Course Name: Industrial Wastewater Treatment

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Lecture 2: Treatment of wastewater produced from Tannery and Pulp and Paper

So, welcome back. We are in module 8, lecture 2, Treatment of wastewater produced from tannery and pulp and paper. So, we will continue our discussion on the tanneries. So, we will talk about the sources of the tannery wastewater. We will talk about the characteristics of the tannery wastewater. We will talk about the environmental impacts because of the discharge or the disposal of the tannery wastewater without treatment and then we will talk about the treatment of the tannery wastewater by using various methods like physical treatment, chemical treatment and biological treatment.

Similarly, we will also talk about that what are the effluent standards for which we can discharge the effluents generated from the tannery wastewater after the treatment into the environment. So, the wastewater that is being produced from the tannery, so it may be continuous in nature, or it can be as intermittent in nature. For example, when we are having the washing processes, so in that case a huge amount of wastewater may be generated and this wastewater that is generated may be continuous in nature. Whereas the wastewater, which is generated from the spent liquors, from the liquors which are used in different processes for the treatment, so they may result in an intermittent flow, and they may result in a wastewater which is highly polluted as well as it is lesser in the fractions.

So, wash waters they are less polluted in comparison to the intermittent flow or the spent liquors wastewater whereas, they may represent a higher fraction of the wastewater in the tannery wastewater. Similarly, the spent liquors they are highly polluted, they may contain a very high amount of chemicals, and they may be smaller in volume in comparison to the wash waters and they represent smaller amount of fraction of the wastewater. For example, when we talk of the spent soak liquor, so it may contain lot of soluble proteins it may contain salts and dirt which are coming out because of the process where we use a high amount of salt as preservatives so that the proteins which are there on the heights similarly, the salts which are there in the spent soak liquor as well as the dirt which is there on the heights, so that comes into the wastewater. And this spent soak liquor may contain lot of soluble proteins because of which the prettification may be very rapid, and it contains lot of nutrients which are required for the bacteria to grow very rapidly and that is why it can lead to a very high prettification of such type of water. Similarly, people have also reported that the pathogenic bacteria like anthrax, so it can also grow on such type of spent liquor wastewater.

So, then we can have the spent lime liquor which can again come from the process like liming, so it may contain very high amount of lime both in the dissolved phases as well as in the suspended phases and similarly it may also contain lot of colloidal proteins which has come out because of the lime reaction with the heights and similarly it can also contain the degraded products of the proteins which again happens due to the reaction. Similarly, it may also contain emulsified fats, and it may also contain sulfides because we know that when we are using the liming process, so in that case we use lime and sulfides so that the liming process may happen. And so, it may also contain number of unreacted limes also, so the sludge that will be generated from such liquor, so it may contain unreacted lime, it may also contain calcium carbonate, it may also contain calcium sulfide. So, this liquor that is generated it may have a very high alkalinity because of the lime, which is there, it may have moderate BOD, and it may also have high ammoniacal nitrogen because of the presence of the proteins and their degraded products. So, now we talk about the baked spent liquor, so it may contain high BOD as well as it may also contain high ammoniacal nitrogen.

So, vegetable tan extract it contains both tannins as well as non-tannins. So, tannins have a very high COD but they have relatively low BOD, so the BOD by COD ratio may be very low if we talk about the tannins and whereas the non-tannins may contain lot of inorganic salts, it may contain organic acids, salts and sugars are also added so that the tanning process may be accomplished and because of which it becomes high in both BOD as well as COD. The spent vegetable liquid, tanning liquid is the strongest individual waste that is found in the tannin wastewater. So, it is one of the individual strongest wastes which is present in the tannin wastewater. So, it may have a very high BOD, it may have a dirty brown color also, so that represents the vegetable tanning liquid.

Similarly, it may have a low pH because we are adding a lot of organic acids and salts so that the tanning process may happen and because of which the pH goes slightly acidic, and pH may be around 4.5 to 5. When this vegetable tan extract may be mixed with the spent lime liquor, so the pH may be enhanced which can also lead to the precipitation of a number of compounds which are there and because of which the tanning wastewater when mixed with spent lime liquor, so it may result in a bulky precipitate. If we talk of the spent pickling and chrome tanning waste, so this wastewater may be small in volume, it may have low BOD, it may have proteinic impurities also, it may have sodium chloride because of salts which are used in the tanning process and similarly it may contain mineral acids as well as the chromium salts. So, the effluent of the spent pickling and chrome tanning may contain trivalent chromium salts because we use chromium salts for the tanning process.

So, these trivalent chromium salts may come into the wastewater and as soon as we mix this spent pickling and chrome tanning liquor with the lime liquor, so it may result in the precipitation of chromium hydroxide because as the pH rises because of this mixing, so the chromium III may be converted to chromium hydroxide precipitate and this way settle

down as a sludge. So, it is very important that we go for segregation of the spent chrome tanning liquor, so that we can result in not only in the pollution abatement, not only in the prevention of the pollution which arises because of the chrome III salts going into the effluents, but it also can help us in the recovery of the chromium that we will talk later. However, in most of the tanneries, it is there that the intermittent wastewater as well as the continuous wastewater, so they are generally combined, and they are disposed of the plant with some sort of treatment or without treatment also. So, if we consider here the raw heights, so they go to the under soaking process and this soaking process may result in lot of salts, organic nitrogen, BOD, COD, dissolved solids and suspended solids and after which we go for the liming process and in the liming process, the waste water that is generated may have a very high alkalinity values, it has sulfides, it has BOD, COD, dissolved solids as well as the suspended solids. Similarly, the baiting and deliming liquor, so it may contain BOD, COD as dissolved solids as well as ammoniacal nitrogen.

So, when we talk of the tanning process, so it may contain lot of vegetable tans, it may also contain synthetic tans, tanning agents, it may contain acidity because of the added chemicals, so that the pH can be lower down because of which the pH of this tanning liquor is low. And similarly, we can also see that when we go for the retaining process after which we go for bleaching and dyeing process, so in that case lot of fats, dyes, the vegetable tans, the synthetic tans, BOD, COD, dissolved solids and suspended solids, so they form a part of the wastewater. In the last when we go for the finishing process, so in that case we use a number of solvents like formaldehyde, so these solvents may be found in the wastewater that is generated from the finishing process. Similarly, we can also see that there can be certain solid pollutants that will be generated from all these processes and the air pollutants may be generated for example, hydrogen sulfide may be generated because of the sulfides are present and this may lead to the order in the wastewater. If we talk about the various types of the waste water generated from different individual processes, so we can see that a spent soak liquor may have a very high flow that is around 176 cubic meters per day whereas, the flow then decreases and we find that during the tanning process this flow may reduce and if we talk about the combined waste that is if we collect the 10 hourly composite sample, so in that case the waste water may be nearly 1310 cubic meters per day.

So, the pH again we see that pH is high during the initial processes where we are using lot of lime and later on when we go for the tanning processes, so then in that case the pH may reduce because of the organic acids or other salts that we add in the tanning process. And if we talk of the composite samples, so in that case the pH is more or less alkaline, so it is nearly 8.9 and this pH value if we talk about it may go to the hourly maximum of nearly 12.3. Similarly, if we talk about the alkalinity, so alkalinity is higher in the initial phases that is in the spent soak liquor, in the spent lime liquor it is the highest and then it may basically reduce, and we find that there is no alkalinity during the tanning processes because we are adding acids to it.

So, then in that case if we talk about the composite samples, so this alkalinity may go as high as 260 milligrams per liter as calcium carbonate. Whereas acidity may be found in the spent tanning liquors and this acidity may be around 1000 or 5400 milligrams per liter as calcium carbonate in case of the chrome tanning liquor. Similarly, the chlorides are also higher because we are using lot of salts in the initial stages when we talk about the spent soak liquor. So here we find that the chloride levels may be as high as 16800 and then basically it reduces later on because then we are not using any salts. So in that case the chloride levels decreases whereas in case of the tanning again this may increase to nearly 3000 because here also we are adding lot of salts and in case of the chrome tanning process this chloride levels may go as high as 7200 milligram per liter and we talk of the composite sample so in that case the chloride levels may be nearly 4280 milligrams per liter and which may go to as high as 10600 milligram per liter when we talk of the hourly maximum.

So total solids are also very high in all the cases, and we see that when we talk about the spent vegetable tan so it may have nearly 34800 milligram per liter of total solids. Similarly, in the spent chrome tanning liquor it may be lower than the vegetable tan chrome liquor and it is nearly 7480 only and if we talk about the composite sample so it may be as high as 10505 milligram per liter. So suspended solids are also high in the initial stages because of the dirt particles and other particles which are present, and this may reduce further, and it may then again increase in the vegetable tan liquor because of the certain material that we use which are which we use as the extracts of the trees and the bark etc. So, this may increase the suspended solids in that case, and this may be again around 1080 in the combined waste. So, COD values are also high for example we see here that in the spent lime liquor the COD values may go as high as 12000 milligrams per liter whereas in case of the vegetable tanning also it may be very high that is nearly 30240 as we have already talked about that this is the individual waste which may contain which is highly polluted which is having a very high COD values as well as the BOD values whereas in the spent lime liquor it may not have so high COD values because here we are adding chromium salts instead of the vegetable tans.

So in the composite sample we can see that these values can reach up to 3700 milligrams per liter whereas the BOD values are also reported here and this BOD values for again for the spent vegetable tan may be as high as 16000 milligrams per liter and in the composite sample it may be nearly 1725 milligrams per liter and the chromium as total chromium may be found in the spent chrome tan liquor only and it may be nearly 2800 milligrams per liter. So, if we allow this waste water to go into the environment without any treatment so it may lead to the lot of environmental impacts for example it can lead to the depletion of the oxygen because of the oxidation of certain reduced compounds which are present for example the sulfites are present or other organic compounds may be present because we have seen that the BOD and COD values are really very high so in that case it will lead to the depletion of oxygen very rapidly and it will lead to the danger to the aquatic life.

Similarly, the deposition from such type of wastewater may also happen near the discharge point and it may lead to the purification of such type of solid materials that is basically deposited near the discharge point, and it may also lead to lot of pathogenic activities in the in such type of solid waste. Similarly, we can also have the gas evolved during this process because we have already seen that the sulfites we are adding so they can result in the formation of H2S and H2S basically may lead to the rotten egg smell, and this may lead to the foul odor in the base water. We have also seen that the chlorides are in excess so if they are going into the water bodies so it may render the water unsuitable for the further uses.

Similarly, the chromium also may go into the wastewater, and this may be highly toxic to the aquatic life, and it will inhibit the growth of the aquatic organism which are present inside the streams. Similarly vegetable tans that we are using so they are generally very having a very dark color that is they are having nearly reddish color, and this may become inky blue color when they come in contact with the water so the water becomes unsuitable for lot of purposes it may also become unsuitable for the domestic purposes also. So, tannins which are present when we are using the vegetable tans so in that case the tannins may be there this may render the water unsuitable for the industrial uses. Some of the tannins may also go for the lagoon process that is they will try to have the untreated waste water in the open they will try to store it in the open land and where basically this may adversely impact not only the ground water but it will also impact the nearby surface waters also and this may also lead to the seepage of the chloride contents as well as it may also lead to the seepage of the chromium. We are also disposing the chrome tan waste also along with it.

So, because of the high chloride content which is present in the wastewater, and it may lead to the salinity in the soil, and it may lead to the loss of fertility of the soil when we are disposing it off as it is on the ground. So, when we are transferring this water through the sewer lines so it may lead to the choking of the sewer line also because lot of precipitation of calcium sulfate and calcium carbonate may happen due to the lime incrustation during the transport processes and it may lead to the reduction in the cross section of the sewer lines which will lead to the choking of the sewer lines. Similarly, as we have seen that the evolution of the hydrogen sulfide may occur because of the sulfides present in the waste water so it may also lead to the corrosion of the concrete surfaces and if the chromium compounds they are present in quantity greater than 10 to 20 milligrams per liter so it will disrupt the operation of the trickling filter it will also cause lot of toxicity to the aquatic life also. And sulfide which are also they are in the wastewater so it may also be toxic to the microorganism so if we are treating the wastewater by using biological methods so it may lead to the toxicity to the microorganism. Similarly, the lime may also be present because you have seen that during the lime process lot of lime basically comes into the wastewater so this lime may also inhibit the biological process during the sewage treatment plant.

So, now let us talk about the treatment of the tannery wastewater so we can have different methods by which we can treat the tannery wastewater so there can be the physical methods, there can be the chemical methods and there can be biological treatment methods. For example, when we talk of the physical treatment methods so in that case the screening is the first of all required the screening is required so that we can remove the bigger particles as well as the some final particles also which can be removed by the screening process and for example we can have lot of flash in the waste water, we can have hairs present in the waste water. Similarly, we can have lot of floating substances also present in the wastewater. So, for example we can have the leather trimmings also basically coming into this wastewater so these all things may be required to be cleaned before we take the wastewater to the further treatment processes. So, in that case we have to go for the screenings and we have to use different size of the screenings for example we can use first of all the coarse screens and then we can go for the fine screen so that we can remove the objects which are of various sizes for example the hairs, the leather trimmings, the other solid materials so they all basically can be should be removed before the waste water goes to the further treatment processes.

So, after the screening process we may go for the sedimentation or settling process where basically we try to remove the particles which are not removed by the screens which are come into the settling tank and it has been seen that if we provide a detention period of nearly 4 hours so it is very effective in removal of suspended solids and nearly 90 percent of the solids can be removed by the sedimentation tank which is having a detention time of 4 hours. Similarly, 98 percent of chromium can also be precipitated in the primary sedimentation tank, and it basically comes out with the sludge because we know that lot of lime basically may be present where in the wastewater so this may react with the chromium III salts which are present in the wastewater so it may lead to the formation of chromium hydroxide. So, ultimately this chromium hydroxide can basically settle down as precipitate and this may also come along with the primary sedimentation tank sludge. However, no appreciable removal of the dissolved solids, BOD, COD, color or chloride can be achieved during the physical treatment by using the sedimentation process. So, if we are treating this wastewater by this method that is if we are trying to treat it by using screening as well as the sedimentation process also then also the lime interstation may happen when we are taking this wastewater to the sewer lines because of precipitation of calcium carbonate and calcium sulfate.

For example, it is possible that in some tanneries they may only go for the physical treatment method and then after that they may take this wastewater to a common effluent treatment plant where the biological methods may be applied for the treatment of the tannery wastewater. So, in that case what happens that this wastewater may again lead to the precipitation of the calcium carbonate and calcium sulfate, and it will lead to the lime incrustation, and it will lead to the choking of the sewer lines in that case. So, after this we

may also go for the chemical treatment method where we can use a number of coagulants for example, we can use alum, we can use ferric chloride, we can use ferrous sulfate and so that we can settle out the correlated particles which are present in the wastewater. For example, we may use ferrous sulfate which is highly effective in the removal of color. Similarly, the chromium can also be removed, the sulfides can also be removed, the BOD and suspended solids have been removed by using the ferrous sulfate, but this is generally applied for the chrome tan waste.

But if we are using the vegetable tan waste, so it can lead to the intensification of the color because we know that the vegetable tan may contain a certain color and we are using ferrous sulfate to it, so it may increase the color in the wastewater. So, that is why the ferrous sulfate is not used for the tanneries which are also using the vegetable tanning process. Instead of using ferrous sulfate we can go for the use of alum but when we are using alum, so we know that the alum precipitation can happen at a proper pH. So, if we see that the alkaline pH is there, so in that case we have to neutralize the wastewater by using acid or carbon dioxide. So, recoronation has to be done so that the pH may be brought down to the optimum pH in which the alum can be effective, and it can lead to the precipitation of aluminum hydroxide.

Similarly, we can also go for ferric chloride, and it has been found that the ferric chloride alone is quite effective in the removal of the tanning and the chemical oxygen demand in the wastewater. So, now we go for the biological treatment after going for the physical and chemical treatment. So, here we use activated sludge process, and it has been found that if we mix it with the municipal wastewater then activated sludge process can lead to the reduction in the BOD, COD and tanning about 90 percent of the direction may happen from here. But here we use a certain acclimatized microorganism so that they can be quite acclimatized to the chromium if it is present in the wastewater. So, that is why it is very essential that we also go for the prior chromium reduction if it is there in the wastewater so that we can treat the wastewater by using the activated sludge process.

The trickling filter has also been used for the removal of BOD, COD and color in the tannery wastewater. However, the biological treatment of the tannery wastewater is not difficult, but the smaller tanner may not be having these facilities because it is relatively costlier because of very high BOD content and that is why if we are having a number of small-scale industries. So, they generally go for the preliminary treatment or the primary treatment of the wastewater and later on they send the wastewater to the common effluent treatment plant where the secondary treatment processes are there where the biological treatment process can be performed and then the wastewater can be discharged off safely. So, it has also been found that the vegetable tanning wastewater can be easily treated by anaerobic contact filters, and it has been found that if we are having a retention time of nearly 12 hours so in that case nearly 89.5 to 90.8 percent removal of COD, 91.9 to 97.5 percent removal of BOD and nearly 73.6 to 90.5 percent of removal of tanning can be

accomplished. So, we can have also had the lagoon system for example, we can have the pond system in which the anaerobic lagoons can be used and if we are having the small tanners or isolated tanners so they can also go for anaerobic lagoon method.

So, because it requires very less land area as well as the nutrient addition is also less in comparison to the oxidation ponds. So, in that case the anaerobic lagoons basically may serve the purpose, and it may help in the reduction of BOD, COD as well as the tannins. But again, here so if we are going for the anaerobic process so in that case the effluent quality may not be very high because the anaerobic lagoons may lead to reduced products which require the oxidation. So, it is very necessary that after anaerobic lagoon we may go for the aerated lagoon so that the oxidation of the reduced species like sulfides or nitrogen so that can take place and that may result in the treatment of certain this type of waste and it may also lead to the reduction in the oxygen demand. So, we can have the two-stage biological treatment method where the oxidation ditches may also be used in place of the aerated lagoons.

So, we can see here a flow sheet which is being used for a combined waste which is emerging out from a vegetable tannery. So, we are having the raw wastewater and here the COD levels are nearly 2900 milligrams per liter and BOD is 1500 milligrams per liter. So, we take it to the screenings then we take it to the primary sedimentation tank where the sludge that is obtained from the primary sedimentation tank may be taken to the sludge drying beds and after which we take it to anaerobic lagoon which may have a retention time of nearly 10 days and it has been reported that the BOD levels has gone down to nearly 190 milligrams per liter. So, after the anaerobic lagoon you have to take it to an aerobic lagoon where the detention time may be nearly 6 days, and it may lead to the further reduction in the BOD and in the up to end we can get a BOD levels as low as 90 milligrams per liter. So, then we can have other processes also where we can have the conventional lagoon system, we can have the fully aerobic system, we can have a combined treatment with the USB also.

So, here what we do that we take the combined waste, the waste coming out from the chrome tanning may be treated separately that is here the chromium may be recovered first of all and then the supernatant may be taken to the evaporation ponds here, but the other waste so they can be mixed here and these mixed wastes it can be first of all passed to the screens and after passing to the screens it may be taken to a pre-settler and then it may be taken to a equalization tank where the waste water may be equalized and after which we may take it to a primary sedimentation tank where we may be doing certain chemical dosing so that the particles can also be removed and the sludge that is generated from here so it may be taken to the sludge dewatering systems. So, after the primary sedimentation tank we can take it to the anaerobic lagoons and the aeration tank and later on we can take it to the secondary settling tank from where the sludge may go to SDWS that is the sludge drying and dewatering facilities. And or we can also take the primary sedimentation tank

to a fully aerobic system where the aeration tank may be used and after which we may go for the extended aeration system and the secondary settling tank is there from which the sludge may be generated, and it may be taken to the drying beds. Or we can also take it through a combined treatment with up flow anaerobic sludge blanket USB where we do not require any primary sedimentation tank we can take the waste water from the equalization tank directly to the USB reactor where the sludge is generated the sludge may be again dewatered and then dried and then we take it to a extended aeration system after which so that the aeration may take place and the reduced product may be converted to the oxidized products and similarly after which we take it to a secondary settling tank from where the sludge generated is taken to the sludge dewatering facilities. So, these are some of the combinations of the various type of treatment methods that can be used for the tannery treatment.

So, if we talk about the standard so if we are having facilities like common apparent treatment plant so in that case it is possible that we may only go for the primary treatment after which it is carried to the secondary treatment plant. So, if we are only doing the primary treatment of the tannery wastewater so in that case the pH should be between 6.5 to 9, suspended solids should not exceed 600 milligrams per liter, the chromium concentration should not exceed 45 milligram per liter. So, this is applicable for an industry which is having the chrome tanning, or we are having the combined chrome as well as the vegetable tanning. So, in that case these are the standards which need to be followed after the primary treatment process.

Similarly, if we are having only the vegetable tannery so in that case the pH should not exceed 6.5 to 9 and the suspended solids should not exceed 600. So, here chromium is not there because we are not using the chrome tanning process. So, these standards may be applied when we are taking this wastewater to a common effluent treatment facility. Similarly, if we are treating the wastewater the tannery wastewater so and if we are discharging it into a inland surface water so in that case it is possible that the standards need to be followed.

So, here the pH should be between 6.5 to 9, the BOD at 27 degrees centigrade in 3 days so this should not basically exceed 100 milliamp per liter. However, the because of the stringent rules and regulations so state pollution control board may also enforce around 30 milliamp per liter BOD in the effluent. Suspended solids should not increase 100 milliamps per liter in the effluent. Similarly, the sulfites may not be greater than 1 milliamp per liter, the total chromium should not be greater than 2 milliamps per liter and similarly the oil in grease should not exceed 10 milliamps per liter in the effluent. Here the wastewater generation may be nearly 20 cubic meters per ton of the raw height which is processed.

So, this gives us an idea that how much wastewater may be generated if we know the quantity of the leather or the raw height which are being processed in a certain tan grease.

So, after the conventional treatment process it is possible that we may require some additional treatment also. For example, it is possible that there may be number of metals that may come into the wastewater during the different processes that are used during the tanning process. So, these metals like for example chromium may also be there so we can we have to treat the metals we have to remove the metals from the effluent by using different methods which you already discussed for example we can use membrane filtration process, or we can also use other chemical technologies like precipitation methods that we have discussed earlier also. So, we can go for those methods, or we can also use adsorption method also so that the metals which are there in the wastewater so they should be removed up to the desired standards.

Similarly, we have to also check the toxicity of the wastewater. So, because toxicity is important if you are discharging the wastewater into the surface water so it may impact the aquatic life. So, in that way we require that the toxicity of the effluent should be removed. So, we have to see that what is the toxicity of toxic levels by performing different type of tests for example we can use a certain type of aquatic organism so that we can check that what is the impact on their reproduction, what is the impact on their growth, what is the impact on the mortality of such type of species and based on that we can decide that the water is toxic or not. So, we can then pass the water through RO process or ion exchange process or adsorption process and then we can again check the toxicity if the toxic levels are less than the desired standards so we can easily dispose of the wastewater into the surface water bodies.

Similarly, the tedious or the provide levels basically they do not go down during the conventional treatment process. So, for that we may go for the either for the reverse of process which may prove to be costly or we may also go for the evaporation process and we should also work on the containment and the neutralization of the order because lot of order is generated from such type of wastewater as you have seen that as to a may be generated which may cause lot of nuisance which may cause lot of smell of the rotten eggs and this has to be contained and the wastewater has to be neutralized for the order so that it can be disposed of properly into the steams. So, these are the differences that we have used during preparation of this lecture, and we stop here.

Thank you.