Effect of metallic mordants on pH and Optical density values of the dyed fabrics by using aqueous extracted eco-friendly natural dye from shells of *Juglans regia*

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Abstract

The present work explores the potential of eco-friendly phytochromic dyeing of walnut shells with two different kinds of fibres viz. cotton and silk by using some metallic mordants such as copper sulphate, potassium dichromate, stannous chloride and ferrous sulphate. The aqueous extracted natural dye of the walnut shells exhibits good range of colours with varying shades of warm beige, caramel brown, funnel seed, yellow beige and golden beige for different metallic mordants for dyeing of cotton fabric whereas shades like almond white, ochre, golden bronze, warm sand and light beige are observed in the case of silk fabric by using different metallic mordants. Pre-mordanting method was used under this study.

The variations in optical density (OD) and pH-values of the solutions (with and without mordanting w.r.t. pre-mordanting method) were also measured (before and after dyeing the fabrics) with the help of UV-Vis-spectrophotometer and pH-meter respectively.

Keywords: *Juglans regia*, Extraction, Natural dye, pH, Optical density and UV-Vis-spectrophotometer.

Introduction

More than 4,000 years have passed since the invention of natural dyes[12]. In the past, people believed that color was a spiritual necessity that was just as important as the physical need for sustenance. The skill of imparting color through dyeing has therefore been crucial in enhancing the beauty of the world in every civilization from the earliest times to the present. Natural dyes derived from plants and animals were the source of bio-color. Dye is a term used to describe organic chemical compounds that have the ability to absorb light and produce color. A substance can retain dyes, which are highly colored molecules, by mechanical retention, physical absorption and the creation of complexes or covalent chemical connections with metals or salts.

A dye molecule is composed of two chemical components: auxochromes and chromophores. Chromophores are unsaturated groups that give compounds their color (Greek: chroma = color, phoros = bearer). Finding effective, affordable and high-quality natural dye sources and extraction methods to satisfy demand is the goal of several ongoing research projects worldwide. In sufficient amounts, natural dyes may be produced without harming the environment and their effluents can be readily broken down using bioremediation techniques.

There is a growing need to develop alternative extraction methods and to improve the fastness properties of eco-friendly natural dyes from plant sources for their reintroduction into dying industries due to the production of toxic chemicals by synthetic dyes that pose serious ecological and human health concerns.

The majority of historically significant natural colorants by phytochemical analysis[7], belong to the carotenoid, anthraquinone, naphthoquinone and indigoid groups. Direct, vat and certain acid dyes are also known as mordant dyes. Organic dyestuffs of vegetable, animal and mineral or inorganic pigments are the general categories into which natural dyes fall.

Therefore, all colors made from plants, insects and minerals are included under the phrase "natural dyes." Additionally, they can be categorized in a number of ways. Several classification techniques were used including:

- Classification according to application method.
- They might be categorized according to their origin or the sources from which they are derived.
- According to their chemical structure.
- Grouping them according to color.

Some introductive points about *Juglans regia*

Scientific classification:

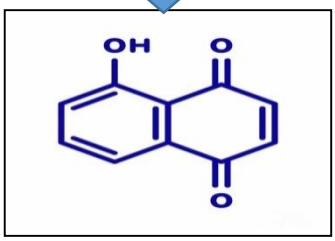
Kingdom	-	Plantae
Division	-	Magnoliophyta
Class	-	Magnoliopsida
Order	-	Fagales
Family	-	Juglandaceae
Genus	-	Juglans
Species	-	*Juglans regia*

Among these dye-bearing plants is the walnut or *Juglans regia L.*, which grows in temperate climates. Typically having a broad crown and short trunk, this huge deciduous tree can reach heights of 25–35 meters (80–120 feet) with a trunk diameter of up to 2 meters (6 feet). Commercial cultivation of it is practiced in Central and Southern Europe, Asia, Western South America and the United States. Leaves, husks and shells have all been explored as possible dyeing ingredients for various textile substrates.

A Walnut fruit

Dried form of walnut shell

Powder form of walnut shell



Juglone (A brown dye pigment)

Fig. 1: Walnut shells and chemical structure of pre-isolated yellow dye component as Juglone from *Juglans regia*

The existence of the napthoquinone class of natural colorants is thought to be responsible for *Juglans regia L.* and has coloring ability. The chemical compound juglone, which belongs to the napthoquinone class, 5-Hydroxy-1, 4-napthoquinone ($C_{10}H_6O_3$), functions as a substantial dye and gives textile substrates a brown hue (Fig. 1). By creating a co-ordination complex with the dye and adhering to the fabric or tissue, a mordant[9] is a material that sets dyes on textiles or tissue sections. The resulting dye-ion coordination complex is colloidal, contains direct bonding, H-bonds and hydrophobic interactions and can be either acidic or alkaline.

In general, mordants come in three varieties:

• Metallic mordants, such as iron, copper, tin and chromium metal salts.
• Myrobalan and Sumach tannins
• Oil mordant, which combines with the primary metal mordant to generate a complex.

Mordants aid in the binding of dyes to fabric by creating a chemical bridge between the dye and the fibre which enhances a dye's staining capacity and fastness characteristics. Insoluble dye compounds are created within the fibre by mordants. When specific functional groups are positioned appropriately inside the dye molecule, the dye molecule coordinates with the metal ion. Coordination usually occurs between two hydroxyl groups or between a hydroxyl group and an adjacent carbonyl and nitroso or azo group. Although a variety of colors with exceptional resistance to wet treatments are produced by the mordant dyes, the tones are not particularly bright.

Current situation of natural dye in India: In the field of natural dyeing, Indians are regarded as pioneers. Presently natural dyes are used to color clothing, medications, cosmetics and other items[6]. They are also utilized to color a variety of food items because of their non-toxic properties. The usage of natural dyes has decreased over generations, despite the fact that indigenous knowledge systems have been practiced for many years. Furthermore, not much is known about natural resource dyeing. The ability of *Juglans regia L.* leaf extract to color various textiles was investigated. Brown napthoquinone colorant, which was extracted from walnut leaves using pre-, meta- and post-mordanting techniques in the presence of copper sulphate, ferrous sulphate and alum sulfate at medium pH[10], was used in this study to dye cotton and wool textiles.

Combination of mordants including lemon juice and potassium dichromate, copper sulfate and lemon juice, lemon juice and ferrous sulfate was used. The color fastness characteristics of *Erythrina suberosa* flowers dyed on wool were previously investigated using a ratio of 1:3, 1:2 and 3:1 for the juice and stannous chloride[14]. The dyeing potential of natural dyes made from *Juglans regia* leaves using a mordant made from Salix albax wood is being investigated. The effectiveness of the dye extraction process using pre-mordanting, instantaneous mordanting and post-mordanting techniques was tested on wool, pashmina, cotton and silk textiles[5].

Previous work focused on standardizing the ancient dyeing process, optimizing[11,15,16] the dyeing and mordating of cotton and wool samples using dye bearing plants including fruit rind of *Juglans regia*[8] and testing the dyed samples against light and washing[3].

Natural dye is becoming more and more popular because it is non-toxic, environmentally friendly and imparts a variety of shades. It was designed to extract natural dye from the bark residue of *Juglans regia* using microwave. Microwave powder, pH, extraction time and dry mass concentration were among the extraction parameters that were examined. Using microwave assistance, the extracted material was dyed and the resulting color yield was assessed. Every time, the amounts of flavonoids and tannins were measured. It was discovered that the ideal extraction parameters were pH = 3, extraction period = 4 min. and microwave powder = 850. Last but not least, FT-IR spectroscopy was employed to differentiate between dyed and undyed acrylic in order to determine how this dye affected the outermost layer of acrylic fibers[2].

Previous research has documented the process of extracting a natural colorant from walnut bark for the purpose of dyeing wool fibers both with and without the use of mordants such as ferrous sulphate, aluminium sulfate and stannous chloride. Additionally, the impact of these mordants on colorimetric and fastness qualities was examined. Juglone served as the primary coloring agent in the walnut bark extract which was characterized with FT-IR and UV-visible spectroscopy techniques. The findings of this study demonstrate that the colorimetric and fastness properties of wool fibers dyed with walnut bark were enhanced by pre-treating them with metallic mordants. According to a previous study, walnut shell extracts were used to dye polyester and polyester/viscose mixes.

To achieve the maximum color depth, many extraction parameters were taken into account, including the material—liquor (M: L) ratio, extraction temperature, extraction duration and pH. The best results for extracting natural dyes from walnut shells (*Juglans regia*) were obtained at 80°C for 75 minutes and with M:L ratio set at 1:30 at pH 2. In order to dye polyester and polyester/viscose blends with the aforementioned walnut shell extract, separate mordanting with $AlKHSO_4$, $AlK(SO_4)_2$, or $FeSO_4$ for 90 minutes was studied. The results showed that pre-mordanting with $FeSO_4$ provides the best dyeing results with good color depth and overall good color fastness, which can be used in future applications for eco-friendly dyeing of polyester and its blended textiles[4].

Material and Methods

Chemicals and reagents: Copper sulphate, potassium dichromate, stannous chloride and ferrous sulphate (Laboratory reagents).

Collection of materials: Pure cotton and silk fabrics were purchased from Khadi Bhandar from a local market in Dehradun district of Uttarakhand. Dried walnut was purchased from local market in Dehradun.

Weight of fabrics was: Cotton - 0.187g, Silk - 0.102g.

The dyeing material (walnut shell) was soaked in distilled water overnight and then dried. This dried walnut shell was then grind into fine powder.

Aqueous dye extraction: The extraction of dyes was carried by the Soxhlet apparatus (Fig. 2).10gram powder of *Juglans regia* shell was taken for the process of aqueous extraction of natural dye. 300 ml of distilled water was taken in the RB flask along with 10 gram of powder and was placed over heating mantle. Temperature was maintained to 100 °C. It was kept for 2 to 3 hours, then allowed to cool down and the coloured extract was obtained (Fig. 3).

Dyeing and Mordanting of fabrics under Pre-mordanting method: The fabrics were washed properly with detergent and then cut into small square shape pieces. Beakers of 100 ml were taken and filled with the extract up to 30 ml, one of them is reference in which no metallic mordant was used. One gram each of metallic mordants such as copper sulphate, potassium dichromate, stannous chloride and ferrous sulphate was dissolved in other four beakers and then fabrics were dissolved in all the five beakers (Fig. 4). Pre-mordanting method was used for the dyeing of fabrics. pH and optical density values of the sample were measured before the dyeing of fabric with the help of pH meter (Fig. 8) and UV-Visible spectrophotometer (Fig. 7) respectively.

Beakers were placed in the water bath along with fabric and temperature was maintained at 80°C onto the water bath (Fig. 5). The solution was stirred continuously for 15 minutes, then fabric was taken out and it was dried in sunlight. Then different colours of fabric were obtained from the different metallic mordants. pH and optical density values of the solutions were again measured after dyeing of the fabrics. Same procedure is followed for both fabrics that were cotton and silk.

Analysis of the dyed samples: UV visible spectrophotometer model no. PerkinElmer lambda 365 was used. The optical density of the solution with metallic mordants and extract (reference) (Fig. 6) was measured with the help of UV-Visible spectrophotometer.

pH metery: The pH values of the different metallic mordants solutions were measured with the help of pH meter before and after dyeing of the cotton and silk.

Results and Discussion

Analysis of pH values for cotton fabric (with and without mordant): The graph (Fig. 9) shows the increase in the value of pH in each case such as from 5.8 to 7.2 in the case of without mordant, 3.6 to 3.9 with copper sulphate, 5.2 to 5.5 with potassium dichromate, 3.3 to 3.4 with ferrous sulphate after dyeing of the cotton fabrics but not in the case of stannous chloride which was reduced from 1.2 to 0.9 respectively. It was observed from the graph that the pH value of reference is highest and the pH value of stannous chloride is lowest before and after dyeing of the fabrics as

compared to other metallic mordants. In case of ferrous sulphate, there is a slightly change in the pH values before and after dyeing of the cotton fabrics.

Analysis of Optical Density (OD) values for cotton fabric (with and without mordant): The graph (Fig. 10) shows the increase in the value of OD in each case such as from 1.417 to 2.027 in the case of without mordant, 0.766 to 1.347 with ferrous sulphate and 1.880 to 2.046 after dyeing of the cotton fabrics but not in the case of copper sulphate and potassium dichromate which were reduced from 0.652 to 0.641and 2.068 to 2.060 respectively.

It was observed from the graph that the OD value of potassium dichromate is highest and the OD value of copper sulphate is lowest before and after dyeing of the fabrics as compared to other metallic mordants. In case of copper sulphate and potassium dichromate, there is a slightly change in the OD values before and after dyeing of the cotton fabrics.

Fig. 2: Soxhlet apparatus

Fig. 3: Dye extracted

Fig. 4: Mordanted and unmordanted dyed samples using selected metallic mordants

Fig. 5: Water bath

Fig 6: Samples for measurement of OD values

Fig 7: UV-visible spectrophotometer

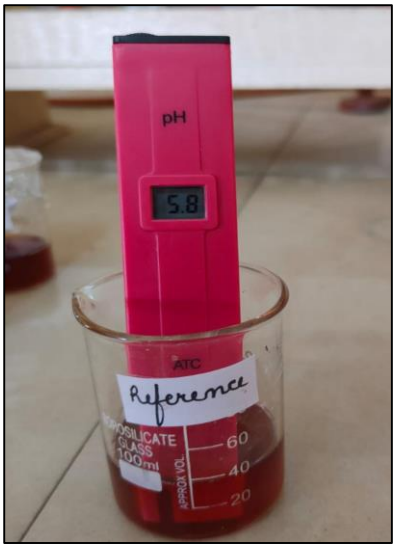


Fig 8: A digital pH meter

Analysis of pH values for silk fabric (with and without mordant): The graph (Fig. 11) shows decrease in the value of pH in each case after dyeing of the silk fabric such as from 5.8 to 4.9 in the case of without mordant, 5.2 to 5.0 with potassium dichromate, 3.3 to 3.2 with ferrous sulphate and 1.2 to 1.0 with stannous chloride after dyeing of the silk fabrics but not in the case of copper sulphate which was increased from 3.6 to 3.7 respectively. It was observed from the graph that the pH value of reference is highest and the pH value of stannous chloride is lowest before and after dyeing of the fabrics as compared to other metallic mordants. In case of ferrous sulphate, potassium dichromate copper sulphate and stannous chloride, there is a slightly change in the pH values before and after dyeing of the silk fabrics.

Analysis of Optical Density (OD) values for silk fabric (with and without mordant): The graph (Fig. 12) shows the decrease in the values of optical density after dyeing of the silk fabric in each case like 1.417 to 0.882 in the case of without mordant, 0.766 to 0.374 with ferrous sulphate and 1.880 to 1.855 with stannous chloride, 0.652 to 0.249 with copper sulphate and 2.068 to 1.846 with potassium dichromate respectively after dyeing of the silk fabrics. It is observed from the graph that the OD value of potassium dichromate is highest and the OD value of copper sulphate is lowest before dyeing of the fabrics. The OD value of stannous chloride is highest and the OD value of copper sulphate is lowest after dyeing of the fabrics as compared to other metallic mordants. In case of stannous chloride, there is a slightly change in the OD values before and after dyeing of the silk fabrics. Here, Tables 1 and 2 also revealed about the variations in pH and OD values using with and without metallic mordants including beautiful colour shades of the dyed fabrics of cotton and silk respectively.

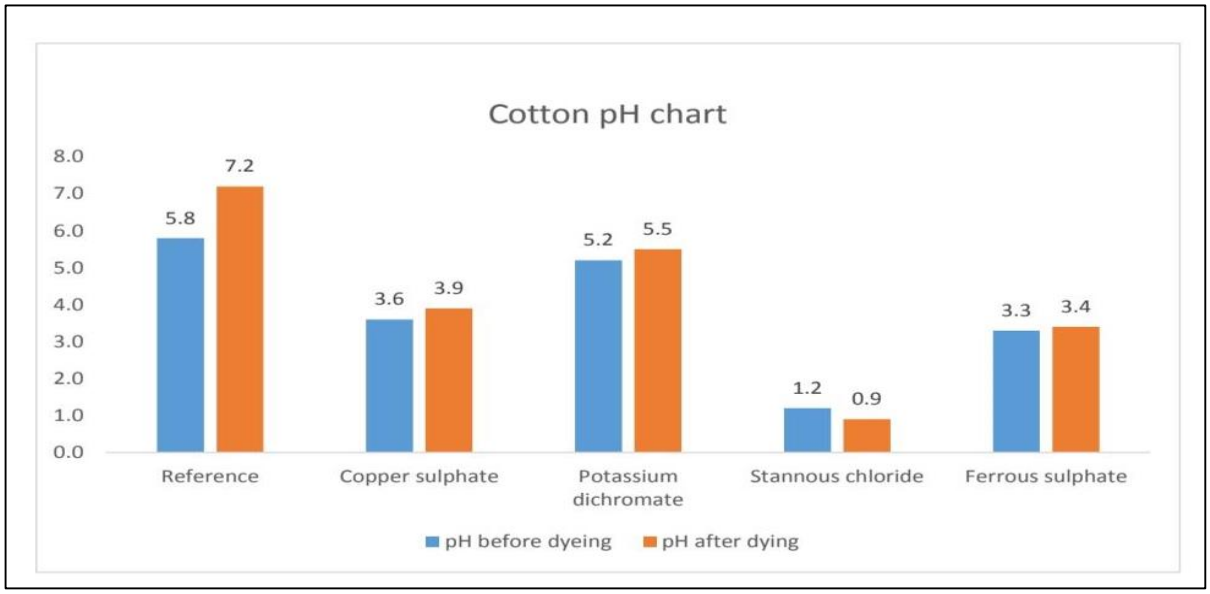


Fig. 9: Variation in pH values before and after dyeing in cotton fabrics

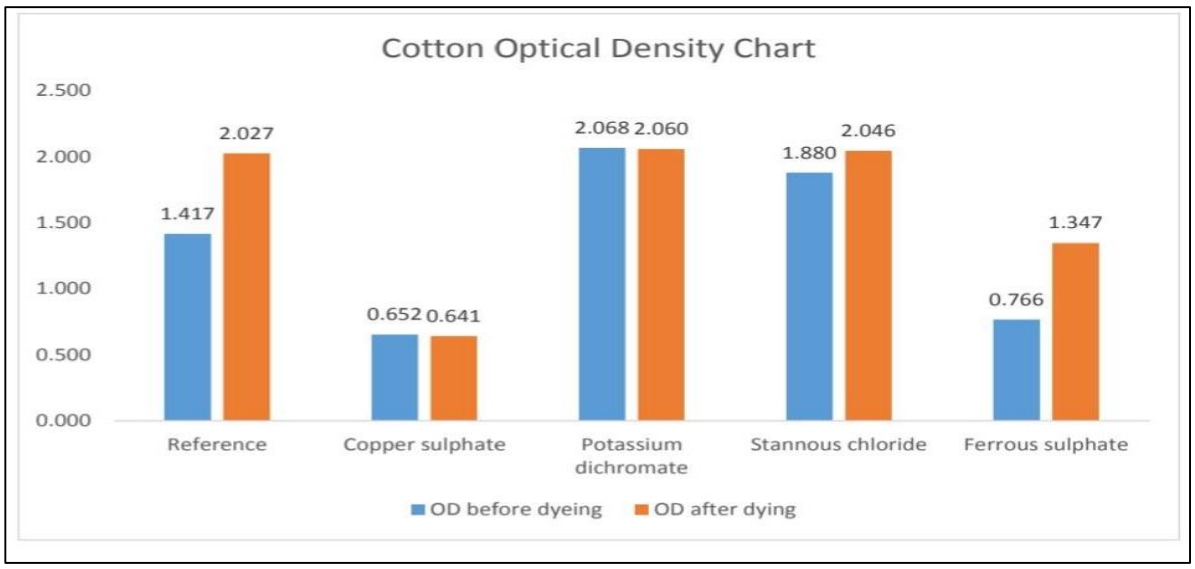


Fig. 10: Variation in OD values before and after dyeing in cotton fabrics

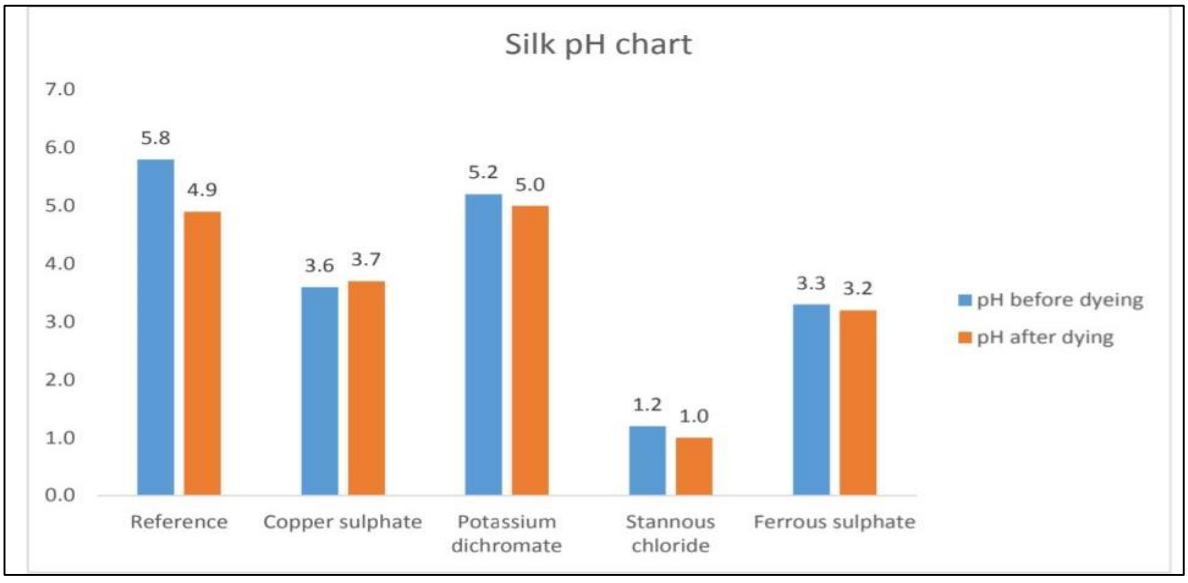


Fig. 11: Variation in pH values before and after dyeing in silk fabrics

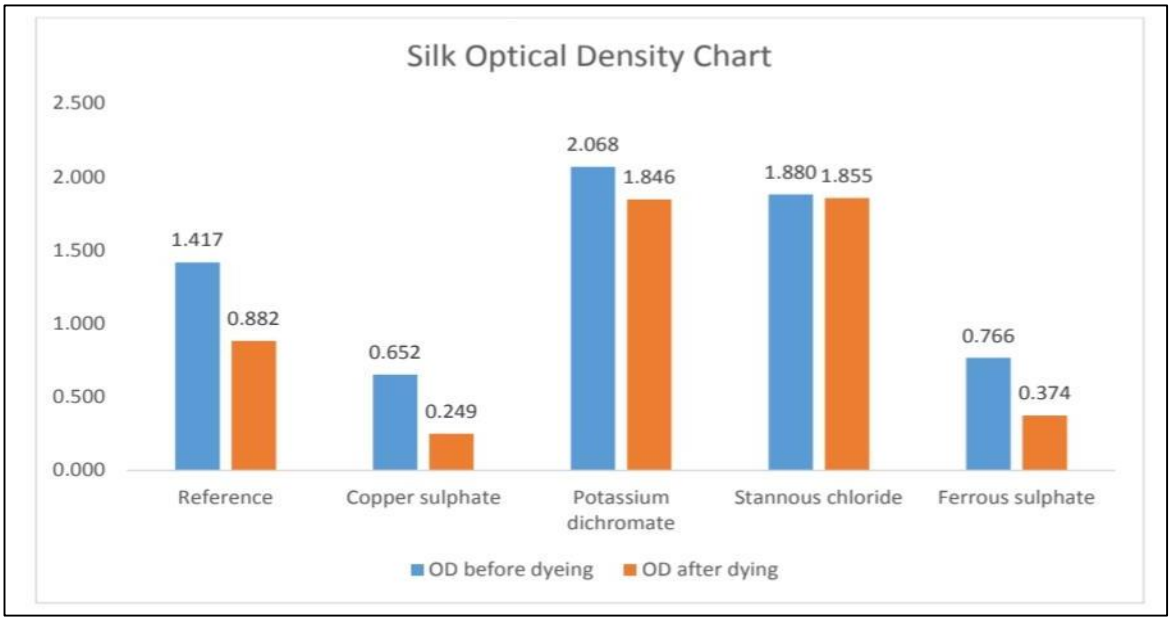


Fig. 12: Variation in OD values before and after dyeing in silk fabrics

Table 1
Variation in pH and OD values by using metallic mordants in case of cotton dyed fabrics with natural dye of seed coat *of Juglans regia*

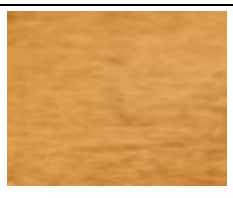
S.N.	Mordants used as metallic mordants	pH value before dyeing	pH value after dyeing	OD value before dyeing	OD value after dyeing	Dyed fabrics (cotton)	Colour observed
1	Reference (Without mordants)	5.8	7.2	1.417	2.027		Warm Beige
2	Copper sulphate	3.6	3.9	0.652	0.641		Yellow beige
3	Potassium dichromate	5.2	5.5	2.068	2.060		Caramel brown
4	Stannous chloride	1.2	0.9	1.880	2.046		Funnel seed
5	Ferrous sulphate	3.3	3.4	0.766	1.347		Golden beige

Table 2
Variation in pH and OD values by using metallic mordants in case of silk dyed fabrics with natural dye of seed coat *of Juglans regia*

S.N.	Mordants used as metallic mordants	pH value before dyeing	pH value after dyeing	OD value before dyeing	OD value after dyeing	Dyed fabrics (cotton)	Colour observed
1	Reference (Without mordants)	5.8	4.9	1.417	0.882		Almond white
2	Copper sulphate	3.6	3.7	0.652	0.249		Warm sand
3	Potassium dichromate	5.2	5.0	2.068	1.846		Ochre
4	Stannous chloride	1.2	1.0	1.880	1.855		Light beige
5	Ferrous sulphate	3.3	3.2	0.766	0.374		Golden bronze

Conclusion

It was concluded that in the fig. 9, the pH value of reference was highest and the pH value of stannous chloride was lowest before and after dyeing of the fabrics as compared to other metallic mordants. In case of ferrous sulphate, there is a slightly change in the pH values before and after dyeing of the cotton fabrics while in the fig. 11, pH value of reference was highest and the pH value of stannous chloride was lowest before and after dyeing of the fabrics as compared to other metallic mordants. In case of ferrous sulphate, potassium dichromate copper sulphate and stannous chloride, there were a slightly change in the pH values before and after dyeing of the silk fabrics. From the fig. 10, OD value of potassium dichromate was highest and the OD value of copper sulphate was lowest before and after dyeing of the fabrics as compared to other metallic mordants.

In case of copper sulphate and potassium dichromate, there were a slightly change in the OD values before and after dyeing of the cotton fabrics whereas in fig. 12, the OD value of potassium dichromate was highest and the OD value of copper sulphate was lowest before dying of the fabrics. The OD value of stannous chloride was observed as highest and the OD value of copper sulphate was lowest after dyeing of the fabrics as compared to other metallic mordants.

In case of stannous chloride, there is a slightly change in the OD values before and after dyeing of the silk fabrics. The aqueous extracted natural dye of the walnut shells exhibits good range of colours varying shades of warm beige, caramel brown, funnel seed, yellow beige and golden beige for different metallic mordants for dyeing of cotton fabric whereas shades like almond white, ochre, golden bronze, warm sand and light beige are observed in the case of silk fabric by using different metallic mordants (Table 1 and table 2) respectively.

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