Anthroquinoid dye-
Rubia/Maddar
Rubia with Biomordant

• Rubia cordifolia (Tamin, local name) produces anthraquinone reddish orange dyes in roots, stem and leaves, which has been used for dyeing textiles since ancient times. Commercial sonicator dyeing with Rubia showed that pretreatment with biomordant, Eurya acuminata DC var euprista

• Karth. (Theaceae family) [local name, Nausankhee (Apatani tribe), Turku (Nyishi tribe) in 2%] shows very good fastness properties for dyed cotton

• using dry powder as 10% of the weight of the fabric is optimum. Use of biomordant replaces metal mordants making natural dyeing ecofriendly.
Abundant source of Rubia

A revived interest in the use of natural dyes in textile coloration has been growing and there is pressing need for the availability of natural dye yielding plants. This is a result of the stringent environmental standards imposed by many countries in a response to the toxic and allergic reactions associated with synthetic dyes. Arunachal Pradesh is recognized as one of the hotspot of biodiversity and the indigenous knowledge system particularly associated with extraction and processing of natural dyes from plants.
Traditionally used by Tribes

From ancient times some tribes of the state were engaged in natural dyeing. The different tribes mainly the Monpas, Apatanis, Nyishis and Adis, respectively, of West Kameng, Tawang, Lower Subansiri and East and West Siang districts of Arunachal Pradesh have been engaged in extraction, processing and preparation of dyes using barks, leaves, fruits and roots of the plants.
Our main focus

- This work was designed with an aim to focus on the innovative methods of dye extraction, mordant study and by means of application of modern technology to sharpen the skills of tribal traditional dyers of Arunachal Pradesh. Although a lot of work has been done on natural dyeing with rubia, our approach is towards development of ecofriendly natural dyeing using biomordant and ultrasound energy.
Characterization of the color components

- R. cordifolia contains mainly alizarin as well as purpurin, pseudo-purpurin, munjistin, and rubiadin, because anthraquinone dyes have poor affinity for cotton fibers, their fastness was often enhanced by mordants. Mordants, which are metal salts that form an insoluble complex with dye molecules, including potassium aluminum sulfate (alum) and ferrous sulfate. The nature of the mordant dye complex is well documented in the literature as shown in Structure I.
How does the chelation happen

- The alizarin molecules are capable of forming six-member chelate rings with aluminum ions. Colored lakes formed by the metal ions and dye molecules resist extraction by water and organic solvents, which readily strip similarly structured acid dyes. The sheer size of the complex may account for some of its insolubility.

- It is also likely that the large complexes are physically trapped within the fiber. The ortho-dihydroxy structure in the hydroxyl-anthraquinone molecules could greatly enhance the chelation. A similar behavior is envisaged for biomordant as well.
Eurya Acuminata

Only a small fraction of plant species takes up high levels of aluminum (Al) in their above-ground tissues. Generally, plants are classified as accumulators if they accumulate at least 1000 mg kg⁻¹ in their leaves. Our knowledge of Al accumulators is built mainly on the substantial contributions made by Chenery starting some 50 years ago. The extract of E. acuminata DC var euprista Karth. leaves is found to contain substantial amount of Al.
Two possible ways of chelation

- The chelation to the anthraquinone moiety of R. cordifolia at two different sites, one with carbonyl and hydroxyl group
- and the other with di-hydroxyl moieties
Important colorant molecules in Maddar/ Rubia

(III)

(IV)

(V)

(VI)

(VII)

(VIII)
Al in Eurya acuminata

- Atomic absorption spectroscopic analysis (GBC Avanta, model-Sigma, Australia) of E. acuminata leaves extract showed 11.767 mg/l of Al content. The high Al content has been suggested to provide useful chelation to the anthraquinone moiety of R. cordifolia at two different sites, one with carbonyl and hydroxyl and the other with di-hydroxyl moieties.
Two dyeing methods

(i) Two-step dyeing (in the ratio of 2% biomordant, owf) was used as pretreatment and then dyeing with Rubia extract (10%, owf) was carried out for 3 h at temperature 30-40 C. The dyed fabrics were rinsed thoroughly in tap water and allowed to dry in open air.

(ii) One-step dyeing (in the ratio of 10% Rubia extract and 2% biomordants) was mixed thoroughly in one bath and the moist fabric was dipped for 3 h at temperature 30-40 C. The dyed fabrics were rinsed thoroughly in tap water and allowed to dry in open air.
Effect of Sonication

In the case of sonication, localized temperature raises and swelling effects due to ultrasound may also improve the diffusion. The stable cavitation bubbles oscillate which is responsible for the enhanced molecular motion and stirring effect of ultrasound.

In case of cotton dyeing, the effects produced due to stable cavitation may be realized at the interface of cotton and dye solution. Dye uptake was studied during the course of the dyeing process for a total dyeing time of 3 h with and without ultrasound. About 58% exhaustion of dye (Rubia) can be achieved in 3 h dyeing time using ultrasound while compared to only 40%, in the absence of ultrasound in stationary condition for this natural dye was observed.
Dye Uptake due to mordant and Biomordant

Dye uptake in different medium

% Dye uptake

Alum treated+dye
BM treated +dye
Dye Uptake

The one-stage and the two-stage dyeing of cotton fabric with and without biomordant by the natural dye R. cordifolia, show that two-stage process with biomordant showed very good results. The dye uptake in case of two-step dyeing is 9.0%, 23.06% and 11.85% for without mordant, biomordant and alum mordant.

- In the case of one-step dyeing, the dye uptake is 38% and 47% for dye- biomordant and dye-alum simultaneous mordanting methods. The effectiveness of biomordant-R. cordifolia in better dye uptake may appear to be slightly less as compared to metal mordanting, however, the reduction in effluent pollution as well as improved fastness properties outweighs its benefit as observed
Fastness properties

• Fastness properties of dyed cotton fabrics under conventional heating and

• ultrasonic conditions of biomordant and R. Cordifolia

• Dyeing methods Wash-perspiration-rubbing-light WF Per-acidic Per-basic Rub dry Rub wet LF

• Conventional 4, 4, 3-4, 3-4, 3-4, 4

• Ultrasonic 5, 4-5, 4-5, 4, 4, 4-5
**pH compatibility**

The pH of *R. cordifolia* extract is 5.7 whereas the pH of *E. acuminata DC var euprista Karth. (Nausankhee)* extract is 7.67.

Thus it can be said that the two extracts are complimentary to each other and that causes the better dye adherence. The suitability of specific biomordant *E. acuminata (Nausankhee)* for this particular natural dye was evaluated on the basis of the traditional information collected.
A-----dye before dyeing
B---- Alum treated fabric +dye (after dyeing) 11.85% dye uptake
C-----Bio modrant treated fabric +dye (after dyeing) 23.06%dye uptake
Conclusion

• R. cordifolia was found to have good agronomic potential as a dye crop in Arunachal Pradesh. Biomordant e E. Acuminata DC var euprista Karth. (Nausankhee) when used in conjunction with R. cordifolia was found to enhance the dyeability due to the Al contents present in the leaves.

• Enhancement of dye uptake was 23.06% with biomordant, 11.85% with alum and 9.8% without any mordant.
Conclusion

• Use of biomordant not only enhances the fastness properties but also gives good colorimetric data on dyeing. Even the fastness properties in this case show good results.

• The two-step biomordant-dye, developed for the ease of industrial application offers an ecofriendly process which should be popularized as an alternate method to the metal mordantedye method.