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Achillea Millefolium, a New Source of Natural Dye for Wool Dyeing

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ABSTRACT

Today, natural colorants are emerging globally due to the fact that they are safer and more environmentally-friendly. Natural dyes have been employed in dyeing Persian carpet piles for many years. In this study, the dried Achillea was used for dyeing wool yarns. The Iranian wool yarn was scoured, mordanted using Cu, Sn, Al salts and then dyed with different amounts of dried Achillea 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_9 orthogonal array (four 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. Achillea found to have good agronomic potential as a natural dye in Iran. Dyeing with Achillea in conjunction with metal mordants showed enhancement in its fastness properties. Therefore it shows commercial capability for dyeing of wool yarns used as Persian carpet piles. Prog. Color Colorants Coat. 2(2009),87-93. © Institute for Color Science and Technology.

1. Introduction

For several centuries humans admired the beautiful natural colors of plants and minerals. The natural dyes have been known and used for thousands of years for painting of body and making foods for ancient humans [1]. The greatest use of natural dyes occurred when the art of weaving developed [2]. The rug weavers also used these dyes for dyeing rug piles but production and development of synthetic dyes limited using of natural dyes [3]. Synthetic dyes offered greater variety and stability of color as compared to natural dyes and the dyers preferred to use synthetic dyes more and more [4]. But today dyeing processes based on natural sources have gained importance in view of stringent environmental and industrial safety conditions which innovative ideas in dyeing industry are being tried to

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cater to such needs. Natural dyes processed for the market do not undergo any chemical operations. Those operations involved are purely physical, such as grinding, drying and water extractions. None of these operations create any great environment problems.

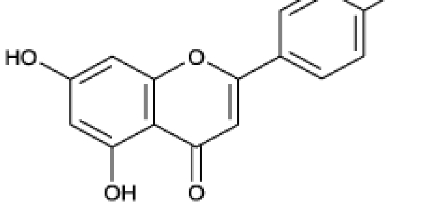
Today, natural colorants are emerging globally due to the fact that they are safer and more environmentally-friendly and thus the application of natural dyes should be considered as a better alternative to synthetic dyes. Using natural dyes contributes to the added value of textiles and also responses to the increasing demand of compatibility with the environment. Recently there has been growing interest in the use of natural dyes in textile applications. This is a result of the stringent environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes. Natural dyes exhibit better biodegradability and are generally more compatible with the environment. In spite of their inferior fastness, natural dyes are more acceptable to environmentally conscious people around the world [5].

From the color chemists' point of 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. Many studies have been done on natural dyes covering such areas as: variation in the quantity of dyes in the natural sources, combination of dyes, properties of natural dyes, effects of mordant and auxiliaries on different properties of dyed samples, light fastness behavior of these dyes, enzymes for improvement of natural dyes absorption, improvement in natural dyes production, the application of natural dyes and discovering other natural dye sources [6-20]. Recently some exhaustive reviews on the subject of natural dyes in textile applications have been published [21, 22]. However, there is very few (if any) work reported in the literature on the use of *Achillea* as a natural dye for its many different applications. Although colorants are considered to be essential in human life, the use of those obtained from natural sources has not been extensively developed. So, it is necessary to study and modify the ways of using natural materials in all different applications such as textile, food, cosmetics and so on.

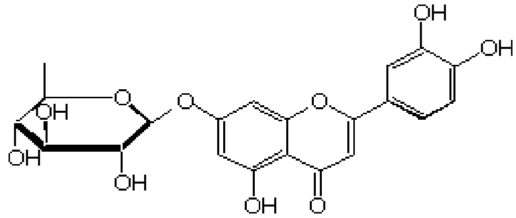
Achillea is a genus of about 85 flowering plants, in the family Asteraceae, commonly referred to as Yarrow. They occur in Europe and temperate areas of Asia and some parts of Iran. A few grow in North America. The genus was named for the Greek mythological character *Achillea*. According to the Iliad, *achilleas,* soldiers used Yarrow to treat wounds [23].

Achillea is a perennial plant with beautiful white to white-yellow or white-purple flowers and grows up to 80 cm tall. The plant also has a long history as a powerful "healing herb" used topically for wounds, cuts and abrasions [24]. *Achillea* contains flavonoids namely as luteolin and Apigenin (Figure 1) which can be used for natural dyeing [25, 26].

In this study, the dried whole *Achillea millefolium* from Kerman province of Iran were powdered and used for dyeing wool yarns which then can be used as Persian carpet piles. Taguchi method was employed to discuss the results of the planned experiments in order to optimize the dyeing parameters. The colorimetric properties and light fastness of the dyed yarns were discussed. The experimental designs were first introduced by Fisher as agricultural research tools in the 1920s [27]. His primary aim was to obtain most information possible about a process with the least number of experiments. The experimental designs and optimization methods for chemists and other engineering branches were reviewed by Bayne and Rubin [28] and Duckworth [29].



Apigenin



Luteolin

Figure 1: Chemical structure of apigenin and luteolin.

Taguchi helped developing these tools so that they now have found much wider acceptance. Taguchi simplified the application of experimental design by using standardized library of the basic designs called orthogonal arrays, along with some simple methods to modify these layouts in order to fit the individual situations. His methodology was also developed within an industrial environment and favored productivity and cost effectiveness over the statistical rigor [30, 31]. Orthogonal arrays were used to assign factors to a series of experimental combinations, in which results could then be analyzed by using a common mathematical procedure. The main effects of these factors and preselected interactions between the factors were independently detected. The emphasize was on the identification of controlling factors and the magnitude quantitation of their effects rather than just the identification of statistically significant effects. The number of trial chosen for an experimental design was based on the desired resolution. In a factorial design, one could study main effects as well as interactions between factors. The latter would be the major advantage of this technique while a major disadvantage for one-at-a-time variable testing method. Main effects and interactions could be confounded, with one another if the experimental design of low resolution were chosen [31].

The significance of a factor is judged by subjecting it to the test of significance. The factors that do not pass this test are considered insignificant and are usually treated as if they have not been present. The process of ignoring a factor once it is deemed insignificant, called pooling, and it is done by combining the influence of the factor with that of the error term. In statistical predictions, two types of mistakes are encountered: alpha and beta mistakes. An alpha mistake is calling something important when it is not. A beta mistake is the significant factor which is mistakenly ignored. Pooling factors that are not significant go toward reducing the chance of making alpha mistakes. As a role, the factor which influence is 10% or lowers than the most influential factor is pooled [32].

2. Experimental

2. 1. Materials

The following materials were used:

- Iranian wool yarns of 434/2 tex with 40 twist per meter.
- *Achillea millefolium* was collected from Kerman, Iran, dried in shadow, ground in a laboratory mill and then sifted.
- Copper sulfate ($CuSO_4$. H_2O), tin chloride ($SnCl_2$), and aluminium sulfate ($Al_2(SO_4)_3$) were purchased from Merck for mordanting process.
- Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck chemical company.
- Nonionic detergent for scouring of wool yarns.

2. 2. Procedures

The wool yarns were treated in five steps as follows:

2. 2. 1. Scouring

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

2. 2. 2. Mordanting

The scoured wool yarns were mordanted with aluminium sulfate, tin chloride, and copper sulfate. The L:G. of the mordanting bath was kept at 40:1. The pH was adjusted using hydrochloric acid at 5. The mordanting temperature was started at 40ºC and then gradually raised to the required temperature within 20 min and kept at this temperature for 1 hr. The mordanted material was then rinsed with water thoroughly, squeezed and dried.

2. 2. 3. Dyeing

First the dye solution was prepared by pouring the appropriate amount of dye powder in water for 24 hr prior to dyeing. Then, the dyeing process was carried out. The L:G of dyeing bath was kept at 30:1. Dyeing started at 40ºC and temperature was raised to required temperature (boiling) within 20 min and maintained at this temperature for 1 hr. The dyebath volume was kept constant by adding excess water during the boiling. 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.

2. 2. 4. Measuring of color strength

The reflectance spectra of dyed samples were measured using 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 10º observer and D65 illuminant. In this study, the reflectance (R) of dyed samples was measured at 360-760 nm. The color strength value (K/S) in the visible region of the spectrum (400-700) is calculated based on the Kubelka–Munk equation:

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

which (K) is the adsorption coefficient, (R) is the reflectance of the dyed sample and (S) is the scattering coefficient.

2. 2. 5. Fastness testing

Light fastness was tested according to ISO 105-B02 method. The dyed samples were exposed to xenon arc lamp using a xenotest model β from Atlas at standard testing conditions. The wash fastness were also measured according to ISO 105-C01.

2. 3. Statistical design of experiments (DOE)

first, it should be emphasized that the experimental design, factorial design and Taguchi method, is merely a tool and would not replace sound technical judgment or creativity in experimental work. In a broad way, the purpose of statistical experimental analysis is 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. Based on years of research and applications, Dr. Genechi Taguchi, a Japaneese engineer, has standardized methods for each of these designs of experiments (DOE) application steps [31].

in general, statistical project consists of five fundamental steps:

1. Problem definition
2. System identification
3. Statistical model formulation
4. Data collection
5. Statistical analysis and results

3. Results and discussion

In this work, the optimization of dyeing factors of applying the *Achillea* as a new source of natural dye was carried out by Taguchi method in order to statistical design of experiments. According to Taguchi parameter design methodology, one experimental design should be selected for the controllable factors. A L_9 orthogonal array (that accommodates four factors in three levels and one factor in two levels each in 9 runs) was employed to identify the optimum conditions for dyeing wool yarns with *Achillea* [32]. Four influencing factors were taken into account and one column was set for the determination of errors as following:

- Type of mordant (A)
- Amount of mordant (B)
- pH (C)
- Amount of colorant (D)

The factors and levels considered for this experiment are shown in Table 1. The color strength values (K/S ratio) for all samples obtained from different conditions was calculated and shown in Table 2. The color strength values may seem low due to the fact that the concentration of dyes in the plants are rather low compared to those of synthetic dyes, but the values are still credible since the K/S ratios were calculated based of the CIE Lab values with at least 4 significant digits [33].

In these experiments, the system was optimized when the response value of (K/S) was as large as possible. The analysis of the variance (ANOVA) was employed to determine the factors influencing the average response (K/S) ratios. Table 3 presents pure sum, the sum of squares (ss), the mean square (variance) and percent.

Table 1: Factors and levels of studied factors.

	Factors	Level 1	Level 2	Level 3	L2-L1
1	A	0. 604	3. 19	2. 061	2. 585
2	B	3. 171	1. 031	1. 653	-2. 14
3	C	1. 688	2. 912	1. 255	1. 223
4	D	0. 98	2. 145	2. 73	1. 165

Table 2: L_9 standard design of experiments for four parameters at 3 levels.

Exp. No	A	B	C	D	K/S
1	Al	5%	2	30%	0.451
2	Al	10%	4	60%	0.922
3	Al	15%	6	90%	0.591
4	Sn	5%	4	90%	2.774
5	Sn	10%	6	30%	0.348
6	Sn	15%	2	60%	2.813
7	Cu	5%	6	60%	2.087
8	Cu	10%	2	90%	1.374
9	Cu	15%	4	30%	1.415

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

	Factors	DOF	Sums of Squares	Variance	F- Ratio	Pure Sum	Percent
1	A	2	2. 819	1. 409	0. 000	2. 819	38. 900
2	B	2	1. 343	0. 671	0. 000	1. 343	18. 543
3	C	2	0. 797	0. 398	0. 000	0. 797	10. 999
4	D	2	2. 286	1. 143	0. 000	2. 286	31. 554
	Other / Error	0	0. 000	0. 000	0. 000		0. 000
	Total	8	7. 247				100. %

The analysis of variance (ANOVA) of each factor on dyeing wool yarn with *Achillea* shows that factor A (type of mordant) is the most important factor with the higher influence percent about 38%. Table 4 displays the colorimetric data of dyeing wool yarn with *Achillea* at CIELAB system. From Table 4, the corresponding assessment shows that, mordant has the most influence in L* as indicates lightness. According to the table, a* and b* as chromaticity coordinates, change shade with different mordant from green to yellow. It shows that the type of mordant affects the shade of color in the product.

For fastness testing the dyed wool samples were tested according to ISO 105-B01 and ISO 105 C01 methods. The light fastness of samples varies between 6-7 compared to Blue Scale and the wash fastness was 4 compared to Gray Scale which both show good light and wash fastnesses.

4. Conclusions

In this paper, experimental design for optimizing analytical methods is described. Four different factors as well as their interactions have been studied. In addition to their significance, they are also reliable since they are studied several times. The Taguchi method simplifies both the assignments of factors and the calculations.

The experimental designs described in this work consist of three level factors. The obtained results along with the analysis of the variance show that the above mentioned conditions can be considered as optimum.

Table 4: CIELAB system of dyeing wool yarn with *Achillea.*

Exp. No.	L*	a*	b*
1	77. 66	-0. 24	25. 29
2	73. 41	-0. 97	38. 28
3	75. 10	-0. 85	29. 00
4	68. 35	16. 51	63. 71
5	78. 87	-1. 0	22. 31
6	72. 62	15. 57	71. 87
7	57. 85	3. 27	29. 45
8	63. 80	0. 87	26. 99
9	61. 19	-5. 75	21. 89

Experiments were carried out at the stated levels, and the optimum conditions were achieved. Confirmation experiments were also carried out.

Obviously, the experimental design has some limitations, but they are worth mentioning because neglecting them often leads to the failing of this approach. The observed variance for a factor is only valid over the range studied for that factor.

Achillea found to have good agronomic potential as a natural dye in Iran. Metal mordants when used in conjunction with *Achillea* were found to enhance the dyeability and its fastness properties. The color shades on wool yarns ranges from light yellow to dark green. 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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