COLOR PALETTE FROM NATURAL DYEING WITH RUBIA DYE (INDIAN MADDAR)

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Scientific paper
UDC: 677:667.7
DOI: 10.5937/tekstind2301031B

Abstract: *Among the natural dyes, one of the most appealing coloration on Textiles comes from Rubia dye. From ancient times this dye has been used. Rubia is one of the species of the Rubiaceae family. The common madder, covers the members such as Rubia tinctorum (common madder), Rubia peregrina (wild madder), and Rubia cordifolia (Indian madder). Figure-1 shows the picture of Rubia cordifolia. It is a source of red pigment which was of economic importance in Asia, Europe, Africa and Mediterranean in the past. The Indian madder plant has 3-4 colorant molecules- manjisthin, purpurin and pseudopurpurin and negligible amount of alizarin. These molecules can form dye-mordant-fabric complexes easily due to appropriately placed functional groups such as - hydroxy and enones. The colorant molecules belong to the class of Anthraquinone dyes. The chelation with the metal ion of the conventional mordants or rare earth (RE) mordants is very facile. Rare earth ions have high positive charge and large ionic radii and this ionic nature of the RE+3 ion forms complexation with oxygen atoms of the dye molecules can take place. It has been observed that there is an increase in K/S value as compared to conventional mordants. This can be attributed to coordination effect of the RE mordant. The colorant molecules are capable of forming intensely colored metal complex with the RE salts. Color palette with Rubia dye are derived from the different metal salts used in the dyeing process. Ecofriendly special auxiliaries add brightness to the dyed fabrics.*

Keywords: Rubia dye, Conventional mordant, Ecofriendly RE mordants, Special auxiliaries.

PALETA BOJA OD BOJENJA PRIRODNOM RUBIA BOJOM (INDIJSKI MADAR)

Apstrakt: *Među prirodnim bojama, jedna od najprivlačnijih boja na tekstilu potiče od boje Rubia. Ova boja se koristi od davnina. Rubia je jedna od vrsta porodice Rubiaceae. Obična mrena, obuhvata članove kao što su Rubia tinctorum (obična mrena), Rubia peregrina (divlja mrena) i Rubia cordifolia (indijska mrena). Slika 1 prikazuje sliku Rubia cordifolia. To je izvor crvenog pigmenta koji je u prošlosti bio od ekonomskog značaja u Aziji, Evropi, Africi i Mediteranu. Biljka indijske mare ima 3-4 molekula boje - manjistin, purpurin i pseudopurpurin i zanemarljivu količinu alizarina. Ovi molekuli mogu lako da formiraju komplekse boje-mordant-tkanina zahvaljujući prikladno postavljenim funkcionalnim grupama kao što su - hidroksi i enoni. Molekuli bojenja pripadaju klasi antrahinonskih boja. Kelacija sa metalnim jonom konvencionalnih jedilica ili jedki za retke zemlje (RE) je vrlo laka. Joni retkih zemalja imaju visoko pozitivno naelektrisanje i velike jonske radijuse i ova jonska priroda RE+3 jona formira kompleksiranje sa atomima kiseonika molekula boje. Primećeno je da postoji povećanje vrednosti K/S u poređenju sa konvencionalnim mordantima. Ovo se može pripisati koordinacionom efektu RE mordanta. Molekuli bojenja su sposobni da formiraju intenzivno obojeni metalni kompleks sa RE solima. Paleta boja sa Rubia bojom je izvedena iz različitih metalnih soli koje se koriste u procesu bojenja. Ekološki prihvatljivi specijalni dodaci daju sjaj obojenim tkaninama.*

Ključne reči: Rubia die, Konvencionalni mordant, Ecofriendli RE mordant, Specijalna pomoćna sredstva.

1. INTRODUCTION

Due to huge biodiversity in India, natural dye yielding plants are found in every zone. It is therefore important to enlist these plants zone wise. The natural colorant present in these plants are in one or the other part of the plant. Root, rhizome, stem, leaves, flower, bark, fruit and fruit skin in varying quantities. These natural dyes yielding plant materials can be sourced from forest wastes, temple wastes, agricultural wastes, food wastes etc. Thus natural dyes can be extracted from these sources and can be used for textile dyeing, paper dyeing, leather dyeing, as food dye, in pharmaceutical formulations and many other purposes.

There are several myths about natural dyes which prevent their commercialization. The main hurdles faced by dyers are extraction of the colorant, uniform application of the colorant and consumer's acceptability towards fastness properties. Earlier the dyers faced several problems while using natural colorants. They are - Less effective extraction techniques, fewer color palette, poor fastness properties, lack of dyeing consistency, use of toxic metal mordants and non-standardized dyeing techniques.

Figure 1: *Rubia cordifolia* plant (Indian Maddar)

In the last few decades research in the area of natural dyes has been instrumental in dealing with these challenges. Several latest extraction methods have been developed for effective and quantitative extraction of the colorant from the plant parts.

In the current times natural dyes can be used effectively using safe auxiliaries. A number of shades can be obtained from the same dye extract. This can be maneuvered using an appropriate mordant.

Standardized dyeing techniques have been developed which have shown good fastness properties in naturally dyed fabrics. Batch dyeing have been shown to have good shade consistency. Toxic metal mordants have been completely eliminated and replaced by biomordants and enzymes. Hence many commercial dyeing units have gradually switched to natural dyes from synthetic dyes. Rubia dye has been extensively used for textile coloration [1-5, 7,8]. Ecofriendly auxiliaries have been used to enhance the fastness properties and also for variation in color. The common metal ions used as mordant with Rubia dye is alum (Al^{3+}) behaves like as Lewis acids in solution, the positively charged of the Al metal ion attracts electron density from an O–H bond which causes the departing proton to lower the pH of 4-5. When the dye is added to the bath the colorant molecules are able of replacing the water molecules by dye molecules thereby forming a dye-mordant-fibre complex [6].

In *Rubia cordifolia* dye the main colorant molecules are munjustin and purpurin as shown in figure-2. These two dye molecules have several metal chelation sites as shown in Figure 3 and Figure 4.

2. EXPERIMENTAL (Rubia dyeing of silk fabrics with metal mordants)

Silk fabric swatches was treated by premodanting and post mordanting with metal mordants such as Alum (2%), $CuSO_4$ (1%) and $Fe_2(SO_4)_3$ (0.5%). In dyeing procedure we added the Na_2CO_3 (1% owf) in Rubia (4% owf) dye solution and got the light purple color (blue tint) of dye bath. For dark shades Vege disperse (4% of solution) was also added in the dye bath and we got the purple color (red tint). Vege Disperse is a dispersing agent. It helps in good solubilization of the natural dye particles particularly in the case of Rubia dyes.

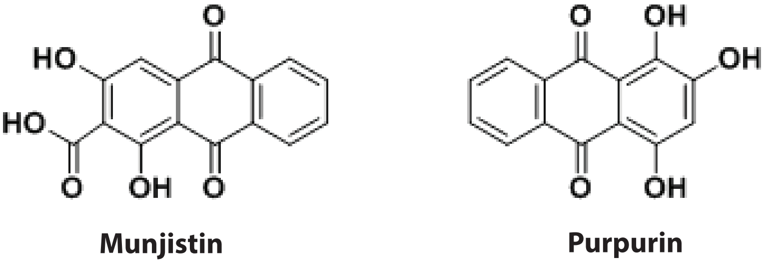


Figure 2: Structures of main colorant – Munjistin and Purpurin of *Rubia cordifolia* dye

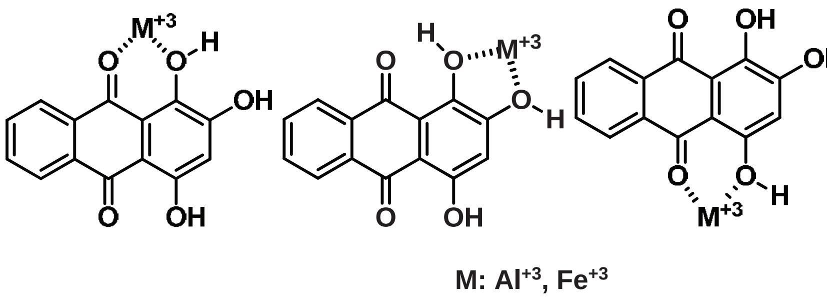


Figure 3: Coordination sites of main colorant molecule Purpurin of *Rubia cordifolia* dye

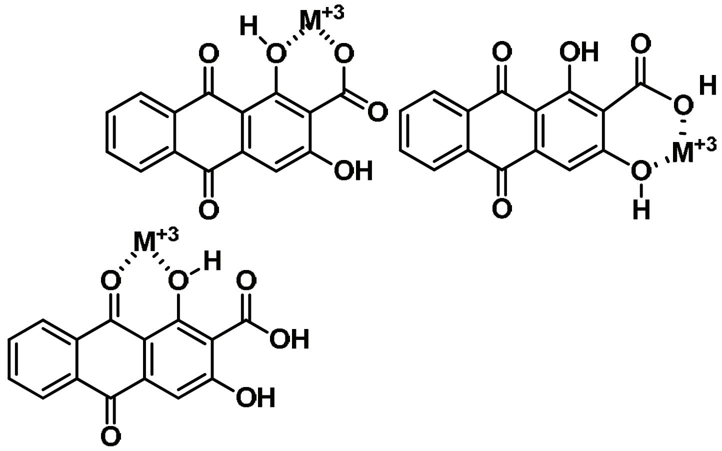


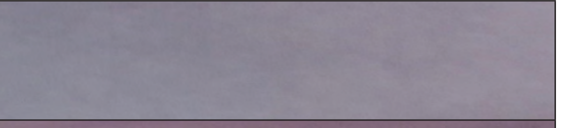
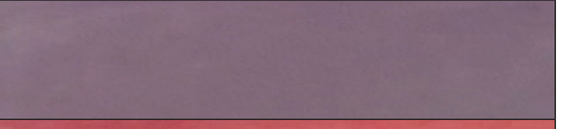
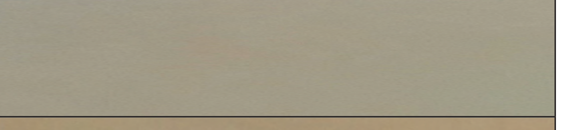
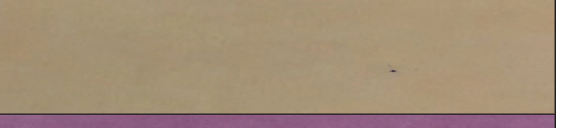
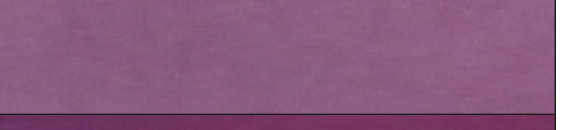
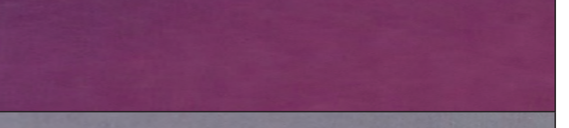
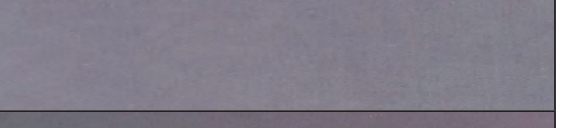
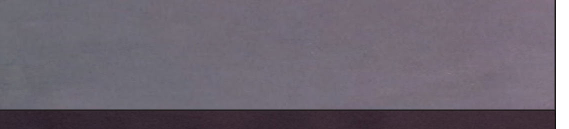
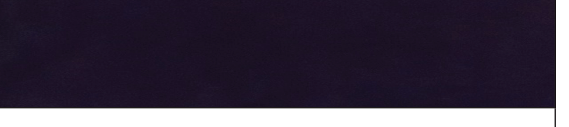
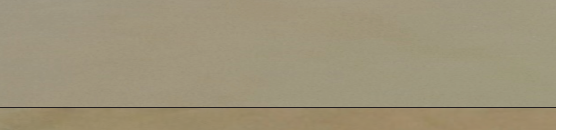
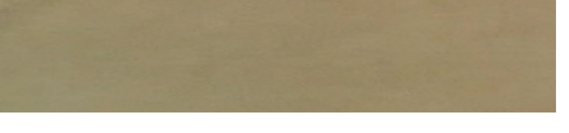
Figure 4: Coordination sites of main colorant molecule Munjisthin of *Rubia cordifolia* dye

Silk swtaches were dipped in dye bath and the temperature was raised to 60˚C slowly, over a period of 30 minutes. The dyeing was continued for 45 minutes with continuous stirring. After dyeing, the samples were removed from the dye bath and dried. Samples were also treated with Vege Super (2% of solution) after drying in the second set of experiments. Vege super is a mild soaping agent ideally suited for natural dyeing final wash.

Role of Auxiliaries in Natural dyeing: Some Auxiliaries have been used with Rubia extract such as Vege Super (VegeS) and Vege Disperse (Vege D) to show further variation in coloration of the fabric. By mere choice of an appropriate auxiliary one can get darker or lighter shades with tonal variation as shown in Table 1 and Table 2. It can be seen that by using only Vege Super the shade is lighter, however when the combination of mordant along with Vege Super and Vege D are used the shades are darker and brighter. Differences in Batch-1 and 2, 3 and 4, 5 and 6, 7 and 8. These were all premordanted before dyeing, where as 9 and 10, 11 and 12, 13 and 14 were post mordanted. It is very apparent that along with a mordant these auxiliaries help in better coloration. Deeper shade with same dye concentration signifies that the dye adherence is better and whenever the dye adherence is better it results in good fastness properties. Different shades can be obtained from Rubia dyeing of silk, Table 1 shows the dyeing results without the use of Vege S only Vege D was used. Table 2 shows results obtained from the use of Vege S and Vege D together. When we see the Table 1 following are the observations-Rubia dye when unmordanted yields bluish purple (1) and when Vege dispearse (Vege D) is used along with unmordanted (2) the shade becomes darker. Rubia dye premordanted with alum mordant (3) gives reddish shade while the same when treated with Vege D yields darker shade (4). However when the same rubia dyed fabric is post mordanted with alum (5) it gives light blue while with Vege D (6) it gives light grey color. Premordanted with copper sulphate (7) alone it gives light purple coloration and further when it is treated with Vege D (8) it gives dark purple color. Post mordanting with $CuSO_4$ (9) gave light blue color and further when it was treated with Vege D the color obtained was grayish blue a tone darker (10). Premordanted by Ferric sulphate rubia dye showed steel grey color (11) while with Vege D it yielded bluish grey (12) color to the silk fabric. Post mordanting with Ferric sulphate gave light bluish grey color (13) and when treated with Vege D it gave grey color (14).

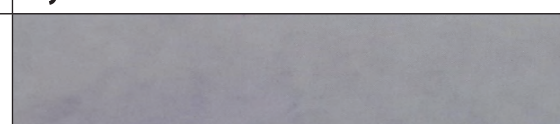
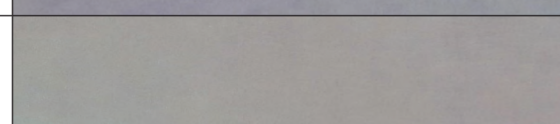
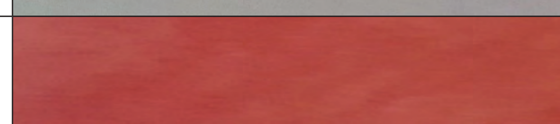
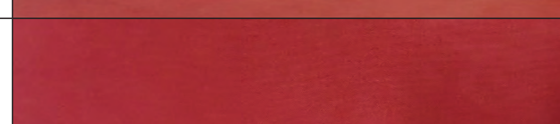
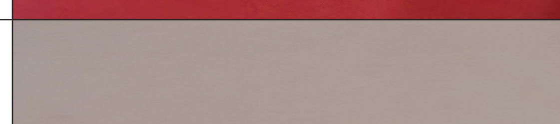
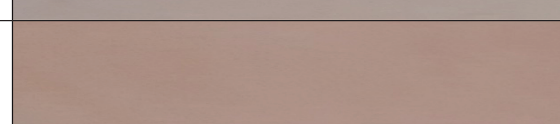
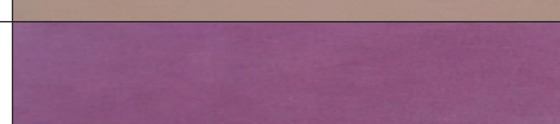
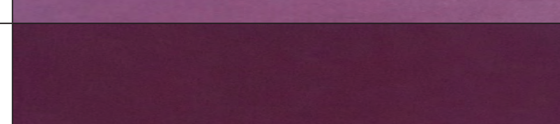
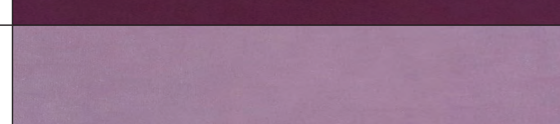
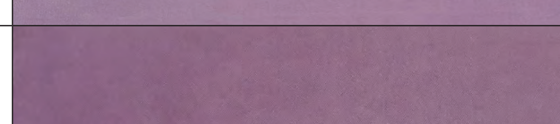
From these dyeing results we can conclude that firstly we can get different hues from the same rubia dye and secondly addition of Vege D in the dye bath yielded darker shades as can seen in sample 2,4,6,8,10,12 and 14 with some toner difference.

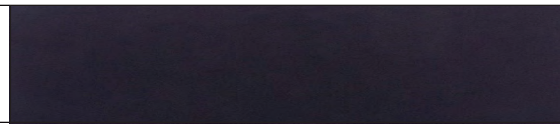
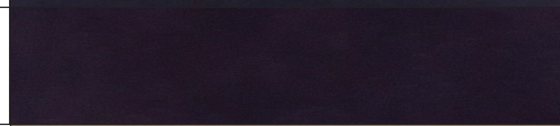
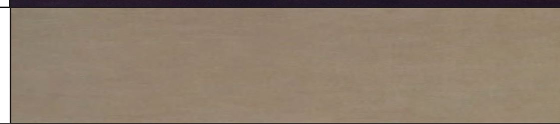
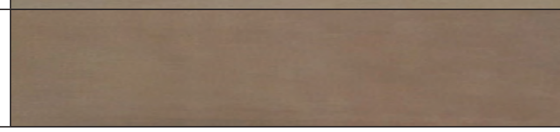
Table 1: Rubia silk swatches (without Vegesuper treated)

S.No	Sample details	Dyed Swatches
1.	Rubia unmordanted	
2.	Rubia unmordanted + Vege D	
3.	Rubia Pre (Alum mordanted)	
4.	Rubia Pre (Alum mordanted)+ Vege D	
5.	Rubia Post (Alum mordanted)	
6.	Rubia Post (Alum mordanted)+ Vege D	
7.	Rubia Pre ($CuSO_4$ mordanted)	
8.	Rubia Pre ($CuSO_4$ mordanted)+Vege D	
9.	Rubia Post ($CuSO_4$ mordanted)	
10.	Rubia Post ($CuSO_4$ mordanted)+Vege D	
11.	Rubia Pre ($Fe_2(SO_4)_3$ mordanted)	
12.	Rubia Pre ($Fe_2(SO_4)_3$ mordanted)+Vege D	
13.	Rubia Post ($Fe_2(SO_4)_3$ mordanted)	
14.	Rubia Post ($Fe_2(SO_4)_3$ mordanted)+Vege D	

When the same sequence was repeated with Vege Super (Vege S) sample-1 which is rubia dye without mordant yields bluish purple (1) while with Vege D and Vege S gave lighter blue shade (2). Rubia dye premordanted with alum mordant (3) gives reddish shade while the same when treated with Vege D and Vege S yields slightly darker shade (4). However when the same rubia dyed fabric is post mordanted with alum (5) it gives light blue while with Vege D+ Vege S (6) it gives light grey color. Premordanted with copper sulphate (7) alone it gives light purple coloration and further when it is treated with Vege D (8) it gives dark purple color. Post mordanting with $CuSO_4$ (9) gave light purple color and further when it was treated with Vege D the color obtained was slightly darker tone (10). Premordanted by Ferric sulphate rubia dye showed bluish grey color (11) while with Vege D and Vege S it yielded navy blue (12) color to the silk fabric. Post mordanting with Ferric sulphate gave light bluish grey color (13) and when treated with Vege D and Vege S it gave light grey color (14). From these dyeing results we can conclude that firstly we can get different hues from the same rubia dye and secondly addition of Vege D and Vege S in the dye bath yielded slightly darker shades as can seen in sample 2,4,6,8,10,12 and 14 with some toner difference. Thus we can conclude that addition of auxiliaries like Vege disperse is advantageous as it helps the dye molecules in the dye bath to be well dispersed for very uniform dyeing. Another observation is that premordanting is better than post mordanting for silk fabrics in the case of Rubia dye.

Table 2. Rubia silk swatches (Vegesuper treated)

S.No	Sample details	Dyed Swatches
1.	Rubia unmordanted	
2.	Rubia unmordanted + Vege D + Vege S	
3.	Rubia Pre (Alum mordanted)	
4.	Rubia Pre (Alum mordanted)+ Vege D + Vege S	
5.	Rubia Post (Alum mordanted	
6.	Rubia Post (Alum mordanted)+ Vege D	
7.	Rubia Pre ($CuSO_4$ mordanted)	
8.	Rubia Pre ($CuSO_4$ mordanted)+Vege D+ Vege S	
9.	Rubia Post ($CuSO_4$ mordanted)	
10.	Rubia Post ($CuSO_4$ mordanted)+Vege D + Vege S	

11.	Rubia Pre ($Fe_2(SO_4)_3$ mordanted)	
12.	Rubia Pre ($Fe_2(SO_4)_3$ mordanted)+Vege D	
13.	Rubia Post ($Fe_2(SO_4)_3$ mordanted)	
14.	Rubia Post ($Fe_2(SO_4)_3$ mordanted)+Vege D	

Rubia dyeing of silk fabrics with Ecofriendly Rare earth (RE) mordants

Silk fabric swatches was treated by premodanting with rare earth mordants along with Alum (4%), cerium nitrate (0.4%), Lanthanum carbonate (0.4%) and Yttrium oxide (0.4%). In dyeing procedure Rubia (4% owf) dye solution was prepared. RFD Silk swatches were dipped in dye bath and the temperature was raised slowly to 60˚C in 30 minutes. The dyeing was continued for 45 minutes with continuous stirring. After dyeing, the dyed samples were removed from the dye bath and dried.

Different shades from same natural dye source

To exemplify that same Rubia extract can yield reddish orange color with alum (Batch 1), camel brown with cerium nitrate (Batch 2) and brown with lanthanum carbonate (Batch 3) and dark purple with yttrium oxide (Batch 4) under premordanting condition with silk fabric as shown in Figure 4. The increase in K/S can be clearly seen in Figure 3 in the case of premordanting with Yttrium oxide. The highest color depth was obtained in the case of Yttrium oxide mordant.

The Visible scan vs the K/S values is shown in Figure 5 for silk fabric dyed with rubia dye. A bathochromic shift for yttrium oxide mordanted fabric was observed with respect to alum mordanted. As the ionic radius of Y^{+3} is close to 1.0, it can show coordination capacity as high as 6,7,8,9, while for Al^{+3} has an ionic radius of 0.53, it can show lower coordinating capacity. The high positive charge with large ionic radii of Y^{+3} ions is responsible for the ionic nature of the Y^{+3} which causes better complexation with - oxygen. Enhancement in K/S value can thus be attributed to RE mordanting. With RE salts, the dye molecules are capable of forming metal complexes.

Figure 4: Standard denotes Unmordanted swatc, Batch -1 Alum mordanted, Batch-2 Cerium nitrate mordanted. Batch-3 Lanthanum carbonate mordanted and Batch-4 Yttrium oxide mordanted

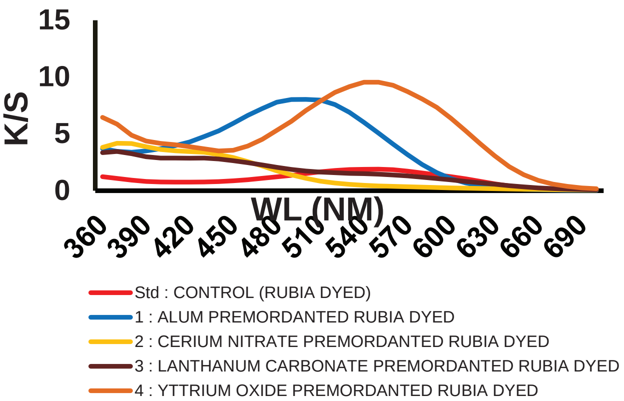


Figure 5: K/S vs wavelength plot for different mordanted silk fabrics

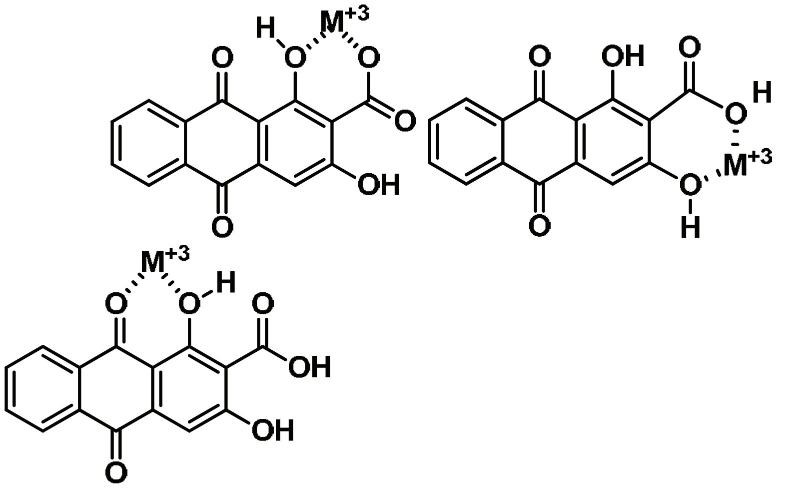


Figure 6: Metal chelation through oxygen centres

RE ions can form bond with hydroxyl and or enone moieties of Natural dye - *Rubia* dye (Munjustin) and the fiber, through their greater coordination complex formation ability, thus rare earth ions can be aptly used in natural dyeing as shown in Figure 6.

In case of silk fibres, the positively charged amino and negatively charged carboxyl groups couple with the dye anions and metal cations due to strong attraction. Ionic bonding is formed between dye and fibre as well as RE metal ions. The dye-RE metal ion forms coordinate bonds with the uncharged amine ($-NH_2$) groups of the silk fabric. One molecule of RE mordant can form a bond with one site of fibre molecule at the same time it can form bonds with several molecules of dyes. As a result, when the mordant molecule binds on to fiber it holds many molecules of dye with it. With the use of lesser concentration (0.4%) of RE salts the color depth was found to be very deep.

3. CONCLUSION

Rubia dye contains well oriented oxygen containing groups for appropriate chetation with metal ion of the mordants, be it conventional mordants or ecofreindly RE mordants.

The lanthanides have the tendency of the metal ion to maximize their coordination number. By using rare earth as mordant the colour fastnesses - washing, and light of the silk fabrics dyed with *Rubia* dye also enhanced. The study showed that premordanting is preferred for *Rubia* dye over post mordanting. Out of three RE salts used for premordanting, the best results were obtained for Yttrium oxide. Yttrium is oxophilic owing to the hard Lewis acid character and large ionic radius. Thus RE^{+3} ions prefer to bond with hard Lewis base donors, such as F, O, and N, and to have high coordination numbers. Munjisthin and purpurin present in *Rubia* dye have ample of oxygen containing functional groups, which are requisite sites for coordination with RE ions. By replacing alum or other transition metal salts with RE salts, there seems to be manifold advantages-firstly better dye uptake, secondly better fastness properties, thirdly possibility of low temperature dyeing, fourthly having low energy consumption and above all being used in lesser quantities they would have lesser pollution load in the effluent, thus being ecofriendly and safe mordant for textile industry.

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Primljeno/Received on: 09.01.2023.
Revidirano/ Revised on: 09.03.2023.
Prihvaćeno/Accepted on: 10.03.2023.