Better Dyeability in Natural Dyeing of Silk using Rare Earth (RE) Salts as Mordant

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Abstract

Natural dyeing requires two main features- a natural colorant and a mordant which can fix the natural colorant to the fabric. Selection of an appropriate metallic compounds as mordants is essential as well as crucial as there is a natural dye and mordant compatibility factor. Mordant is required for dyeing natural fibers with natural dyes. This paper presents the application of rare earth (RE)salts as mordant for the dyeing of pure silk fabrics by two different modes of mordanting using a natural dye—Rubia cordifolia. The influence of pre-and post -mordanting on silk dyeing were explored. The rare earth mordant dyeing was found to improve dye-uptake, the fixation of dyestuff, and thus causing better adherence of the colorant and good colour fastness. Another speciality of RE salts is that they provide different hues to the fabric with Rubia dye extract.

Through this study we wish to report that with the use of rare earth salts, there has been manifold advantages such as better dye uptake, better fastness properties, low temperature dyeing, low energy consumption, and above all would have lesser pollution load in the effluent, thus proving them to be ecofriendly and safe mordant.

Keywords

Rare earth salts; Lanthanum carbonate; Yttrium oxide; Cerium nitrate; Premordanting; Postmordanting; Rubia cordifolia.

Citation

Archana Gangwar and Padma S Vankar - Better dyeability in Natural dyeing of Silk using Rare earth (RE) salts as mordant, *BTRA Scan* - Vol. LI No. 2 July 2022, Page no. 4 to 9

1.0 Introduction:

With natural dyes mordanting with metal salts is an integral part of the dyeing process. These are metallic salts which are applied onto the fabric before, or after the dyeing step (they are called pre and post-mordanting respectively). Conventionally salts such as alum, copper sulphate, ferrous sulphate, and tin chlorides metal salts are being used with natural dyes. Other methods of mordanting could involve the use of biomordants which are derived from plants such compounds are polyphenolic commonly called tannins and tannic acid as well as enzymes[1-3]. The use of some metal accumulating plants such as Eurya acuminata DC var euprista Karth in natural dyeing has been reported by Vankar et al [4]. This plant inherently contained Aluminium which was responsible for dye adherence.

The role of a mordant is well defined. It acts like a bridging head between the colorant and the fabric and thus is responsible for better dye adherence. Mordants help to bind the dyestuff to the fibre. There are many mordants commonly used in natural dyeing and each one will give a different shade from a particular dyestuff as per its chelating capacity. Depending on the oxidation state of the metal of the mordant, the dye chelation takes place[5].

Rare earth element (Rare Earth) salts are also called (RE salts); salts from lanthanide series such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), terbium (Tb), ytterbium (Yb), dysprosium (Dy), holmium (Ho), gadolinium (Gd), erbium (Er), thulium (Tm), lutetium (Lu), and with closely-related two elements such as yttrium (Y), scandium (Sc). The Rare earth (RE) are a unique group of elements. Their f electronic configurations, the hard Lewis acid character of their ions, and their large ionic radii render their coordination chemistry distinctly different from that of transition metal elements. Specifically, because of the large ionic size, a high coordination number is required unless sterically bulky ligands are utilized. The insignificant involvement of the f orbitals in chemical bonding means lanthanide–ligand interactions are primarily ionic, leading to

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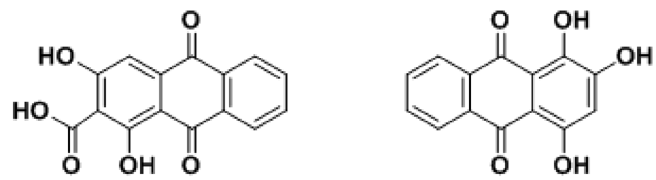
generally labile lanthanide complexes with flexible and irregular coordination environments. Because of their hard Lewis acid character, lanthanide coordination toward O-based ligands is strongly preferred. Thus natural colorants in Rubia dye have oxygen containing functional groups which bind with RE metal.

Rare-earth elements are more reactive than other metallic elements. The rare earth ion is capable of making a combination with hydroxyl, azo group, or sulfonic group to form stable complexes, which makes the rare earth salts suitable candidates for dyeing and printing industries. The application of the rare earth as mordant in the silk dyeing with natural dyes was found to improve dye-uptake and apparent depth (K/S value) and have a distinct darkening effect along with colour fastness [6].

Application of rare earth chloride in dyeing wool fiber with gardenia yellow colorant was studied. Variables such as pH, temperature, the concentration of lanthanum chloride, and its mode of addition in the dyeing process were investigated. The optimum dyeing conditions were obtained as follows:pH value of 4, the concentration of lanthanum chloride 7%(owf) added during the constant temperature period, and the dyeing temperature was 90 ℃. Results showed that the dye uptake could be raised to 96.27% with excellent washing fastness and slight strength loss.[7]

Light fastness improvement with metal salt mordants is mainly due to the formation of metal–colourant complexes, this complexation increases dye uptake, and, as dye adherence is better, the light energy transmitted through the surface to the inner layers is reduced also the complexation induces dye aggregation on the surface of the fabric which is exposed to irradiation. This causes quenching of the dye molecule's photoexcited states [8].Dye–metal complexation is generally accompanied with colour changes, which is attributed to the formation of charge transfer complexes and an increase in conjugation lengths [9].

We aimed to use rare earth salts instead of conventional mordants for the natural dyeing of silk fabric with Lanthanum carbonate, Cerium nitrate, and yttrium oxide. The effects of dyeing conditions such as dyeing temperature, time of dyeing, and the concentration of rare earth(RE) salts were taken into consideration. The RE salts used were Lanthanum carbonate, Yttrium oxide, and Cerium nitrate on the silk fabric for checking the dyeability. These mordants were investigated systematically and compared with conventional mordant- Alum. The fabrics dyed with natural dyes in presence of rare earth as mordant exhibited high colour and shade stability as reflected through their K/S values and E values. Employing rare earth as mordant apparently raised the colour fastness - washing, and light of the silk fabrics dyed with Rubia dye. The main colorant molecules in Rubia cordifolia dye are munjustin and purpurin as shown in figure-1



Munjustin *Purpurin*

Figure-1 Structures of main colorant molecules of Rubia cordifolia dye

In the case of silk fibres, dye anions and metal cations have a strong attraction towards positively charged amino and negatively charged carboxyl groups, respectively. Hence, they enter the fibre and form ionic bonding between dye and fibre as well as metal ions. The dye-metal chelates thus produced also form coordinate bonds with the uncharged amine (–NH2) groups of the silk fabric. One molecule of RE mordant can form a bond with one site of fibre molecule. But one molecule of RE mordant can form bonds with several molecules of dyes. As a result, when the mordant molecule binds to fiber it holds many molecules of dye with it.

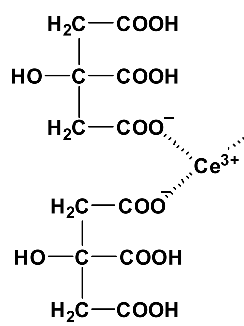


Figure 2 - Complex of RE ion (Ce) with citric acid

Two possible mechanisms of dissolution with citric acid include metal ion displacement with hydronium ions and the formation of soluble metal-ligand complexes by RE metal chelation have been suggested [10].

2.0 Material and Methods

2.1 Material

Pure silk (RFD) was purchased from Shah Company, Rare earth salts- Lanthanum carbonate, Yttrium oxide, and Cerium nitrate were procured from IRELlimited. Citric acid and alum were purchased from Loba chemicals.

These rare earth salts were not readily miscible in water, hence citric acid was used for dissolution.

2.2 Method

The flow chart of the premordanting and post-mordanting dyeing processes are shown in figure-3.

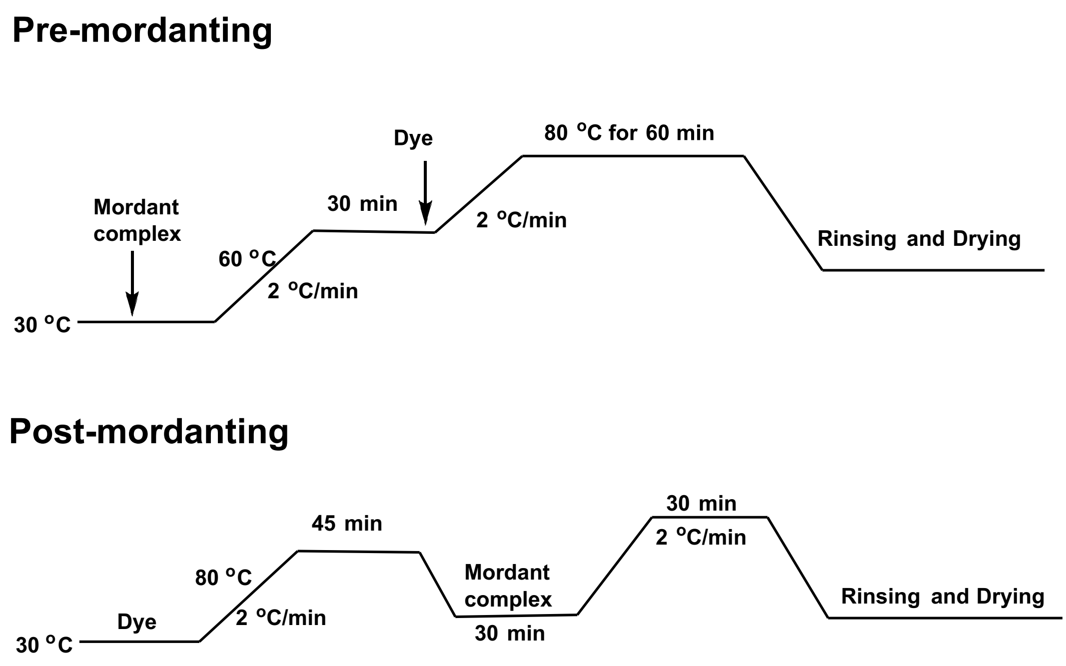


Figure 3 - Schematic representation of Pre and post mordanted dyeing

Rubia dyeing with RE salts (Pre and post mordanting)

The dyeing bath was heated to 60^{0}C where it was mainotained for a particular time (60 minutes). The silk fabrics were then rinsed with clean water at ambient temperature followed by being squeezed and dried. In the pre-mordanting method, the wet fabrics were first immersed in a solution of the mordant and heated to 60^{0}C where they were kept for 30 minutes. After being added with the natural dyes the bath was heated to 80^{0}C where the fabrics were treated for a particular time (45minutes). Then the dyed samples were rinsed with clean water and dried via similar processes as mentioned above. In the post-mordanting method, the silk fabrics were first dyed in an aqueous solution containing a natural dye at 80^{0}C for 30 minutes followed by being cooled to 60^{0}C where the mordant was added. Then the fabrics were kept at 60^{0}C for another 30 minutes. Subsequently, the dyeing bath was heated to 80^{0}C again where the fabrics were dyed for a time in the range of 45-50 minutes. At last, the dyed fabrics were rinsed and dried. The effects of dyeing temperature and time on the dyeing of silk fabrics with the Rubia natural dye was studied as shown in figure-3. Silk swatched (RFD) were premordanted by 4% mordants such as alum (Conventional) and the rare earth salts 0.4%(Lanthanum carbonate, Yttrium oxide, and Cerium nitrate separately with citric acid in the ratio of (1:3). Mordanting was done at room temperature for 30 mins. After drying the samples were dipped in (Rubia 5% owf) dye bath and slowly the temperature was raised to 70-80^{0}C over a period of 30 minutes, and stirring of the fabric was done for 45 minutes. After dyeing the samples were washed with water and dried. Similarly post mordanting was done after dyeing with similar concentrations of the mordant.

K/S Measurements

The dye uptake in the dyed silk swatches was obtained through the measurement of the light absorbances at the wavelength of maximum absorption, of the dye bath before and after dyeing with an ultraviolet-visible (UV-Vis) spectrophotometer. The dye uptake was calculated with the following equation:

$$\text{Dye uptake} = \frac{A_b - A_a}{A_b} \times 100\%$$

where Aband Aarefer to the absorbance of the dye solutions at the beginning and the end of dyeing, respectively.oThe CIELAB colorimetric values including ΔE, L*, a*, b*, C*, and the color strength K/S of the dyed fabrics were measured by Premier Computer Color Matching System using illuminant D65 and 10standard observer. K/S was calculated from the reflectance values K/S using the Kubelka-Munk equation as follows:

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

Where R represents the reflectance of the dyed fabric and K/S stands for the ratio of the absorption coefficient (K) to scattering coefficient (S). The higher the K/S value the greater the color strength.

The color fastness of washing of the silk fabrics was determined according to the standard ISO method ISO 105-C10 (2006). The measurement was carried out with both sample and standard silk fabrics that were sewn together and tested under the same conditions. The dyed silk fabric was washed at 40oC for 30 minutes in a non-ionic soap solution with material to liquid ratio of 1:50. All dyed fabrics were then separately rinsed and dried. The colorfastness to washing levels, observed against a grey scale, were classified as numbers ranging from 1 and 5, which corresponds to poor to excellent fastness, respectively. Colorfastness to light was tested according to ISO 105-BO2 method.

3.0 Results and Discussion:

The dye uptake in the case of premordanted dyed silk swatch was from 52-58 % in the case of Cerium nitrate, 62-64% in the case of premordanted lanthanum carbonate, and 85-87% in the case of Yttrium oxide. This is in accordance with the K/S values.

The graph of K/S values shown in figure-4 is showing a bathochromic shift for yttrium oxide mordanted fabric with respect to alum mordanted. The plausible explanation could be that coordination through Y+3RE(III)could be 6,7,8,9 due to its ionic radius being close to 1.0, while for Al+3 coordination can be only 4,5,6 as the ionic radius is 0.53. Owing to the high positive charge, large ionic radii of RE(III) ions,0, and the ionic nature of the RE(III)–oxygen bonds, RE(III) ions tend to share the carboxylato-groups to form polymeric complexes. The increase in values due to RE mordanting reveals that dye molecules are capable of forming a metal complex with the positively charged metals as shown in figure-5.

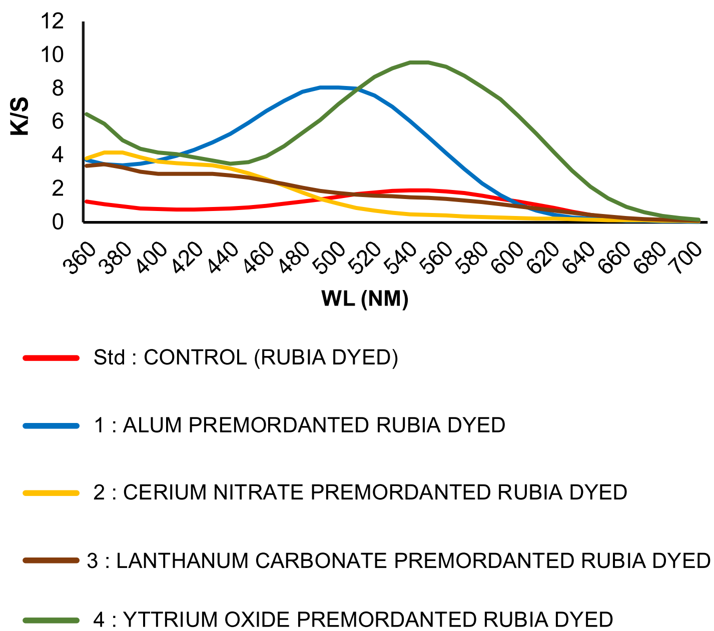


Figure 4 - K/S value graph for different mordants.

The ion of rare earth element can form a bond with hydroxyl and or enone moieties of Natural dye- Rubia dye and the fiber, through their greater coordination complex formation ability, thus rare earth can be aptly used in natural dyeing.

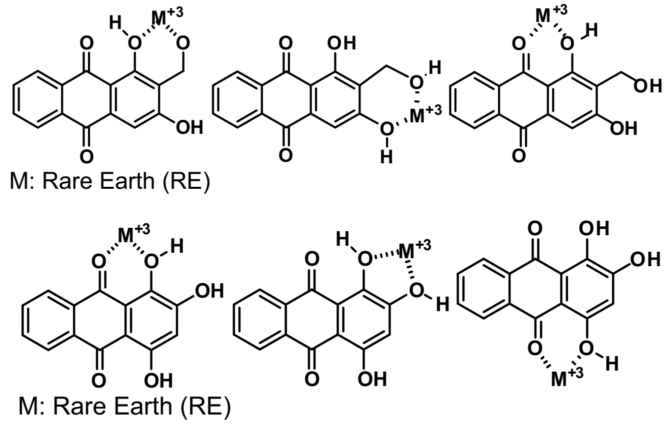
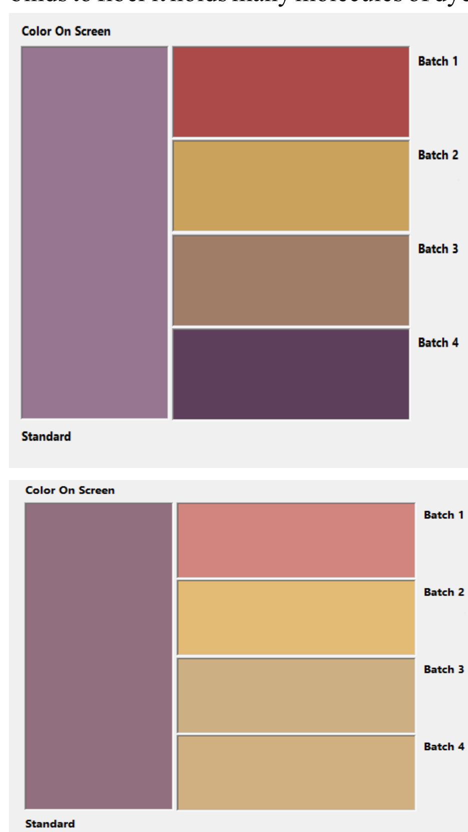


Figure - 5 Metal chelation through oxygen centres

In the case of silk fibres, dye anions and metal cations have a strong attraction towards positively charged amino and negatively charged carboxyl groups, respectively. Hence, they enter the fibre and form ionic bonding between dye and fibre as well as metal ions. The dye-metal chelates thus produced also form coordinate bonds with the uncharged amine (–NH2) groups of the silk fabric. One molecule of RE mordant can form a bond with one site of fibre molecule. But one molecule of RE mordant can form bonds with several molecules of dyes. As a result, when the mordant molecule binds to fiber it holds many molecules of dye with it.



Pre- mordanting with RE salts

Post-mordanting with RE salts

Figure-6 Standard-Unmordanted, Batch-1 Alum mordanted, Batch-2 Cerium nitrate mordanted, Batch-3 Lanthanum carbonate mordanted, Batch-4 Yttrium oxide mordanted.

Therefore, using RE mordant, the colour yield was seen to have enhanced considerably. Thus by the choice of an appropriate RE salt in the premordanting step, we can get different colour from the same dye extract- alum yields orangish red, Cerium salt yields yellowish brown, Lanthanum yields camel brown, and yttrium yields dark purple as shown in figure -5. However, in the post mordanting of the same dye extract, colours obtained on the swatches were very different and were lighter in shade.

The dyeing results of Rubia dye clearly shown in Table-1 and figure-4, clearly indicates that pre-mordanting with yttrium oxide gave K/S value better than that obtained by pre-mordanting with alum. Another observable fact is that premordanting with RE salts is preferred over postmordanting for Rubia dye, considering the CIELab values and K/S values. Out of the three chosen RE salts- Lanthanum carbonate, Cerium nitrate, and Yttrium oxide- the best results were obtained by Yttrium oxide in just 0.4% concentration.

The dyed swatches showed improved wash and light fastnesses as shown in table 2 and the best result was observed in the case of the Yttrium oxide pre-mordanting method. With the use of 0.4% RE salts, the color depth was found to be very good. Post mordanting did not yield the desired color depth or shades.

4.0 Conclusion:

An intrinsic feature of the lanthanide coordination chemistry is the tendency of the metal ion to maximize its coordination number. Employing rare earth as mordant apparently raised the colour fastness - washing, and light of the silk fabrics dyed with Rubia dye. The study showed that premordanting is preferred over postmordanting for Rubia dye. Out of three RE salts used for premordanting, the best results were obtained for Yttrium oxide. The oxophilicity of Yttrium is owing to the hard Lewis acid character and large ionic radius. RE(III) ions prefer bonding with hard Lewis base donors, such as F, O, and N, and have high coordination numbers. The colorant molecules Manjisthin and purpurin present in Rubia dye have the requisite sites for coordination. By using RE salts in place of alum or other transition metal salts there seems to be manifold advantages-better dye uptake, better fastness properties, low-temperature dyeing, low energy consumption, and above all would have lesser pollution load in the effluent, thus proving them to be ecofriendly and safe mordant.

Table 1 - CIELab values Rubia dyed silk swatches

S.No	Name	K/S	L*	a*	b*	dE*	Remark
Std	Rubia unmordanted	29.05	49.65	17.51	-6.40	--	
Batch1	Alum Pre Mord	**99.18**	40.87	46.19	16.34	37.62	Change in colour
Batch2	Alum Post Mord	17.10	63.22	29.15	15.65	26.47	Change in colour
Batch3	CeN Pre Mord	25.58	66.28	8.59	38.25	48.47	Change in colour
Batch4	CeN Post Mord	12.06	77.84	5.95	40.71	52.93	Change in colour
Batch1	LaC Pre Mord	28.83	56.75	9.30	19.93	28.48	Change in colour
Batch2	LaC Post Mord	10.76	72.91	4.63	25.88	38.65	Change in colour
Batch3	YO Pre Mord	**105.81**	30.73	17.89	-9.51	19.17	**Premordanting/YO**
Batch4	YO Post Mord	11.13	73.29	5.87	27.97	40.13	Change in colour

CeN- Ceriun nitrate, LaC- Lanthanum carbonate, YO-Yttrium oxide, Pre Mord- Premordanting, Post Mord-Postmordanting.

Table 2 - Washing and Lightfastness of the Rubia dyed swatches

S.No	Name	Washing Fastness	Lightfastness
Std	Rubia unmordanted	2-3	3
Batch1	Alum Pre Mord	3-4	3
Batch2	Alum Post Mord	2-3	2
Batch3	CeN Pre Mord	3-4	3
Batch4	CeN Post Mord	3	2-3
Batch1	LaC Pre Mord	3-4	3
Batch2	LaC Post Mord	3	2-3
Batch3	YO Pre Mord	**4-5**	**5**
Batch4	YO Post Mord	4	3-4

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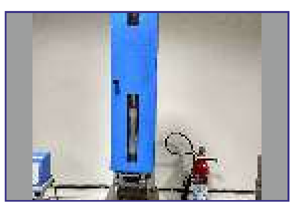
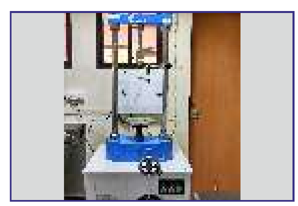
Installation Damage of Geosynthetics

The geosynthetics are prone to some amount of damage during their installation. To assess the quantity of the installation damage, a standard method was initially developed by Watts and Brady of the Transport Research Laboratory in the United Kingdom. The procedure has also discussed in the ASTM D 5818 with similar requirements. We are at BTRA doing the test following same ASTM D 5818 method followed by respective tensile strength. For the time being we are using the construction site for the sample preparation. If customer will agree, BTRA will collect the sample from site after standard procedure and provide ethe report.



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