Natural Dyes

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Lecture No. # 37

In the series of natural dyes, we now come to yet another natural dye which is in the category of flavonoid dyes, and the representative plant that we have chosen with which we did work in great detail in order to show its usability, and the plant is called Eclipta Alba. Eclipta Alba was found abundantly in our place and as a result we thought this can be taken up as a representative flavonoid dye component from the natural dye series.

We have learnt about anthocyanins, we have learnt about indigoids, we have learnt about anthraquinoids and we have also learnt about carotenoids. Now, it is time to look at the most abundantly available colorant called the flavonoids, and the plant that we choose which was for the first time used as a natural dye component for textiles from our laboratory.

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This is how the plant looks like. This is a common Eclipta Alba plant which is like a creeper and this was used.

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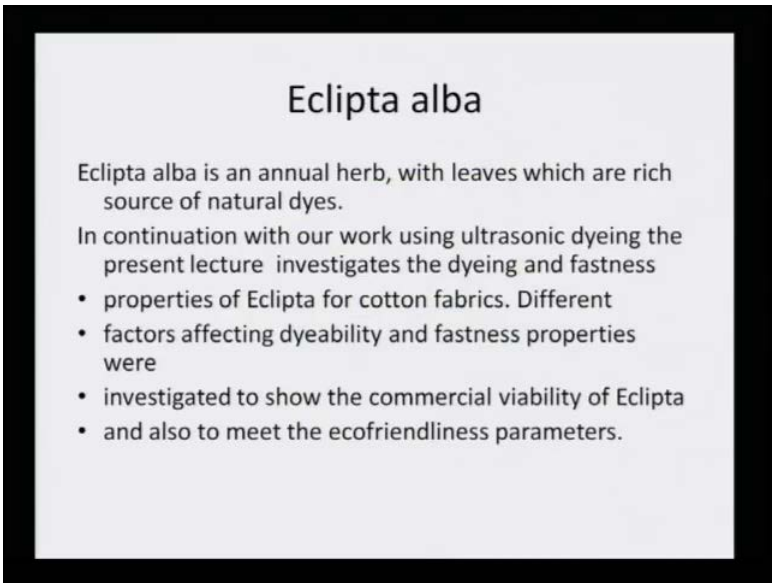

So, Eclipta Alba is an annual herb, with leaves which are rich source of natural dyes. In continuation with our work using ultrasonic dyeing the present lecture investigates the dyeing and fastness properties of Eclipta on cotton fabrics. Different factors affecting dye ability and fastness properties were investigated to show the commercial viability of Eclipta and also to meet the eco-friendliness parameters.

So we were trying to see, whether it be fits a dye category or not, and for fitting into the dyeing category, the dye source or the extract must be very compatible with the cellulosic material, because time and again I have told you that cellulosic material are most difficult to dye. And if we can use any extract for cellulosic fiber using it for other fibers like protein, proteinaceous fibers or synthetic fibers will not be such a big challenge and that is why we use, we try to use this extract primarily for cotton. Because if as it the saying goes if the (( )) is you know one by cotton dyeing then the rest will all follow.

So, the same way we try to look at the fastness properties that were related whether it is giving good fastness property and whether it is first and the fore most thing that comes to our mind, does it give a continuous source of colorant? Because if we are dependent on seasonal plant. We will have to wait for that season to come then only the flower will be available or the plant part will be available for dye extraction, but here was an annual

herb which is a perennial herb and leaves could be taken off, it is a renewable source of material that can be utilize for extraction of dye.

The next point that comes to mind is, what is the kind of dye to fiber compatibility and we found that yes it has a good compatibility. Then we try to in our exercise of popularizing sonicator, we tried to show that does it you know also does this dye from the Eclipta - the Flavonoid dye from the Eclipta help to get adhered more by sonication method or is it that the conventional method is better for this dye.

So, this kind of continuous parallel studies we did for various dyes of different origins or belonging to different chemically chemical class of compounds and we came to a conclusion that flavonoids are also very compatible - first thing. Second thing is that we found out that, these Flavonoid dyes have a very beautiful chemistry of chelation just the way the anthraquinoid dyes or the anthrocynin dyes chelate with the metal. So, now the question was can we also replace the metal because the second exercise that we were emphasizing in our laboratory that is, it possible to replace the metal mordanting step with either a bio mordant or a by enzymes and those kind of exercises we did with the Eclipta and we came to a conclusion that yes it is a good, you know member of the natural dye series which can be explored for commercial dyeing.

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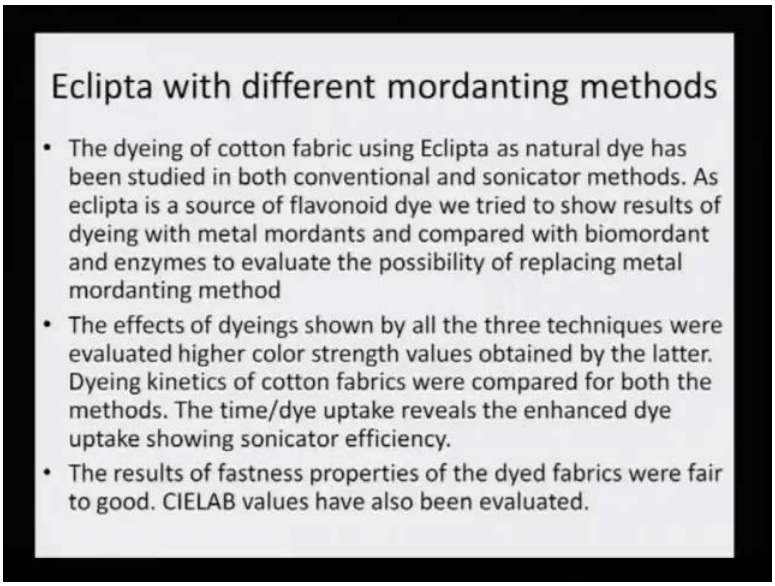

So therefore, we try to work with Eclipta with different mordanting methods the dyeing of cotton fabric using Eclipta as natural dye has been studyied in both conventional and

sonicator methods. As Eclipta is a source of Flavonoid dyes, we tried to show results of dyeing with metal mordants and compared it with biomordant and enzymes to evaluate the possibility of metal mordant replacing the metal mordanting method.

So you see that, the whole exercise may appear to be similar but since this is different class of compound called the flavonoid dyes. We did this exercise with anthrophinoid dyes, we did the same exercise with anthrocynin dyes and when we were successful in finding that natural dyes are having a good compatibility with cotton then, those were screened out in the lab and suggested to the industry, that these are some of the newer sources of natural dyes.

The effect of dyeing shown by all three techniques were evaluated higher color strength values obtained by the latter. That is the possibility of using bio mordants and the enzymes. Dyeing kinetics of cotton fabric were compared for both the methods. We tried to see, whether really there is any kind of dye enhancement, dye uptake enhancement with the help of sonicator or not because unless and until we establish that, we cannot say that sonicator is better than conventional. So, that is the reason why conventional dyeing method that is the regular you know boiling method was tried out and let me tell you, that Eclipta gave a very good solution or extraction with water.

So, there was no need to add any HCL or any base, because the dye itself precipitated in a very fine manner. The time and dye uptake reveals the enhanced dye uptake showing sonicator efficiency. So with even tried to see, whether rarely there is any contribution or efficiency made by the dye or not, or by the sonicator method or not, because each dye as I told you, has its own reactivity with the fiber. How much it will penetrate, what kind of bonding it will form with the fiber, whether it will be ionic bonding or coordinate bonding or covalent bonding or hydrogen bonding or wander wall forces or electrostatic forces, we have learnt it all in different aspects. Now is the time to co-relate these with keeping in mind the chemistry of the fiber and the dye.

So, it was important to take a look at what is the structural detail of the Flavonoid dyes. The results of fastness properties of the dyed fabrics were fair to good. CIELAB values were also evaluated because you see, unless and until we evaluate the CIELAB values, it will not be clear what kind of shades are obtained from these dyes, because you may think it is giving green, I may think it is giving some other shade of light yellowish

green. So, that discrepancy can be completely removed if we have IUPAC nomenclature kind of naming system and here it is a numeric number system for describing a color which is done by the CIELAB values.

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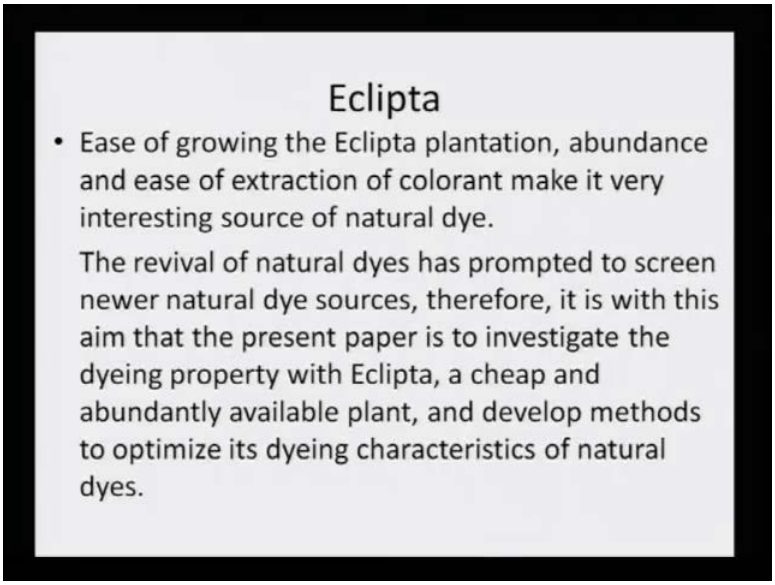

So now this Eclipta plant let us try to see, how easy it is to grow the ease of growing the Eclipta plantation, abundance and ease of extraction of the colorant make it an interesting source of natural dye. Because you see, if the extraction process or the availability or (( )) you know agronomics is very difficult. One cannot depend on this kind of natural dye source. So, here was a candidate which had ease of growing, ease of plantation, ease of extraction and it was abundantly available to the user. The revival of natural dyes has prompted to screen newer natural dye sources therefore, it is with this aim that the present world, I has been investigated and the dyeing property of Eclipta a cheap and abundantly available plant and developed methods to optimize it is dyeing characteristics has been described. Because see, this is a new source, so we have to find out all the details of this new source.

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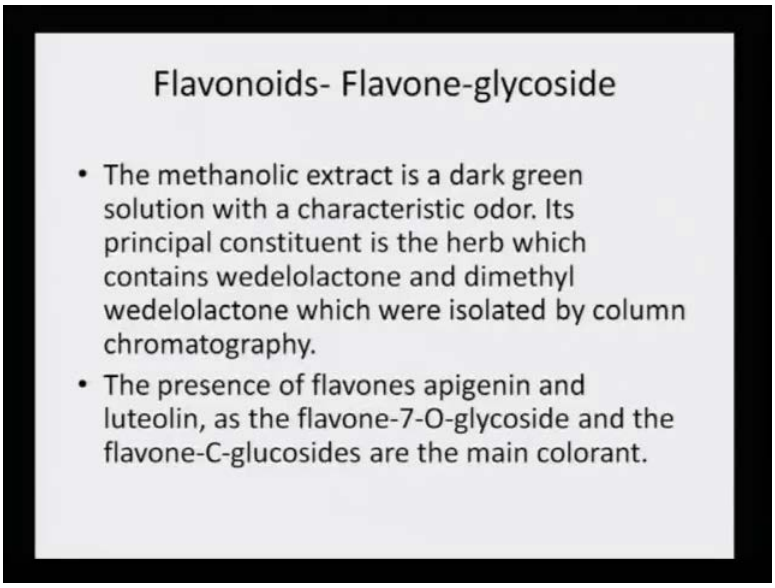

So looking at the chemistry, because I have already mentioned that, it is a flavonoid dyes, it is basically a flavones- glycoside. The methanolic extract is a dark green solution because it is a leaves extract, so obviously, some chlorophyll will run into it with the characteristic odor. It is a principle constituent is the herb which contains wedelolactone and dimethyl wedelolactone, which were isolated by column chromatography,but these lactones do not participate in dyeing.

It is the presence of the flavone particularly the apigenin and the luteolin, as the flavone 7-0-glycoside rather 7-O-glycoside and the flavones-C-glucosides are the main colorant. So you see that, these are the two main compounds which are abundantly present in the leaves apart from chlorophyll, and because of the green color of the chlorophyll this yellow looking dyes are completely must when it comes to the extract, but never the less they are prominently present and are the main constituent of the extract.

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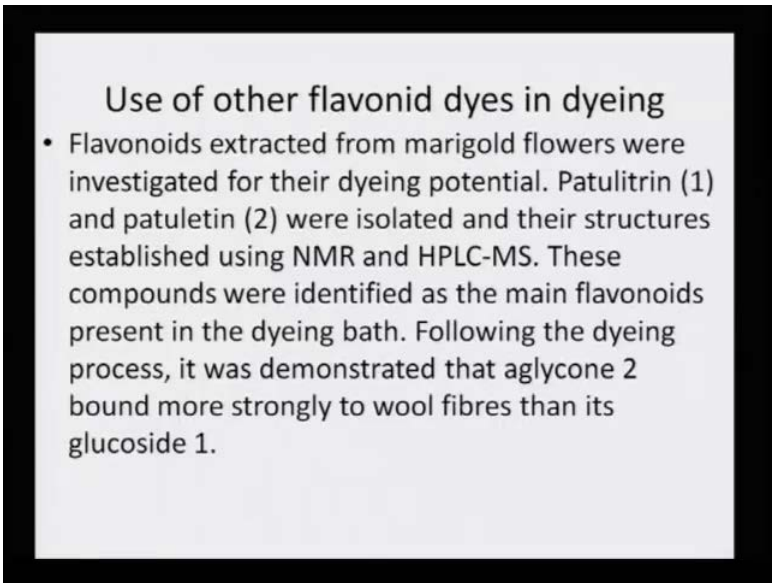

The use of other flavonoid dye has been presidentent in the literature. So, we know that it is not the first time or the first dye of the flavonoid series that we have used. Nobody use Eclipta, as a source of flavonoid dye that is true, but there were other flavonoids extracted from marigold flowers and were investigated for dyeing potential. Patulitrin and patuletin were isolated and their structures established using NMR and HPLC-MS. These compounds were identified as the main flavonoids present in the dye bath. following the dyeing process, it was demonstrated that the aglycone 2 bound more strongly to the wool fibers than it is glycoside which is one.

So that means, the aglycone is the one which is more deeply or strongly attached to the fiber. The glucoside is just hanging there because it is present in the nature or in when it is extracted, it has a glucoside. But that glucoside or glycoside is hydrolyzed and the aglycone is the one which form the strong bond with the fiber.

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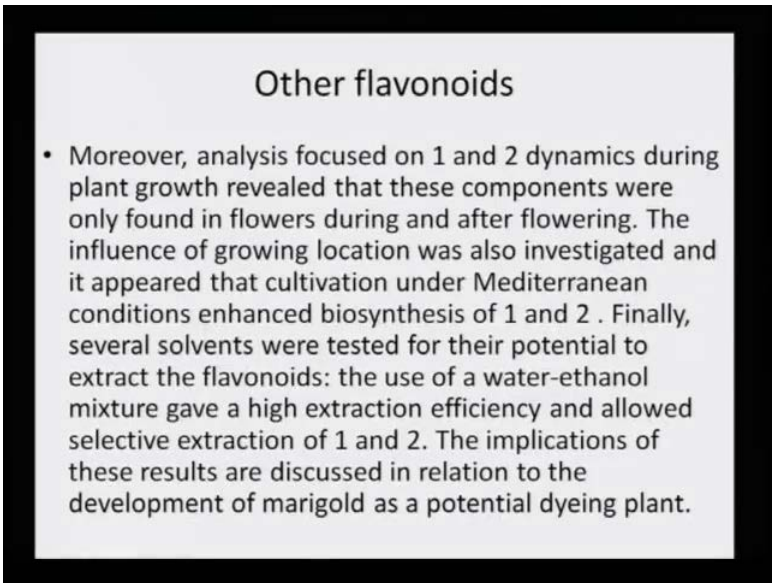

Other flavonoids documented are moreover analysis focus that, the number one; that is the glucoside and number two dynamics during the plant growth revealed that these components were only found in flowers during and after flowering. The influence of growing location was also investigated and it appeared that cultivation under mediterranean conditions enhance the biosynthesis of the formation of the aglycone and the glucoside.

Finally several solvents were tested for their potential to extract the flavonoids the use of water ethanol mixture gave high extraction efficiency and allowed selective extraction of the aglycone and the glucoside.

The implications of these results are discussed in relation to the development of marigold as a potential dyeing plant. So, a whole lot of exercise with marigold flavonoids had been carried out. So, we had a kind of you know, chart to work with, we knew how to proceed, what are the essential steps that we should take in order to extract the flavonoid dye, how should we isolate the flavonoid or how should we characterize it, because it is important to then be able to say with lot of confirmation that the Eclipta alba extract has abundance of flavonoid which participate in the dyeing process.

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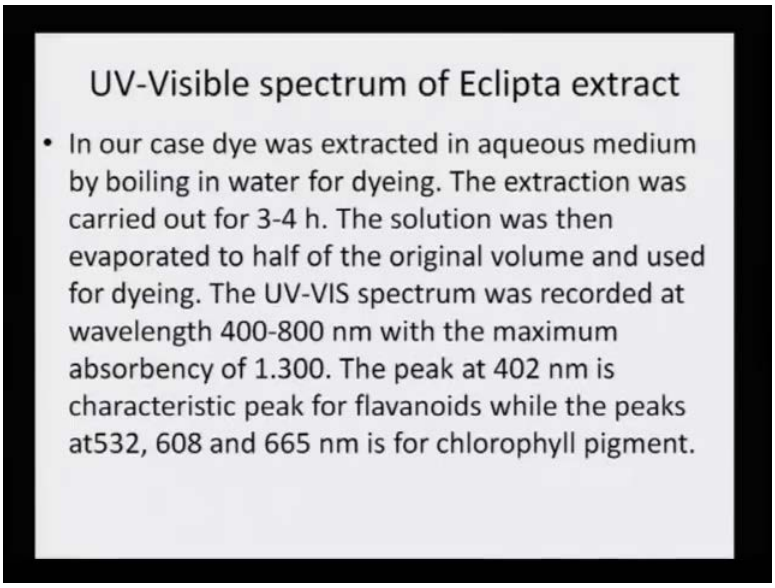

So, we took help of the UV visible spectrum of Eclipta, and we found that in our case the dye was extracted in aqueous medium by boiling in water, and then it was the same extract was actually used for dying after concentrating it for by fifty percent. So you see, no acid is added. Simply the leaves of ecliptic Alba plant are taken even the stems have a lot of colorant. So, they are all chopped off and boiled in water.

The extraction was carried out for three to four hours. The solution was then evaporated to half of its original volume that is what I said that it was reduced for dyeing, because you see, otherwise it will be a very dilute solution and the color will on the fabric will appear very faded. So, for that matter, we need to concentrate the dye extract and once it is evaporated to fifty percent. That means, it is concentrated to 50 percent.

The UV visible spectrum was recorded at wavelength between 400 to 800. Now, this is a visible region with the maximum absorbency of 1.300. The peak that appeared at 4.2 nanometer is characteristic peak for flavonoids while the peaks at 432, 608 665 nanometers were for chlorophyll pigment. So, it co extracted because water is such a universal solvent that along with flavonoids both the chlorophyll pigments also came along. Now, if one has to take a look at the UV visible spectrum of the extract, if the visible region that is from four hundred to eight hundred nanometer in shows, that there is the distinct peak at 402 then, there is a peak at about 475 and so on, and so forth. So,

these are some very characteristic flavonoid peaks and it at atleast goes to proof partially that flavonoids are definitely a part of the extract.

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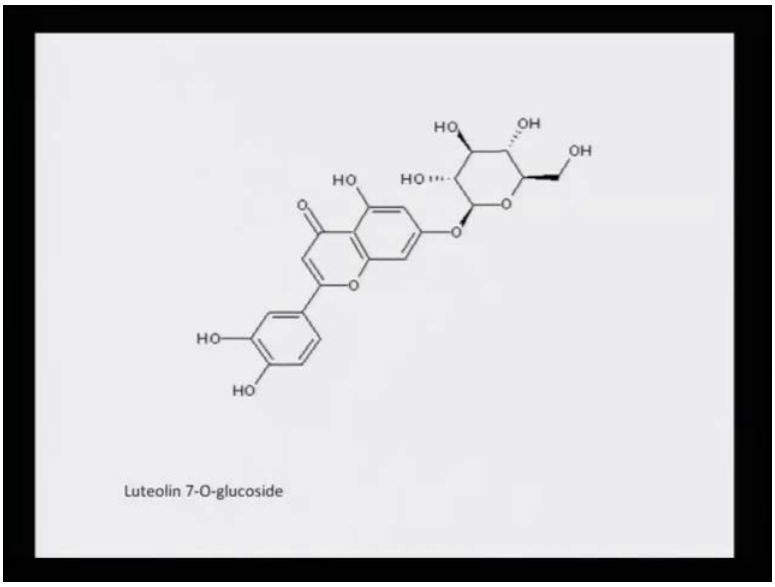

Now, looking at one of the molecules, see this is the structure of luteolin 7-O-glucoside. Now, the glucoside is hanging on the top and then is the benzonoid ring which has one hydroxy and the thirds ring has two hydroxy. Now, these two hydroxy's are actually ortho to each other very ideally suited for metal chelation. So you understand that now, by looking at this particular one flavonoid I have taken, although it has epigenin and other flavons also. But this itself give you an insight that how beautifully now the metal or the enzyme or the bio-mordant can chelate, because it has the right kind of appendage for chelation.

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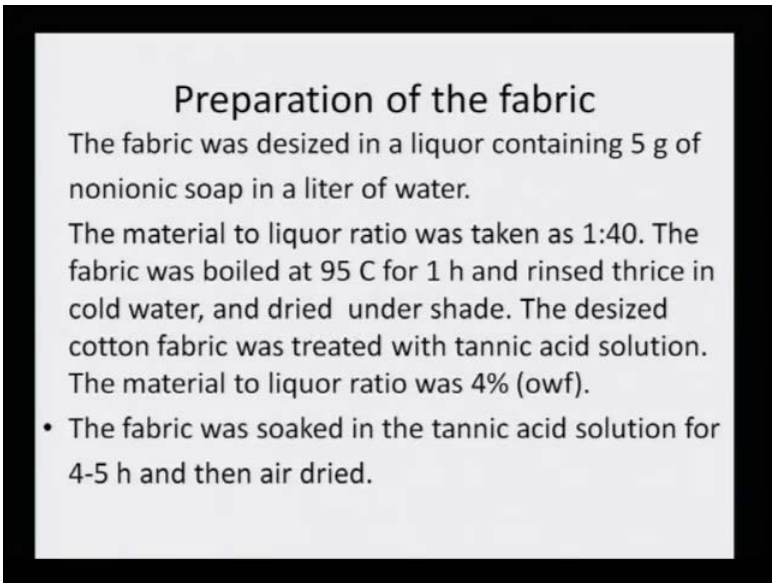

Now as what we know, that every fabric has to be treated before dyeing can be started. So, the fabric was desized in a liquor containing five gram of nonionic soap in a liter of water. The material to liquor ratio was taken as 1:40. The fabric was boiled at ninety five degrees for one hour and rinsed thrice in cold water, and dried under shade. The desized cotton fabric was rather discovered fabric was then treated with tannic acid solution.

The material to liquor ratio was four percent the weight of the fabric. Tannic acid treatment is a must, when we are dyeing cotton and time and again, when we have spoken about natural dyeing I have told you that this particular step cannot be avoided. For the simple reason, that cotton does not have enough of hydroxy groups free to chelate with the metal or with the dye or the metal chelated dye. So, in that case, this tannic acid treatment then offers linking group or attachment groups ready to attach the chelated dye. So, that is the role of tannic acid.

This treatment is not required in when we are doing the dyeing of silicon wool. For the simple reason, that there the amide linkages have CO and NH 2 and these are quite efficient in forming hydrogen bonding and covalent bonding and so on. And therefore, this kind of tannic acid treatment is just not required, when we are talking about dyeing of silicon wool, but in case of cotton I have told you, and again I am telling you, that tannic acid treatment is a must and the role of tannic acid is to provide appendages or linking heads. So, that the chelated dye can attach.

The fabric was soaked in tannic acid solution for three to four hours even or it can be four to five hours, but it should be freshly treated with tannic acid. One cannot keep the tannic acid treated fabric for too long. And then, it is air dried.

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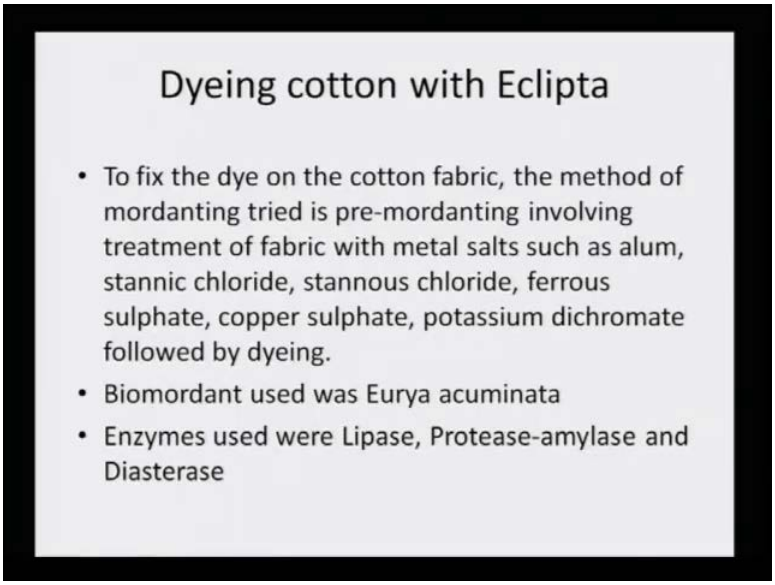

The Dyeing cotton with Eclipta extract to fix the dye on the cotton fabric, the method of mordanting tried is pre-mordanting involving treatment of fabric with metal salts such as alum, stannic acid, stannous chloride, stannic chloride, stannous chloride, ferrous sulphate, copper sulphate, potassium dichromate and then it is followed by dyeing.

Or we can use bio-mordant such as Eurya acuminate and we know that, in Eurya acuminata there is sufficient amount of aluminum or we can use enzymes such as lipase or protease-amylase combination or Diasterase. So, these are some of the mordanting methods that we applied. Metal mordanting was only done for comparison say, because we were trying to replace this metal mordanting with the help that and in order to show the efficacy of the biomordant and the enzyme. We had to make a comparative data between the metal mordanting prevalent method with these two methods. Now, we have learnt one thing that pre mordanting and dyeing gives raise to two different steps.

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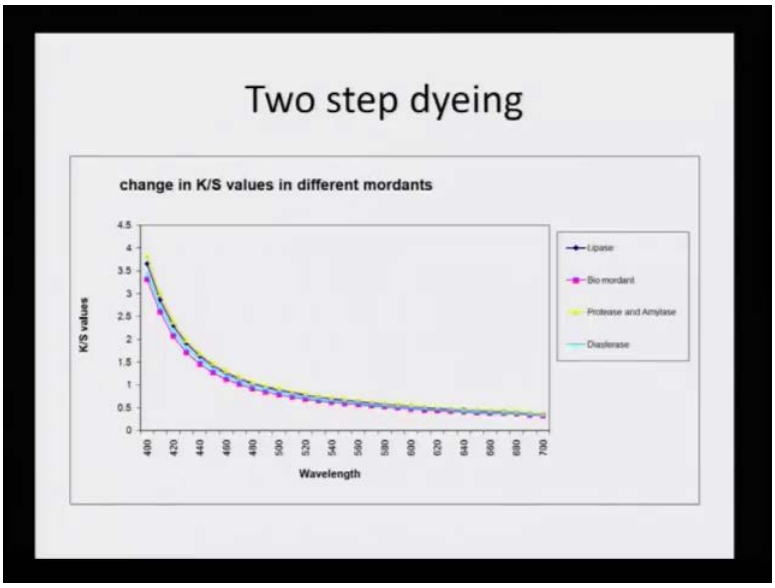

So, we call it two step and the change in K by S values when noted for lipase, bio-mordant, protease-amylase and diasterase was found that the protease-amylase showed the best result with Eclipta. Never the less even the bio-mordant was not far to behind you can see that, they are all very competitive in terms of their efficacy. Similarly, if the enzyme or the bio-mordant was put it the dye bath with the Eclipta extract the changing K by S shows that lipase shows the best result. So you see that, whether we take a one step methodology for dyeing or we take two step methodologies for dyeing, we need to understand which is the best option.

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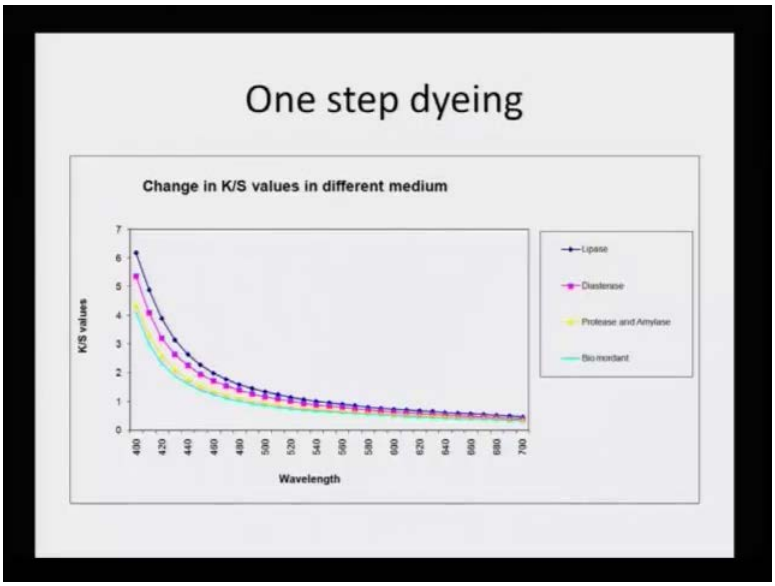

And in the case of one step, definitely it is lipase, which is very well compatible with the natural dye eclipta. Earlier also we have seen that, with enzyme there is a small drawback that the compatibility of the enzyme and the dye has to be worked out. It is not that all dyes and all enzyme work together and with the same efficiency. So, that kind of exercise needs to be always done, when we are dealing with enzymes and new natural dyes. Never the less bio-mordant also showed very efficient result and that was of prime importance.

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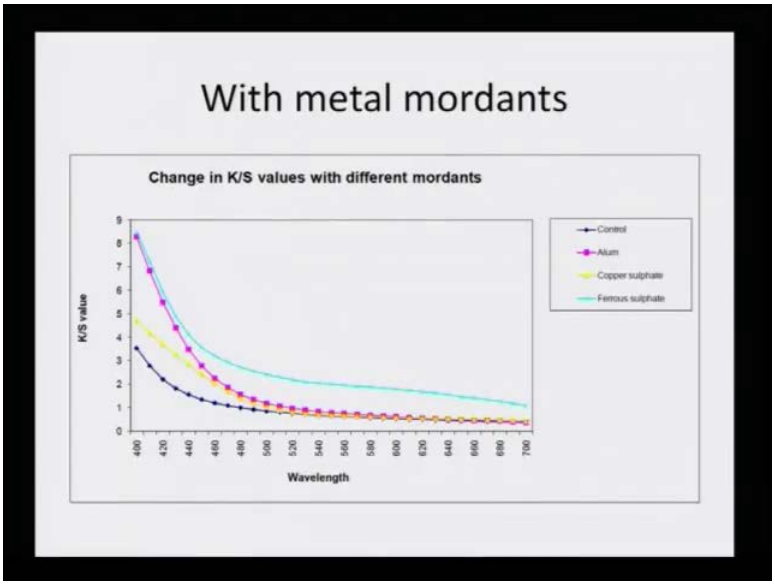

In order to make comparison, we also did and the same analysis with metal mordant. And metal mordants like alum, copper sulphate, ferrous sulphate and stannous and stannic chloride were all tried out, but this particular slide shows. The comparison between or the changing K by S of the control sample which has no mordant with alum, copper sulphate and ferrous sulphate.

So that one can see, that ferrous sulphate shows the best result, but because it has you know, a tendency to form kind of a lake with a tannic acid and ferrous stannate is generated. There is a lot of darkening of the fabric, because of the ferrous mordanting. But we were not interested in looking at that we were trying to see, how efficient is the tannic acid process and we found that the K by S values in the one step is ranging from six to seven and the two step it is ranging from 3.5 to 4.5. But in the metal mordanting step although, it is almost reaching six to seven, but at what cost. The disposal of these

metal mordants become a very big problem. So therefore, there is a need for the replacement of metal mordanting step with either the use of bio-mordant or the use of enzymes.

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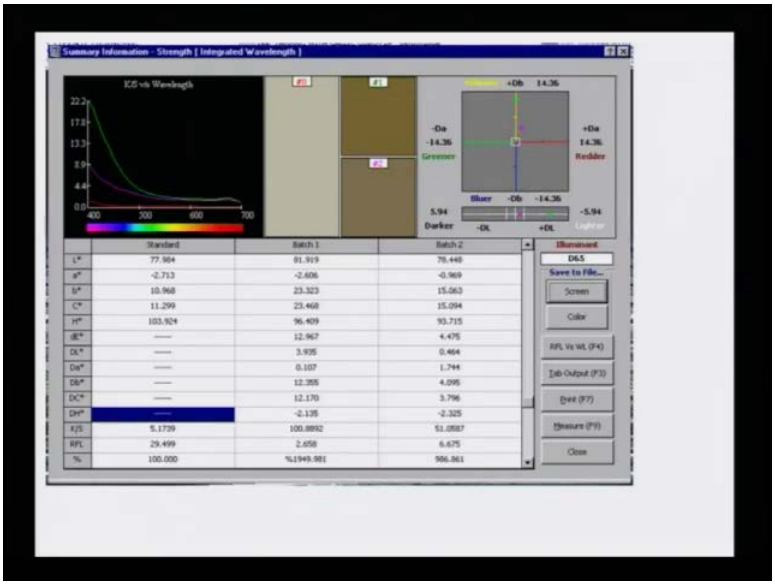

Now, if we try to look at this particular slide, you will see that, this Eclipta can show beautiful results and this is how this color scan machine gives it is result. The output of the result output of the color scan machine is that the k by s value is shown that with different substate, that is by using bio-mordant and lipase. The second one is the lipase and number one is bio-mordant and you see how beautifully the color or the greenish olive green color is obtained from the Eclipta extract.

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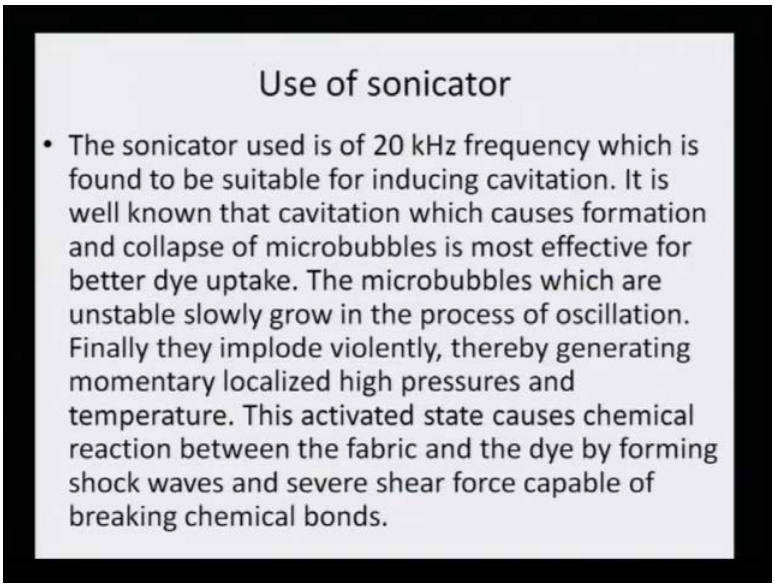

Now, time and again, we have been talking about sonicator. And we have understood, that this agitation mode definitely helps in dye uptake, what else does it do to the fabric. The sonicator used here is a twenty kilohertz frequency machine, which is found to be suitable for inducing cavitation. It is well known that cavitation which causes formation and collapse of the microbubbles is most effective for better dye uptake, time and again we have shown, with not less than thirty different natural dyes, that sonicator method is certainly very good for dyeing. We have also shown that sonicator was used in certain dyes where it was used for extraction because the dyes were heat sensitive.

So therefore, it has a very positive role to play in the dyeing process. The micro bubbles which are unstable slowly grow in the process of oscillation. Finally, they implode violently, thereby generating momentary localized high pressures and temperature. This activated state causes chemical reaction between the fabric and the dye by forming shock waves and severe shear force capable of breaking chemical bonds.

So you see that, at that kind of agitation, what happens to the chemistry of the dye and the fiber. There has to be some alteration, there has to be some reason which enhances the dye uptake and it is clearly now understood, that the dye forming activity with the fiber is happening only because of these kind of shock waves and the sheer force which are very severe in nature. And they kind of tend to break certain bonds and make certain new bonds.

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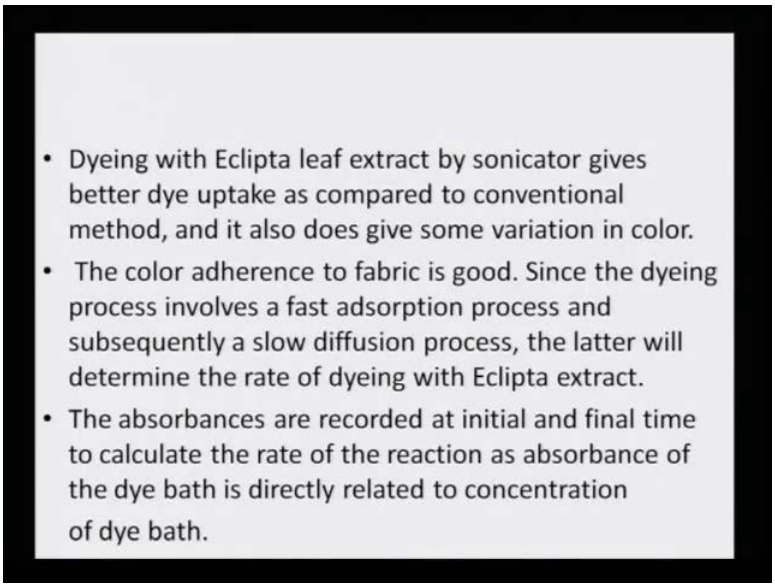

Dyeing with Eclipta leaf extract by sonicator gives better dye uptake as compare to the conventional method, and it also does give some variation in color. The color adherence to fabric is good. Since the dyeing process involves a fast adsorption process and subsequently a slow diffusion process, the latter will determine the rate of dyeing with Eclipta extract.

So, there are two different processes occurring, one is a fast absorption and the other one is a slow diffusion. So, these two rates have to match and then only the dyeing will be complete or it has to be given enough time for the dye to completely diffuse. So, that you know, the extortion of the dye is complete. Because the ultimate aim is that, this kind of sonicator agitation must cause an enhancement in the dye uptake. The absorbance's are recorded at initial and final time to calculate the rate of reaction as absorbance of the dye bath is directly related to concentration of the dye bath. See, what will happen as the time proceeds, the dye from the dye bath will be going into the fabric.

Now, if the rate is you know fairly medium or slow, even if it is slow. At whatever rate it is diffusing, the dye is getting depleted from the dye bath, but it is getting enhanced on the fabric. So, the rate of loss in the dye bath will be equivalent to the rate of gain in the fabric. And that is, what is taken into account because instead of destroying the fabric or doing a desorption study, it is better to just evaluate the concentration of the dye that is

present before, during and after the dyeing. So, that will give an idea at what time till what time how much has diffused and that helps us to understand the kinetics of dyeing.

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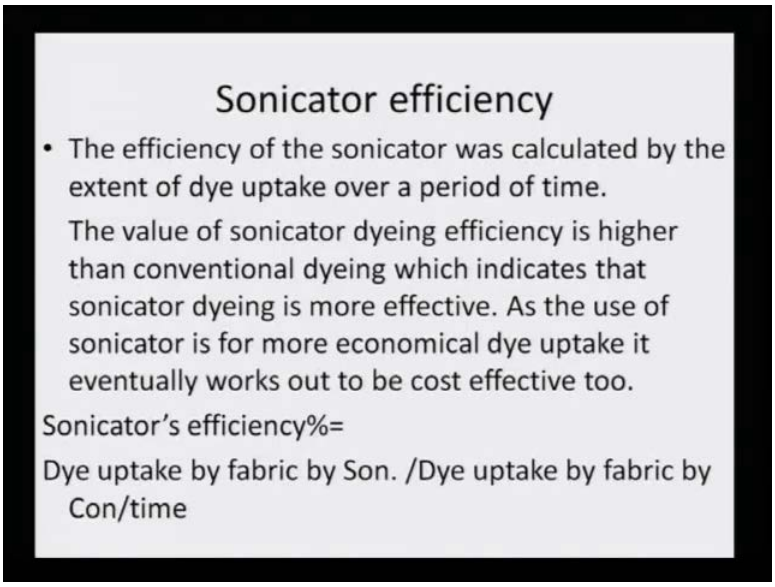

Sonicator efficiency, when we say, it is good, it is good, it is good, how good it is. So, that efficiency also can be calculated. The efficiency of sonicator was calculated by the extent of dye uptake over a period of time. The value of sonicator dyeing efficiency is higher than the conventional dyeing which indicates that sonicator dyeing is more effective. As the use of sonicator is for more economical dye uptake it eventually works out to be cost effective too, because you see, if the dye uptake is faster. The fabric will not need to be heated or boiled as in the conventional method, it takes almost three to six hours, whereas in sonicator it takes only 1 to 3 hours. So, that time saving is there, energy saving is there, and obviously, money saving comes automatically.

So, that is why it is not only cost effective, but one can even find out the sonicator efficiency percentage by the dye uptake taken by the fabric, by the sonicator method over the dye uptake by fabric, by the conventional method in a given period of time. So, we cannot have variables here, the time has to be fixed. In one hour, how much fabric has taken up the dye in sonicator method. That can be evaluated from the UV visible you know, evaluation of the dye bath solution after dyeing of one hour and the same experiment is you know conducted for the conventional dye bath. And that, those value will show us how much of the dye uptake has taken by sonicator method and how much

of dye bath dye uptake has been taken by the conventional method. So, the time factor should remain the same. It is not that in three hours how much it has been taken and in six hours how much it has taken, that will be wrong calculations. So, that will not give correct sonicator efficiency.

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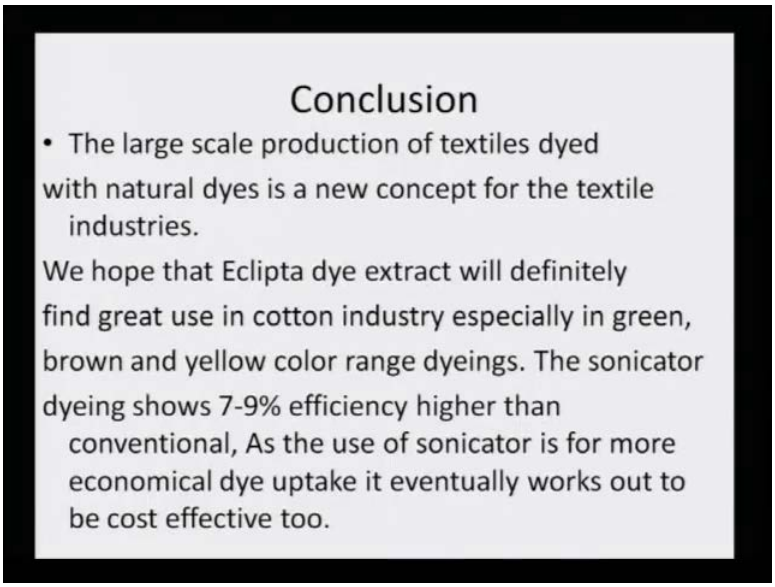

So, if I have to Conclude, I will say that a large scale production of textile dyed with natural dye is a new concept for textile industries. We hope that Eclipta dye extract will definitely find great use in cotton industry especially when green's, brown's and yellow color range dyeings have to be done. The sonicator shows about seven to nine percent efficiency higher than the conventional dye.

As the use of sonicator is for more economical dye uptake is eventually worked out to be most cost effective also. Because when we try to offer a methodology to the industry, we have to show that, it has an edge over the conventional method. Otherwise, nobody is going to take this technology. And also, whether all the parameters of a good dye is being fulfilled by a new dye that has been screened from the natural dye series of dye yielding plants.

We have to see many factors, we have to take into account many factors and those factors are that it should be water soluble, it should be easily extractable, it should have all the goodness of be compatible with toughest of the tough material that is cotton. If it can dye cotton, it can definitely dye silk and wool. There is no doubt about it and anyway

natural dyes are not meant for synthetic fibers like polyester, polyacrylamide. So, we need not worry about the synthetic fibers at all. Looking at the natural fiber demand if any dye can dye cotton then that dye comes into a good dye category.

The next point that needs to be remembered is that the fastness properties should be good. It should not be that in one wash the dye has run off or striped off. In such a case, it will not be a good member of good natural dye. Therefore, sonication method is definitely adding on to the efficiency replacement of metal mordants with bio-mordants or enzyme is not only taking care of the eco friendliness and the disposal problem of the dye affluent, but it is also bio-degradable.

So, there is no problem of an affluent disposal at all what so ever. And the dye you know, can be actually the dye disposal or the dye bath affluent disposal can easily be done into the agricultural lands without destroying the chemistry of the soil and it can be very well used for irrigation purposes. So, that is the whole idea of talking about today's Flavonoid dye which was extracted from the plant called Eclipta Alba.