Course Name: Industrial Wastewater Treatment

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Lecture 1: Treatment of wastewater produced from Tannery and Pulp and Paper

Welcome back. We are in module 8, lecture 1 and in this lecture, we will discuss about the treatment of wastewater produced from tannery and pulp and paper. So, here in this lecture we will cover the concepts on the introduction on the tannery's manufacturing processes and we will talk about that how the manufacturing of the leather is done and how the hides which are used for the preparation of the leather. So, they are prepared so that they can be amenable to the tanning process. Similarly, the tanning process will be discussed. We will also discuss about the finishing processes which are involved during the manufacturing of the leather, and we will also talk about the flow diagram of the vegetable and chrome tanning process in this lecture.

So, tanning industries is one of the oldest industries where the animal hides are converted into leather. So, we talk here about the hides not about the skin because the skin mainly applied for the living animals whereas, hides is applied for the dead animals. So, we will be converting here the hides into the leather. So, this process is known as the tanning process, and we are converting the hides into product which is very highly resistant to the degradation because we know that the animal hides.

So, they may contain lot of hairs on it, they may contain lot of protein material attached to it, they may also contain lot of flesh attached to it and as well as the blood will be there. So, these things we need to be converted into a product which is more stable, which is more resistant to the further degradation because if we leave these hides as it is so then they will be degraded because of the bacteria which will thrive on the flesh that is available on the organic material which is available to them and on the proteins which is available to them. So, they will try to degrade it further. So, we try to make the hides completely resistant to the degradation process. So, this is known as the tanning process and we also do this tanning process so that we can make the leather softer, we can make the leather more uniform, and which can be used for number of purposes like it can be used for the clothing, it can be used for the apparel, it can be used for making of the shoes etc.

So, that is why the tanning is very old industry because from the ancient times it has been used for the clothing of the ancient peoples. So, that is why this industry can be classified as one of the oldest industries. The tannery wastewater that is produced because of this process because of the conversion of the hides into the leather. So, this may be characterized by a strong color. So, we can have a very high color in it not only because of

the natural things which are present in the hides, but also of the dyeing or basically we can say the coloring of the hides because of which the color comes into the wastewater.

Similarly, it may contain very high amount of BOD values because a lot of proteins, lot of flesh, lot of organics so they are going into the wastewater. And similarly, it may also contain a number of highly dissolved salts where basically we can have the concentration of the salts because the salts are used for the preservation of the leather and during the other processes also, we use number of salts so that we can make the leather more receptive to the tanning process. So, that is why this wastewater may contain very high content of the salts in it. And similarly, the pH will vary depending upon what process we are using. So, the wastewater coming out from that process, the pH will depend upon that process and based on the chemicals that we are using for that process.

So, the pH will depend upon that, and pH varies from it may be basic when we are using lime salts whereas it can be highly acidic when we are using acids and other acidic salts. So, here the main concern is that that we can have a growth of a number of clusters of these industries. So, these industries may grow side by side and they may start dumping their waste outside the their premises which may contain lot of chromium salts and these chromium salts may again leach into the groundwater and it may cause damage not only to the groundwater, but it can also cause the damage to the surface water wherever the water leaches because it contains a highly carcinogenic salt that is basically chromium 3 is used which may be converted to chromium 6 on the oxidation process and this may go to the surface water bodies as well as it may also contaminate the groundwater. A case has also been reported where it was found that a cluster of the industries that the groundwater was totally contaminated by hexavalent chromium and the concentration was more than 1000 times of the drinking water standards. So, that is why it is very important that when we are having this wastewater which is being generated from the tanneries.

So, this basically should be treated properly, so that it may not cause irreversible damage to the environment. So, that is why it is very important that we try to treat this waste up to a certain degree, so that we can go for its safe disposal. Similarly, the hexavalent chromium is here a major concern because all of us know that we have already talked about the metals and hexavalent chromium is highly carcinogenic in nature. So, this may pose a major threat to the environment because hexavalent chromium if it goes into the water obviously into the surface water or into the groundwater. So, it may contaminate that water, and people may be drinking it without knowing that it is containing hexavalent chromium.

So, the tanning process involves a number of combinations of mechanical as well as chemical processes. For example, we can have number of chemicals to be added so that we can preserve, we can cure, we can make the leather soft, and we can also basically involve the mechanical processes. For example, we have to have a uniform thickness of the leather which we want. So, for that some mechanical processes may also be used. Similarly, we

can use a number of chemicals. For example, we can use lime here, we can use sulfites here, we can use number of salts here as well as we can use acids here and number of enzymes are also used during the tanning process which we will be discussing just now. So, here the heights which are there so they are converted into the non-deteriorated product by preserving it by adding a certain chemical which may be organic or inorganic in nature. So, these materials may become chemically bound to the protein structure of these heights and then they can preserve it from the further degradation. So, we can have two types of tanning operations where we can have the chrome tanning as well as we can have the vegetable tanning. So, in the chrome tanning as the name suggests we have to use chromium salts so that the tanning process is accomplished.

Similarly, for the vegetable tanning we use the extracts which are received from bark of the trees for example chestnuts, or we can also use certain plants so that we can tan the leather by using vegetable tanning. So, the manufacturing of the leather it involves a number of operations for where we convert this raw animal heights into different type of leather. For example, we can have the raw leathers, we can have the finished leathers, we can have the colored leathers, we can have a very highly soft leather which is of very very high qualities. So, for different type of leathers we have to have a different type of operations which are involved so that we can convert the raw heights into the leather. So, basically, we have three stages where we first of all prepare the heights for the tanning process so that the heights may become receptive to the tanning.

The second process is the tanning process itself where we tan the leather where we try to convert the leather into a stable product. Similarly, we have to go for finishing process after the tanning process we convert the leather into a finished product. So, the preparation of heights may involve for example when we are having the heights which are coming from the slaughterhouses. So, we have to see that the heights, so they are properly cleaned they are hydrated, and they are ready to undergo the tanning process. So, the preparation of heights means that is we try to prepare the heights we try to make the heights we are in the process of the tanning.

So, that it can receive the tanning chemicals into it and then basically it can be converted to a degradation resistant product. So, we can have different steps here for the preparation of heights where basically we use curing or preservations. Then we go for the soaking process, we go for liming and de-liming process, we go for bedding, we go for pickling process. So, preparation of heights covers the first step is the curing or preservation. So, the heights are brought from the slaughterhouses.

So, we receive the heights in the tanneries from the slaughterhouses. So, that we can convert it into the leather. So, here these heights may be first of all preserved by adding certain salts. So, that there is no decomposition or bacterial growth taking place. So, that is

why for preventing it from the bacterial growth or basically from the further decomposition or degradation before it is converted to the leather.

So, it has to be cured or preserved. So, this means that the whatever the salts we have used here which for the preservatives. So, that also needs to be removed during the preservation and curing processes. We have to wash the heights to so that we can remove the dirt as well as the salt preservatives. Similarly, we also soak it further into the fresh water which contains NaCl, or it may also contain the preservative chemicals like anti-mucin, and we have to soak it for at least for 1 to 5 days.

So, that it may become receptive for the further processes. After curing process, we go for soaking where the cured heights which have been soaked in the salt water or in the preservative water. So, they are now soaked in the water. So, that whatever the salt is there. So, salt that we have used.

So, it may have dried the leather. So, to rehydrate the heights we generally go for the soaking process where it is soaked in the water for long time. So, that it becomes receptive to the subsequent processes. So, for the preparation of heights we have to treat it by using a paste of lime as well as sodium sulfide. So, here we use a combination of lime and sodium sulfide in the ratio of 8 is to 1 and this is basically done in the wooden vats, and this process is called liming where it serves a number of purposes. For example, we can have first of all the hair removal where the limes it helps in the loosening of the hair follicles, and this facilitates the removal of the hair from the heights. So, this may be done so that the hairs are first of all removed from the heights. Then we go for flushing process. So, here the lime also aids in the removal of the flesh and also basically helps in the removal of the non-collagen proteins which are there in the heights. So, that the height may become free from these materials and later on basically we can go for the tanning process.

Similarly, it also opens up the fibers where the collagen fibers they can become more permeable to the tanning agents which we are using during the tanning process. So, that is how the preparation of the heights is done so that the lime may be used for making the heights more receptive to the tanning process as well as it removes a number of unwanted things which are there on the heights so that it may be further used for the tanning process. So, we can have the preparation of the height the liming may be done, and it may lose the hairs. So, these hairs may be removed mechanically also the hairs which are removed mechanically. So, they can be washed they can be dried, and they can also be sold as a byproduct. For example, it can be used for a number of other materials for example, it can be used for carpet pads, and we can use these hairs for other purposes also. So, this is one of the things by which we can use these hairs. However, the common method is that that we generally go for the liming process, and we completely dissolve these hairs, and these hairs may find their way in the wastewater stream. So, here after the hairs are removed so then basically these heights are really prepared for the actual tanning process. So, then you

go for the deliming process where the deliming process means that is we remove the excess lime which has been added in the heights.

So, during the liming process we have added lime as well as the sodium sulfide. So, we generally wash it so that we try to remove the extra lime, which is there, and which has also raised the pH of that height. So, basically we also try to wash it so that we can adjust the pH and then it may become more suitable for the next stage of processing because the next stage of processing may require a low pH values that is why it is very important that we wash the heights completely after the liming process so that they may be delimed as well as the pH may be reduced. Then the process comes which is known as the baiting process which is used so that we can further soften the heights, or we can also condition the heights the collagen fibers are also conditioned so that it becomes more soft and more receptive to the next processes. So, here we use a number of enzymes for example, we may use here proteolytic enzyme solutions which may be dissolving the proteins which will be converting these proteins into the simpler compounds and then basically it can be discharged into the wastewater.

So, here we the heights are placed into a large rotating drums which you can see on the right. So, these types of drums are used here we place the heights, and we place the enzyme solutions, and they are rotated and for a long time so that this proteolytic enzyme may get enough time so that the baiting process may be completed. So, baiting not only reduces the pH, but it also helps in reduction of the swelling of the heights which have been done during the liming process. Similarly, it also helps in the protein degradation of the proteins which are attached to the heights. So, after the baiting process we go for a process which is known as the pickling.

Now, we place the heights in the rotating drums, and we treat it by using the salt acid solutions. So, here we try to further lower the pH so that the heights may become receptive to the tanning agents which basically acts very well in the acidic environment. So, now the heights become ready for undergoing the tanning process. So, these are some of the preparation processes which are used so that the tanning process may be may start. So, the main advantage of the tanning process is that it treats the heights so that it can become more durable.

Similarly, it will treat the height so that it becomes resistant to the decay, it will be resistant to the quantification process otherwise it will degrade further, and we will not be able to utilize it for our further use if it is not properly tanned. Similarly, it is also used for a number of other applications. For example, when we are going for the coloring process and we are going for the dyeing process, so in that case also the tanning process is very essential. So, here we can have two types of tanning. For example, we can have the vegetable tanning and the chrome tanning.

So, we will discuss the vegetable tanning and chrome tanning one by one. So, let us start with the chrome tanning process and most of the leather which are produced which are of very good quality, so they are mostly chrome tanned. That is, we use here the chromium solutions, the chromium III solutions so that we can tan the leather and this type of leather which are produced from the chrome tanning. So, they may be used for the upper parts of the boots and shoes, they may be used for clothing, they may be used for apparels, they are used for preparing a very good quality of light leathers. So, for example, when we go for the vegetable tanning generally the leather that is produced is of a thick quality whereas in this case the very light and soft leather is produced by the chrome tanning process.

And chrome tanning process also requires a very less processing time in comparison to traditional vegetable tanning where we may require longer contact hours so that the tanning process may be completed. And in the tanning process we use the same wet as we have used for the pickling in the previous step, and we add a solution of chromium sulphate to it, and we mix it for 24 hours. So, what happens that this chromium sulphate may be having a characteristic color. So, this characteristic color goes on to the chrome tanned heights. So, this may convert the heights into blue color height that is why a characteristic blue color is caused after the chrome tanning process is completed.

Now, some color has been added on to this height. So, we used a bleaching agent so that we can remove this color, and we can use a dilute solution of sodium thiosulfate or sodium carbonate in the same bath so that this leather which is having a certain color after the chrome tanning so this can be removed from the heights. After this we may throw out the half of the spent liquor which is there in the chrome tanning process and then we can reuse the half other half for by using fresh volume of the water and this liquor which is thrown out from the chrome tanning process it may contain lot of chromium salts into it. So, that may be a matter of concern, and it should be properly treated before we put it for the safe disposal. So, after this process the excess moisture which is there so it may be removed from the heights by using operation which is called the ringing operation.

So, ringing operation is the similar operation as we try to ring our clothes after bathing. So, we try to apply a force in the opposite direction so that whatever the excess water which is there or excess moisture which is there in the height. So, this can be removed from the heights. So, it also results in the soft leather for example, when we are going for the applications like upholstery, clothing and other accessories. So, we generally try to prepare a soft leather so that these types of items can be made with good quality.

So, after the chrome tanning process since the cattle heights they are too thick so what we do here that we try to split it that is we try to remove the upper portion and the lower portion here so that we can get a leather which is of uniform thickness, and it is having a lower thickness also which results from the splitting of the heights. So, for example, it will produce two surfaces one surface will be grain side which is on the top whereas, the lower

portion which is there which is basically containing no grains. So, that is basically thin portion also so that is known as a split, or it is also the blue drop. So, this is splatted into two parts. So, here the one surface which has the grain side retains the natural grain whereas, the other surface which is the lower portion so it basically has no grains and it is smoother in nature and because of the no graining they may be used for making of the suede garments or the suede shoes where basically suede may be used for a more permeable and softer leather which we require for some type of shoes or we may require for some type of clothing.

So, both the grain side as well as the split so they may be further processed so they can have the uniform thickness. So, for this we go for a process which is called shaving where we try to remove the small pieces of the leather which are there so when we try to make the thickness uniform so it may result into a very small pieces of leather which are very similar to the coarse sawdust. This may be removed from the leather, and these are called shavings, and they may result in the solid waste generation. So, after this process the tanned hides which are there so they are retained and then basically they are colored and then they are fat liquid. For example, retaining is a very short span of second tanning process where basically we use some other salts rather than the chromium salts so that is known as the retaining process.

So, this may further increase the durability of the leather, so we go for the retaining process. After retaining we go for the coloring process that is we try to add certain pigment we try to add certain dyes to the hides so that basically whatever the leather is produced we try to add certain pigments we try to add certain dyes to the leather so that we can get the desired color in the leather and then after that the hides are again taken out and they are run so that the excess moisture which is present so that may be removed from the produced leather. After this we take it to a process which is called fat liquid where we add a number of mixture of the oils for example we can use mineral oils we can use the crude oils so that the desired softness in the leather may be attained and so these hides are now added into the oil into a rotating drum where these oils may be added or the mixture of the oils or grease basically may also be added so that the leather may be fat liquid. So, after this the leather is dried and then it is physically conditioned so for the physically conditioning of the leather we go for the processes which are known as the staking and buffing where we staking means that is we try to massage the leather further so that becomes more pliable more resistant to the cracks etc. and becomes more softer and similarly the buffing operation may also be done where light sanding operation may be done so that whatever the imperfections are there on the underside on the grain side also so that can be smoothen out and these surface imperfections can be removed from the leather and leather becomes more soft and more durable. So, the finishing processes may also be used here for example we can provide a further gloss to the leather that is produced so this may enhance the waterproof qualities of the leather.

So, here we try to have the liquid finish materials which we try to roll it on it, or we try to spray it for example we can apply three to four coats of those finishing liquids which is again followed by the drying cycles. After that we may also go for making some patterns we can have the embossing done on the leather which is now totally prepared so that we can have the hallmarks the industrial marks present on that or basically we can have other information embossed on the surface of the leather so this basically can be done so this comes under the finishing process and finally the area of each of these leather is measured electronically and then it may be stamped on the underside so that which means that the now the leather is finished and then it may be packed and it can be stored for the for the shipment. Vegetable tanning is may also be done for example here we use the tannins which are received from the plant sources for example we can use certain type of tree bags we can use certain type of leaves we can use certain type of fruits so that we can tan the heights. So, when we are going for the vegetable tanning so in that case, we may produce a leather which is more of thicker quality which is more of more firm as well as durable and as well as it produces the products for example when you want to produce the leather belts, saddles, the work gloves, the shoes, the soles of the shoes, the craft works etc.

So, we generally go for the vegetable tanning process. So, this vegetable tanning process may result in a leather which is not of very high quality, but it can be used for our daily use items or basically we can use it for a rougher work that can be done, and we are basically this type of tanning may be used. So, the vegetable tanning has also the similar basic steps as we have seen in the previous in the chrome tanning. So, however the sequence may be somewhat different and there may be some few finishing operations which are associated only with the vegetable tanning process only and here the brushing process is done after the hair removal and the baiting process is also similar to that of the chrome tanning process, but the pickling may not be done in this vegetable tanning. So, here the coloring is done by using a very weak tanning solutions and that's why we find that the vegetable tan leather is not highly colored and we generally find that the vegetable tan leather they are more or less brownish in color and they do not have other colors on it or the colors are there but these colors may be quite light in comparison to the colors that we see in the chrome tanning leather. So, here after coloring the heights may be produced may be added into the wets which may contain the bark extract which basically we take it from the strong tanning solution and then later on we take it to a weaker tanning solution and then it can be rinsed and then it can be dried.

Here the splitting process is not required because the leather is basically not split into two parts, we use we try to convert the leather into a thick leather only and here however the leveling process may be done so that we can get a uniform piece of thickness of the leather and that's why in this case there is no split that is produced during the vegetable tanning. So, after this the heights are generally oiled so that it can be fat liquid as we do in the chrome tanning and after the oiling we can dry and then we can mechanically condition it

and virtually we require no finishing process in the vegetable tanning processes and some spray finishes may be applied and the only finishing process that is employed is to press it so that we can get a very smooth grain surfaces and then later on it can be measured and it can be packaged prior to the shipment. So, in the finishing processes we may go for the stuffing fat liquid as well as the dyeing process that is the coloring of the leather that is produced after the tanning process and here we may also go for adding oil and grease so that the leather that is produced basically becomes more soft it becomes more pliable and it becomes more resistant to the tearing of the leather and here we can also go for using synthetic dye stuffs for providing different type of colors to the leather. So, if we talk about the flow diagram of the vegetable as well as the chrome tanning process so we can see here that the raw heights are taken first of all to the soaking process where we add sodium chloride to it certain salts are added so that whatever the proteins are there whatever the flesh is there whatever the dirt is there so that can be removed from the system and here we can see that it may lead to the intermittent and strong waste from the soaking process and after the soaking process we can take it to the flushing where basically we try to remove the flushing by washing it further right by soaking it further and this flushing basically may produce a waste which is a continuous and it is a weak type of waste that is produced after the flushing we can take it to a lime process where we add lime as well as we may add sodium sulfide to it so that the hairs the proteins and the resistance or basically the opening of the collagen fibers so this may happen and then basically it may result into a again a strong and the intermittent waste. So, from the liming process we can take it to the hair removal process where we can de-hair the heights which are there and these de-haring may be done where we can loosely remove the hair from there which results in a by-product or we can also completely dissolve the hairs so this may result into a continuous and the weak waste after the hair removal process we can take it to the process of the wetting where basically we can go for addition of certain enzymes like here we can use chymotrypsin or trypsin as well as ammonium sulfate can be used and the wetting process may also result into the intermittent strong waste and then we wash the heights so that may result into the continuous and the weak waste.

So, after the wetting process if we talk of the chrome tanning process so we can take the heights to the pickling process where we add certain salts we add certain acid to it so that the heights may become receptive to the chrome tanning process and in the tanning process we add a certain chromium salts that is chromium sulfate and we also add certain salts to it after the tanning is done we may go for the splitting process then after that we may go for washing process and washing process may result in a continuous and the weak waste. So, after the washing process we can go for coloring and fat liquoring and then we go for the finishing and this fat coloring and fat liquoring may result in an intermittent strong waste here also. Similarly, when we talk of the vegetable tanning process so in that case we may use a certain extract which are generated from the bark or from the nuts or from the vegetables so this tanning process is done and this tanning process may lead to the

intermittent strong waste and similarly after this we may bleach the heights and by using a solution of sodium sulfate and sulfuric acid and after which we may go for oiling and loading where we add certain oil salts and sugar also and we go for the finishing process. So, that is how the vegetable tanning and the chrome tanning process may differ in their processes. So, if we talk about this flow diagram of the vegetable tanning process so here, we can see that we are taking the raw heights the soaking pits so this may result into the continuous flow of the wastewater also.

So, for example, we can have the washing which is being done so this may result in a continuous wastewater whereas the spent liquid which is being generated from the liming wet so it may result in the intermittent flow of wastewater. De-flashing and hair removal may lead to the continuous generation of the wastewater. The De-liming and wetting may result in a in the continuous flow of wastewater when we are going for the washing it and whereas the solution that we are using for the De-liming and the wetting process so this spent liquid may result in an intermittent flow of the wastewater. So, tanning process here also may lead to a continuous generation of the wastewater after the tanning process when we go for the washing process. So, it may lead to the continuous generation of the wastewater whereas the tanning extract that we are using the spent liquid of the tanning process may result in an intermittent flow of wastewater.

Similarly, the washing and finishing process may lead to the generation of the continuous flow of the wastewater as well as it may lead to the intermittent flow of the wastewater and then we get the finished leather. So, we stop here, and we will be discussing about the characteristics of the wastewater that is generated from the various processes which are involved in the tanning process in the next lecture. So, these are the differences that we have used for the preparation of this lecture.

Thank you.