

Extraction of rubiadin dye from *Swietenia mahagoni* and its dyeing characteristics onto silk fabric using metallic mordants

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Rubiadin dye extracted from *Swietenia mahagoni* has been applied onto silk fabric and its dyeing properties are evaluated using metallic mordants $MgCl_2$ and $FeSO_4$ as a function of dye concentration, dyeing temperature, dyeing time and pH. It is observed that the dye exhaustion significantly increases in case of $FeSO_4$ as compared to that in case of $MgCl_2$. Colour shades of dyed silk fabrics are found to be dark dull red, dark bright yellow and too dark red for unmordanted, $MgCl_2$ mordanted and $FeSO_4$ mordanted dyeing respectively. The colour strength of $FeSO_4$ mordanted dyed fabric is found to be 3.19 times higher than unmordanted and 1.11 times higher than $MgCl_2$ mordanted dyed fabrics. Dyed fabrics show good fastness properties. $FeSO_4$ mordanted dyed fabric shows more resistance against light, washing, rubbing and perspiration as compared with the other mordanted and dyed fabrics.

Keywords: Colour values, Dyeing, Fastness properties, Metallic mordant, Rubiadin dye, Silk fabric, *Swietenia mahagoni*

1 Introduction

The natural dyes/colourants are being used in textile since ancient age throughout the world. But their use has decreased to a large extent due to the arrival of cheaper synthetic dyes. However, now a day, the use and production of natural dyes are becoming more popular owing to the growing awareness about environmental problems coupled with the toxicity associated with synthetic dyes. As a result, renewable resources are now being reinvestigated as the alternative raw materials. Natural dyes exhibit better biodegradability and are more environment friendly alternative to synthetic dyes¹⁻³.

The plant kingdom has a vast source of natural dyes/colourants that can be extracted from many parts of plant such as leaves, fruits, seeds, flowers, barks and roots. Bangladesh has an abundance of plant species with dye yielding properties. The rural people extract dyes from leaves, roots, flowers or barks of some plant species mostly by boiling, scrapping, powdering and mixing with other materials to get the desired colour. Though several workers have been reported the extraction of dye from different plant species^{4,5}, even today many species remain unexplored. So, it is crucial to explore the extraction

of natural dyes from abundantly occurring plant sources. Mahagony plant (*Swietenia mahagoni*) which is very much familiar to the mass people of Bangladesh can be an important source for the extraction of natural dye. Its bark contains rubiadin (Natural Red 8) dye compound. However, no work has been reported till date on the use of *Swietenia mahagoni* as a natural dye for textile applications.

The dye specialists use dyes onto different types of textile fabrics based on their fixation properties. For example, basic dyes are suitable for cotton dyeing. Also there are some other natural dyes sources such as *Mangifera Indica*, *Eclipta alba* and *Lawsonia inermis* L. that could be used for dyeing cotton fabric⁶⁻⁸. Gupta *et al.*⁹ has developed a dyeing process of silk with natural dye cutch in presence of different mordants. They observed that dyed silk fabrics exhibit good wash and colour fastness properties. Goel and Geol¹⁰ reported the natural tissue flower dye in presence of different mordants that exhibited fair to good wash and light fastness when applied onto silk.

However, tedious extraction process of dyes from the raw materials, low colour value and long dyeing time push the cost of dyeing with natural dyes considerably higher than with synthetic dyes. To overcome these drawbacks, bacterial dyeing, enzyme

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dyeing and ultrasonic dyeing are being considered as an alternatives^{8,11,12}. But in most cases colourfastness properties of dyed fabrics are not satisfactory. Again, some natural dyes are fugitive and need a mordant for the enhancement of their fastness properties. When fabrics are treated with mordants, it may create more functional groups (amino and methylol groups) than are present on untreated fabrics. This phenomenon provides more reactive sites to attach dye molecules, and hence improves dyeing properties. Some metallic salts such as alum, stannous chloride, stannic chloride, ferrous sulphate, copper sulphate and potassium dichromate are widely used as mordant.

In the present study, dye component is extracted from the bark of *Swietenia mahagoni* plant by solvent extraction method and its dyeing properties are studied onto silk fabric. Different factors affecting dyeability and fastness properties are studied to show the commercial viability of *Swietenia mahagoni*.

2 Materials and Methods

2.1 Materials

The bark of mahogany (*Swietenia mahagoni*) plant was collected from Kushtia, Bangladesh. The bark sample was washed with fresh water to remove dust and other impurities and finally air dried. The air dried sample was stored at an ambient temperature in an air tight container.

The raw silk fabric (Fibroin, $C_{15}H_{23}N_5O_6$ 65-80%; Sericin, $C_{15}H_{25}N_5O_8$ 12-25%; tenacity 4.6 g/den) was collected from Usha Silk Factory, Rajshahi, Bangladesh. The silk fabric was degummed for 3-4 times with 3 g/L soap solution at 95-100 °C for 1 h. The pH was maintained at 10.0-10.5 by using soda ash solution. The fabric to liquor ratio was maintained at 1:30. The fabric was then washed with distilled water and dried at room temperature.

Silica gel of 200 mesh for column chromatography was purchased from Loba Chemie, India. All the chemicals used in column chromatography as well as other purposes were of analytical grade. The dyeing of silk fabric was carried out using de-ionized water.

2.2 Methods

The dried bark sample was cut into small pieces and grinded to make fine powder. The powder (100 g) was submersed in 1 L ethanol for 24 h. This crude

extract was subjected to solvent-solvent partitioning by methanol, petroleum ether and carbon tetrachloride respectively. Initial screening was performed by TLC. Only carbon tetrachloride fraction showed good resolution. As a result, this fraction was injected in chromatographic column packed by silica gel, eluted with a mixture of petroleum ether and ethanol in an increasing polarity to yield several fractions (S_1 - S_7). About 2.3 g of S_3 fraction in powder form obtained from petroleum ether and ethanol (49:1) was preserved for dyeing. For sophisticated analysis, S_3 fraction was subjected again in column over silica gel using chloroform and methanol to fractionate and finally purified 16 mg dye component was obtained.

The extracted red colour dye was sparingly soluble in water. The dye baths were prepared by adding 0.2-1.8% dye and 1% mordant on the basis of the weight of fabric. The pH of dye bath was maintained at 8 using dilute sodium carbonate solution. The fabric-liquor ratio was maintained at 1:30. Before dyeing, silk fabric was wetted well in distilled water and squeezed for even absorption of dye particle. Dyeing was performed at 30- 90 °C for 30-210 min with occasional stirring, and allowed for further 30 min as the bath cools down. After dyeing, the fabric was squeezed over the dye bath. Finally, the fabric was thoroughly washed with soap solution and distilled water for several times and then dried at room temperature¹³.

2.3 Measurements

Fourier-transform infrared (FTIR) spectra of the extracted compound were recorded with $CHCl_3$ using Perkin Elmer spectrophotometer in the frequency range 4000-600 cm^{-1} . The UV-visible absorption was recorded on a Shimadzu 1601 PC UV/Vis spectrophotometer. ^1H -NMR and ^{13}C -NMR spectra were measured at 25 °C on a Bruker AV200 and Bruker DRX NMR spectrometer respectively at 200 MHz. The melting point of the compound was determined using SMP1 apparatus. The elemental analyses were done in a Perkin Elmer 2400 elemental analyzer.

The absorbance of the dye solution was recorded at 480 nm before and after dyeing on a Shimadzu 1601 PC UV/Vis spectrophotometer. The amount of dye absorbed was calculated using the following relationship:

$$\% \text{ Dye absorbance} = [(W_1 - W_2) / W_1] \times 100$$

where W_1 is the absorbance before dyeing; and W_2 , the absorbance after dyeing.

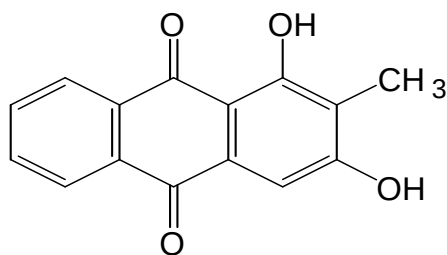
The colour strength (K/S values) and CIE lab values (L^* , a^* , b^*) were measured by Macbeth CE-3100 spectrometer. The K/S values of dyed samples were evaluated by light reflectance technique and assessed using the Kubelka-Munk equation¹¹.

Colour fastness properties of unmordanted and mordanted dyed silk fabrics were determined by standard test methods, ISO 105 B02:1994; ISO 105 C06:1994; ISO 105 X12:2001 and ISO 105 E04:1994 for light, washing, rubbing and perspiration respectively¹⁴⁻¹⁷.

3 Results and Discussion

3.1 Structure Elucidation

The structure of extracted dye is confirmed by the FTIR, UV/Vis, ^1H NMR, ^{13}C NMR, elementary analysis and melting point data. The results show that the dye component is anthraquinone compound i.e. rubiadin (1, 3 dihydroxy 2 methyl anthraquinone) and its structure is shown below:



Rubiadin (1, 3 dihydroxy 2 methyl anthraquinone)

The characterization details of compounds are: reddish powder (mp. 290°C); FTIR (KBr) (cm^{-1}) — 3415 (-OH), 3055 (aromatic C-H), 1615 (-C=O), 1548, 1458, 1436 (aromatic -C=C-) (CHCl_3), 898 (-CH₃); ^1H NMR ($\text{DMSO}-d_6$, 500MHz) (δ) — 13.25 (s, Cl-OH), 8.21-8.26 (2H, m, C5-H and C8-H), 7.80-7.87 (2H, m, C6-H and C7-H), 7.30 (1H, s, C4-H); ^{13}C NMR ($\text{DMSO}-d_6$, 125MHz) (δ) — 186.7 (C9), 182.1 (C10), 164.1 (C3), 161.7 (C1), 134.2 (C7), 133.9 (C6), 134.0 (C10a), 133.4 (C8a), 133.5 (C4a), 127.1 (C5), 126.9 (C8), 116.2 (C2), 109.6 (C4), 109.6 (C9a). The composition of dye component is found to be C 70.86%; H 3.96%; and O 25.17%.

3.2 Dyeing

The effect of dye concentration, dyeing time, dyeing temperature and pH on dye exhaustion is shown in Fig. 1. It is observed that dye absorption by silk fabric decreases with the increase in dye concentration. This may be due to the high

concentration of dye ions which hinder the absorption of dye by the fabric, whereas the low concentration of dye ions favours it. With the increase in dye concentration, the absolute quantity of absorbed dye also increases while the relative quantity diminishes. Thus, the fabric absorbs a relatively greater amount of dye from a dilute solution¹⁴.

Figure 1 also shows that the absorption of dye by the silk fabric increases with the progress of dyeing time and it reaches maximum when dyeing time is 150 min. The dye absorption then remains nearly the same even after further increase in dyeing time. The possible reason of such behaviour is that fabric immersed in a dye solution absorbs dye until equilibrium is reached. At any temperature and mordant concentration, the actual equilibrium is reached when each fabric is dyed throughout its cross-section and when even after the lapse of a longer period of time, no further exchange of dye in the fabric or in the solution takes place¹⁵.

It is also observed that the absorption of dye by silk fabric increases with the increase in temperature and becomes maximum at 60 °C. At high temperature the size of the fibre pores increases and dye particles easily penetrate into the fabric. When the dye bath cools down, the fibre pores contract and the dye particles remain in the fibre. Hence, at higher temperature, dye absorption is higher, but above 70°C desorption of dye might be occurred.

In presence of mordant, the dye absorption is higher than in unmordant one. The mordant dissociates into positive and negative ions in the aqueous solution of dye. The positively charged ions migrate towards the negatively charged fibre surface. As a result, dye ions can easily attach with fibre surface and hence improve the dye ability¹⁴. It is also observed that the absorption of dye by degummed silk fabric increases with increase in pH, and it reaches maximum at pH 8. At above or below pH 8, the shades of the fabric are uneven and dull.

The above results reveal that bright and even shades are obtained under the optimized conditions when silk fabric is dyed with 1.25% dye for 150 min at 60 °C, maintaining pH at 8. Shades are not uniform and acceptable above or below these marks.

3.3 Colorimetric Values

The fabrics dyed under optimized condition are tested for CIE LAB values. The colour values are taken at three different illuminations as shown in Table 1. The positive values of DL^* , Da^* , Db^*

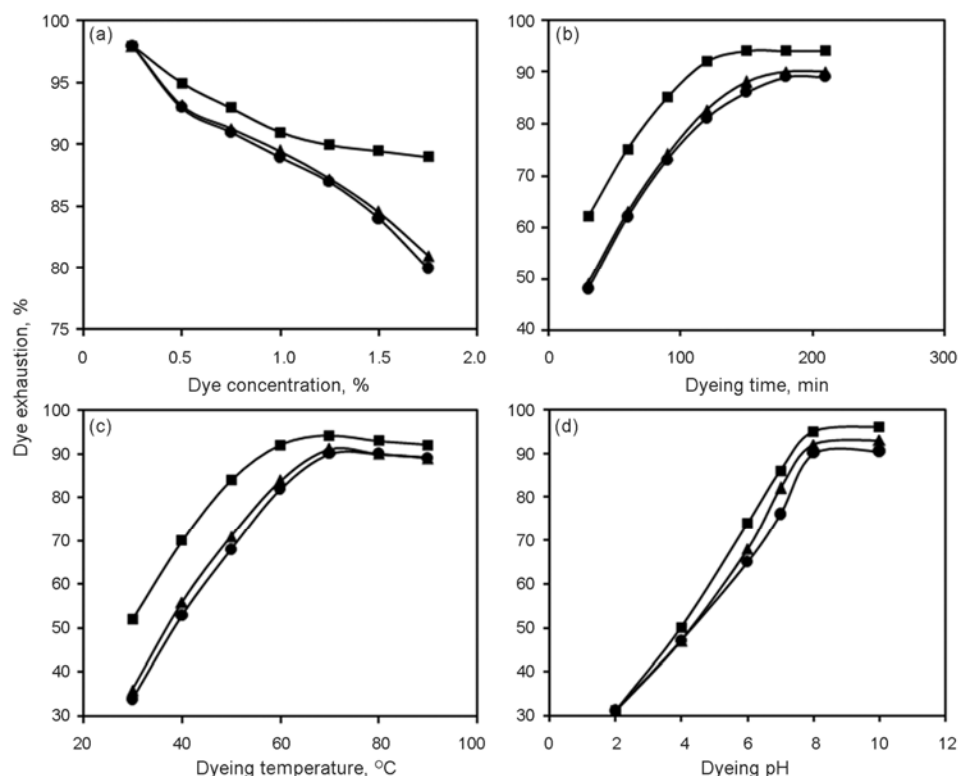


Fig. 1—Effect of dyeing parameters on dye exhaustion (●) un-mordanted, (▲) MgCl₂ mordanted and (■) FeSO₄ mordanted dyeing system

Table 1—Data colour analysis of dyed silk fabric

Illumination	Dyed sample	DL*	Da*	Db*	K/S
D65 10 Deg	Unmordanted	0.00	0.00	0.00	20
	MgCl ₂ mordanted	-1.13	-1.21	1.22	22.2
	FeSO ₄ mordanted	-9.19	-24.57	-31.13	63.6
msTL84-10	Unmordanted	0.00	0.00	0.00	20.8
	MgCl ₂ mordanted	-1.09	-1.63	1.23	23.1
	FeSO ₄ mordanted	-9.97	-21.88	-34.95	66.4
TL83 10 Deg	Unmordanted	0.00	0.00	0.00	21.5
	MgCl ₂ mordanted	-1.11	-1.67	1.05	23.9
	FeSO ₄ mordanted	-10.50	-21.91	-37.62	68.6

Table 2—Colour fastness properties

Dyed samples	Light fastness	Wash fastness	Rub fastness (dry)	Perspiration
Unmordanted	3-4	4	3-4	3-4
Mordanted with				
MgCl ₂	4	4-5	4	3-4
FeSO ₄	4-5	4-5	4-5	4-5

indicate more brightness, redness and yellowness respectively, whereas negative values indicate less brightness, greenness and blueness. Unmordanted, magnesium chloride mordanted and ferrous sulphate mordanted fabrics show dark dull red shade,

dark bright yellow shade and dark red shade respectively. Maximum strength is obtained using ferrous sulphate mordant.

3.4 Fastness Properties

Table 2 shows the colourfastness properties of dyed fabrics. The colour change is assessed by using gray scale within the range 1-5, where 5 is outstanding and 1 is poor. The satisfactory colour fastness properties are showed by dyed silk fabric both for mordanted and unmordanted system. FeSO₄ mordanted dyed fabric shows outstanding fastness properties compared with the other dyed fabrics.

4 Conclusion

Rubiadin dye was extracted from the bark of mahogany plant using simple solvent extraction technique. The dye yield in bark sample was found high enough to utilize on fabric dyeing without using metallic mordant. However, higher *K/S* value and better colour fastness properties of dyed silk fabric was found by using metallic mordants (MgCl_2 and FeSO_4). Thus, this dye can be commercialized for protein fabrics dyeing.

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