

A review of some significant trends in dyeing of silk with natural dyes

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Abstract

The article comprehensively reviews recent breakthroughs in use of newer types of natural dyes for improvement of the properties. The dyeing of silk fabric has been done using four types of natural dyes that include indigo, turmeric, madder and Terminalia cecuba. The parameters evaluated include color measurement, light fastness, wash fastness and rubbing fastness. There has been improvement in properties. In another innovative research, dyeing could be done with and without mordants. In another innovative research, silk fabrics have been mordanted with alum and dyed with cochineal and gall oak shellac extracts. Optimum dyeing parameters have been determined by using different concentrations of these natural colorants.

Key words: *Silk, Natural dyeing, Mordants, Fastness properties, Herbal extracts, Textile processing.*

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I. Introduction

Natural dyes can be obtained from plants, animals, or minerals. They have been used for the coloration of fibers such as silk, wool, cotton, and flax for many centuries. Cochineal was derived from the dried bodies of females of the *Dactylopius coccus* Costa insects and used for the coloration of textile fibers as a red dye in Asia from the 18th to the 19th centuries and in Europe from the 16th to the 19th centuries. This natural dye presents good light stability. Its color varies from orange to red, depending on the pH [1-4]. The coloring principle of the cochineal extract is carminic acid, a hydroxyanthraquinone linked to a glucose unit, comprising 10% of the cochineal and 2–4% of its extract. Treatment of carminic acid with an aluminum salt produces carmine, the soluble aluminum lake. Carmine has normally 50% or more carminic acid [5].

Quercus infectoria Olivier is a semi-deciduous little tree that grows in Asian, Mediterranean countries, and south-eastern Europe. This plant is rich in tannins and has been used for dye and ink manufacture from Sumerian time to the present day. Generally, the obtained colors are black for silk dyeing and between soiled yellow-brown for wool dyeing [6]. Although energy conversion efficiencies of natural dyes are very low, many of them have important advantages such as easy preparation, minimal toxicity, lower allergenic reaction, and cost compared to synthetic dyes. Some researchers have focused on the investigation of dye-cocktail solutions, which use two different natural dyes to overcome this energy conversion problem [7].

Dyes obtained from natural resources are non-pollutant, non-allergic, shade rich and warm [8]. However, they have poor colour yield, reproducibility, dyeing efficiency and cultivation efficiency besides having limited shade range and non-availability; hence they have been replaced by synthetic dyes [9]. They are advantageous as they are stronger, brighter, reproducible, cheap, easily available and have better fastness but, during the manufacturing process, many carcinogenic chemicals are required and effluent created on using them can be damaging to the environment apart from causing allergies to human skin and cancer, unlike natural dyes [10-13]. Yet, it would be improper to classify all the synthetic dyes as harmful or all the natural dyes good for health. However, natural dyes still possess high potential to substitute certain harmful synthetic dyes owing to their eco-friendliness, biodegradability, less toxicity and irritation to skin [14-16].

II. Dyeing with natural herb extracts

HPLC analysis

The dye compositions were based on the literature, the chromatograms and the absorption spectra acquired with the standard reference compounds [17-20]. After HPLC analysis, it is well known that the methanol extract of the dried cochineal led to the elucidation of some new anthraquinones, along with to known compounds carminic acid, kermesic acid, and flavokermesic acid. The structure of the new compounds such as 2-C-glucoside of flavokermesic acid, 4-aminocarmesic acid, α/β C-glucofuransides of kermesic acid, etc. were identified [21]. One of the metal salts, i.e. the aluminum salt, was used as a mordant in the traditional dyeing process with the natural dyes, consisting of tannin and anthraquinones. The sample preparation for the extraction of the dye components from the dyed silk fibers was commonly used hydrolysis procedure with hydrochloric acid. For the extracts, with this treatment it is necessary to HPLC analysis. The dye compositions were based on the literature, the chromatograms and the absorption spectra acquired with the standard reference compounds. After HPLC analysis, it is well known that the methanol extract of the dried cochineal led to the elucidation of some new anthraquinones, along with to known compounds carminic acid, kermesic acid, and flavokermesic acid. The structure of the new compounds such as 2-C-glucoside of flavokermesic acid, 4-aminocarmesic acid, α/β C-glucofuransides of kermesic acid, etc. were identified. One of the metal salts, i.e. the aluminum salt, was used as a mordant in the traditional dyeing process with the natural dyes, consisting of tannin and anthraquinones. The sample preparation for the extraction of the dye components from the dyed silk fibers was commonly used hydrolysis procedure with hydrochloric acid. For the extracts, with this treatment it is necessary to Dyeing Code Alum (%) (Premordant) Cochineal (*Dactylopius coccus* Costa) (%) Gall oak (*Quercus infectoria* Olivier) (%) FeSO₄ (%) (postmordant)

The natural dyes were identified in the silk fabrics dyed according to the different concentrations. Carminic acid, gallic acid, ellagic acid and minor colorants were determined in the acid-hydrolyzed silk extract. In this study, spectrum intensity of color compounds was increased in all dyeings as the dye ratio increases, especially for minor colorants. On the other hands, it was determined that the a-coded samples generally contained more minor colorants when compared to the b-coded samples. Even though in the samples with dyeing code 4 with lowest cochineal ratio gallic acid was detected; in the samples with dyeing codes 14 and 24 with lowest gall oak ratio gallic acid was not detected. This result showed that the color compounds in the cochineal were bound more strongly to the fabric when compared to gall oak.

Color measurement values of dyed fabrics

The CIEL*a*b*, color strength (K/S), and color differences values obtained for the dyed fabrics have been determined. The coloristic properties of the dyed fabrics were enhanced because of high concentration of cochineal and gall oak in the dye bath, which used alum. Generally, FeSO₄ usage as a mordant salt improved the dyeability of the silk fabrics. The highest K/S values for the dyed silk fabric sample at the maximum absorption wavelength were 6.30 and 5.79 for the samples 32b and 33b [22]. This means that the highest color yield was obtained in dyeing with 6% alum, 15% cochineal, 9–10% gall oak, and 3% FeSO₄. When the sample 1a-coded was taken as standard, the K/S values of samples 'b-coded' (premordanted with alum and post-mordanted with FeSO₄) were found high compared to the samples 'a-coded', but in some cases (dyeing code 3, 24–33) the K/S values of the dyed samples 'a-coded' were determined high compared to the dyed samples 'b-coded'. When the samples 'a-coded' was taken as a standard, the color difference (ΔE^*) values of the dyed 'b-coded' were found in the range from 12.82 to 32.21. The highest color difference value was found as 32.21 for the sample 13b dyed with 6% alum, 5% cochineal, 10% gall oak, and 3% FeSO₄.

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Color fastness results of the dyed fabrics

The washing, perspiration, rubbing, and light fastness values of the dyed fabrics have been determined. The color change values of the samples after the washing, perspiration and rubbing fastness tests in general were found to be 3+ in gray scale rating. The color fastness values of dyed samples to light without gall oak and used a high proportion of cochineal were found to be 3 in blue scale rating.

For samples 'a-coded', dyeing code 8 and 9, light fastness rating on the blue scale were determined as 5, for samples 'a-coded' and 'b-coded', dyeing code 2–3 and 24–31 light fastness values were determined as 3 and rest of the samples exhibited light fastness values as 4. Post-mordanting with FeSO₄ did not improve the light fastness properties. The acidic perspiration color fastness test results were quite good when compared to the alkaline perspiration for all dyed samples. In general, both the acidic and alkaline perspiration color fastness test results were adequate.

Using FeSO₄ as a mordant salt after dyeing affected the color change of washing, acidic and alkaline perspiration fastness test results. But, the mordant salt did not improve the light fastness properties.

III. Top dyeing of silk with natural dyes

Textile processing is mainly associated with colouration of various fibres. The merits of synthetic dyes have been discussed earlier on as being cheap, brilliant shades, wider spectrum of shades and so on. The major hurdle in replacement of natural dyes with synthetic dyes. They are advantageous as they are stronger, brighter, reproducible, cheap, easily available and have better fastness but, during the manufacturing process, many carcinogenic chemicals are required and effluent created on using them can be damaging to the environment apart from causing allergies to human skin and cancer, unlike natural dyes. Yet, it would be improper to classify all the synthetic dyes as harmful or all the natural dyes good for health. However, natural dyes still possess high potential to substitute certain harmful synthetic dyes owing to their eco-friendliness, biodegradability, less toxicity and irritation to skin. Textile processing is mainly associated with colouration of various fibres. The merits of synthetic dyes have been discussed earlier on as being cheap, brilliant shades, wider spectrum of shades and so on. The major hurdle in replacement of natural dyes with synthetic dyes Top dyeing of silk using natural dyes however is the non-availability of standard shade card and application procedure that follows a modern and scientific technique [24-26]. Various literatures pertaining to different natural dye sources report their use for other than textile applications [27,28]. Literature of their application with the help of mordants and conventional dyeing procedures on different textile materials is also available [29-31]. But research work reported related to application of these dyes using padding techniques on natural as well as on artificial textiles are few and the same also report that natural dyestuffs have colour limitations [32-34]. Nonetheless, a textile craftsman has an unusual opportunity to mix colours to achieve unique effects when working on textiles. Top dyeing is the most obvious way of expanding the range of colours that consists of dipping a textile into several different dye baths in succession. Dipping a cloth into a blue vat, and then in a yellow dye bath will create green colour. Similarly, dipping in red dye bath followed by yellow one will result in orange, and so on. This technique can be applied to any combination of colours, although the dyes producing the clearest colours are generally best for top dyeing. However, no scientific work on the production of wider shade range with the standard procedure has been reported. In our earlier work, production of primary and secondary shades on textiles is reported [35,36]. This work is mainly concerned with the production of standard primary, secondary and tertiary shades on silk material from four commercially available natural dyes, its colour characterisation and finding out its fastness properties against various agencies.

Silk fabric was dyed with four individual as well as with the combination of the dyes at 50 gm/l concentration by a hot padding method. The results in terms of L*, a*, b* and K/S values are presented in Table 1, where L* represents the lightness or darkness of the samples, the variation in a* values shows the redness of dyed samples, while b* is indicative of the yellowness of the sample. From the results, it is evident that variety of shades viz, yellow, red, blue, orange, green and purple could be produced on silk fabric using four natural dyes namely, turmeric, indigo, Terminalia chebula and madder by the top dyeing technique. It has also been observed that by dipping silk fabric into individual dye bath unique shades can be produced using hot padding technique. Colours that are developed by using individual natural resources depend on the chromophoric group present in that particular natural dye. In case of turmeric, the yellow colour appears due to the presence of curcumin (β -diketone), while in case of madder (Rubia Tinctom), the chromophoric group is flavone derivative that gives orange to red colour with or without the use of mordants. Similarly, in case of indigo, chromophores containing disulfide donor groups are responsible for shades of blue colour whereas, in case of Terminalia chebula different shades of beige to brown can be obtained, where the chromophoric group responsible for the colour is condensation product of tannins. After individual application, padding of silk fabric in different dye baths, in succession, gave compound shades (combination of two or three natural colours) using top dyeing technique. The various colours and shades which can be produced on silk fabric with selected commercially available natural dyes have been determined, individually and with the combination of two or three dyes using

top dyeing method. Fastness to light, washing and rubbing of samples dyed individual colour or with mix colour have been determined. It can be seen that all samples dyed either with individual dye or with the combination of dyes, exhibits adequate all round fastness properties except turmeric which shows poor light fastness than others; whereas rubbing fastness was found poor in indigo dyes compared to terminalia chebula. D-3 has excellent fastness to washing, light and rubbing. Fastness properties of the dyed samples depend on the attachment of the dye with the fibre and the dye to fibre attachment depends on the presence of auxochromic group and its affinity towards the fibre. Turmeric contains curcumin which may have formed hydrogen bond with the silk fibre resulting in poor light fastness. Terminalia chebula and madder showed good to very good all round fastness that may be due to the stronger attachment between the fibre and dye. Finally, in case of indigo, rubbing fastness was found to be poor - an indirect indication of the fact that the auxochromic group present in indigo, may have poor affinity towards the fibre. It may have been retained on the surface or to remain partially trapped, thus adversely affect the rubbing fastness property.

IV. Conclusion

In this study, various concentrations of the cochineal and gall oak natural dyes were used with pre-mordanted and post-mordanted methods on silk fabric samples. Identification of the dyed silk fabrics was carried out by using reversed-phase high-performance liquid chromatography with diode-array detection. In accordance with HPLC results, a-coded samples that not comprise iron contain more colorant against b-coded samples, which consist of iron. These results show that while more colorants are complexed with aluminum, use of aluminum and iron together are done in combination with less colorant. The color variety can be achieved with a different ratio of the cochineal and gall oak. The highest color yields (K/S) were obtained in the dyed samples without post-mordanted with 15% cochineal, 1% gall oak (such as dyeing codes 31, 11b-13b, 24a-33a) and with alum, 15% cochineal, 9% gall oak, and post-mordanted with FeSO₄ (3b, 11b-13b, 19b-33b).

The washing, alkaline/acidic perspiration and dry/wet rubbing fastness values of these samples were quite good, at 4. The light fastness results were at level 3–5. The best light fastness values were determined at dyeing codes 8a and 9a. As a result, it was determined that in the natural dyeings two different mordanting processes can be applied by using cochineal and gall oak together on silk fabrics according to dyestuff analysis, color measurements and fastness tests. The consequences of all the results are at the desired grade.

Silk fabric can be dyed successfully with Indigo, Turmeric, Madder and Terminalia chebula either independently or with the help of metallic mordants. Various shades of yellow, red and blue can be produced using four natural dyes individually or in combination by means of a new hot padding method. Further shades of orange, green, purple and so on could be produced with adequate fastness properties using top dyeing method. The most significant part of the study is that the use of hot padding and top dyeing methods can successfully produce diverse shades, besides being lower on energy and equipment requirements. Hence, the process can be considered as cost effective and best suited for small scale industries or in cottage dyeing industry

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