Course Name: Industrial Wastewater Treatment

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Lecture 3: Treatment of wastewater produced from Tannery and Pulp and Paper

So, welcome back, we are in module 8, lecture 3 and we are talking about the treatment of the wastewater produced from tannery and pulp and paper industries. So, we will cover in this lecture the chromium removal and recovery process which basically comes out from the tannery wastewater. Similarly, we will talk about the chromium chloride removal and the recovery processes that we need to follow so that we can treat the tannery wastewater fully and we can get rid of the chloride levels. Similarly, after this we will talk about the pulp and paper mills, we will talk about the raw materials which are used in the pulp and paper industries, we will talk about the pulp manufacturing process where we will talk about the mechanical pulping, we will talk about the chemical pulping and we will talk about the chemo mechanical pulping also we will talk about the properties of the pulp and similarly, then we will talk about the flow diagram of the integrated mill where basically, the pulp as well as the paper may be produced. So, we have seen that the chromium is generated during the chrome tanning process and this chromium III salts may go into the sludge that is generated from the chromium III may be present in the base water that is generated from the chrome tanning process. So, the major portion we have already seen that the major portion of the chromium III may be removed in the primary sedimentation tank.

For example, we have seen that when we are having a combined chrome tanning waste, so in that case nearly 98 percent of the chromium III may be removed during the primary sedimentation tank, and it may come out as the primary sediment settling tank sludge. So, this sludge may contain lot of other impurities also because we are having other impurities which are for example, colloidal impurities which are there. So, they may also become the part of those that sludge. So, it is not easy for us to recover the chromium during that process.

And similarly, when we are treating the waste water by using the primary sedimentation tank in a combined chrome tanning waste water, so in that case the chromium concentration is reduced in the primary sedimentation tank which may further be reduced when we are going for the dilution by using domestic wastewater as we have seen that when we are treating the wastewater by using the biological methods like active research process. So, in that case we can have the combined treatment where the domestic wastewater may be treated along with the tanning wastewater. So, in that case the chromium concentration may reduce, or the chromium concentration may also reduce further when we are having

the dilution by the river water. And this residual concentration may not also impair the BOD removal process until unless the concentration of the chromium in the effluent may be really very very high. But it is very important that we segregate the chrome tan liquid and then we try to recover the chromium from it because the chromium is highly toxic also and as well as it is quite costly also.

So, it is better that we segregate the chromium from the chrome tan liquid. So, here what we do that we add lime to it so that the pH may be raised beyond 6.6 or so and then the chromium III salts are present in the wastewater. So, they may be precipitated as chromium hydroxide, and they may settle down as a sludge and later on this sludge basically can be separated out by filtration process or by settling process and then this sludge basically can be used for the recovery of the chromium III. So, if we treat this sludge by using a concentrated sulfuric acid so in that case the chromium sulfate solution may be formed and this chromium sulfate solution may again be used for the chrome tanning process.

So, it is possible that we can recover nearly 90 percent of the chromium by this process, and it is nearly 25 ml of the concentrated H_2SO_4 may be required per liter of the spent chrome tan liquid so that we can recover the 90 percent of chromium from the chrome tan liquid. So, the recovered chrome tan liquid is very highly comparable to the freshly prepared liquors, but they may need certain adjustment of the pH because the pH of the recovered chrome tan liquid may be high because of the addition of the lime that we have added there or the raising the pH. So, we can adjust the pH by adding soda ash or other salts so that we can or other chemicals so that the pH can be brought down to the value which is required for the chrome tanning process. Similarly, the filtrate which comes out from this the recovery of the chrome tan liquid so this may also contain chromium, and it may be further sent for the treatment with the other base water. So, the cost of the recovery may be less than the cost of the fresh chromium powder that we are using so it is feasible that we can go for the recovery process and here the profit margin may be of the order of 27 percent of the total cost of the chrome powder, so it becomes beneficial that we try to recover the chromium out of it.

Though it is possible that some of the tannors may not go for this recovery because of not so high profit rate but again this when we are going for the recovery of the chromium so then it is first of all it will reduce the chromium pollution load in the environment as well as it will also lead to the lot of saving of the foreign exchange as the commercial chromium is generally imported from the abroad and then basically it is used in the chrome tanning process. Similarly, we also will reduce the load on the chromite mining. Now after talking for the chromium so chloride is also a problematic thing in the tannish base water so here the chloride cannot be removed by the conventional treatment process as we have already seen so we can go for the solar evaporation of the soaked liquor or the spent pickling liquor where the lot of salt is used but however the salt that basically becomes very impure because of the other impurities also coming into the salt so the disposal of these salts may

become a problem. However, we can reuse the salt which is used in the spent liquors. For example, the spent soaked liquor may contain nearly 10% of the salt whereas the pickling liquor may only require 8%.

So, what we can do here that the spent soaked liquor may be used as a pickling liquor after adjusting the percentage of salt here that is we can go for the addition of acids or we can go for the addition of alum for example 0.2% of alum may be used and later on the settling may be done and after which the spent soaked liquor may become suitable for the pickling liquor. And similarly, we can also reuse the pickling liquor so it can be reused several times with or without make up water so that the salt usage is reduced. Or we can also go for technologies where we can use saltless preservatives like neem oil can also be used for the preservation purposes. So, this completes our tandoori base water part and now we go on to the next industry that is the pulp and paper mills.

So, this pulp and paper mills are also one of the oldest industries as we have seen that the tandoori industries, they are one of the oldest industries. So here also this pulp and paper is a very old industry, and it has seen a tremendous expansion during the last 25 years. But the main problem of the pulp and paper industry is that it is a highly water intensive industrial process. So, it leads a very high amount of water for its different processes that we will be discussing just now, and it may require because of the large amount of water that is required so it may lead to the huge generation of the wastewater. So here the basic process is that the pulp is generated first of all.

So, the pulp that is generated is generated from a raw material which contains cellulosic materials. For example, we can generate the pulp from the bamboo, from the wood, from the recycled papers also. So, this cellulosic material is used for the preparation of the paper. So here the wastewater may contain very high amount of CODs and as well as the color because we are using lot of organic material here which contains lot of lignin into it. So this lignin may have very very high COD content into it and this imparts also the low biodegradability also and the color may be used when we are using the colored paper or when we are going for the bleaching process also.

So then also the color may be coming into the wastewater. Similarly, when we are going for the chemical pulping process so in that case also a lot of color basically comes into the wastewater. And presence of the lignin so it basically makes the wastewater highly non-biodegradable because the BOD by COD ratios may be very very low in such case because lignin is highly non-biodegradable in nature, and which makes the wastewater non-biodegradable. So, as we have talked about that it is a highly water intensive process. So generally the industries that is the pulp and paper mills so they are located near the banks of the small rivers and because lot of awareness have come for the conservation of the waters and lot of research is also being done for finding out the economical solution for

recycling the water for treating the water so that the water can be reused and we can conserve the water so that has lead to the reduction in the utilization of the water.

For example, earlier the industries used to consume nearly 200 cubic meters of water per ton of the paper that was produced but now in 2023 it has been reported that the integrated mills have reduced it to nearly 40 cubic meters per ton of the paper that is produced. So, we can divide the pulp and paper operations into two major sections that is first is the pulp mills where the pulp is produced and other is the paper mills where the papers are basically produced. So pulp mills they generally separate the fibers of wood from other materials for example which we can have waste materials like rags, we can have waste water, we can have straws so we can also have other things which are basically attached to the cellulosic fiber for example here we want to remove lignin from the cellulosic fiber so these all things when we remove it and then we try to create a certain material which is pulpy in nature which basically forms a pulp which can be used for the generation of the paper later on. So, this is known as the pulping operation and this is generally performed in the pulp mills whereas when the pulp is produced so it may be taken to the paper mills where the manufacturing of the papers different type of papers for example the paper products the converted paper products and papers so they may be manufactured from the pulp that is generated from the pulp mills. So, when we are having these both the industries together, so they are known as the integrated pulp and paper mills.

So the raw materials that are used in the pulp and paper industries the first is first and the foremost is the wood that is we can use different type of woods here for example we can use softwood which are coming out from the coniferous trees such as pines, fruits or fir and these softwood fibers they are long so they can provide a strength to the paper. Whereas we can also go for the hardwood where basically we use deciduous trees like ecliptus we can use birch we can use oak so these fibers which are produced from the hardwood so they are shorter and they also produce weaker fibers they are not having that strength as which are having the long fibers but they can contribute a lot to the paper smoothness to the opacity to the printability which can be used for other purposes. So, we can also use recycled paper also as a raw material for example the base paper the used paper so they also can be collected sorted, and they can be processed for the recycling of the paper. This will reduce the demand for the virgin fibers, and it will also minimize the environmental impact in the sense that it will lead to the lower deforestation that is the demand of the pulp and paper industry. So here we can use a number of chemicals for example we can use chlorine, chlorine dioxide, hydrogen peroxide and oxygen we can bleach the pulp so that the color may not go into the paper that we are having so it will not only remove the color from the pulp, which is there, but it also adds to the desired brightness to the pulp.

So, similarly we can also use a chemicals like sodium hydroxide, sodium sulfite or sulfonate acid which are employed so that we can break down the complex molecules of

the lignin and they can be separated out from the collagenous fibers and we use such type of chemicals during the chemical pulping process where we try to cook the wood that we are having so that the wood can be digested and lignin can be separated out. So, it can be used during the craft process, it can be used during the sulfite pulping process which we will be discussing in the coming lectures. So, we have to use a large amount of water as we have already discussed so this large amount of water can be used for the pulping process, it can be used for the washing process, and it is generally used for the paper making process also. So, as we have already discussed that the efforts are being made so that we can recycle, we can use this wastewater, we can treat the water so that we can minimize the environmental impacts. Then there is a requirement for the energy sources for example, there can be various stages like pulping, refining, drying and finishing so they all require lot of machines, and they may require lot of electricity in that, and steam may also be used during certain pulping processes like when we are using them, when we are drying the paper in that case the steam may be used.

Similarly, a number of fillers and additives may also be used for example, the calcium carbonate may be used to improve the brightness, to improve the opacity and the printability of the paper. Similarly, we also use stars so that we can improve the paper strength, we can also control the ink absorption by the paper. Dyes and pigments may also be used so that we can produce the colored papers. So chemical additives may also be used for example, we may have added the retention aids which can retain the fine particles so that it can improve the sheet formation from the pulp that we are having. Similarly, lot of de-foaming agents are also used so that whatever the foam is formed during the paper making process so that can be removed, and we also have to add wet strength agents which can enhance the paper strength of the paper when it is wet.

So, we can also use other fibrous materials also for example, which are generally non-wood fibers for example, we can use cotton, we can use hemp, or we can use KNF for the production of the paper. And lot of biomass and residues are generated for example, lot of bar, sawdust and wood chips will be generated when we are going for the processing of the logs and so this can be used as a fuel for the energy generation. Similarly black liquid that we will be discussing during the craft process so it may also contain lot of dissolved lignin. So, it may also be used as a fuel for the energy recovery. And we may also go for adding number of chemicals like we may go for the pulping agents, de-foamers, de-inking chemicals so they also are added during the paper making process.

So, the paper making process can be divided into two phases. One is the pulp making and other is the final product of the paper. So, the pulping process is the crucial step where the wood fibers so they are separated from the other components of the wood so that we can produce pulp. For example, here we separate out the lignin, we separate out the other waste materials which are there in the wood which we do not require, and we separate out the cellulosic fibers so that we can produce the pulp out of it. And we know that the pulp is

the essential and the key part or we can say the key raw material for the production of the paper.

So, we can produce the pulp by different methods for example, we can go for the mechanical pulping, we can go for the chemical pulping, and we can go for the chemo-mechanical pulping. So, in the pulp making phase the chipped cellulosic raw materials so they are digested by using different chemicals. So, we generally do it at high temperature and pressure. So, this process basically loosens the cellulose fibers, it can dissolve the lignin, it can dissolve the resins, it can dissolve other non-cellulosic materials which are there in the raw material so that we can separate out the cellulosic fibers. So, we can use number of raw materials like for example, wood is there, cotton or linen racks are there, straw, hemp, sparto, flax and jute or wastepaper so they all can be used as a raw material for the pulping phase.

So, when we go for the mechanical pulping, so we are separating out the fibers without the addition of the chemicals. For example, this here we use number of mechanical processes, here we use number of machineries so that we can separate out these fibers from the rest part of the wood. So, this may be a very highly energy intensive because we are using a number of machining processes there and the fibers which are produced so they basically may be shorter fibers and we have already seen that these shorter fibers may be very weak in nature because they are not long, they may not provide enough strength to the paper. So, and these papers that is produced from this mechanical pulping so they may be weak paper which can discolor very fast, which can also become brittle with the age. So that's why generally the paper that is produced from the mechanical pulping, so they are used for the newsprint, they are used for the tissue papers, they are used for paper board.

So, we can go for the mechanical pulping by two methods. For example, the first method is called ground wood pulping where the wood locks so they are mechanically ground grounded by using a very very huge stones or metal surfaces so they are grinded and these fibers during the grinding process they are separated from the wood because of the mechanical action and then we may get a certain fibers out of it which are shorter in nature and they can be used for the manufacture of the newsprint paper. Similarly, we can also go for refiner mechanical pulping where the locks are not used, where the wood chips are used and these wood chips are basically taken to a mechanical refining process where we use the grinding plates or the refiners as you can see here so these are the grinding plates which are being used for grinding of these wood chips and this action the refining action may separate out the fibers without using the significant chemicals and this may lead to the generation of the pulp and this pulp may also be generated when we are going for the thermo mechanical pulp that is where we are using the thermal application along with the mechanical applications so that we can get a thermo mechanical pulp or we can also go for chemi thermo mechanical pulp which is also called CTMP where we use certain chemical treatment and then we can go for the thermal and mechanical treatment for the production

of the pulp. So after the mechanical pulping we may also go for a process which is called chemical pulping where we try to use a number of chemicals which break down the lignin that is which this lignin is a very complex polymer that binds the cellulosic fibers very tightly so we use a number of chemicals so that we can digest these lignin and it comes out in the waste water that is generated from there and we get the cellulose fibers intact. So, these cellulose fibers can be used for the production of the pulp, and this may produce a very high-quality pulp, and which can be used for a number of ranges of the paper products.

So, the chemical pulping can be done by using two processes for example we can go for the craft pulping process where the wood chips they are mixed with the solution of sodium hydroxide and sodium sulfide and this mixture of sodium hydroxide and sodium sulfide, so it is known as the white liquid. Then this mixture is heated in a digester at a very high temperatures and pressure so this cooking process basically breakdowns the lignin and it separates the fibers from the other unwanted materials. Then the resulting pulp is known as the craft pulps, and it is basically washed further so that whatever the residual chemicals which are there on this pulp so this may be removed from the pulp. So, sulfide pulping will also be done where the wood chips they are treated with the different chemicals that is here we use the sulfurous acid and a calcium-based chemical that is the calcium bisulfite or calcium sulfite may be used for the digestion of this mixture. So here we cook the mixture at a very high temperature and pressure so that the lignin is dissolved from the wood that we have used during this process and then whatever the pulp we get from here that is known as the sulfide pulp is washed and then basically so that we can remove the chemicals which are there and then it is taken for the further use.

We can also use other chemicals also for example we can use sodium carbonate so that we can break down the lignin in that case so it is basically soda ash is used for the soda pulping and similarly we can also add anthraquinone during the craft pulping process, so it improves the yield of the pulp. So we can see here that when we are going for the chemical pulping so we take the wood chips here so in that case we may go for the cooking or the alkaline treatment so we add white liquor here for example when we talk of the craft process so this white liquor may be added or whatever the chemicals we are using for the process so they may be added here and the wood chips are added here and this is basically digested at very high temperature and pressure and then basically whatever the waste water is generated after this so these materials are washed and this may result in a generation of the waste water which is known as the black liquor and this black liquor may again be converted to white liquor we will be discussing this that is it can be recycled and reused in the digestion process. And now whatever the wood has been generated whatever the digested wood has been generated from here, so it is taken to the delugification process to the bleaching and drying process and finally it is basically the pulp is formed. So here lot of wastewaters is generated from the dying process the wastewater is also generated from the washing brown stock. So then we can also go for the mechanical pulping where we

may use wood chips or we may also use the wood locks also so here it will go for the mechanical process like we can go for the disc refining and after which we go for the screening and cleaning and then basically we wash the cleanings that basically we have received from here and this may again go for the further thickening the bleaching and drying process and thickening may lead to the generation of the waste water which may ultimately lead to the generation of the pulp.

So, after this we may also go for the chemo mechanical process where semi-chemical pulping is used so this is a hybrid process which uses the chemical as well as the mechanical pulping so here we go for initially chemical pre-treatment before the refining mechanical refining and basically this may be used but the chemical treatment may not be as intensive as we have done in the in the pure mechanical process so here the mechanical refining process we may treat it by using the chemicals so it not only increases the pulp brightness but it also decreases the presence of the shives so shives are the undigested wood that basically is present in the brown stock. So here we can use neutral sulfite semi-chemical approach for example here the the wood chips they are treated with sodium sulfite and sodium carbonate before the the pulp is taken to a to the mechanical pulping and this mixture is heated but it is not heated in the severe conditions as you have seen in the craft of the sulfite pulping and after which the pulp that is produced so this can be taken to a refining process and then basically the pulp that is the NSSC pulp that is produced it combines the chemical as well as the mechanical pulping characteristics. So, after the pulping process the resulting pulp is first of all bleached so that the color is removed and then it is taken to the manufacturing process of the paper. So, the choice of the pulping method will depend on number of factors for example it will depend upon the type of the paper that you want to produce it will also depend upon the cost consideration it will also depend upon the environmental considerations so depending upon that we choose the method which we can apply for the pulping operations. So then we can have the number of properties of the pulp that is generated so that we can have the suitability for different type of papers or paper board products that we are generating out of it so we can have the fiber length so it also decides that if the fiber are long we have already discussed if the fiber are short so it may be a weak paper if the fiber are long so it may result in a strong paper.

Similarly the fiber morphology also gives us insight regarding the quality of the pulp and the freeness basically it tells us about the ability of the pulp to drain water during the pulp making process so higher the pulp ability to drain the water the better it is and similarly the opacity means that is how much it can block the transmission of the light and it is very very essential when we are going for the printing papers or when we are going for the writing papers so in that case opacity is very much required. So, we have to also see the bulk density that is bulk density will tell us that what will be the yield of the paper from the given amount of pulp that we are having so that's why it is this property is also very

important. Similarly the tensile strength it gives the indication about the strength of the paper that is produced from the pulp and the tear resistance also helps us to assess the durability of the paper against the tearing and other environmental conditions and similarly the moisture control is also very important which is a very very crucial in controlling the water content in the paper during the paper making process. So this is a simplified flow diagram of the integrated mill where we can see that there is a wood yard and the chipping basically is taking place here and from the wood yard and the chipping so various logs of the wood or we can say the chips that are formed from the wood so they are taken to a cooking process for example here we are talking of the chemical pulping process so here it is taken to the cooking digesters where we add a number of chemicals which are required for the digestion of the wood and after the digestion process is over then we take it to the washing process where again a number of very large amount of waste water may be generated after which we take it to the screens one so that the lumps of the wood or basically the chives so they can be removed from the pulp that is formed and then we take it for the bleaching process where the color which is there on the on the pulp so this can be removed by the bleaching process by using different type of chemicals and after the bleaching it may again go for the screening so that we can have a uniform material which is which is generated from the screens and then we may take it to the drying machines where the pulp is dried further and then we may take it to a rolling or the finishing department where the ultimate product that is we require that is either we require paper or we require the paper products or other products that are generated for example cardboard so they can be produced from here and this is how the paper is generated. So, these are the differences that we've used during the preparation of this lecture, and we'll continue our talk regarding the pulp in paper mills in the coming lectures.

Thank you.