DISCOVERY

58(319), July 2022

Effect of mordants and mordanting methods on the dyeing property of anthraquinone based dye from *Rubia cordifolia*

Devi Priya M[1], Siril EA[2]

To Cite:
Devi Priya M, Siril EA. Effect of mordants and mordanting methods on the dyeing property of anthraquinone based dye from *Rubia cordifolia*. *Discovery*, 2022, 58(319), 742-749

Author Affiliation:
[1]Department of Botany, St. Thomas College, Ranni, Pazhavangadi PO, Pathanamthitta 689673, India
[2]Department of Botany, University of Kerala, Kariavattom, Trivandrum 695 581, India

***Corresponding Author:**
Dr. Devi Priya M.
Assistant Professor and Head
Department of Botany
St. Thomas College, Ranni
Pazhavangadi PO, Pathanamthitta, India
Email: devi.priya.m@gmail.com

Peer-Review History
Received: 04 May 2022
Reviewed & Revised: 05/May/2022 to 09/June/2022
Accepted: 11 June 2022
Published: July 2022

Peer-Review Model
External peer-review was done through double-blind method.

ABSTRACT

Natural dyes are eco-friendly and sustainable source of colourants than its synthetic counterparts. The present investigation deals with extraction of anthraquinone based dyes from roots of *Rubia cordifolia* and its utilization in dyeing cotton fabrics using diverse mordants and mordanting methods *viz.*, pre, post or simultaneous mordanting. Dye bath was prepared by boiling the powdered root in water at 100°C. Dyeing efficiency was tested using mordants like myrobalan, aluminium potassium sulphate, copper sulphate, ferrous sulphate or acetic acid. A wide range of colours/shades was produced. pH of dye bath before and after dyeing varied significantly among different mordants used. Percentage dye uptake due to various mordant was significantly ($P < 0.001$) varied on mordanting methods. Highest dye uptake (72.09 %) was recorded in myrobalan based post mordanting method. Wash fastness and rubbing fastness were in the range of 1/2nd–4/5th acceptable grades. Thus suggest the use of madder roots along with mordants to get flamboyant shades on cotton fabric.

Keywords: Dye, Cotton fabric, Mordant, Natural dyes, Madder, *Rubia cordifolia*

1. INTRODUCTION

The use of natural dyes dates back to ancient periods and continued as coloring source until the turn of twentieth century. Even though the earliest dyes were discovered accidently using berries and fruits, with the experimentation and gradual development, the art of dying using natural dyes was perfected in ancient civilizations. (Kharbade. and Agrawal, 1998; Mishra and Patni, 2001). However, industrialization at the turn of 20th century, natural dyes was mostly replaced with its synthetic alternatives. Madder is such a neglected red dye once largely been used as textile dye that gives wide and diverse shades of red, indigo or even black. Source of Indian madder is the roots of *Rubia cordifolia* L., belongs to family rubiaceae, and is native to high elevations of Indian subcontinent (Gupta, 2003). Root derived powder of madder was an important dye source for the Asian cotton industry and is still used by craft dyers in Nepal. It is ascribed as

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

"the queen of natural dyes" and is used for imparting red, scarlet, brown and mauve colours to wool, fibres and fabrics. In textile industry, it is known as rose madder and in painting industry, as it is a colourant for paint, referred to as madder lake (Zomlefer, 1994). Its dye stuff is called as madder with C.I. name natural red 6, 8, 9, 10, 11, 12, 14 and 16 (Saxena and Raja, 2014), is based on the anthraquinoid structure. The roots of *R. cordifolia* contain more than 20 major anthraquinone constituents, like alizarin (chief colouring compound), munjistin, purpurin, pseudopurpurin, xanthopurpurin, rubiadin, anthragallol, lucidin, damnacanthal, nordamncanthal etc. (Gupta et al., 2011; Gokhale et al., 2004). In *R. cordifolia*, the anthraquinones are generally present as the glycosides in younger roots. Literature suggests that about one year old madder contained mostly a yellow dyestuff and the red dyestuff appeared during the second year of growth (Chenciner, 2000). The madder dye imparts brilliant colours of red depending on the mordants and dye concentrations. Depending on the mordant used, the colour shade of madder dye can be modified through red, pink, orange, lilac and brown (Green, 1995).

Even though natural dyes have several problems like colour yield, blending and fastness problems, the utilization of natural resources is gaining attention of the world mostly because of its eco-friendly nature. Though Indian madder is acclaimed as dye source since ancient period, its utilization remain neglected in the modern era. Therefore in the present study communication we evaluate the colouring property of madder dye on cotton fabrics with different mordants and methods. The optimizations of dye and mordant for different color shades ultimately lead to utilization of madder in the commercial dyeing of cotton fabrics.

2. MATERIALS AND METHODS

The roots of *R. cordifolia* were collected from the natural habitat, Ellappara (Latitude 9º36', 49.89" N, Longitude 77º00', 6.59"E Elevation 1158m) of Idukki district, Kerala state, India. The collected roots were washed well in water, cut into small pieces (2-3 cm), shade dried for 2 weeks, and powdered in a grinder (Preethi Silver Mixer Grinder 149, Mumbai, India) for 2 minutes.

Extraction of crude dyestuff

For dye extraction, root powder was weighed, boiled in a beaker (1000 ml) containing twelve times more tap water (1: 12) for 1 h, to reduce the volume (80 %) to 1: 10 by boiling. The suspension was filtered while hot using single layered, fine muslin cloth. This crude dye stuff was kept in a steel container (1000 ml) for one week at room temperature in dark, providing proper aeration without any agitation facilitated fermentation.

Preparation of the fabrics

Pure white, bleached poplin, zero-zero finish, 100 % cotton fabric (Mfg. Shree Geetha Fabrics, Burhanpur, Maharashtra, India) was used to test dying property of madder. These cotton fabrics were cut into small pieces (1 gm; approximately 10 × 10 cm size) and were scoured prior to dyeing using 2 % non-ionic, sorbatan detergent, Labolene (Fischer Scientific India Pvt. Ltd., Mumbai, India) for 2 minutes to remove drosses, and also to facilitates adsorption and penetration of applied dye. The scoured fabrics were gently agitated in tap water for a minute and the process was repeated (4-5 times), till the last traces of detergent was removed and then dried under shade at room temperature. The scoured fabrics was soaked in tap water for 30 minutes[10], prior to dyeing or mordanting to improve the even spreading of dyestuff to fabrics.

Preparation of mordants

In the present investigation, metallic mordants *viz.*, aluminium potassium sulphate (Alum; Loba Chemie Pvt. Ltd., Mumbai, India), ferrous sulphate (Spectrum, Reagents and Chemicals Pvt. Ltd, Cochin, India), copper sulphate (SD Fine Chemicals, Mumbai, India), and non-metal mordant glacial acetic acid (Merck India Pvt. Ltd., Mumbai, India) and a natural mordant myrobalan (dried and powdered fruits of *Terminalia chebula* L.) purchased from local market were used. Chemical mordants were dissolved in required quantity of tap water to obtain the desired concentration, 5 % on weight of fabric (o.w.f.). The myrobalan powder was soaked in tap water (1: 10) for 12hrs at room temperature, which was then mixed with 100 ml of tap water and heated at 80°C for 30 minutes (Anitha and Prasad, 2007). The cooled solution was used as final mordanting solution after filtrating in a muslin cloth.

Dyeing and mordanting

Scoured cotton fabric (1 g; approx. 10 X 10 cm) was treated with different mordanting solutions. Three types of mordanting *viz.*, pre-mordanting (onchrome), simultaneous mordanting (metachrome) and post mordanting (afterchrome) methods were tried to determine the colour shades and reflectance. In pre-mordanting method, the mordant was applied first, followed by dyeing the samples. In simultaneous mordanting, the mordant was added in the dye bath itself, where as in post mordanting method, dyeing

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

was done first and then mordanting was carried out. Prior to dying, the pH of the dye bath was adjusted to 7.5 by using 1 N sodium bicarbonate (Merck Specialties India Pvt. Ltd., Mumbai) by using pH meter (Eutech pH Tester 10, Thermo scientific). The dye bath taken in a beaker (100 ml) was then heated on a hot plate and the temperature was maintained at 95°C for 45 minutes. The material to dye-liquor ratio (MLR) was fixed as 1: 20. After dyeing and mordanting, in case of post mordanting treatment, the fabrics were rinsed successively in hot water followed by cold water, and then dried under shade. The pH and OD (436 nm) of dye bath, before and after dying was duly recorded.

Percentage of dye uptake

The percentage of the dye uptake was determined through the measurement of the difference in the absorbance of the dye before and after dyeing at 434nm, the absorption maxima of dye solution. The experiment was repeated three times and the average OD was recorded. The % of dye uptake (% of exhaustion) was calculated as per Badoni et al., 2009). The spectrophotometric measurements were carried out by using UV-Visible Spectrophotometer (UV-VIS-1700; Shimadzu, Japan). Further, the absorption of the dye by the fabric was determined by using reflectance spectroscopy (Shimadzu UV-1700) at 434 nm and was graphically presented.

Analysis of colour fastness

Colour fastness to wash was determined by washing with diluted soap solution. IS/ISO C10105 was designed to determine the effect of washing only on the colour fastness of the textile (Anon, 2008) and colour fastness to rubbing (Anon, 1984) by using a manually operated crock meter by employing IS 766: 1984 method.

3. RESULT AND DISCUSSION

In the present study, the mature roots were used for dye extraction (Fig.1). The dyestuff produced deeper colours when it is fermented. Naturally cotton fibers show reluctance to absorb natural dyes because of its cellulosic nature. In a preliminary trial, anthraquinone dye extract of Indian madder showed less affinity to cotton fibers. To enhance the affinity, different mordants were used, which also influence the fastness property of dye on fabrics.

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

Fig 1: *R. cordifolia A*: freshly harvested roots, B: root powder, C: dye stuff obtained from madder, D: dyeing the fabrics in fermented dyebath

Fig 2: Colour shades produced by madder in presence of different mordants and different mordanting methods used for the study identified with the help of Pantone Formula Guide (Anon, 2000)

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

Table 1: Colour shades produced by cotton fabrics by using madder dye by different mordants

Mordants	Pre Mordanting	Simultaneous Mordanting	Post Mordanting
Acetic Acid	Yellow Pantone 7520 U	Orange Pantone 720 U	Orange Pantone 726 U
Alum	Red 032 Pantone 1765 U	Red 032 Pantone 1767 U	Red 032 Pantone 700 U
$CuSO_4$	Purple Pantone 263 U	Rubia Red Pantone 7429 U	Rubia Red Pantone 7431 U
$FeSO_4$	Prossian Blue Pantone 5155 U	Warm Red Pantone 5225 U	Warm Red Pantone 436 U
Myrobalan	Yellow Pantone 7250 U	Yellow Pantone 7415 U	Yellow Pantone 4665 U
Dye alone (Control)	Warm Red Pantone 508 U		

Colouring effect of madder dye

When cotton fabrics were dyed with madder with or without mordants, produced varying colour shades (Table 1; Fig.2), which were identified with Pantone formula guide (Anon, 2000) and were photo documented.

Most of the colours obtained were the varying shades of red, orange or yellow. When aluminium potassium sulphate (alum) was used, varying shades of red colour was produced, irrespective of mordanting methods adopted. Mordanting using copper sulphate produced rubia red colour during simultaneous and post mordanting, while ferrous sulphate produced warm red colour, and is comparatively duller than in alum mordanted fabrics. In pre mordanting, copper sulphate produced purple colour and prossian blue colour by ferrous sulphate. Mordanting by different methods using acetic acid showed yellow to orange shade. Myrobalan produced yellow shades only. The yellow shade obtained from acetic acid and myrobalan in pre-mordanting were same having the same pantone number (7520U). The madder dye alone produced warm red colour.

Earlier, Samanta (2010) reported the production of maroon red colour on jute fabric from Indian madder at alkaline conditions under aqueous medium. The use of alum, copper sulphate and ferrous sulphate as mordants for madder dye produced shades of creamish brown, chocolate brown, pink respectively as reported by Agarwal and Gupta (2003). In the present study, these mordants could produce various shades of red and purple colour. It is also reported that madder dyed fabrics were brilliant shades of bright red to scarlet depending on mordants and dye concentrations (Yusuf et al., 2013).

Percentage dye uptake

The percentage of dye uptake for each treatment was calculated using OD value of dye bath before and after dyeing. The dye uptake due to various mordant was significantly ($P < 0.001$) varies in three methods of mordanting tested. When dye alone was used, the percentage was 28.91 %. The highest dye uptake (72.09 %) percentage was recorded in myrobalan based post mordanting method of dyeing and was significant ($P < 0.05$). Among all the methods, simultaneous mordanting recorded the significantly ($P < 0.05$) low dye uptake irrespective of the mordants used (Table 2). Copper sulphate when used as mordant in simultaneous mordanting the lowest percentage dye uptake (12.17 %) among all the treatments was recorded. When pre and post mordanting were compared, except alum, the other mordants showed an increased uptake of dye in post mordanting method.

Table 2: Percentage of R. cordifolia (madder) dye uptake in cotton fabric mordanted using five different types of mordants through pre, simultaneous or post mordanting methods

Mordant	Pre Mordanting (%)	Simultaneous Mordanting (%)	Post Mordanting (%)	Mordant mean
Acetic Acid	50.70 ± 0.49^{c}	20.97 ± 0.56^{c}	55.78 ± 0.04^{d}	42.48
Alum	59.38 ± 0.55^{a}	20.68 ± 0.25^{c}	38.33 ± 0.16^{e}	39.46
$CuSO_4$	48.25 ± 0.55^{d}	12.17 ± 0.27^{d}	66.00 ± 0.58^{b}	42.14

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

$FeSO_4$	46.50±1.64[d]	38.42±0.55[a]	58.53±0.33[c]	47.82
Myrobalan	56.12±0.48[b]	33.85±0.09[b]	72.09±0.25[a]	54.02
Dye alone	28.91±0.89[e]	-	-	28.91
Treatment mean	48.31	25.22	58.15	
Treatment df (n-1)=5	297.599***	1558.422***	7873.025***	

Means within a column followed by same letters are not significantly ($p < 0.05$) different as determined by Duncan's multiple range test. ***highly significant ($p < 0.001$) F value; LSD ($p < 0.05$) for treatment mean 14.18; LSD ($p < 0.05$) mordant mean 35.98

Table 3: Fastness values of madder dyed cotton fabric with or without mordant

Test Parameters		I	II	III	IV	V	VI
Colour Fastness to Wash (IS/ISO C 10-105)	Colour Change	2	2/3	2/3	1/2	2	1/2
	Stain on Cotton	4/5	4/5	4/5	4/5	4/5	4/5
	Stain on Wool	4/5	4/5	4/5	4/5	4/5	4/5
Colour Fastness to Rubbing (IS 766: 1984)	Dry	4	4/5	4	4/5	4	4
	Wet	3/4	3	4	3/4	3/4	3/4

I: Alum, II: Myrobalan, III: $CuSO_4$, IV: Madder, V: Acetic Acid, VI: $FeSO_4$

Analysis of colour fastness

Colour fastness is the resistance of a material to change any of its colour characteristics and it is a prerequisite in textile industry. Wash and rubbing fastness of dyed fabrics were analyzed by using grey scale, which helps to identify visual difference and contrast. The grey scale has the 9, possible values: 5, 4/5, 4, 3/4, 3, 2/3, 2, 1/2, and 1 of which 5 represents the best rating and 1 the worst rating. In the present study, the colour change was poor (1/2) for non-mordanted and copper sulphate used as mordant on cotton fabric. The value was 2/3 for both myrobalan and ferrous sulphate mordanted fabric while alum and acetic acid rated as 2. Stain on cotton and wool were 4/5 for all the mordants (Table 3). Dry rubbing fastness values were very good or good for all the dyed fabrics. It was very good (4/5) for dye alone and myrobalan while others showed good (4) dry rubbing fastness. Wet rubbing fastness values was good to average and was found to be good for copper sulphate and fair (3/4) for other samples except myrobalan mordanted fabrics (3). Hence our study proved that the madder dye can be recommended for textile dyeing along with mordants like myrobalan, ferrous sulphate, acetic acid, copper sulphate etc... Previously, various types of mordants were used to assess the fastness property of madder dye. Good washing, perspiration fastness and fair light fastness of silk fabrics dyed with mixture of *R. cordifolia* and *Tagetus erecta* dye extracts (Katti et a., 1996). Good or very good washing and moderate or fair light fastness was observed with mordants such as copper sulphate, potassium dichromate or stannous chloride (Bhuyan et al., 2004); myrobalan and alum (Mondal et al., 2004); ferrous sulphate and tannic acid (Teli et al., 2004); alum, copper sulphate, ferrous sulphate and myrobalan (Patel, 2011); tin (II) chloride (Yusuf et al., 2015). The color fastness with respect to light exposure, washing and rubbing was quite satisfactory on woolen yarn when henna and madder dyed samples were analyzed (Yusuf et al., 2013). A comparative study on dyeing of cotton and silk fabric with madder by using alum and copper sulphate as mordants reported lesser wash fastness and somewhat similar rub fastness value (Jahan and Datta, 2015) as in the present investigation.

4. CONCLUSION

In the modern era wide spread emphasis is given to utilization of natural dyes as it is safe and eco-friendly resource for the sustenance of human. Though there are some problems associated with the use of natural dyes, natural dyes have regained the attention of the world. The whole process of extraction and dyeing of madder that is used for the present work is ecologically safe, and cost effective. Since dye content in intact plants varies with season, age, soil type, processing methods etc…, special care is necessary in selecting the root material to reproduce the same result as such. Brilliant colour shades obtained from madder with different mordants will definitely attract the attention of textile industry. It was also shown that these mordants can improve the

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

fastness property of the textile. There are reports that certain natural dyes can impart antimicrobial property to the dyed fabric. In India, there are so many dye producing plants, which are under-utilized, and to enhance its utilization potential it is necessary to assess and improve the available techniques to safe guard the future generations.

Acknowledgements:
We are thankful to Head, Department of Botany, for providing all the facilities to carry out this work. We are thankful to Mr. Baiju B., Foam Mattings India Ltd., Alleppey for technical support. We also thank Mr. Prakash N. Bhat, Central Silk Board, CSTRI, Bangalore for textile analysis. Devi Priya M. is grateful to University Grants Commission, (Govt. of India) New Delhi for Teacher Fellow grant (F.No.FIP/KLMG 052, TF05) through FDP program.

Author contributions
Dr. DEVI PRIYA M.: First author did the study
Dr. E.A. SIRIL: Research Guide of the first author, who provided instructions for the present study and corrected the manuscript
There are no potential conflicts of interest
Devi Priya M. is grateful to University Grants Commission, (Govt. of India) New Delhi for Teacher Fellow grant (F.No.FIP/KLMG 052, TF05) through FDP program.

Funding
This study has received funding from University Grants Commission, (Govt. of India) New Delhi for Teacher Fellow grant (F.No.FIP/KLMG 052, TF05) through FDP program.

Conflicts of interests
The authors declare that there are no conflicts of interests.

Data and materials availability
All data associated with this study are present in the paper.

REFERENCES AND NOTES

1. Agarwal S, Gupta K. Optimization of dyeing conditions for natural dye madder roots (*Rubia cordifolia*). Colourage, 2007: 50: 43-6.
2. Anitha K, Prasad SN. Developing multiple natural dyes from flower parts of Gulmohur. Curr Sci, 2007: 92: 1681-2.
3. Anon. ISI Handbook of Textile Testing, Determination of colour fastness of textile materials to rubbing. Indian Standard Institution, New Delhi: 1984: 1-6.
4. Anon. Pantone Formula Guide solid uncoated. Pantone Inc., USA: 2000.
5. Anon. Indian Standard Textiles - Tests for Colour Fastness Part C10 Colour Fastness to washing with Soap or Soap and Soda. Bureau of Indian Standards (BIS), New Delhi: 2008.
6. Badoni R, Semwal DK, Sati SC, Rawat U. Optimization of dyeing procedure on wool yarn with *Pistacia integerrima* dye using synthetic and natural mordants. Colourage, 2009: 56: 67-70.
7. Chenciner R. Madder red: a history of luxury and trade. Routledge, USA: 2000.
8. Dixit S, Jahan S. Colour fastness properties of *Euphorbia continifolia* leaves dye on silk fabric. Man-made Text India, 2005: 58: 252-4.
9. Gokhale SB, Tatiya AU, Bakliwal SR, Fursule RA. Natural dye yielding plants in India. Nat Prod Radiance, 2004: 3: 228-34.
10. Green CL. Natural colourants and dyestuffs - A review of production, markets and development potential. Food and Agriculture Organization of the United Nations, Rome: 1995: 1-34
11. Gupta AK. Quality standards of Indian Medicinal Plants. Indian Council of Medicinal Research, New Delhi: 2005: 317.
12. Gupta D, Kumari S, Gulrajani M. Dyeing studies with hydroxyl anthraquinones extracted from Indian madder. Part 2: dyeing of nylon and polyester with nor damnacanthal. Colouration Technol, 2011: 117: 333-6.
13. Jahan N, Datta EA. Comparative study on dyeing of cotton and silk fabric using madder as a natural dye. J Polym and Text Eng, 2015: 2: 05-11
14. Katti MR, Ramnik K, Shrihari N. Dyeing of silk with mixture of natural dyes. Colourage, 1996: 43: 37-8.
15. Kharbade BV, Agrawal OP. Analysis of natural dyes in Indian historic textiles. Studies in Conservation, 1998: 33**:** 1-8.

16. Mishra P, Patni V. Extraction and application of dye extracted from eriophyid leaf galls of *Quercus leucotrichophora*- A Himalayan blue jack oak. Afr J Biochem Res, 2001: 5: 90-4.
17. Mondal S, Dutta C, Bhattacherya S, et al. The effect of dyeing conditions on fastness properties of natural dyes on silk fibers. Colourage, 2004: 51: 33-6.
18. Patel AR. Pink shade developed on Cotton yarn from *Rubia cordifolia* Linn. Life Sci Leafl, 2011: 19: 780-4.
19. Samanta AK. Effect of different mordants , extraction conditions and dyeing process variables on colour interaction parameters and colour fastness properties in dyeing of jute fabric with manjistha, a natural dye. J Institution of Engineers (India)-Textile Engg, 2010: 91: 7-15
20. Saxena S, Raja ASM. Natural dyes: Sources, Chemistry, Application and sustainability issues. In Muthu, S.S. (Ed.) Road map to sustainable textile and clothing Eco friendly Raw Materials, Technologies, and Processing Methods. SGS Hong Kong Limited, Hong Kong: 2014: 37-80
21. Sudhakar R, Gowda KNN, Padaki NV. Natural dyeing of silk with the nut extract of *Areca catechu*. Colourage, 2006: 53: 61-6.
22. Teli MD, Adivarekar RV, Pardeshi PD. Dyeing of pretreated cotton substrate with madder extract. Colourage, 2004: 51: 23-32.
23. Yusuf M, Shahid M, Khan SA. Eco-dyeing of wool using aqueous extract of roots of Indian madder (*Rubia cordifolia*) as natural dye. J Nat fibres, 2013: 10: 14-8.
24. Yusuf M, Shahid M, Khan MI, et al. Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant. J. Saudi Chem Soc, 2015: 19: 64-72.
25. Zomlefer WB. Flowering Plant of the World. University of North Carolina Press, London. 1994: 1-430.

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS