Natural Dyes

Prof. Padma Vankar

Department of Chemistry

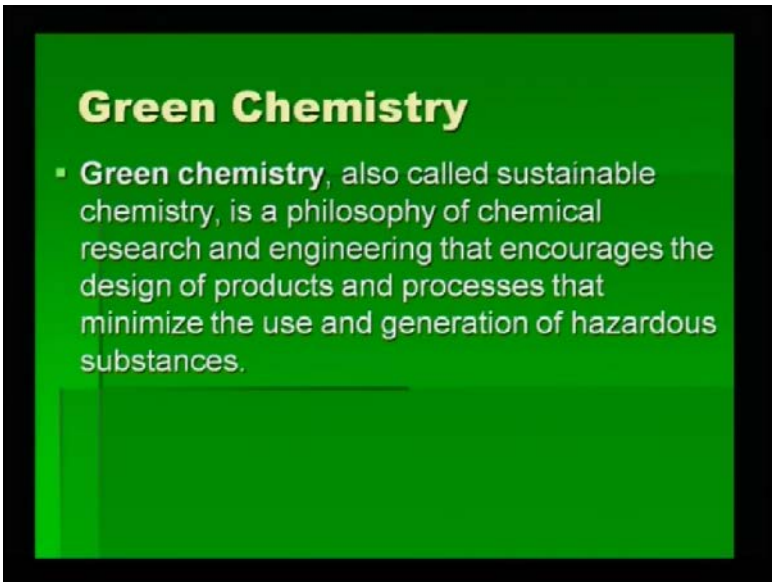
Indian Institute of Technology, Kanpur

Lecture No. # 23

Let us now try to look at the natural dyeing concept from the green chemistry view, because there has been a big drive of having a green approach towards all industrial processes. And similarly processes which actually give out a lot of toxins or are creating environmental pollution must take a green chemistry approach towards their processing. And therefore, now let us try to evaluate the eco friendly dyeing with of cotton by using enzyme pretreatment. So, how does it be fits into the definition of green chemistry? Let us take an overview of that in this lecture. Although a few things will be repetitive, but the emphasis is on the fact - that this particular process has been developed in a manner that it be fits the green approach of the industrial processing.

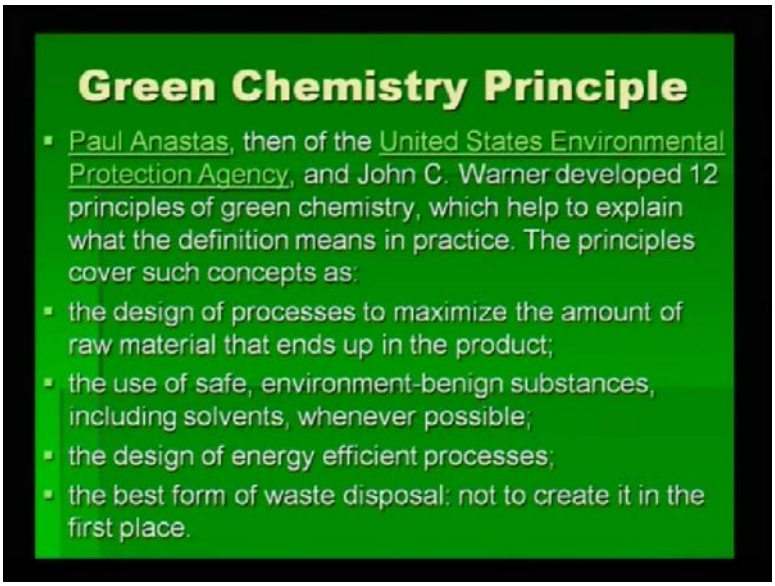
So, a green approach which talks about ultrasonic natural dyeing of cotton fabric with enzyme pretreatment. And we will get into a little more deeper, you know we just fleetingly mention that enzymes are good, but what is the kind of enzyme reaction, what is the kind of dye enzyme interaction, all those things we will take a more serious look in this particular lecture. You must have seen that many a times I mention a few things in the lectures, and then later on in the subsequent few lectures I elaborate upon it. This is mainly because first the term should be introduced to you. And once you are familiar with the terminology, then its significant role in the dyeing process is then emphasized. And more and more details are given to you, so that you can understand the concept in a better manner.

(Refer Slide Time: 02:39)



Green chemistry, also is called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of product and processes that minimize the use and generation of hazardous substance. So, any process or product if it can be made by not generating hazardous material will come under the category of green chemistry. So, that is what is meant by green approach. And so, now at least you are clear that not only the slide looks green, but actually the color has been just taken up just to match with the green approach. But it has nothing to do with the green coloration. It is not that ultra sound dyeing of cotton with enzyme will green give green color, you know that is not the concept the green approach means that any product or process should not liberate any kind of environmental hazardous material. And if that is so then that approach or the process will come under the green chemistry approach.

(Refer Slide Time: 04:08)



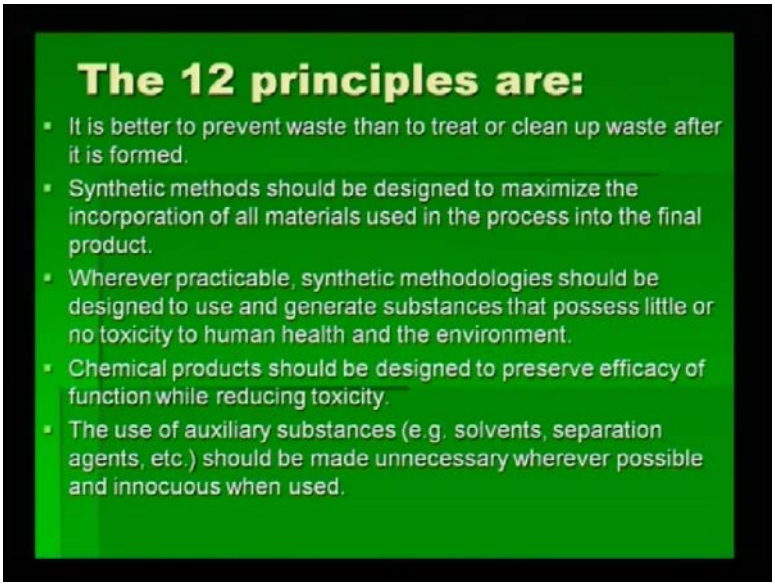
Green chemistry principle was first you know introduced by Paul Anastas, then of the United States Environmental Protection Agency that is U. S. E. P. A and John C. Warner who developed 12 principles of green chemistry which help to explain what the definition means in practice. So, what they did? They in order to explain the green approach; they said that the green chemistry approach has 12 principles, and these 12 principles will cover all the aspects that what will categorize or what will help them to categorize under the green approach. The principle covers such concepts as the design of the process to maximum the to maximize the amount of raw material that ends up in the product, the use of safe, environmentally benign substances including solvents, whenever possible, the design of energy efficient processes, the best form of waste disposal not to create it in the first place. So, first few points are very, very relevant to even natural dyeing.

The design of the process should be such that maximum amount of the product can be used for the as the raw material. So, there will be very little waste, and the product that will be generated will be more and more useful. And there should the process should be safe, environmentally benign substance means there should not be use of any hazardous chemical. And therefore, solvent and use of any such chemical which may generate toxins should be avoided as far as possible. Now, I will give you an example. For leather, there is a chemical that is used for preservation of leather and that is called pentachlorophenol. Now, it is impossible to preserve the leather of good quality for a

longer period of time, unless and until it is treated with pentachlorophenol or for that matter, the chromium tanning of the leather. These two things are very, very important chemicals, and both of them are very hazardous.

Although they were many, many substitutes that were brought in, but nothing could match the affectivity of the that of chrome-6 in tanning and or rather chrome-3 in tanning and pentachlorophenol. So, the substituent's, though they were environmentally benign, were not showing their required affectivity. Therefore, wherever they have to be used, they should be used, but in the minimal quantity. And the design should be that it should be energy efficient and as far as possible least amount of waste should be then generated and that should be disposed properly.

(Refer Slide Time: 07:22)

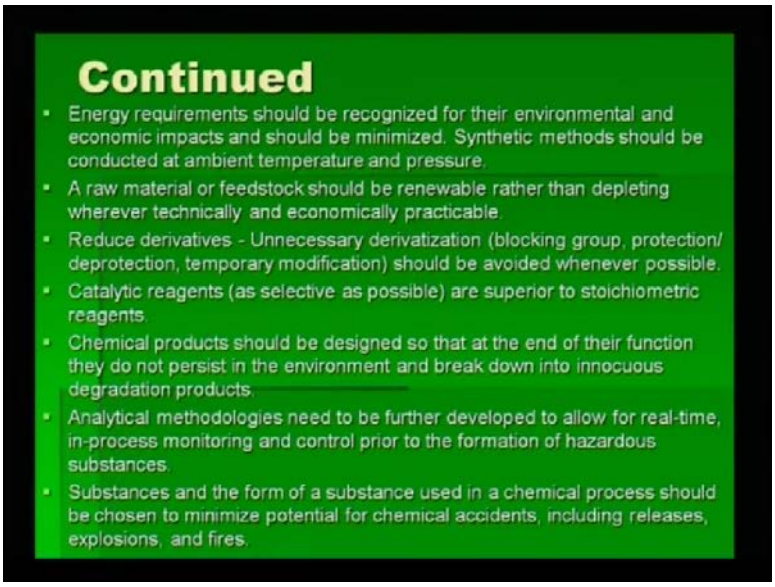


The other principles are it is better to prevent waste than to create or clean the waste after it is formed. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and to the environment. Chemical products should be designed to preserve efficacy of function while reducing toxicity. The use of auxiliary substances like solvents, separation agents should be made unnecessary wherever possible and innocuous when used. So, it should be as safe of chemical process that minimum amount of waste is generated, minimum amount of hazardous chemical are used. And wherever

possible, the chemical product should be designed to preserve the efficacy of the function; while it should reduce the toxicity.

Similarly, synthetic method should be designed to maximize the incorporation of all the material. So, there will be less wastage. So, like that there were 12 principles designed by these two scientists of U. S. E. P. A. And they found that these, you know, principle cover by and large most of the areas of chemical processing and chemical reactions where waste are generated and more toxins are created. Energy requirement should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

(Refer Slide Time: 09:35)

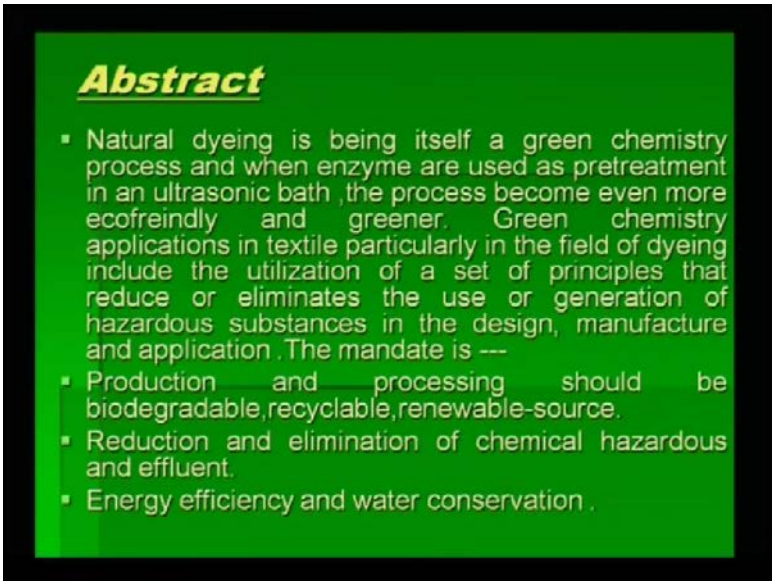


Raw material or feed stock should be renewable rather than depleting wherever technically and economically practical. Reduce derivatives - unnecessary derivatization blocking group, protection, deprotection, temporary modification should be avoided whenever possible. Catalytic reagents as selective as possible are superior to stoichiometric reagents. Chemical products should be designed, so that at the end of their function they do not persist in the environment and break down into innocuous degradation products. Analytical methodologies need to be further developed to allow the real-time, in-process monitoring and control prior to the formation of hazardous substances. Substances and the form of the substance used in a chemical process should

be chosen to minimize potential for chemical accidents, including releases, explosion and fires.

So, it covers a whole range of possible contamination and possible polluting situations. And it also says that all what should be avoided, and so one can make the whole chemical process more green in its approach. Now, when we try to evaluate this green approach with the kind of innovative dyeing system that we had developed; I will be able to explain to you, how we were able to save the use of metal mordants which create a environmental problems to switching over to enzyme pretreatments, because enzymes are bio degradable and so on and so forth. And the use of ultra sonification for dyeing also is a a cost effective, time effective, and you know resource effective, technology for dyeing.

(Refer Slide Time: 11:48)



Natural dyeing is being itself a green chemistry process and when enzymes are used as pretreatments in an ultrasonic bath, the process becomes even more eco friendly and greener. Green chemistry applications in textile particularly in the field of dyeing include the utilization of a set of principles that reduce or eliminates the use or generation of hazardous substance in the design, manufacture and application. So, you see we quite rightly be be we are befitting the green chemistry approach. The mandate is that production and processing should be biodegradable, recyclable, renewable resources;

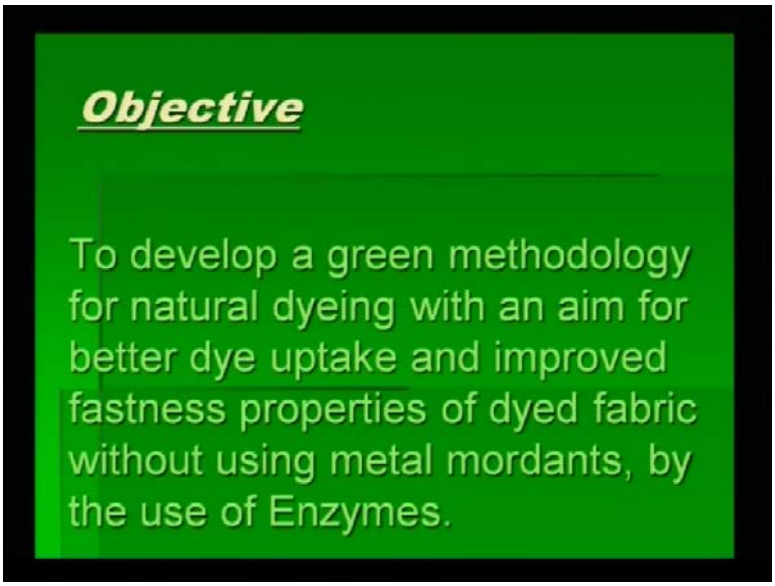
reduction and elimination of chemical hazards and effluent; energy efficiency and water conservation.

Now, all these points will we were taken into account. So that it truly fits into the green chemistry approach. And therefore, you know we try to see where all the environmentally polluting substances were generated, where all the time was being consumed more, where all the energy was being consumed more and those processes were then looked into thoroughly and more innovative technology was develop in those specific area.

(Refer Slide Time: 13:26)

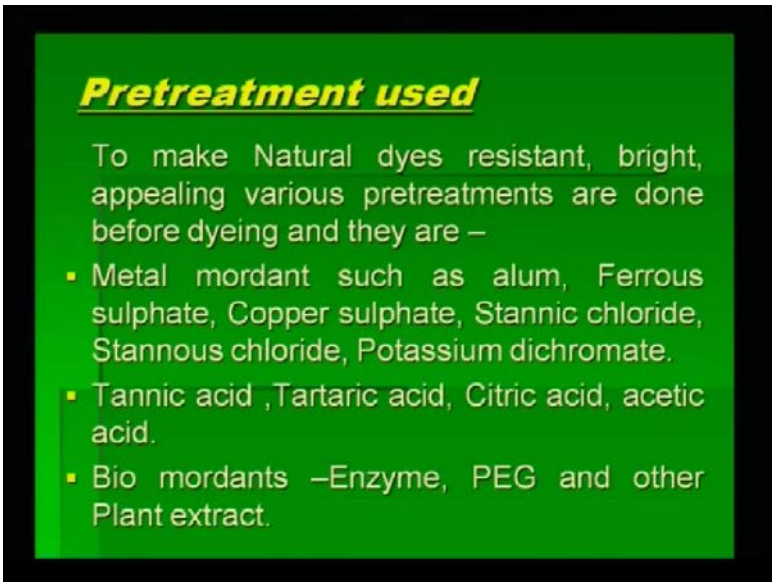
Now, if I have to introduce this topic to you. Innovation in natural dyeing due to the advance technology now available to the dyers has brought back old traditional dyeing once again into limelight. The main focus of research in this area covers four major issues; one is the extraction of natural dye, innovation in dyeing, effluent management and green approach that is eliminating the use of metal salts. So, we have tried to actually make the process - the entire natural dyeing process more green by looking at all these four aspects that is extraction of natural dye, innovation in dyeing and effluent management and green approach eliminating use of metal salts. Because metals were the ones which were actually used in the conventional dyeing process and these metals created toxins, and therefore, the environment became polluted.

(Refer Slide Time: 14:31)



The main objective of this whole exercise are the of this lecture is to develop a green methodology and introduce it to you, so that you can now understand the process from the green chemistry approach; for natural dyeing with an aim for better dye uptake and improved fastness properties of the dyed fabric without using metal mordants or by using instead of that using enzymes. So, how can we get similar results as what we procured by natural dyeing with metals in the same manner. If we repeat the process by using enzyme, does it really help and get us the same dye uptake or the same color strength or the same hue color, and that is what we will take a very serious look at.

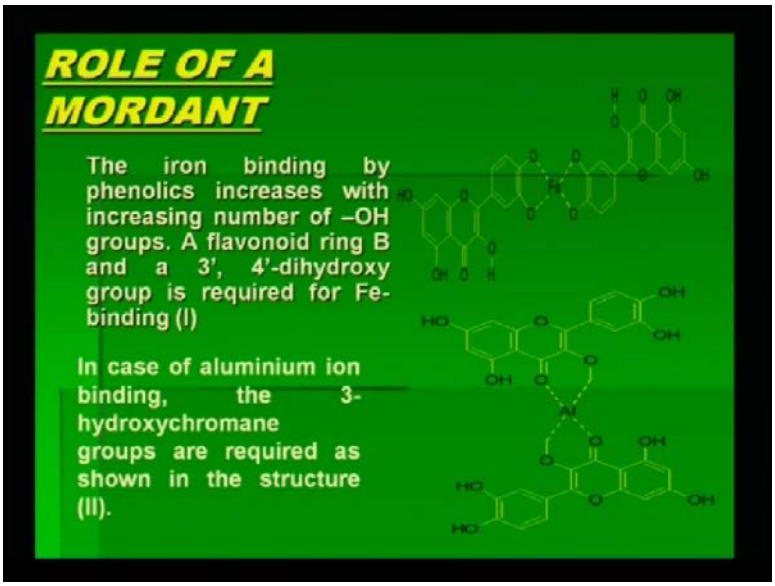
(Refer Slide Time: 15:29)



Pretreatment used here to make natural dyes resistant, bright, appealing various pretreatments are done before dyeing and we have learn that. Time and again I have told you the importance of pretreatment and the importance of metal mordanting. We will dedicate another lecture for pretreatments in the following few lectures. But right now you should understand that mordanting goes hand in hand with natural dyeing. And therefore, mordanting with metal mordant such as Alum, Ferrous sulphate, Copper sulphate, Stannic chloride, Stannous chloride, Potassium dichromate are very, very common.

Sometimes mordanting or pretreatments are done with the help of tannic acid, tartaric acid, citric acid, acetic acid. And biomordants are used such as enzymes, PEG and other plant extract. We just talk spoke about the plant extract, pyrus perschia and urea, accuminata this morning. So, you would recollect that there are biomordants of plant origin also, where the metal is hidden or present in the plant in a very small quantity, but still in the requisite quantity where it can effectively do the mordanting.

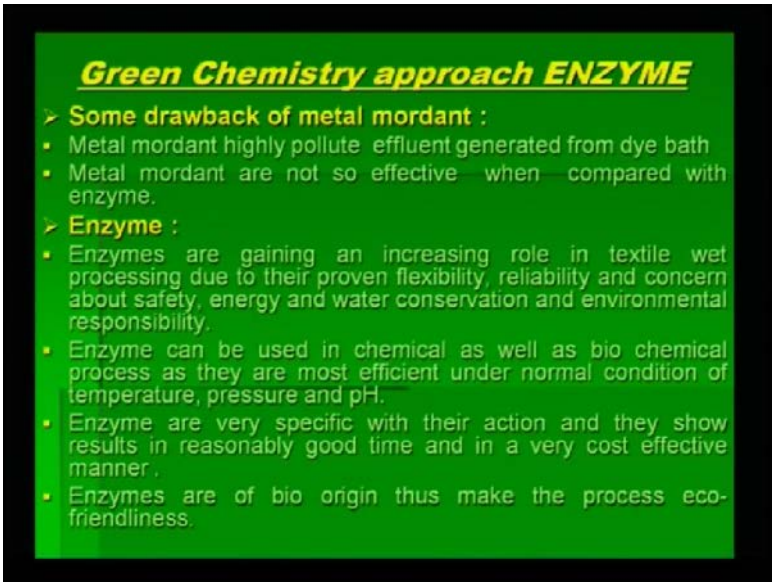
(Refer Slide Time: 17:01)



What is the role of mordant? Now, if you look at this, the iron binding by phenolic group increases with the increasing number of the OH groups. A flavonoid ring B and the 3 prime, 4 prime-dihydroxy group is required for iron binding and which can be seen in the first structure. You see how nicely the two structures are flavonoid structures are linked up with the iron. And in the case of aluminium, the binding occurs with 3-

hydroxychromane group where the requirement of hydroxy plus carbonyl is a must as shown in the structure number two. Time and again I am showing you this structure. So that you can understand where does the metal come and what is the role of the metal. And if this metal has to be replaced then why how does it help, what will be the new linkages with the enzymes or with the PEG or with the tannic acid that will be facilitated.

(Refer Slide Time: 18:08)



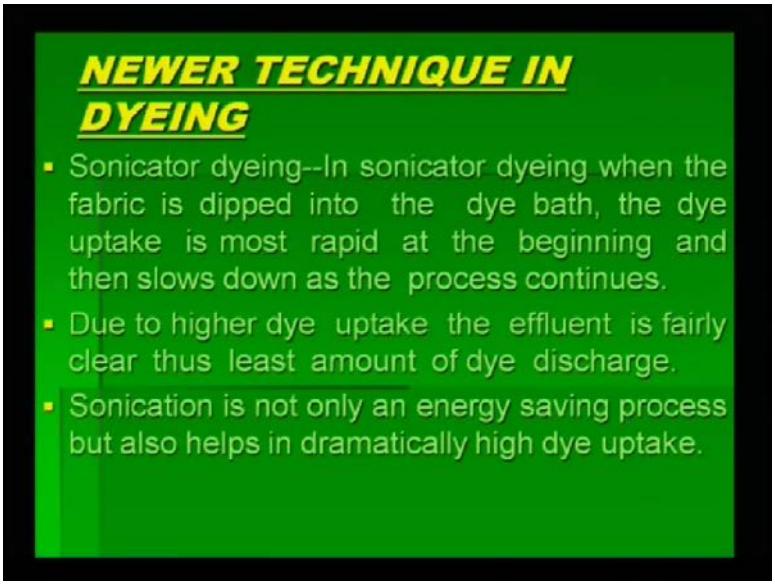
Green chemistry approach and the answer is enzyme. Some drawbacks of metal mordants; first you have to understand. Metal mordants highly pollute effluent generated from the dye bath. Metal mordants are not so effective when compared with enzyme. So, we saw that you know when metal mordants have to be used; it was something like 2 to 4 percent of the weight of the fabric. It could not be used less than that. And only in the case of copper and chromium, we showed that even use of 1 to 2 percent was kept low only from the point of view of environmental pollution or it may not create any hazardous situation. But enzymes are actually used only in 0.05 percent of the weight of the fabric. So, you see that if the quantity of enzyme that is required by itself it is too little.

Enzymes are gaining and increasing role in textile wet processing due to their proven flexibility, reliability and concern about safety, energy and water conservation and environmental responsibility. Enzyme can be used in chemical as well as bio chemical process as they are most efficient under normal conditions of temperature, pressure and

pH. Enzymes are very specific with their action and they show results in reasonably good time in a very cost effective manner, cost effective why because the amount use is very small. Enzymes are of bio origin thus make the process eco friendly. So, you see that - that is how it is like using enzyme as a pretreatment in place of metal mordant is a big achievement by itself, because we are removing one of the most, you know, notorious chemical from the process which is responsible for creating environmental hazards.

Now, at the same time we were also looking at the technological up gradation, effective and efficient exploitation of new technology will keep us in competitiveness with the world. Utilization of ultra sound energy for extraction as well as dyeing, cotton, silk and wool with natural dyes is a definitive improvement, and green approach in modern textile processing. And this has been developed by us in the (( )) laboratory.

(Refer Slide Time: 20:59)

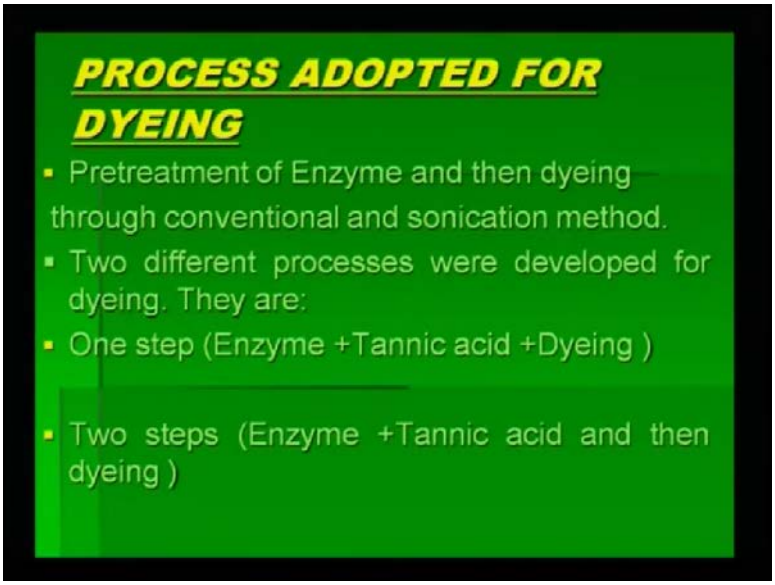


Now, newer technique of dyeing, we have already discussed this morning about the sonicator dyeing. But we will now see how sonicator dyeing has become a part of the green chemistry approach. Sonicator dyeing when the fabric is dipped into the dye bath, the dye uptake is most rapid at the beginning and then slows down as the process continues. Due to higher dye up take, the effluent is fairly clear, thus least amount of dye discharge is actually observed. So, the dye bath when the job is over, when the dyeing is over, the dye bath in conventional case still has a huge amount of dye left, and it is fairly difficult to remove this colored water or to treat this colored water. Because in order to

have a safe disposal, a lot of treatment processes like coagulation and many kinds of other treatments have to be done to decolorize this colored water.

But in sonicator, because the dye content is taken up largely by the fabric, the solution becomes very, very poor in its optical density, which means that the concentration of the dye in the dye bath after the dyeing is very poor. And thus it it can be discharge even with mild treatment methods. Sonication is not only an energy saving process, but also helps dramatically in high dye uptake. And we have seen that how cavitation, how this formation of the micro bubbles coming together, including create a localized temperature and pressure, and enhance the capillary action of the dye to be taken into the fabric pores; so, all that is possible, because of the initial cavitation or agitation caused by the sonicator.

(Refer Slide Time: 23:19)



Process adopted for dyeing; pretreatment of enzyme and then dyeing through conventional and sonicator methods were carried out. If one has to prove that this method is better than that method, it has to go through a comparative test. Otherwise it is very hard to make an evaluation just by looking at only one parameter. Two different processes were developed for dyeing. They were they are one step where enzyme tannic acid and dyeing was done together, and in the other process, two step process was done. First the enzyme and the tannic acid were treated to the fabric and then the fabric was

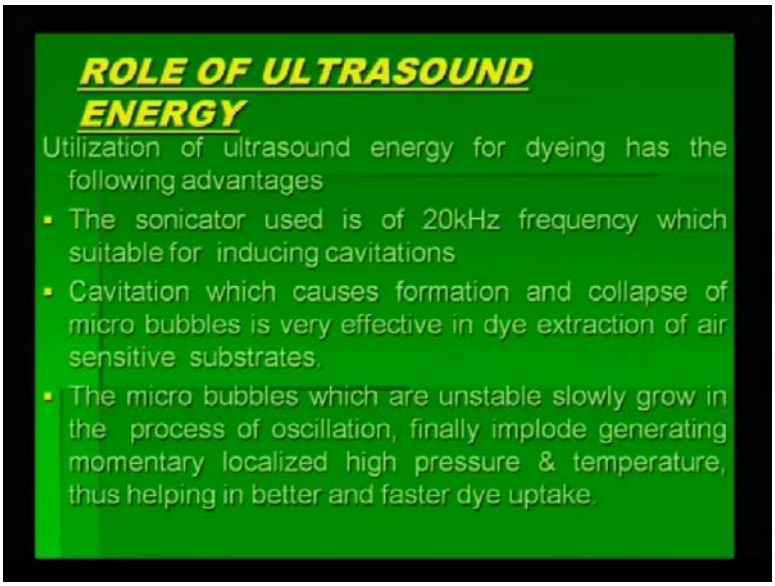
then dyed. Pretreatment of enzyme and then dyeing through the sonication and conventional method were the being two methods that were used for comparative study.

The fabric cotton was pretreated with enzyme as well as metal mordant. And then if you also made a parallel study with metal mordant, because if we have to show that is this enzyme method is better than the metal mordanted method. We have to make a comparison between these two. And if we have to prove that conventional method is not as good as sonication method, we have to make study of that. So, actually four tests were going on parallel.

(Refer Slide Time: 24:55)

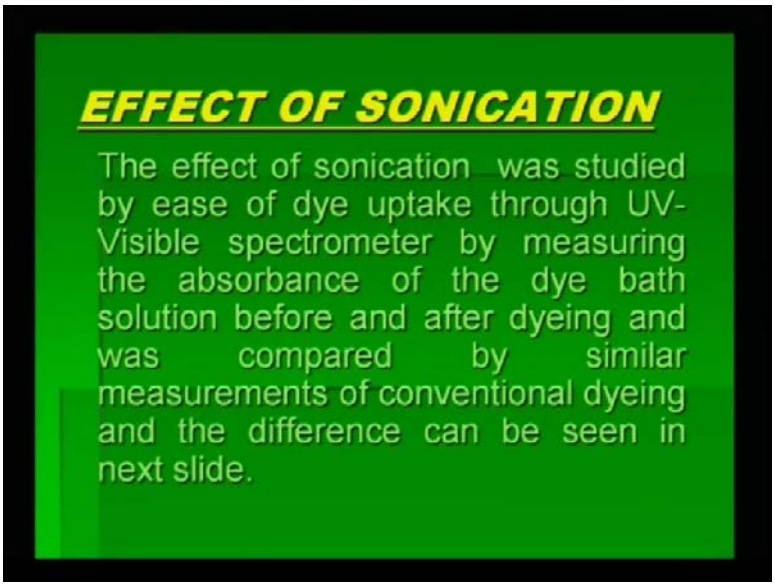
The pretreated fabric both with enzyme and mordant separately were dyed with two natural dyes that is catechu and tectona. Catechu is brown in color and tectona gives reddish color. In sonicator bath at liquor ratio 30 is to 1. We were keeping it more dilute, 30 is water and 1 is part is the dye. The temperature of the dye bath was kept not higher than 45 degree centigrade and maintain at this level for 1 hour. In sonicator dyeing the process showed accelerated dye uptake. Conventional dyeing was also carried out simultaneously to compare the dye uptake. So, basically if we have to prove that this is a faster method, we have to do both of them together and see in 1 hour, how much dye uptake has taken place in the in both the cases.

(Refer Slide Time: 25:54)



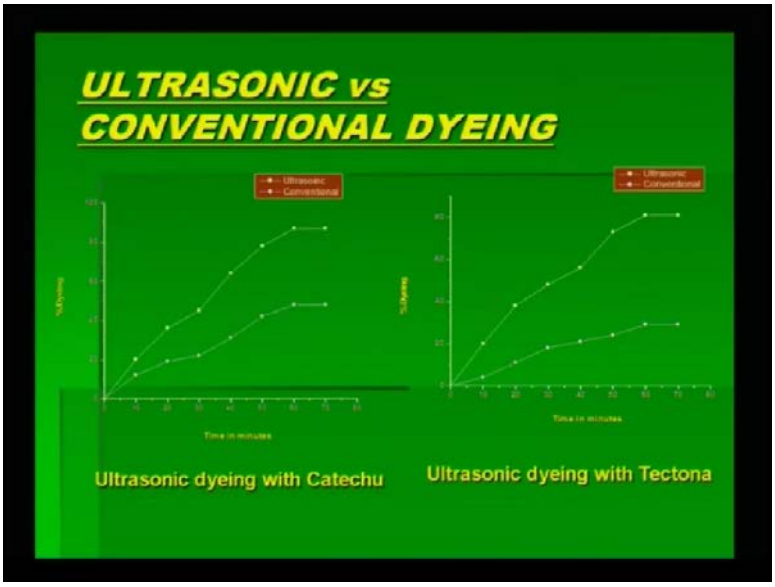
Role of ultra sound energy: Utilization of ultra sound energy for dying has the following advantages. The sonicator use is of 2 20 kilo hertz frequency which is suitable for inducing cavitation. And has what I said cavitation which causes formation and collapse of micro bubbles is very effective in dye extraction as well as in dyeing. The micro bubbles which are unstable slowly grow in the process of oscillation, finally implode, one is explode and the one which breaks inside in implosion; generating momentary localized high pressure and temperature, thus helping in better and faster dye uptake. So, that is how the sonication effect works.

(Refer Slide Time: 26:40)



The effect of sonication was studied by ease of dye uptake through the UV - visible spectrometer by measuring the absorbance of the dye bath solution before and after dyeing, and was compared by similar measurements of the conventional dyeing, and the difference is shown in the next slide. So, you see that if we have to say, this is better, that is better, we have to make a comparison and so a comparative study was done.

(Refer Slide Time: 27:15)

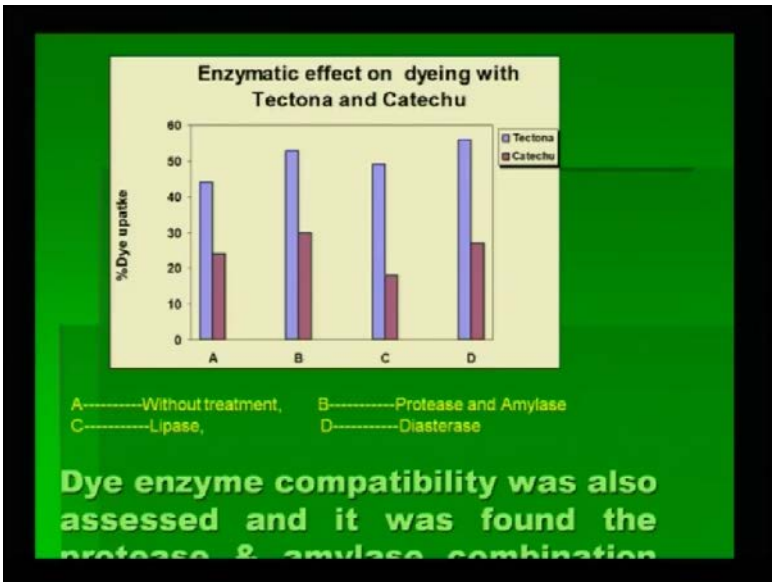


Here is a graph which clearly shows that the line mark with ultra sound energy system and the line mark with convention. In both the dye cases like in the case of this catechu as well as in the case of tectona, the ultra sound shows a higher line. So, this shows that the dye uptake in the case of ultra sound method or ultra sonic method of dyeing has been much higher as compared to the… So, the graph itself speaks for its utility. One does not have and these measurements were done by UV - visible spectrophotometer. And I just covered that chapter where we were discussing about evaluation of the optical density of the dye bath. So, before and after both were evaluated; obviously, the loss of dye has been the gain on the fabric. So, nothing has got lost in the process whatever has been the luring of optical density in the left behind dye bath has actually been incorporated on the fabric. So that is how one evaluates the dye uptake.

(Refer Slide Time: 28:34)

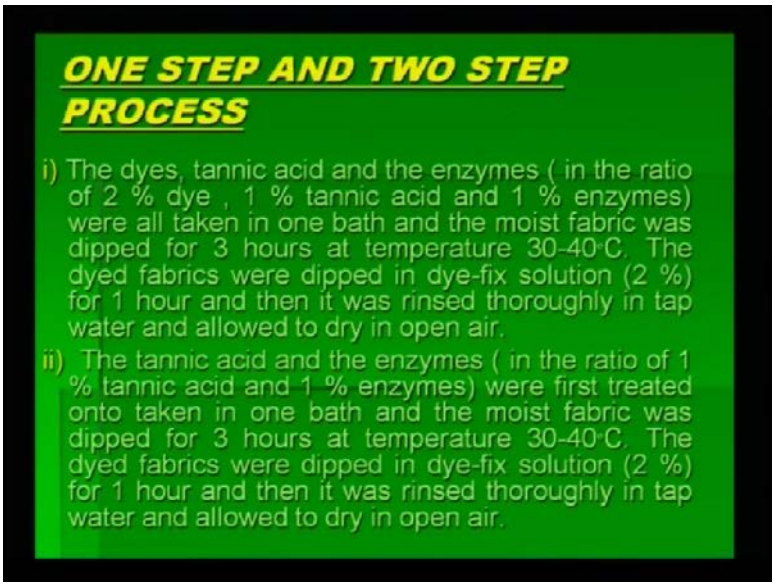
So, if we try to look at now, the CIE lab values of course these are not so important from the point of view of studying it. But from the point of view of enzyme treatment and metal mordanted treatment; you will see that the metal mordanted treat are lighter in shade, whereas the dye which was treated with the enzyme like pro-amylase, diasterase and so on and so forth, showed very good fastness property. So, the fastness properties actually varied between 4 and 5 in the case of washing fastness and light fastness and I told you that for a dye to be categorized as a good dye. The better the wash fastness, the better the light fastness, the better categorization it gets. Similarly, comparative study was done between the enzyme treated fabric and dyed with catechu and tectona. And the metal mordanted fabric treated with catechu and tectona and these were the results. Now, if we have to look at the, you know, study of what is the enzymatic effect on dyeing with tectona and catechu between the two dyes, if we have to make a comparison.

(Refer Slide Time: 30:01)



Tectona seems to be very, very good with the enzyme treatment. Now, remember that I had very clearly told that enzymes are very specific in nature, because they are like catalyst and enzymes are just like lock and key arrangement, not every lock can be opened by any key on vice versa. So similarly, we have enzyme and dye reactivity. And this graph shows that the dye uptake for tectona dye under without treatment also it was much better, and in lipase with protease and with diasterase, but among all the diasterase showed the best compatibility. So, the dye enzyme compatibility was also assessed and it was found that protease and amylase combination plus diasterase. They both are very good, either we use protease and amylase for tectona or we use diasterase for tectona, both are suited. But it was not so good with lipase or with the other dye with the other enzyme. So, that is how the compatibility of the enzyme and the dye is evaluated.

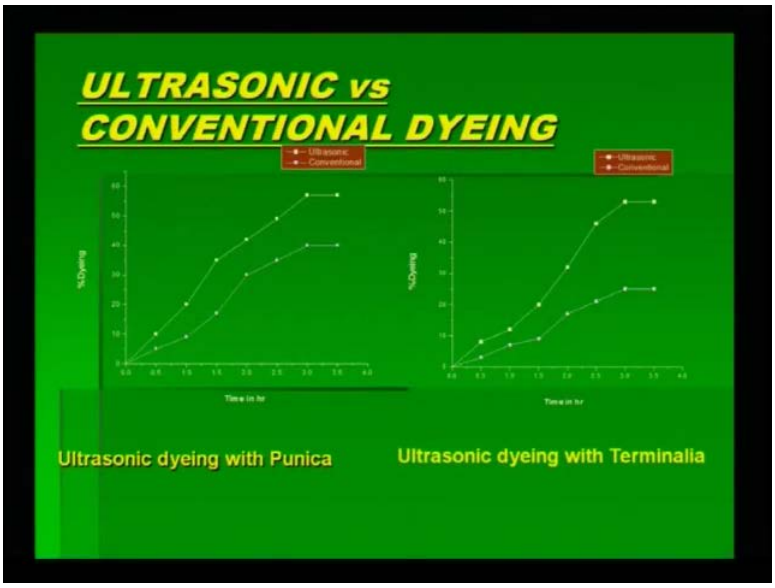
(Refer Slide Time: 31:21)



One step process and two step process: Now, we spoke about the preparation of the dyeing methods and there we saw that you know, if we can reduce the number of steps, it is always advantageous. The dye, tannic acid and the enzyme are all put in one bath in 2 percent, 1 percent and 1 percent ratio; of course here the enzyme quantity has been raised. But we were taken in the one bath and the moist fabric was then dipped for 3 hours at a temperature between 30 to 40 degrees. The fabric dyed were dipped in dye-fix solution 2 percent, and then for 1 hour it was left in that dye-fix, and then thoroughly wash with water and dry.

The second method was that the tannic acid and the enzyme were mixed in the ratio of 1 is to 1, and were first treated on to the fabric, and then it was dyed for 3 hours in the dyeing solution. So, these were the two one step and two step processes where step wise addition or simultaneous addition were done and a comparative analysis was done.

(Refer Slide Time: 32:36)

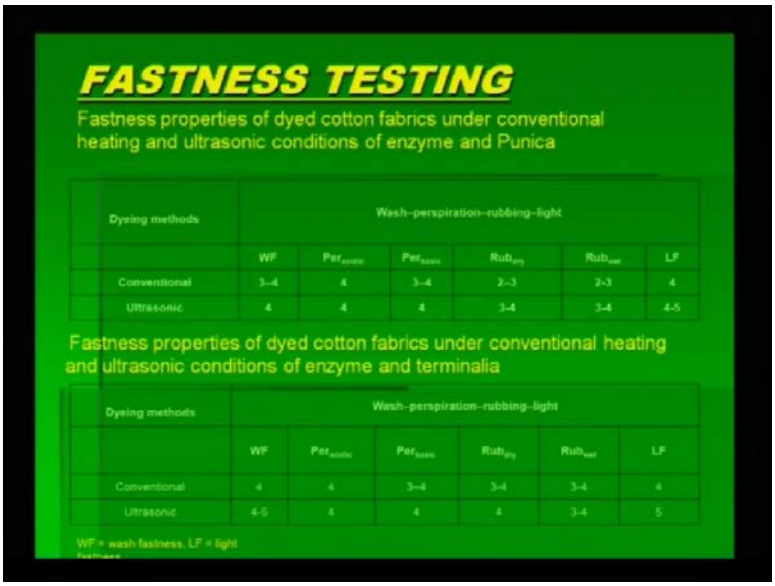


And it was found that you know, if one tries to look at other dyes also like punica and terminalia. And makes a comparative analysis between in the ultra sound and the conventional, it is always that ultra sound was superior to the conventional dyeing.

(Refer Slide Time: 32:54)

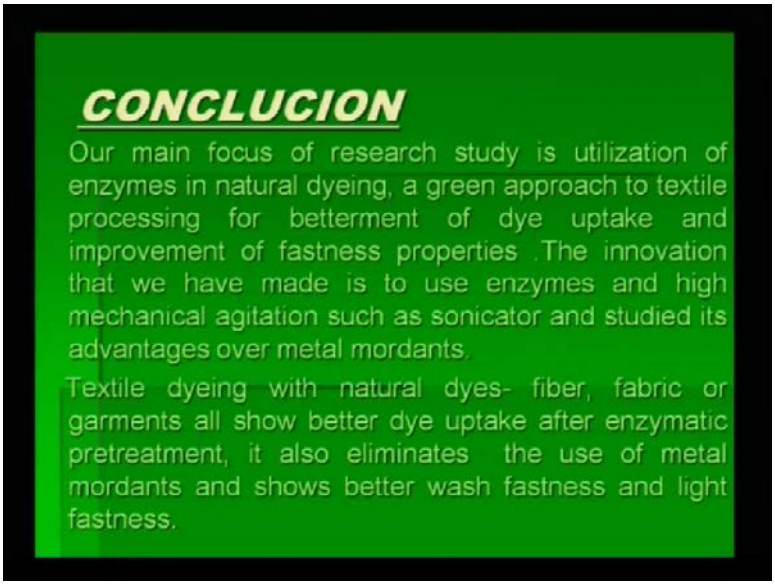
And the even the value color measurements for these two dyes that is the punica and rheum emodi shows that you know, these dyes have good compatibility with a specific enzyme.

(Refer Slide Time: 33:10)



Even fastness properties were enhanced by the use of enzymes and when it was seen that you know if the fastness properties are evaluated between conventional and ultra sound. It was found that it showed very good fastness properties and all the time it was superior to the conventional. So, sonicator dyed fabric, because it had better dye uptake showed better result, the bottom line is that. And we made many studies with many different dyes and there you know compatibility study with which enzyme it works the best and so on and so forth.

(Refer Slide Time: 33:57)



In conclusion, if I have to talk about this green approach of the research. Our main focus of research study is was focused on the utilization of enzyme first thing. And because it is a green approach to the textile processing, it is meant for a the betterment of the dye uptake and improvement of fastness property. So, the main goal of any dye and any method is whether you carry it out by conventional or whether you carry it out by any other dyeing process. The aim should be that the dye uptake should be very good. And if it is better than the existing method that innovation will be definitely taken up and will fall in the category of green chemistry approach. The innovation that we have made is to use enzymes and high mechanical agitation such as sonicator and studied its advantages over metal mordants; textile dyeing with natural dyes, fiber, fabric or garments also better dye uptake after enzymatic pretreatment. It also eliminates the use of metal mordants and shows better wash fastness and light fastness.

So, it is now it can be very confidently told that the role of metal mordant can be rightly substituted by the use of enzyme or bio mordant. We studied about the bio mordant in the previous class, but this class was mainly dedicated for the enzyme, specificity, enzyme compatibility, and why we should use or substitute metal mordant, and why we should take a greener approach towards natural dyeing. It was a completely new ball gain which I tried to show it to you, because you see the trend of reducing the pollution has been you know globally this is an excepted fact and it is the industrial revolution which is causing more and more pollution. So, there has a the time has come, when this pollution problem needs to be checked.

And unless and until we make a check on every process - industrial process, we will be not ending up in doing any good to the environment. And in order to reduce the technologies that must be promoted or the technological innovation that are should be taking place or research should be oriented, such that we generate least amount of waste first thing. The process should be energy intensive, so that it is cost effective. When the waste is reduced and no toxins are utilized, and natural compounds are used from the natural source which are renewable, it will definitely have a very green impact on the whole textile processing. So, that was the whole aim of doing this lecture to give you a green chemistry approach to the natural dyeing process.