic detergent and mordanted using some metal salts including Cu, Cr and Al. It was then dyed with different amounts of dried pistachio hull powder. Taguchi statistical method was employed to find the effective factors and results of the planned experiments, in order to optimize the dyeing factors. A  $L_{18}$  orthogonal array (seven factors in three levels) was employed to evaluate the effects of different parameters in dyeing process. The colorimetric properties of the dyed yarns were evaluated in CIELAB system. Pistachio hulls found to have good agronomic potential as a natural dye in Iran. Metal mordants when used in conjunction with pistachio hulls were found to enhance the dyeability and its fastness properties. The stepwise process of dyeing with pre-mordanting showed to be energy and time saving and found to achieve high dye retention. Therefore this natural dye has good scope in the commercial dyeing of wool yarns used as Persian carpet piles.

**Keywords:** Natural dye; Wool dyeing; Mordant; Pistachio hull; Taguchi

### Introduction

Today, natural colorants are emerging globally due to the fact that are safer and environment-friendly and thus the application of natural dyes should be considered as a better alternative to synthetic dyes. Using natural dyes contributes to the added value of textiles and also responses to the increasing demand of compatibility with the environment [1-7]. From the point of color chemist view, the actual coloring matters used and the methods by which they were so skillfully applied are of considerable interest. So, it is necessary to study and modify the ways of using natural materials in textiles [5,7]. Many studies have been done on natural dyes covering such areas as: variation in the quantity of dyes concerning natural sources, combination of dyes, properties of natural dyes, effects of mordant and auxiliaries on different properties of dyed samples, light fastness behavior of natural dyes, improvement in natural dyes production and discovering other natural dye sources [8-16]. The colorimetric properties of natural yellow dyes including henna (*lawsonia inermis*), dolu (*rheum emodi*), kamala (*mallotus philippinensis*), onion (*allium cepa*) and turmeric (*curcuma tinctoria*) with different mordants have been studied by Gulrajani et al. [11-13]. Tsatsaroni and Eleftheriadis also discussed the color and fastness of natural saffron [17]. Many research papers have been published on natural dyes and mordanting but a few papers have been published on the alteration of all different factors in one approach. *Pistacia vera L.*, from family *Anacardiaceae*, genus *Pistacia* is a small tree up to 10 meters tall, with deciduous pinnate leaves and edible delicious nuts. It is native to southwestern Asia and Asia Minor, from Syria to the Caucasus, Iran, Turkey and Afghanistan. There are archaeological evidences of pistachio nuts were used for food as early as 7,000 B.C. The plant was then introduced to Italy from Syria early in the first century A.D. Subsequently, its cultivation spread over other Mediterranean countries, USA, Australia and China. Botanically a drupe consists of Pericarp (ovary wall) (hull), Endocarp (shell) and ripened ovule (seed) that is the edible portion. Pericarp, in turn, consists of Exocarp and Mesocarp. Pistachio hulls are the byproduct of nut production, which is usually useless. Iran is the world's leading pistachio producer and produces over 350 thousands metric tons every year. There are thousands tons of pistachio hull wastes which can be

used as a valuable source of natural dye for carpet piles. To optimize the design of an existing process, it is necessary to identify which factors have the greatest influences and which appropriate values produce the most consistent performance. Experimenting with the design variables, one at a time or by trial and error, until a first feasible design found would be a common approach to process optimization. However, this approach could lead one to a very long and expensive time span in completing the design process. A technique for laying out the experiments when multiple factors involved is popularly known as the "factorial design of experiments". This method helps researchers to determine possible combinations of factors and to identify the best combination. Since it is extremely costly to run a number of experiments to test all combinations, application of a full factorial design of experiments is restricted when many factors and levels are studied. The statistical experimental analysis is proposed to investigate the significances of systematic effects. The application of this kind of experiments requires careful planning, prudent layout of experiment, and expert analysis of results. A commonly applied statistical method, Taguchi experimental design and analysis of variance (ANOVA), could be used to analyze results of the experiments on the response and to determine how much variation quality influencing factors contribute [18-25]. Orthogonal arrays can be used to assign factors to a series of experimental combinations, in which results could then be analyzed by using a common mathematical procedure. The variables can generally be grouped into two major classifications: (a) independent variables or factors, and (b) dependent variables or responses. In this factorial design, the main effects of independent variables and the interactions between dependent variables can be studied. The latter would be the

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major advantage of this technique while a major disadvantage for one-at-a-time variable testing method.

In this research, the usage of the dried pistachio hulls for dyeing wool yarns was studied. To achieve the maximum color strength of wool samples dyed with the pistachio hulls with a minimum number of experiments, a Taguchi experimental design  $L_{18}$  orthogonal array (seven factors in three levels and one factor in 2 levels) was employed to evaluate the effect of different factors in the dyeing process. The Iranian wool yarn was first scoured with a nonionic detergent and mordanted with some metal salts including:  $KAl(SO_4)_2$ ,  $CuSO_4$ , and  $K_2Cr_2O_7$ . The yarn was then dyed with different amounts of dried pistachio hull powder. The colorimetric properties of the dyed yarns were evaluated in CIELAB system.

## Experimental

### Materials

The following materials were used:

- Iranian wool yarns of 432/2 Tex with 144 twists per meter.
- Nonionic detergent (Shirley Development Limited) for scouring of wool yarns.
- Aluminum potassium sulfate ( $KAl(SO_4)_2$ ), copper sulfate ( $CuSO_4$ ) and potassium dichromate ( $K_2Cr_2O_7$ ) from Merck for mordanting process.
- Hydrochloric acid and sodium hydroxide for controlling the pH.
- Dried powdered pistachio hulls from genus *Pistacia vera* L. collected from Kerman province, Iran.

### Procedure

The wool yarns were treated in four steps as follows:

**Scouring:** Wool yarns were scoured with 0.5% nonionic detergents for 30 minutes at 50°C. The L:G (Liquor to Good ratio) of the scouring bath was kept at 40:1. The scoured material was thoroughly washed with tap water and dried at room temperature. The scoured material was soaked in clean water for 30 minutes prior to dyeing or mordanting.

**Mordanting:** The scoured wool yarns were mordanted with  $KAl(SO_4)_2$ ,  $CuSO_4$ , and  $K_2Cr_2O_7$ . The L:G of the mordanting bath was kept at 40:1. Hydrochloric acid was used in the mordanting bath for adjusting the pH at 5. The mordanting temperature was started at 40°C and then gradually raised to the required temperature during 20 min and kept at this temperature for 1 hr. The mordanted material was then rinsed with water thoroughly, squeezed and dried.

**Dyeing:** First the dye solution was prepared by pouring the appropriate amount of dye powder in water for 24 hours before dyeing. Then, the dyeing process was carried out. Dyeing started at 40°C and temperature was raised to required temperature in 20 minutes and resumed at this temperature 1 hr. The pH of the dyebath was kept at

pH=5 using dilute acid or base. The dyed material was then rinsed with water thoroughly, squeezed and dried.

**Measuring of color strength:** To investigate the effects of different parameters on the reflectance spectra of dyed samples, a GretagMacbeth spectrophotometer model 7000A computer integrated, was used. CIELAB color co-ordinates ( $L^*$ ,  $a^*$ ,  $b^*$ , C) and color strength values (K/S) were calculated from the reflectance data (R) of dyed samples for 10° observer and D65 illuminant based on the Kubelka–Munk equation:

$$K/S = \frac{(1-R)^2}{2R}$$

In which, K, is the sorption coefficient, R is the reflectance of the dyed sample and S is the scattering coefficient.

## Results and Discussion

In this research work, the optimization of the dyeing factors in applying the pistachio hulls as a new source of natural dye for wool yarns was carried out employing Taguchi method for statistical design of experiments. According to Taguchi parameter design methodology, one experimental design should be selected for the controllable factors. A  $L_{18}$  orthogonal array (that accommodates seven factors in three levels and one factor in two levels each in 18 runs) was employed to identify the optimum conditions for dyeing wool yarns with pistachio hulls [25]. Seven influencing factors were taken into account and one column was set for the determination of errors as following:

- Amount of colorant (A)
- Amount of mordant (B)
- Type of mordant (C)
- Temperature of mordanting bath (D)
- Temperature of dyeing bath (E)
- Duration of mordanting (F)
- Duration of dyeing (G)

The three levels of factors were selected in accordance with the preliminary test and the previous author's experience [26,27]. The factors and levels considered for this experiment are shown in Table 1. The K/S ratios for all samples from different conditions was calculated and shown in Table 2. In these experiments, the system was optimized according to the maximum response value of (K/S). The analysis of the variance (ANOVA) was employed to determine the factors influencing the average response (K/S) ratios. Table 3 presents the degree of freedom (df), the sum of squares (SS), the mean square (variance, V), and the F ratio of variances (F). The insignificant factors are pooled to reduce the chance of making alpha mistakes. As a role, the factor, which influence is 10% or lower than the most influential factor is pooled [25]. The F-Value implies that the model is significant. One column was set for the determination of errors to consider the effects

Levels	Amount of colorant, A (g)	Amount of mordant, B (g)	Type of mordant, C	Temp. of mordanting bath, D (°C)	Temp. of dyeing bath, E (°C)	Duration of mordanting, F min	Duration of dyeing, G min
1	0.4	2	Cr	50	60	30	60
2	0.1	5	Al	70	80	60	90
3	2	10	Cu	Boil	Boil	120	120
Optimum	0.4	2	Cu	50	60	120	120

Table 1: Studied levels of different factors and the optimum level.

Factors	Error	A	B	C	D	E	F	G	K/S
Exp. No									
1	1	1	1	1	1	1	1	1	0.06077
2	1	1	2	2	2	2	2	2	0.05804
3	1	1	3	3	3	3	3	3	0.06073
4	1	2	1	1	2	2	3	3	0.05729
5	1	2	2	2	3	3	1	1	0.04999
6	1	2	3	3	1	1	2	2	0.05730
7	1	3	1	2	1	3	2	3	0.05911
8	1	3	2	3	2	1	3	1	0.05747
9	1	3	3	1	3	2	1	2	0.04033
10	2	1	1	3	3	2	2	1	0.06026
11	2	1	2	1	1	3	3	2	0.05847
12	2	1	3	2	2	1	1	3	0.05652
13	2	2	1	2	3	1	3	2	0.05753
14	2	2	2	3	1	2	1	3	0.06043
15	2	2	3	1	2	3	2	1	0.05233
16	2	3	1	3	2	3	1	2	0.05796
17	2	3	2	1	3	1	2	3	0.05720
18	2	3	3	2	1	2	3	1	0.05714

Table 2: Design of experiments (DOE) and the calculated K/S ratios for different conditions.

	df	SS	V	F
Error	1	1.56968E-05	1.56968E-05	1.742903
A	2	6.01627E-05	3.00813E-05	3.340098
B	2	6.90913E-05	3.45457E-05	3.835796
C	2	6.45276E-05	3.22638E-05	3.582426
D	2	6.15764E-05	3.07882E-05	3.418584
E	2	1.49631E-05	7.48157E-06	0.83072
F	2	4.80049E-05	2.40024E-05	2.665124
G	2	3.9758E-05		
e	2	3.2291E-05		
(e)	4	3.60245E-05	9.00613E-06	
Sum	17	4.06072E-04		

Table 3: The analysis of the variance (ANOVA) for samples dyed with pistachio hulls.

of factors excluded from the experiment and/or Uncontrollable factors (beta mistakes).

The variation of K/S against the different levels of factors is shown in Figure 1.

The response of software calculation shows that the optimum levels of each factor are as follows:

- Amount of colorant at level 1 (0.4 g).
- Amount of mordant at level 1 (2.0 g).
- Type of mordant at level 3 (CuSO<sub>4</sub>).
- Temperature of mordanting bath at level 1 (50°C).
- Temperature of dyeing bath at level 1 (60°C).
- Duration of mordanting at level 3 (120 min).
- Duration of dyeing at level 3 (120 min).

The ANOVA predicts the maximum value of K/S=0.7 for the above optimum conditions. It also suggests that the factors influencing the dye absorption of the wool yarn are of different importance and that the most important factor is the amount of mordant (F=3.835796)

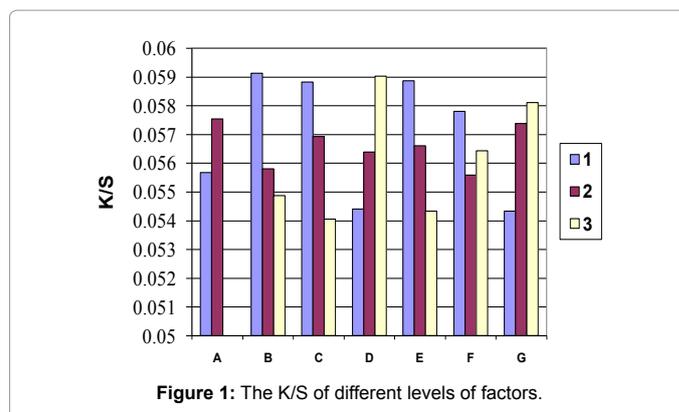


Figure 1: The K/S of different levels of factors.

followed by the type of mordant (F=3.582426), and temperature of mordanting bath (F=3.418584). The amount of colorant is the fourth most important factor presenting the F ratio of 3.340098. The higher the percent influence of a factor, the tighter the tolerance, and vice versa.

### Effect of mordant

Most of the natural dyes have poor affinity for natural fibers. Moreover, their fastness is often enhanced by metal mordants, which form an insoluble complex with the dye molecules. It is known that flavonols have greater tendency towards chelate formation due to the presence of hydroxyl-keto functionality [28,29]. The probable way of chelation depends on the nature of the mordant-dye complex which has been discussed earlier [27]. Mordant makes strong coordination bonds with the wool yarn on one side and the colorant molecule on the other side. The dye molecules are capable of forming five- and six-membered chelate rings with different metal ions. These chelates utilize the ortho-dihydroxy structure and/or carbonyl ortho to the hydroxyl group in the flavonol dye molecules, which in turn greatly enhance the affinity of natural dye and fiber. Therefore the type and amount of mordant is of the great importance to make such chelation [27].

### Conclusion

The use of the experimental design is described for optimizing analytical methods. Many factors can be studied, so the interactions can be determined. In addition to the factors identified as being significant, they have more credibility since they are studied several times. The Taguchi's method simplifies both the assignments of factors and the calculations.

The designs described in this work include three level factors. The results and analysis of the variance show that the above-mentioned conditions were considered as optimum. Experiments were carried out at the stated levels, and the optimum conditions were achieved. Confirming experiments were also carried out. Limitations to the experimental design may be seemed obvious, but they are worth being stated, neglecting them often leads to the failing of this approach. The variance observed for a factor is only valid over the range studied for that factor. Pistachio hulls found to have good agronomic potential as a natural dye in Iran. Metal mordants when used in conjunction with pistachio hulls were found to enhance the dyeability and its fastness properties. The color shades on wool yarns ranges from light orange to dark orange. The stepwise process of dyeing with pre-mordanting showed to be energy and time saving and found to achieve high dye

retention. Therefore this natural dye has good scope in the commercial dyeing of wool yarns used as Persian carpet piles.

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