**Course Name: Industrial Wastewater Treatment**

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**Lecture 4: Treatment of wastewater produced from Tannery and Pulp and Paper**

Welcome back. We are in module 8, lecture 4 and we are discussing about the treatment of wastewater produced from tannery and pulp and paper. So, in this lecture we will be discussing about the craft process for pulping. We will discuss about the flow diagram of a craft pulp and paper mill. We will talk about the sulfide pulping. We will talk about the sources of the wastewater generation and then we will talk about the wastewater characteristics which are generated from the pulp and paper industries, and we will also talk about the typical pollution load per ton of the production of the paper.

So, the craft process, which is involved in the making of the pulp, so it uses a number of chemicals for example these chemicals may be sodium sulfate, sodium hydroxide and sodium sulfide. So, these chemicals are added in the digester along with the chips of the wood so that they can be digested and the spent liquor which is produced from this reaction is known as the black liquor. So black liquor may be treated separately so that we can recover whatever the chemicals we have added during the digestion process. So, these cellulosic fibers which are there so they are separated from the lignin that is present in the wood and then basically these fibers are washed and after which they are partially dewatered in a cylindrical screen which is known as the decker.

A concentrated wash water may be sent for the chemical recovery and the dilute wash water it forms the wastewater. So, whatever the concentrate or we can say the spent liquor is there so that is used for the chemical recovery and the washing water, so this basically forms the part of the wastewater. So, the volume of the wastewater which is generated from the washing of the digestion material, so this is known as the brown stock wash, or it is also known as the unbleached decker waste. So, after this these cellulosic fibers so they are sent for the bleaching where we employ three stages for example, we can use chlorine here first of all and then we can use caustic and then we use hypochlorite in successive stages so that the color that is there on this pulp which is generated so that may be removed. So here the wastewater which is generated from the chlorine as well as the hypochlorite stage so this is light yellow in color whereas when we employ the caustic for the extraction of the color so this may be highly colored in nature and after this the bleach pulp is sent to the paper mill for the making of the paper.

So, when we talk of the paper mill so here the pulp is first of all disintegrated it is mixed with the number of materials like for example which are known as the filler materials so that the paper may be formed the strength of the paper may come the luster of the paper may come as well as the consistency of the paper is maintained. So here we use alum we use talc we use ties so that we can have the required requisite properties and here this is done in a tank which is known as the beater and this tank is of the oblong shape and here after this process the of the beating the pulp is then refined in a machine which is known as the Jordan and then the refined paper is diluted so that we can have the proper consistency which is required for the paper making and later on it is passed through the screens where the knots and lumps which have been formed during the process so they can be removed and then later on this may be sieved through a fine screens or a series of rollers so that basically we can produce the papers and the water which is drained out from this rollers when we are rolling the paper so this is known as the white water and this also forms the waste water from the paper mill sections. So, this wastewater as because we are rolling the paper so it may contain lot of fine fibers it may contain the chemicals that we have added as the filler materials for example alum can be there, talc can be there so these things comes into the wastewater generated from the paper making section. So here we have already talked about that the black liquor that is formed from the digestion of the wood chips so this may be recycled. So for the recycling of the black liquor so we generally go for the concentration first of all by the evaporation method and then we incinerate it with the addition of the sodium sulphate so whatever the organics are there for example lignin will be there, resins will be there so they will be burnt out and the smelt which is now left so this is dissolved in the water and after dissolving it in the water it will result in a liquid which is known as the green liquor.

So, when we add lime to this liquor so white liquor and the lime mud basically forms and this white liquor can be used again for the digestion process. So, when we are recovering the black liquor so it may result in a formation of number of toxic compounds for example we can have the dimethyl sulphide, we can have methyl mercaptan which can be highly highly toxic to the environment. So now we will discuss about the flow diagrams of the craft pulp in paper mill. So here we can see here that the raw wood is taken to the chipper plant and in this chipper we are chipping the wood so that it forms the chips and these chips are later on washed by the water which is recycled from the paper mill and this washing results in the generation of the waste water which is light colored waste and it is basically mixed with other waste so that we can treat it separately. Similarly when we take these chips to a digester so here we add the desired chemicals for example in the craft process we may add sodium sulphate or we may add sodium hydroxide or sulphide so here these chemicals are added and the digestion process at high temperature and pressure is performed so this may also result in the spills which forms the wastewater condensed wastewater here and this wastewater is taken separately for the treatment.

So, here we can have the separator where we separate out the pulp that is generated and the spent liquor so this results in the black liquor and this black liquor may be taken for the recycling where we again evaporate this black liquor we try to incinerate in the furnace and then we after this incineration we can go for addition of the water and to the smelt and this may result in the formation of the green liquor and when the lime is added to this green liquor so lime mud may be formed and the white liquor that is formed so that can be again taken back to the digester for the digestion process. So here we are now after separating the pulp is there and this pulp is again washed and by the water and this wash water may again be mixed with the black liquor water for the recovery of the chemicals. Similarly, then we can add some water here then we again wash it and this wash water that is the brown stock wash so this may be resulting in a colored waste so that is taken separately for the treatment of the color. After this process we add chlorine to it so that the bleaching may be done, and the chlorination waste is then added along with the waste that is being generated from the chipper house and this result yields in the light-colored waste. So, after the chlorine bleaching, we take this pulp that is generated for the further bleaching that is by caustic, and this results in a generation of the highly colored water and this water is again mixed with the water which is generated from the washing of the brown stock as well as the water that is generated from the spills of the digestion process.

So, after the caustic bleaching, we take the pulp further to the hypochlorite bleaching which results in a light-colored waste and this waste is again mixed with the waste water which is coming from the chlorine bleaching as well as from the chipper house waste. And then we get the finished pulp so this finished pulp is now then taken to the pulp chest and where after this certain chemicals like glue, alum and tal has been added so which acts as a filler materials for the formation of the paper and this is done in the beater and after the beater we take it to the Jordan and then we add water to it so that we can have the required consistency which is required for the paper formation and then we take it through the screens where the knots and lumps basically they can be removed and then it is taken to the paper machines or the rollers where it is rolled and whatever the water is generated that is the white water is generated so that may be again recycled may be taken for the washing of the chips wooden chips and here the fibers that are generated from here so this may be taken back to the paper machine or formation of the paper and later on from the paper machine the papers are taken to the dryers and then they are taken to the reelers and then the final product is formed. So, then we come to the sulfite pulping so in addition to draft pulping we can also use sulfite pulping where it produces the cellulose fibers which are very pure in nature and here, we add sulfite ions and bisulfite ions for the digestion of the wood chips. So, these chemicals which we add for example sulfite and bisulfite ions so they may leave the bonds which is there between the cellulose and the lignin components, and it may result in the formation of lignocellulose. So, here we can add number of salts of the sulfite and bisulfite for example these salts may be of sodium these salts may be of calcium these salts may be of potassium magnesium lime as well as ammonium ions.

So, we can add a number of salts which can lead to the digestion of the wood chips and here one more thing we have to keep in mind that the soft wood is primarily used for the sulfite pulping process. So, lignin which is converted to lignosulfates here in this case so it can be soluble, and it can be separated out from the cellulose fibers. So in the sulfite process whatever the digestion liquid is formed so it is not treated for the chemical recovery while we in the craft process we generally take the black liquid for the chemical recovery but in case of the sulfite process we do not take it for the chemical recovery and the entire quantity of the liquid that is generated so it forms a colored waste while in craft process only the colored waste is formed due to the leakage the spillages or the overflow of the digestion liquid or the black liquid. So, the efficiency and effectiveness of the sulfite process it also depends upon the type of woods that we are using so we should have a wood that should be soft in nature, and it should also have the absence of bark, so this limits the process of the sulfite pulping and because of which the sulfite pulping has declined in comparison to the black pulping. So, sulfite process however does not degrade the lignin, and it converts the lignin into lignosulfates and these lignosulfates can be used as a byproduct.

So in the sulfite pulping the brown liquor that is generated that is also in sulfite pulping the spent liquor that is there the digestion liquor that is generated so this is also known as the brown liquor it is also known as red liquor it is called the thick liquor or sulfite liquor also whereas in case of the craft process we give it a term as the black liquor for the digestion liquid which is spent after the digestion. After this process the pulp is washed by using counter current flow and so that the whatever the cooking chemicals or the degraded lignin and hemicellulose are left on the pulp so that can be washed and this extracted brown liquor is concentrated in multiple evaporators and it can be taken to the recovery boiler where it can be burned and we can generate the steam out of it or we can generate the energy out of it and we can recover the inorganic or we can also recover the inorganic chemicals for the reuse and it is also possible that after this pulping process this brown liquor may be neutralized and so that we can recover the useful byproducts of the pulping. So the waste water that is generated in the sulfite pulping so it may contain number of chemicals for example we can have the resin acids here we can have the unsaturated fatty acids alcohols, protonated resin acids etc. and in the digester house we find that the common waste water pollutants are again resin the fatty acids, color is there, BOD, COD and adsorbable organic halides so they may be there or volatile organic compounds so they may found the way in the waste water for example if we talk about the VOCs so we can have terpenes, we can have alcohols, phenols, methanol, acetone, chloroform etc. So we can see here that the sulfite condensate that has been generated so this may have a very low pH so the pH may be between 2.5 to 2.8 to 2.9 and similarly the BOD may be as high as nearly 2000 and it can vary up to as high as 5110 and COD may vary from 4000 and it may go as high as 27100 so methanol may also be released here for example here we see that the methanol is 250 milligrams per liter and the sulfites will obviously come in the

waste water and nearly 800 to 1270 milligrams per liter of sulfite comes into the waste water. So, we have certain advantages of the craft pulping which includes the increased pulp strength so when we are using the craft pulping process so the pulp that is generated is having a higher strength in comparison to the pulp generated from the sulfite processes. The craft process also requires less cooking time in comparison to the sulfite process and we can also recover the heat as well as the chemicals when we are using the craft processes so this recovery may result in the economics of the process as well as it may also result in the reduced cost due to the chemical recovery which we are having during this process. And similarly, this process is highly effective in digesting nearly every type of species for example we have already discussed that in case of the sulfite process the soft wood is required whereas in case of the craft process we can use any wood that is available. And similarly, the bleaching process is followed in case of the craft pulping, so it increases the pulp brightness.

So, these are some of the advantages of the craft pulping because of which the craft pulping is used predominantly in the pulp and paper mills. So the waste water that is generated from the craft process so it may include number of contaminants for example when we go for the wood preparation so we may have soil, dirts and the bars which are removed and the chips they are separated and the water is used to clean the wood so the waste water that is generated from this process contains lot of suspended solids it will contain BOD, it will contain dirt, it will also contain grit materials and it will also contain fibers. So, after the wood preparation the digester house where basically we go for the cooking of the wood chips so here the black liquor is generated so it may contain number of cooking chemicals which we are using, and we are also finding out the lignin which is being extracted from the wood chips so they will also come into the wastewater. So, now here the wastewater will contain the resins which basically comes out from the wood, the fatty acids, similarly lot of color which basically because of the lignin coming out extracting into the digestion liquid so color will be there similarly BOD will be there and then we will have a number of absorbable organic halides, we will have BOCs like alcohols, phenols, methanol, acetones and chloroform. So, this will be forming the part of the wastewater which is generated from the digester house.

Similarly, when we go for the pulp washing so the wastewater that is generated from the pulp washing process so it may have high pH, it may contain BOD, it may contain COD as well as the suspended solids and the color basically that is we want from here maybe dark brown in color. After this we go for the pulp bleaching process and this pulp bleaching process may contain lot of dissolved lignins, it may contains carbohydrates, it may contain color right which is basically coming out from the pulp that we are bleaching and similarly it may contains COD, it may also contain absorbable organic halides, it may contains chlorine compounds, it may contains chlorate, it may contain organochlorine compounds which have been formed due to the reaction of the chlorine with the organics. So, for

example we can have the very very lethal compounds like dioxins, and we can have VOCs like acetone, methylene chloride, carbon di-sulphide, chloroform, chloromethane so they all will be formed during the process. Lastly when we go for the paper making paper making process, so in that case the wastewater may contain particulate waste, it may contain organic compounds, it may contain inorganic dyes where we are coloring the paper similarly it may contain COD, acetone etc. So the waste water characteristics which is coming out from the pulp in paper mill, so here if we talk about the small pulp in paper mills for example here we are having 20 tons of paper produced per day so in that case the flow may be of the tune of 330 cubic meters per ton of the paper produced, the pH may lie between 8.2 to 8.5 and the suspended solids are very high for example 900 to 2000 milligrams per liter, the COD may be varying from 3400 to 5780 milligrams per liter and the BOD may be varying between 682 to 1250 milligrams per liter and here the COD by BOD ratio is very very high so this means that biodegradability of this waste water is very very low. Similarly when we talk of the mills which produce nearly 2000 tons of papers per day so in that case the waste water that is generated will be nearly 222 cubic meter per ton and we may be having the colors very high color that is nearly 7800 units and the pH may be alkaline here that is 8.5 to 9.5 and we can have the total solids nearly 4410 whereas the suspended solids is 3300 so we see that the suspended solids fraction is higher in the total solids and we can have the COD nearly 716 milligrams per liter this may be due to because of the high water used during the process so dilution may happen because of which the COD is basically lesser than the COD that is produced from the smaller production mills. Similarly, the BOD values are nearly 155 milligrams per liter and here also we can see that the COD by BOD ratio is very high.

So, when we talk about the characteristics of waste water which is generated from the various pulp and paper processes so we can find that in the large mills for example if we talk of the composite waste water so here the pH basically which is generated in India in the large mills so this is nearly 11 the total solids may be 5250 the suspended solids may be 1233 and here the BOD is 983 milligrams per liter the COD may be 2530 and the color basically which is there is black in color. Similarly when we talk of the small mills so in that case the pH may be 12.3 and we have a very high total solids again because of the smaller usage of water the solid concentration may increase and it is 15000 where the suspended solids is nearly 4890 and we see that the BOD 5 concentration is nearly 2628 6145 for the COD values and this may have a color which is dark black in color. Similarly we can see that the waste coming out from the digester house so it may contain alkaline pH and it may also contain very high amount of total solids as well as the suspended solids the BOD 5 is also very very high and similarly we see that the COD values are very very high and we see that there is a color that is basically it is measured in the optical density so this is nearly 16.6. So when we talk of the combined up to end so the pH nearly is 7.6 whereas the total solids and the suspended solids may decline in comparison to the digester house values and similarly we find that the BOD and the COD values are also low and the

color basically is also low because we are combining the waste water that is being generated from various processes and similarly we can see here that the bleaching results in a waste which is highly acidic in nature and it has lot of total solids is very very high where suspended solids concentration is low in this case and we find that the dissolved solids are really high and the BOD is nearly 140 milligrams per liter in this case and the COD in the color is not basically there because of the presence of the chlorine and similarly we see here that when we talk of the paper mills so this value of the waste water is alkaline in pH it may have total solids of 2415 and 935 milligram per liter with suspended solids so here again we see that the dissolved solids are higher in comparison and then we see that the BOD is 425 milligram per liter COD is 845 milligram per liter and the color of the waste water that is generated from the paper mill is also dark black in color. So if we talk about the distribution load which is being generated from different sections of the pulp in paper mills so we see that when we are having the small industries so in that case the flow percentage from the digester section is highest right whereas in case of the bleaching it is more than the paper mill section whereas if we see in the large mills so the digester section may have smaller flow because of the usage of water in the later stages to be higher and we find that the highest amount of the waste water flow it comes from the bleaching section. The BOD values for the small pulp in paper mills so it is highest in case of the digester section whereas in the is lowest in case of the paper mill section whereas if we see the large mills so we find that the digester section and the bleaching section so they may have the similar percentage of the BOD load. So suspended solids load in case of the small pulp in paper mills so it may be nearly 60 percent that is it is the highest of the bleaching section as well as the paper mill section whereas in case of the large industries so we find that the digester section is having the highest of the suspended solids so it is comparable to the mill section suspended solids concentration whereas in the bleaching section we find that the suspended solids is the lowest in this case.

So, we come to the typical pollution load per ton of the production so we see here that when we are having the process like when we are talking about the ODR so in this case the suspended solids which are produced during the this process so this may be 3.75 kgs per ton so here in the pulping the suspended solids is nearly 13.5 kgs per ton in the bleaching it is 6 kgs per ton in the paper making it is nearly 30.8 kgs per ton. So here we see that in case in all these processes the paper making processes produces the highest load of the suspended solids whereas if we talk about the BOD so we can find that the bleaching process so it may impart to the highest BOD load in comparison to the other processes.

Similarly the COD has not been reported here but if you see the color so we find that the color is very very high in case of the bleaching section and if we talk about the large mills so we find that the 31.2 kgs per ton of the suspended solids are produced whereas BOD is nearly 13 kgs per ton and the COD is 82.4 kgs per ton whereas in the small mills it is 140.3 kgs per ton of suspended solids is produced whereas BOD may be nearly 152.26 kgs per

ton and the COD may be 639.4 kgs per ton. So, here the color is measured on the basis of the platinum cobalt scale. So now if this wastewater is allowed to be put into the environment without any treatment so it will cause a number of environmental impacts. For example when we talk of the wastewater going into the water bodies so here the fishes so they may be exposed to this toxic elements which are present in the pulp and paper mill base water and it can lead to a number of problems in the aquatic life for example it can lead to the respiratory stress, it can lead to the mix function oxygenase activity, it can lead to the toxicity, it can lead to the mutagenicity, it can lead to the liver damage and it can lead to genotoxic as well as the other lethal effects. So, it has been found that the surface plankton population declined when the untreated wastewater was being discharged into a wetland. Similarly, it can also have a number of health effects on the humans also for example we can have diarrhea, we can have vomiting, headaches, nausea and high irritation to the people to the children or to the workers who are involved in the pulp and paper mill base water handling.

Similarly, the high carbon dioxide level so it can be a potential source of the distress and toxicity so it has been reported for the rainbow trout where basically it is found that the high carbon dioxide level so it can cause toxicity to rainbow trout. Similarly, it has been found that in the crayfish that the manganese accumulation may take place when we are having the pulp and paper mill wastewater going directly without treatment into the water bodies. Reaching agents and dyes can also be toxic when it is going to the aquatic organism and even at very low concentrations so if we are putting the wastewater directly without any treatment so this can lead to the toxicity to the aquatic life. And these toxic compounds are continuously discharged into the wastewater into the water bodies so it can disrupt the reproductive systems, it can impair the growth, it can lead to the genetic mutations in the aquatic organism. So one of the main problem is that if the excessive nutrients which are present in the base water so it may lead to the eutrophication process also so it will lead to the growth of the algal bloom and this basically will lead to number of problems for example when these algal blooms will be degraded so they will decompose and they will deplete the oxygen as well as the depletion of oxygen may also happen during the night time when basically these algal blooms may respire.

So, this will ultimately impact the aquatic life in an adverse way. Similarly, the pulp in paper if it is without any treatment if it is taken to the irrigation fields so this may lead to the soil infertility it may lead to the deterioration of the quality of the soil and it can also lead to the reduction in the yield of the crops. So here when we use chlorine bleaching for the bleaching process which is involved in the pulp in paper, it can also lead to the depletion of the soil. So here this may leach into the ground water, or it may go into the surface water also and it has been found that number of cases of the diabetes, hyperactivity, reproductive failures, number of allergies so this can be reported in the human bodies, and this will also impact the immune system of the human body. So we can see that the pulp in paper mill

so number of gases toxic gases may be released and similarly it can go to the surface water bodies, it can go to the rivers, it can also go to the ground waters here and basically it can be also go where you are going for the land filling or soil contamination may happen from this and this may lead to the infertile soils or the contaminated soils basically may come and again it may come back to the humans and it may impact human health.

So, we stop here, and we will continue our discussion on the treatment of the pulp in paper wastewater in the next lecture and these are the references that we have used for the preparation of this lecture.

Thank you.