Natural Dyes

Prof. Padma Vankar

Department of Chemistry

Indian Institute of Technology, Kanpur

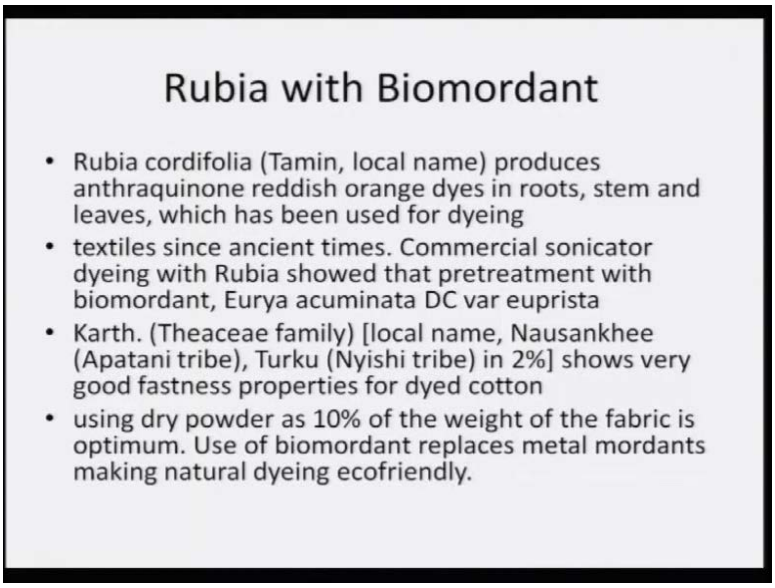
Lecture No. # 34

When we were taking the classification of natural dyes, we had talked about various types of dyes according to their structural detail. We had named as indigoid dyes, anthraquinoid dyes, anthocyanin dyes, carotenoid dyes and many such classification we had dealt with. So far when we have been doing the detail study of these structurally important natural dyes among them we have already discussed in great detail anthocyanidin dyes or anthocyanin dyes with respect to rows, with respect to hibiscus.

Then just this morning we took at another detail account of carotenoid dyes in terms of (( )) and now we will take a look at a very important very old very ancient yet very important dye from the anthroquinoid series from the Rubia or Maddar extract. Now the structural detail that chemical compositions, the metal chelation and its dyeing effect with the help of the innovative technology that we have develop using bio-mordants in this case; we have shown that Rubia can be a very multi festive dye also you know because it is so largely used or it has a big scope to be use in the industry.

So, we try to put up some innovative technological up gradations steps. So that this dye can be popularly used among the local people and as well as not only for the domestic market, but also for the international market. For the simple reason that everybody likes to wear clothes which are dyed with you know natural dyes and secondly, because this has the bright orangish, brick red color which is very appealing to one and all. So, that is the reason why we spend enormous amount of time trying to a find out its large availability and then it is you know how traditionally it is being extracted and used for dyeing and what are the steps that we can upgrade. So, that it can be industrially very useful.

(Refer Slide Time: 03:19)



Rubia with biomordant what was try to explode in a big way. Rubia cordifolia or maddar are in Arunachal Pradesh it is commonly known as Tamin produces anthraquinone reddish orange dyes in the roots, stem and leaves, which have been used for dyeing. Now, one thing I want to make it clear right from the beginning that we have been trying to popularize you know all those parts to be used which do not destroyed the plant. And in case we use the roots of rubia; obviously, the plant would be dead. So, we propagated the use of only the leaves and the stems, because the stem and leaves have enough amount of dye, but the roots have the maximum amount. So, it does not matter because we need not destroyed the plant.

Textiles in ancient times have been used have been using this particular dye from madder or rubia. Commercial sonicator dyeing with Rubia showed that pretreatment with bio mordant that is Eurya acuminata DC var euprista karth from the theaceae family also known as Nausankhee by the Apatani tribe, Turku - Nyishi tribe in 2 percent shows very good fastness properties for dyed cotton. So, here we were trying to concentrate on dyeing of cotton because as I have told many times that cotton dyeing with natural dye is a big challenge and we were trying to explore how to combart this challenge and that is why we wanted to use this biomordant and along with the the cotton, how does it how does the maddar extract actually behave. Using dry powder of about 10 percent weight of the fabric is optimum; use of bio mordant replaces metal mordant making natural dye completely eco friendly.

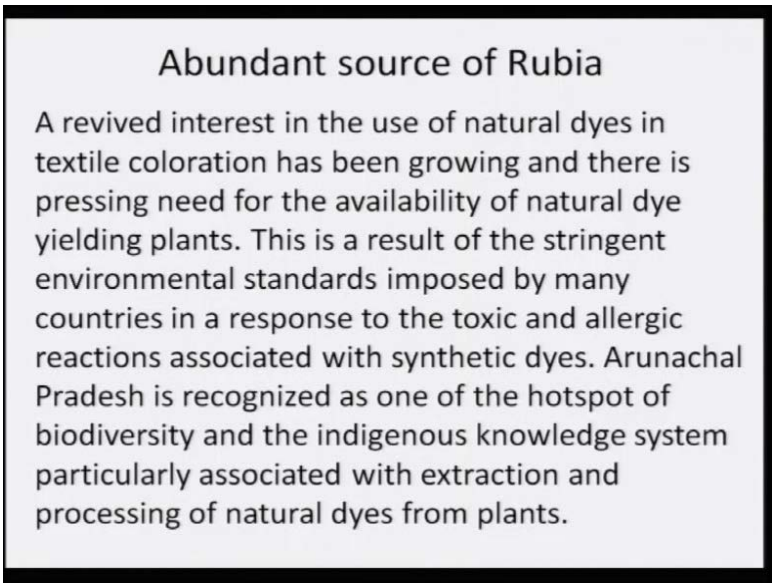
Now, time and again I am emphasizing on three main facts. One is show do we bring about a technological up gradation in the process of extraction or dyeing. Second is how can we replace the metal mordant, because that creates later on problems with the dye bath a fluent treatment, and thirdly how to enhance the light and wash fastness which is the prerequisite for a dye to be accepted in the commercial market.

So, this dye had no problems in its acceptance in the commercial market, because it is the ancient dye, but how can we bring about improvement through our technological advancement, and one such thing we did was to carry out the dyeing process in a sonicator. Now, sonicator ultrasound waves have a particular frequency of agitation in the dye bath which is very, very good for dye uptake. So, this we had already established in the laboratory.

And we were trying to explore with as many new dyes in order to establish it is you know validity because any process need not be valid for all the dyes. So, we wanted to show through our sonication dyeing method which we introduce for the first time with natural dyes that if sonicator bath is used for dyeing process. The dye uptake is definitely enhanced and enhanced by several force; it is not just that it is marginally enhanced by one or two percentage. It is substantially, you know improved by 10 to 15 or sometimes even 20 percent. Now in commercial scale this 20 percent extra dye uptake can definitely make a lot of difference on the hue color and also on the requirement for the disposal of the dye bath effluent.

So, looking at the whole picture in a very holistic manner, one has to keep these points in mind that dyeing with natural dye would requires certain you know adjustments, and these adjustments should be beneficial in the wrong in the long run not only in terms of dye uptake, but also it should have good dye penetration; it should create good light and wash fastness, because that is the ultimate goal. So, we try to take the toughest material that is cotton, we try to replace the metal mordant which is the problem creating chemical in the whole process by using bio material, and we called this as bio-mordant and that bio mordant was Eurya acuminata. Now with this background we started you know exploring where all Rubia is actually present because you see we have to look for a plant material which should be abundantly available.

(Refer Slide Time: 09:21)



So, the abundant source of Rubia, a revived interest in the use of natural dyes in textile coloration has been growing and there is a 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 the biodiversity and the indigenous knowledge system particularly associated with extraction and processing of natural dyes from the plants, because it has very rich flora. So, the flora being so rich it is adds on to the possibility of finding many more dye yielding plant then what we have in the planes or at this altitude.

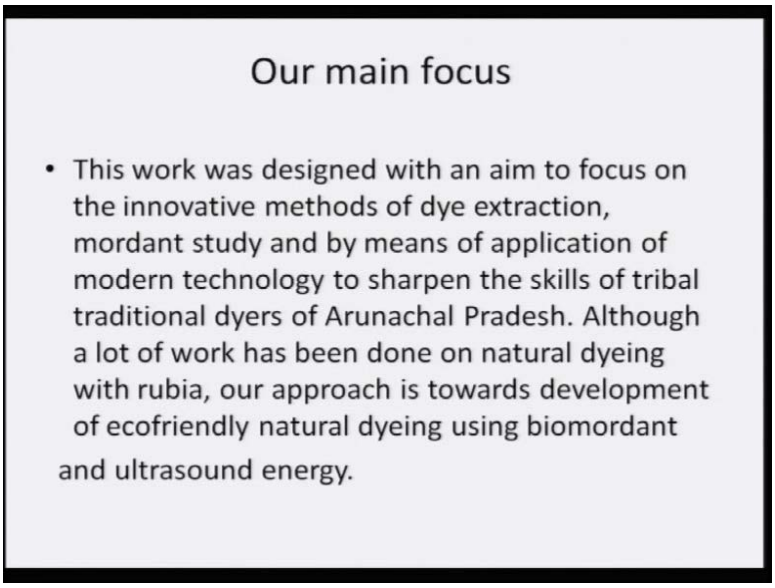
So, altitude, latitude really makes a lot of different plus soil condition, climatic condition everything adds on to different varieties of plants, and many, many dye yielding plants have been identified. And this identification was possible only because the local tribal people gave us this information that these are probable dye yielding plants, also although they did not know how to use it, and many times their extraction procedure was much tedious and as a result, because of the combustion process they were not a you know extracting the dyes instead they now switched over to synthetic dye. But they were still pockets of tribes who are practicing natural dyeing we make them we took lot of a you know traditional knowledge information from them and try to document, because otherwise this information would be loosed. And now is the time of the computer age

where we have to document all traditional information, so that it can be preserved for much greater time.

(Refer Slide Time: 11:47)

Traditionally some of the dyes of this maddar were being used by some 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 the 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 plant. So, since these were the few tribes which were at one point of time interested and were using natural dyes, we thought of contacting them because we could get the traditional knowledge from them.

(Refer Slide Time: 12:30)

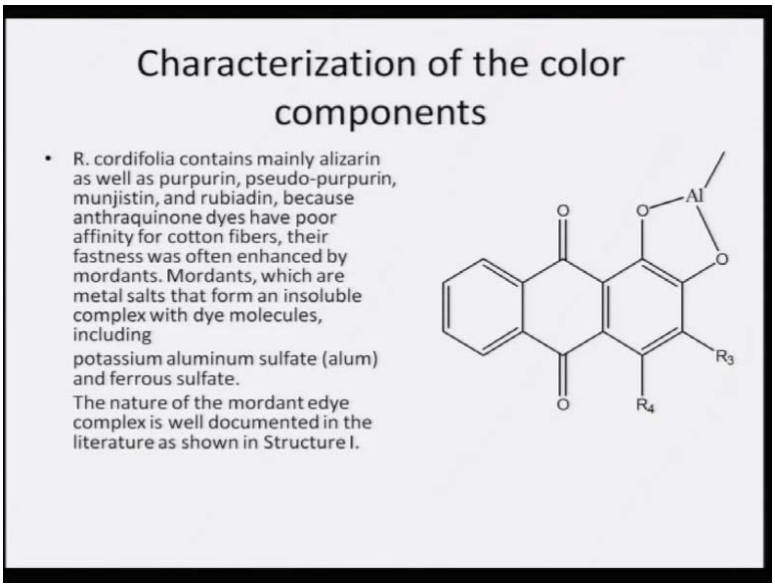


Our main focus: This work was designed with an aim to focus on the innovative methods of dye extraction, mordant study and by means of application of modern technology to sharpen the skills of tribal traditional dyer's of the Arunachal Pradesh. Although a lot of work has been done on natural dyeing with rubia, our approach is towards the development of eco friendly natural dyeing using bio mordant and ultra sound energy.

So, what we try to do? We did not invent a new dye; we did not discover a new dye; the dye was already there, but what we try to do? Because dyeing with rubia extract or maddar extract cotton was one of the biggest challenges that the textile industry would face, and we try to ease out that process by bringing in the use of bio mordant taking care of the echo friendliness of the process. So that less and less amount of affluent is generated and affluent which is non hazardous and most of the components should be bio degradable of that affluent.

The second point was how to enhance the dye uptake, because the toughness of the cotton dyeing is because cotton is very reluctant to take up the dye. The dye penetration is very poor. So, is there any other method which can enhance this process, and yes, we have an answer there is a process of ultra sound energy usage which can enhance the cotton the toughest of the tough material to have good dye penetration.

(Refer Slide Time: 14:31)

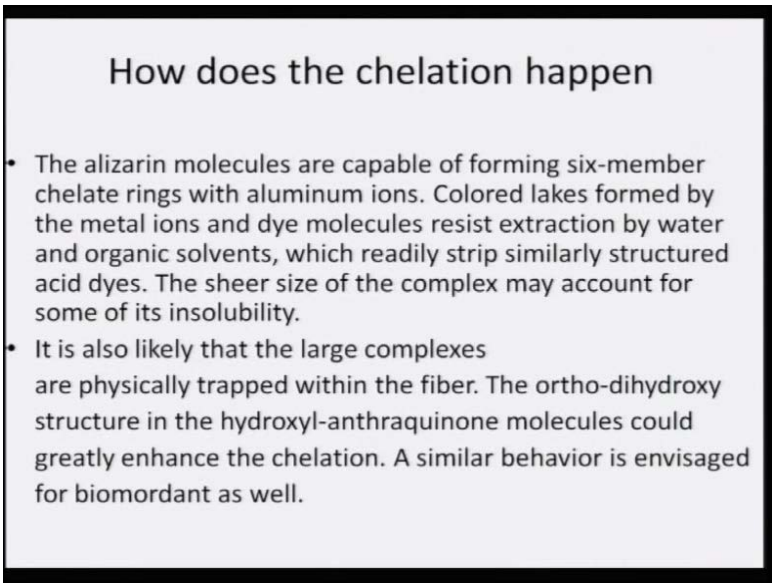


Now, then the next step is to look for the characterization of the color components, because as I have been talking about the dye compatibility - the dye structure compatibility with the fiber compatibility, unless until that is matched the dye will not be taken up by the fiber. So, it is it goes hand in hand unless we have a good understanding of what is the structure of the dye that is in the maddar extract; we will not be able to proceed.

Rubia cordifolia mainly consists of 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 potash alum sulphate that is the common aluminum sulphate which is commonly called as alum and with ferrous sulphate.

The nature of mordant dye complex is well documented in the literature and it has been shown; that this is how that the dye hydroxyl compound of the anthraquinone moiety actually chelates with the aluminum trivalent aluminum then forms a bond covalent bond with the dye hydroxyl which are ortho to each other. So, this is a common structural detail of one of the alizarin - this is an alizarin molecule, and pseudo purpurin or purpurin are nothing but differently substituted groups that are present on the a, b, c ring under a and c ring rather.

(Refer Slide Time: 16:40)

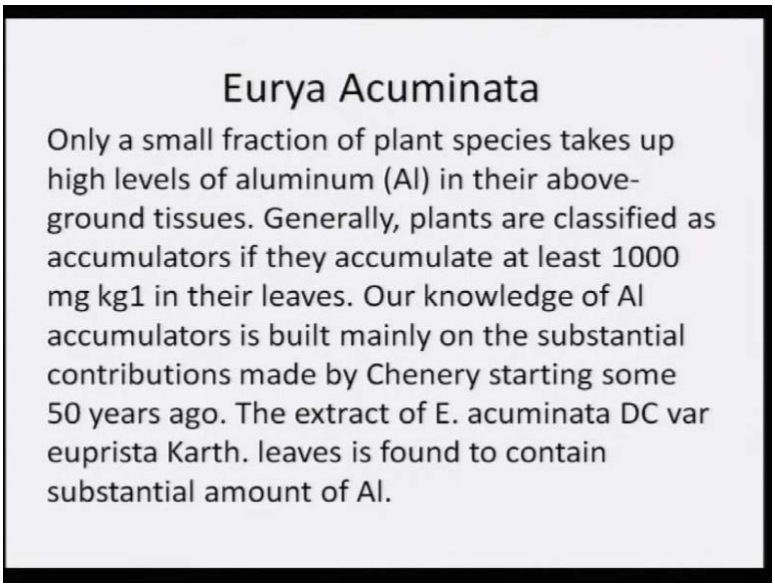


How does the chelation actually happen? The alizarin molecules are capable of forming six-member chelate rings with aluminum ions. Colored lakes formed by the metal ions and dye molecules resist extraction by water and organic solvents, which readily strip similarly structured acid dyes. The sheer size of the metal may or the complex may be may account for some of its insolubility. It is also likely that large complexes are physically trapped within the fiber. The ortho-dihydroxyl structure in the hydroxyl-anthraquinone molecules could be greatly enhance it could be responsible for the chelation. A similar behavior in envisaged for bio mordants as well.

So, just now I showed you that if alum is added to alizarin how does the structure look like, and how does the chelation with the covalent bond forming between the aluminum and the oxygen of the hydroxyl group present on the anthraquinone moiety can be envisaged.

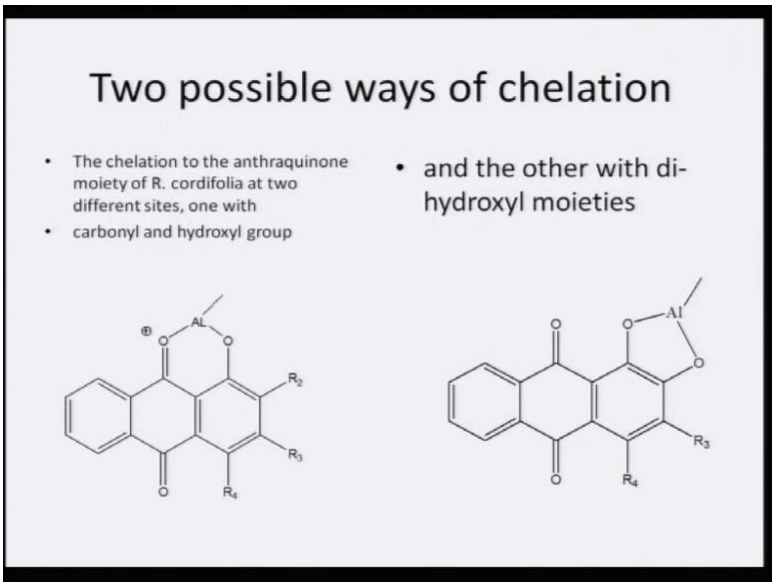
When we try to look at the, you know details of analytical details of eurya acuminata plant which is also one of the plants available in Arunachal Pradesh and the tribal people told us that they always use this plant and co extracted with madder leaves, stems, and roots. So, we did not know why they were using this particular plant, and in order to understand and they said that color definitely showed deepening and the fastness improved if they added this plant also at the time of extraction. Obviously there has to be some kind of chemical which must be responsible for this dye enhancement.

(Refer Slide Time: 18:52)



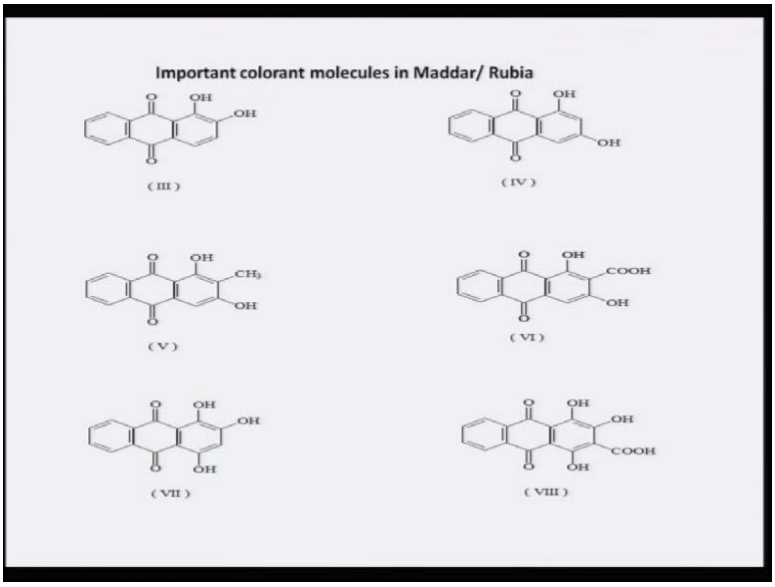
Only a small fraction of the plant species takes up high levels of aluminum in their above ground tissues. Generally, plants are classified as accumulators if they accumulate at least 1000 mille gram per kilogram in their leaves. Our knowledge of aluminum accumulator is built mainly on the substantial contribution made by Chenery starting some 50 years ago. The extract of aluminum Eurya acuminata DC var euprista euprista Karth. leaves is found to contain substantial amount of aluminum. And the low and we hold we found that it does contain aluminum and that is what is playing a very vital role when the extraction process was carried out.

(Refer Slide Time: 20:15)



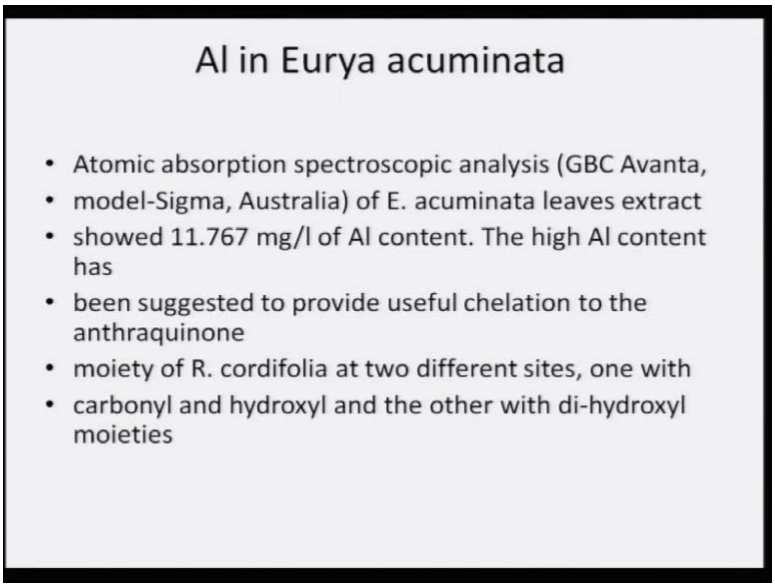
Two possible ways of chelation is either the two hydroxyl groups on the ortho position can chelate with aluminum, or the carbonyl and the hydroxyl you know which are adjacent to each other can chelate. So, these are the two possible ways of chelation. So, in both the cases the aluminum still remains tridentate, but the oxygen when it becomes trivalent has a positive charge when the carbonyl is participating.

(Refer Slide Time: 20:28)



Now, from the maddar extract it was possible to identify although the literature is already very full of the information that madder has these 6 compounds; that is we just named them that alizarin, purpurin, pseudo purpurin, rubiadin and so on and so forth. And you will see that the basic skeletal structure remains the same. It has an anthraquinone structure and apart from that it has auxochromes which could be different; it could be ortho dihydroxyl; it could be meta dihydroxyl; it could be meta dihydroxyl with the methyl group in between; it can have a carboxyl group in between, and it can have you know tri hydroxyl groups or it can have tri hydroxyl with the carboxylic groups. So, various types of structural structurally different compounds substituted or a work the present in the maddar extract.

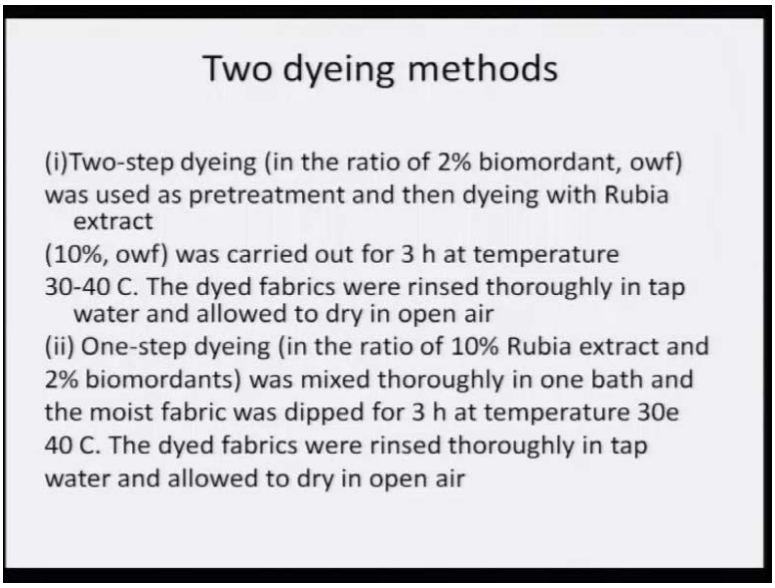
(Refer Slide Time: 21:44)



We try to analyze the aluminum content in Eurya acuminata. Atomic absorption spectroscopic analysis by, you know this GBC Avanta, model showed that the leaves showed 11.767 mille gram per liter of aluminum content. The high aluminum content has been suggested to provide useful chelation to the anthraquinone moiety of the rubia cordifolia at two different sites, one with the carbonyl and hydroxyl and the other with the dihydroxyl moieties. So, we have shown both the structural details, how the chelation is possible at two sites, and with two types of participation - one with carbonyl and hydroxyl between carbonyl and hydroxyl; and the other one between two hydroxyl.

Once you understand the chemistry, it will be able it will be easy for you to understand why this eurya was added at all; what was the role of eurya, because of the aluminum that is present and that is enough amount of aluminum is present to do these two types of chelation. And because the maddar consists of six different types anthraquinone quinoid dyes it is not just one single alizarin compound we have seen that. So, these six structures actually all are participating in the dyeing process and that is why it is understandable to see that structure plays a very vital role in proper understanding of the chemistry of dyeing.

(Refer Slide Time: 23:37)

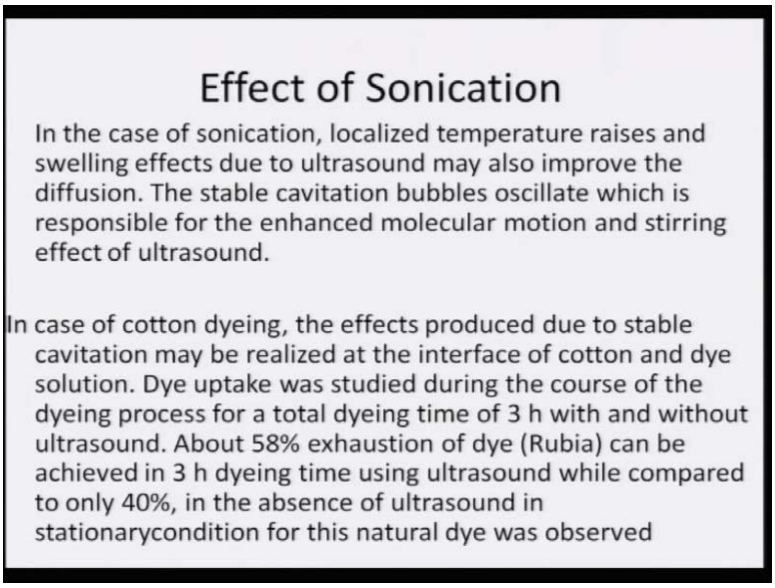


Then we develop two different methods for dyeing. As what we have done mostly, we have used two step dyeing in this in the ratio of 2 percent bio mordant, 2 percent with respect to the fabric weight was used as pretreatment and then and then the dyeing with Rubia cardifolia extract was carried out which was about 10 percent weight of the fabric and it was carried out for 3 hours at temperature between 30 to 40 degrees. The dyed fabric was rinse thoroughly in tap water and allowed to dry in open air.

Similarly, the process was repeated in sonicator because every time we say that any method is better we cannot just say it is better, but we have to make a comparison the conventional method was compared with the sonicator method both the two method as well as the one step method.

The ratio's and all other parameters were kept at the same, except in the case of conventional method - it was heated to about 72 to 80 degrees for 3 hours where as in the case of sonicator. It was just sonicated at room temperature between 30 to 40 degrees, and it was not heated externally. One step dyeing process in the ratio of 10 percent Rubia extract and 2 percent by bio-mordant was mix thoroughly in one bath and the moist fabric was dipped for three hours at room temperature between 30 to 40 degrees. The dyed fabrics were rinse thoroughly in tap and allowed to dry in open air. So, the process of the one step was that the mordant that is the bio mordant was added to the dye bath simultaneous or meta mordanting with bio mordant was carried out.

(Refer Slide Time: 25:34)

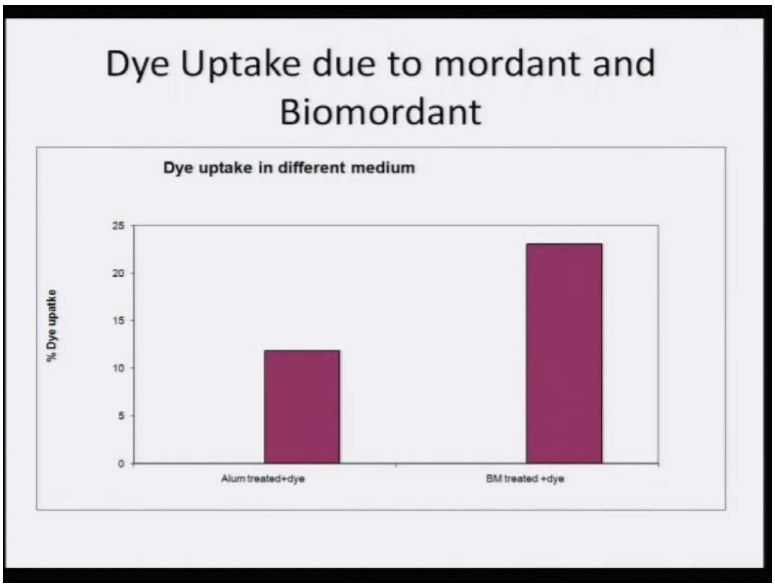


Effect of sonication: Now, as what I said we tried to do both the process, so that we can compare. In case of sonication, localized temperature raises and swelling effects due to ultrasound may also improve the diffusion; the diffusion of the dye extract. The stable cavitation bubbles oscillate which is responsible for the enhanced molecular motion and stirring effect of the ultrasound. So, because of this particular you know agitation method, it is possible to do this in a much faster manner and in a more effective manner.

In case of cotton dyeing, the effects produced due to stable cavitations may be realized at the interface of the cotton and dye solution. The dye uptake was studied during the course of dyeing process for a total dyeing time of 3 hours with and without ultrasound. So, that is what I mean that conventional method and ultrasound method was done side by side. So, has to come to a conclusion whether this method is better or not so good.

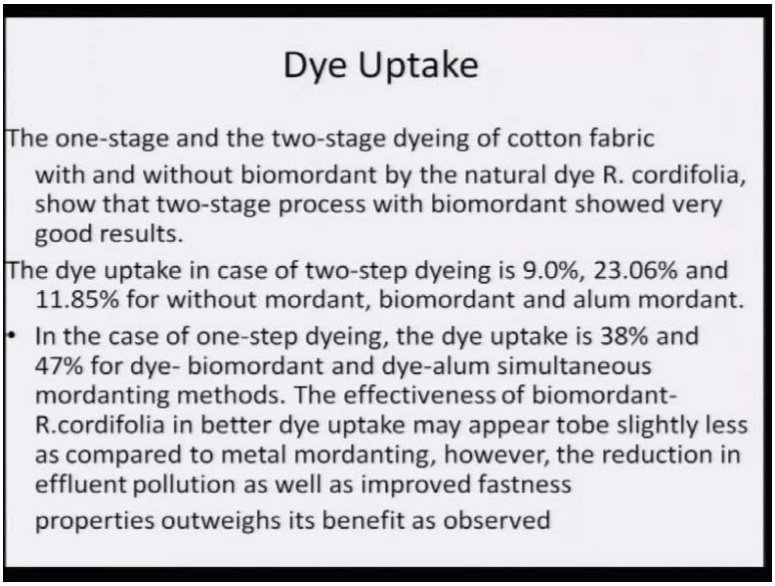
About 58 percent exhaustion of the dye that is Rubia can be achieved in 3 hours dyeing time using ultra sound, while compare to that only 40 percent in the absence of ultra sound in stationary condition for this dye natural dye was observed. So, they were very discrete and very you know different values it is not just marginal enhancement. So, 58 percent, we service 40 percent 18 percent enhancement is a big amount of dye uptake if one tries to look at the industrial process.

(Refer Slide Time: 28:06)



Now, dye uptake due to mordant and bio mordant also work and you know compare, and it was seen that alum treated material; that means, if a metal salt is used. Then the the enhancement as compare to the bio-mordant when it is you know used. You can see from the graph that the dye uptake in different medium that is different mordant medium; one is alum added separately or bio-mardant treated fabric shows this kind of dye uptake changes.

(Refer Slide Time: 28:27)



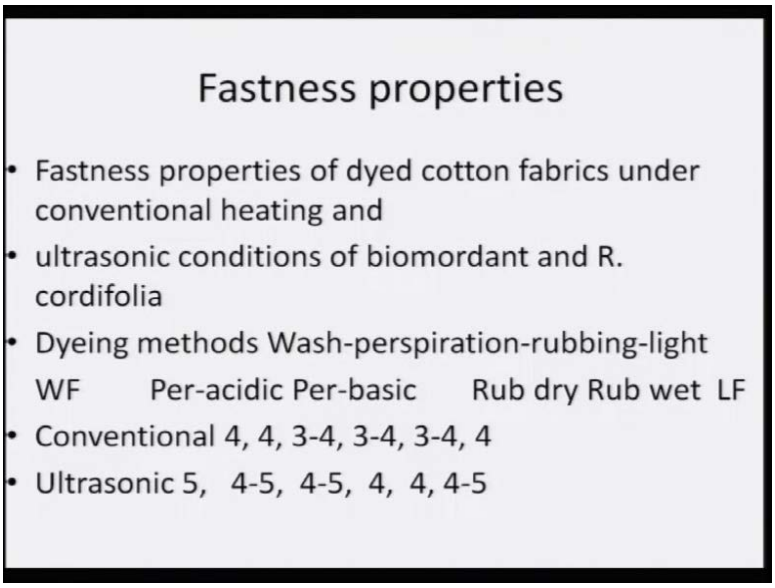
The one-stage and the two-stage dyeing of cotton fabric with and without bio-mordant by the natural dye Rubia cordifolia, show that two stage process with bio-mordant showed very good results. The dye uptake in the case of two-step dyeing is 9 percent, 23 percent and 11 percent for without mordant, bio-mordant and alum mordant respectively.

So, you see that if no mordant was used nine percent dye up take that can taken place. But if bio mordant was used 23 percent of the dye uptake took place, and almost half of that or even less than half eleven percent was taken up by the alum mordanted fabric. In case of one step dyeing the uptake is 38 percent, and 47 percent for dye bio-mordant and dye alum simultaneous mordanting method.

Now, there in the simultaneous mordanting method we did not find the effectiveness of bio mordant Rubia cordifolia in better dye uptake may appear to be slightly less, but looking at the metal mordanting problems; however, the reduction in effluent pollution as well as improved fastness properties actually out ways the benefit. So, the difference here is only 9 percent, but the enhancement if you try to look at so you know one has to say what is good and how can it be done. It is not always that you know you have to just look at one parameter, of course, that one parameter dye up take is the most important parameter, but a fluent treatment the cost of affluent treatment and all those, and the time consumption and the you know energy consumption, everything needs to be calculated when we are dealing with industrial processes.

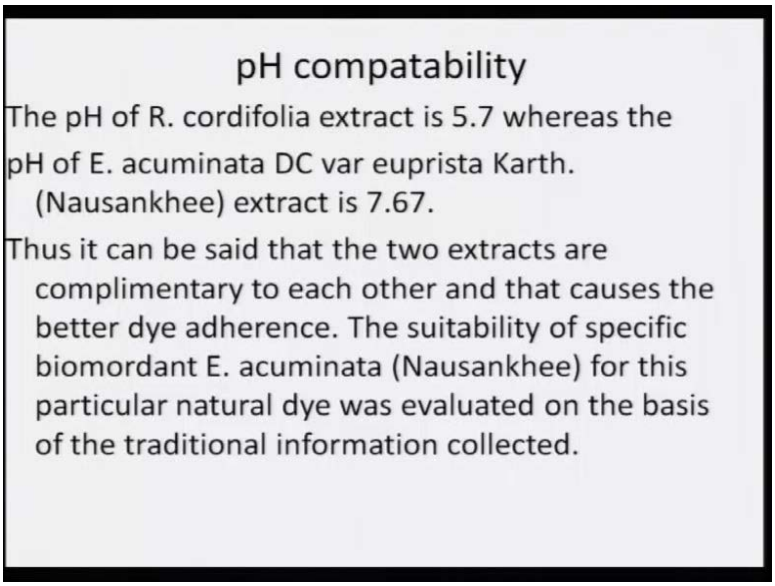
When we try to look at the fastness properties of the dyed fabric, we find that ultrasonic fabrics have superior fastness properties as compare to the conventional ones. And you will see that washing perspiration, rubbing, light fastness everything both the perspiration acidic and the perspiration basic then rubbing dry, rubbing wet, light fastness, wash fastness they are all lower in value, when we look at the conventionally dyed swatches, but when we look at this ultra sonic dyed swatches they are all one step you know above in the gradation scale.

(Refer Slide Time: 31:16)



If these are in the 4 scale they are in the 5 scale. So, you one can understand that the fastness as also improve by the use of ultrasound. Actual aim of using any new technology should go in the betterment and in ways of either reducing the time, reducing the cost or doing some kind of additional property which did not exist in the conventional processes. Thus then only it will be accepted by the industry; otherwise it has no meaning it will just be an academic exercise, and it will just remain in the laboratory, and nobody will practice it. When it order to make it more popular, it has to have some you know added advantage.

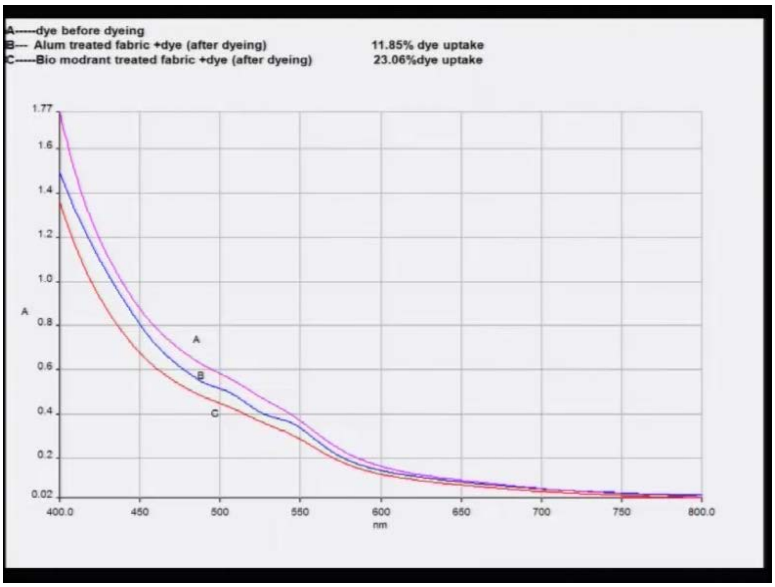
(Refer Slide Time: 32:34)



Another you know observation that we made was that it has a pH compatibility also the pH of the Rubia cordifolia extract is about 5.7 where as the pH of the Eurya acuminata extract was found to be 7.67. Now does it can be said that the two extracts are complimentary to each other and that causes the better dye adherence. The suitability or specific bio mordant that is Eurya acuminata or Nausankhee as what the tribal people call it for this particular natural dye was evaluated on the basis of the traditional information collected.

Now we also try to look at you know whether it is making any pH change or whether it is rarely you know just adding as a source of aluminum, you know all those details we try to narrow down all the information. So that now every information about this new bio-mordant planned should be available to everybody, and that is why you know we try to do all this analytical methods to find out the amount of aluminum that is present in eurya and amount of you know the the pH of each of this each of this solution and so on and so forth.

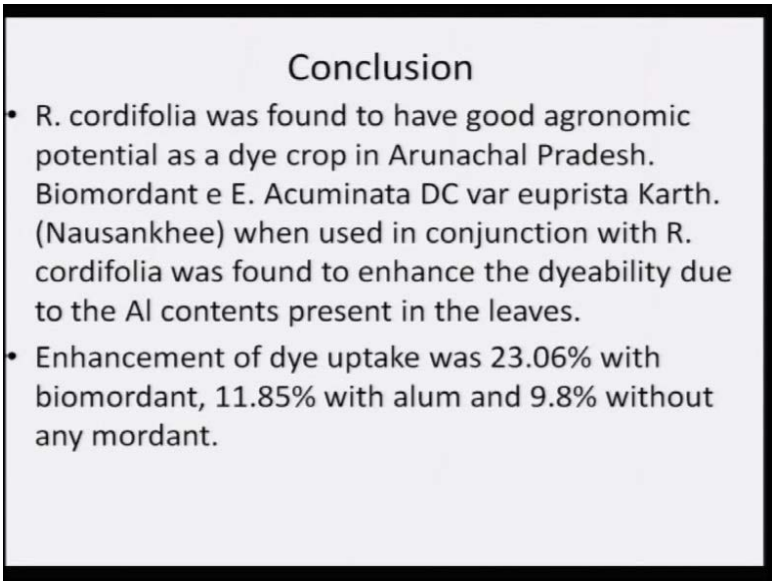
(Refer Slide Time: 34:02)



Now I would like to show you this graph particularly because if the dye concentration is represented by A - that is dye is the dye solution before dyeing; no fabric has been dipped. When alum mordanted fabric is a dipped into this dye solution it gives a graph of B, and when bio-mordanted treated fabric is dipped in to the same dye bath of the same concentration, and that is how we were able to calculate the dye uptake with the help of

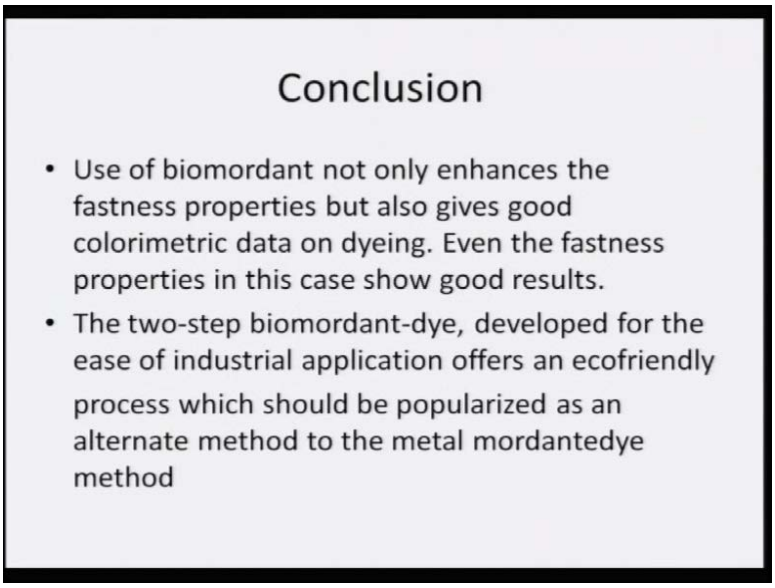
UV visible spectrometer. So, it is not an arbitrary way of calculation, but whatever remains back in the dye bath is the dye solution after dyeing, and whatever has been the loss from the initial dye bath concentration to the present dye bath concentration has gone into the fabric. So, this difference actually gave us the percentage of dye uptake and in the alum treated case, it was 11.85 percent whereas bio-mordant treated fabric showed 23.06 percent dye uptake.

(Refer Slide Time: 35:27)



So, if we have to conclude, I would say that Rubia cordifolia a very prominent anthroquinone dye was found to have good agronomic potential as a dye crop in Arunachal Pradesh. Bio-mordant that is a Eurya acuminata or Nausankhee when used in conjunction with Rubia cordifolia was found to enhance the dye ability due to the aluminum content present in its leaves. Enhancement of dye up take was about 23.06 percent with bio-mordant and 11.85 percent with alum, and if no mordant was used the dye uptake was about 9 percent.

(Refer Slide Time: 36:16)



Use of biomordant not only enhances the fastness properties, but also gives good colormetric data on dyeing - that is the CIELAB values, the L A B values, the k by s values were very good. Even the fastness properties in this case show very good results, and we have seen that ultrasound use has rarely brought the dye to A grade dye category; even for cotton where it was almost like C grade category, because of the problems of the poor dye uptake can poor fastness properties and so on and so forth.

The two-step bio mordant dye, develop for the ease of industrial application offers an eco friendly process which should be popularized in an alternate method to the metal mordant dye method. So, you see what we try to do? We try to you know summarize the whole process or the dyeing process could be popularize in a different way by popularizing. Firstly, the use of Eurya acuminata in place of metal mordanting then in the process of dyeing we eliminated the conventional long method on the contrary we did the ultrasonic dyeing at room temperature thereby saving the cost of energy, and even time. And we service we got benefits which were much important for a dyer, because it showed very s good dye uptake. As a result the dye bath also had now lower concentrations of dye remaining for disposal. So, the whole process was developed with keeping in mind that how technology can be coupled with traditional information.