

**Course Name: Industrial Wastewater Treatment**

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**Lecture 5: Treatment of wastewater produced from Tannery and Pulp and Paper**

So, welcome back, we are in module 8, lecture 5 and we are discussing the treatment of the wastewater produced from tannery and pulp and paper. So, in this lecture, we will talk about the treatment of the pulp and paper mill waste by different processes. So, the treatment of the pulp and paper mill waste, so it can be done by a combination of number of processes. For example, here we will talk about the recovery process first of all, then we will talk about the chemical treatment for the colour removal, we will talk about the activated carbon for the color removal process. Similarly, then we will talk about the physical treatment by using clarification process or the sedimentation process, then we will talk about the biological treatment for wastewater, then we will talk about the lagooning process, and the land treatment method and we can also talk about the disposal of waste by the irrigation process. So, when we talk about the recovery process, so the recovery of the process chemicals and the fibers, so it reduces a lot of loads on the wastewater treatment.

So, here we have to try to recover the process chemicals as well as the fibers during the processes itself, so that the wastewater may have a lower load of these materials coming on to into the further treatment. So, when we talk about the recovery process, so in the recovery process the lignin is generally destroyed so we can try to recover the lignin by using the precipitation of the black liquid. So, we generally add certain acids to it, for example we can add carbon dioxide, we can go for the recombination, we can go for addition of the sulfuric acid, so that this lignin may be recovered without any destruction, and this can be reused further. For example, the recovered lignin may be used as a dispersing agent in various types of suspension so the lignin may also be used as raw material for the preparation of dimethyl oxide, so this can be used as a spinning solvent for polyacrylonitrile fibers.

So, the activated carbon may also be manufactured, so whatever the lignin we are recovering from the black liquid, so it can be used for the conversion to the activated carbon, for example we can go for the process of the activation by adding acids or other basically taking it to the pyrolysis process and then basically we can convert the lignin that is generated from here into the activated carbon which can be used for the adsorption process. Similarly, we can also go for the fibers which are there in the white water, so they can be recovered by the sedimentation process or by the flotation process, so we can use air flotation here so that if the fibers which are having the lighter in nature, so they can basically come on the surface by the air flotation process and then these fibers can be

separated out from the white water and they can be then reused and this will also decrease the load on the waste water treatment. Similarly, the lime can be recovered, and we can use the recalcination process for the recovery of the lime which can be done from the lime mud, but it is generally not practiced in India because it has got lot of silica content into it and because of which the recovery of lime in the pulp and paper mills may not be feasible. So, the coagulation process can also be used for the colour removal, however it has been found to be uneconomical for the removal of the colour in the pulp and paper wastewater. And similarly, the removal of colour by using the lime sludge is also not found to be very effective.

However, a massive lime treatment process has been proposed by the National Council for Stream Improvement in USA where they can remove 90 percent of color 40 percent to 60 percent of the BOD from the waste by using this massive lime treatment process. So, here a large quantity of lime which is required for the recausticisation of the green liquor into the white liquor is first of all taken to the coloured waste effluent where it is reacted with the coloured waste water and the colour from that waste water is generally removed by reaction with this lime and then the sludge that is generated from this process which has got lot of color. So, the colour is absorbed by the lime and then the sludge, which is settled, so this can be used for the recausticisation of the green liquor later on. So, this treatment may result in the formation of the dark brown liquor and this liquor contains both the cooking chemicals as well as the colour producing components like lignin and later on this lignin bearing liquor can be used as a digester liquid. So, now this is the flow diagram for the massive lime treatment for color removal in pulp and paper mills.

For example, here the colored waste water may be taken to the grid chamber where the larger size particles or we can say the heavier particles they can be removed and then basically we add lime here which may be required for the recausticisation of the green liquor and here whatever the waste water is there which is having lot of colour, so that colour basically may come on to the lime mud. So, this lime mud becomes coloured in now and this is this lime mud may be used for the treatment of the green liquor right and this green liquor which we got get from the recovery from the black liquor. So, this green liquor after addition of the lime, so it basically turns into the white liquor which is taken to the digester for the digestion process and the sludge generated from here may contain lot of calcium carbonate. So, this may be taken to the lime kiln for the calcination process and the recovery of the lime. Similarly, when we are having the wastewater which is where we are adding the high amount of lime, so this is coming out.

So, here we can do go for the decarbonation process, so that the pH may be lowered and then basically it is again taken to another clarifier where the sludge may settle down further and which may be taken for the recovery of the lime, and the effluent may be taken for the further processes. So, activated carbon can also be used for the color removal. For example, a study conducted by NEERI has observed that the activated carbon can remove nearly 94

percent of the colour from the pulp and paper mill based. However, we have to adjust the pH before we go for the adsorption process. So, in this case it has been found that if the pH is nearly 3, then we can get the maximum removal of the colour by using the activated carbon treatment.

Similarly, it has been found that nearly 90 percent of the colour COD, DOC and AOX can be removed from the bleaching wastewater by using activated coke as an adsorbent. So, after the colour removal, we can go for the physical treatment for the clarification by using sedimentation process where we try to remove the total suspended solids. So, these total suspended solids may be comprised of the bark particles, the fibers, the fiber debris, fillers and coating materials. So, they can be removed by using the sedimentation process. So, we have seen that the circular clarifiers, so they are able to remove nearly 70 to 80 percent of the total suspended solids from the combined mill effluent, and it has been found that nearly 95 to 99 percent removal of the settleable solids can be accomplished in the clarifier. So, settleable solids basically they are different from the suspended solids. So, here the settleable solids can be removed nearly 99 percent when we are going for the sedimentation process. However, when we go for the sedimentation process, so in that case the BOD reduction is very small, it is only of the order of 25 to 40 percent only. So, here the average removal rate of the total suspended solids by the sedimentation is reported to be nearly 70 to 80 percent, and it has been seen that if we are going for a surface loading of nearly 30 to 31 cubic meter per square meter per day, so it is adequate for the removal of nearly 79 percent of the total suspended solids and 52 percent removal of COD was also observed when we provide a hydraulic retention time of nearly 30 minutes. The primary sludge that is produced from this process, so it can be thickened easily as well as it can be dewatered mechanically easily and so this may be one of the advantages of this process. And it has also been found that the dissolved air flotation may be able to remove nearly 95 percent of the total suspended solids because it is possible that very fine particles like fiber particles or other bark particles etcetera which are lighter in nature, so they may not be removed during the sedimentation process and that is why we see that the efficiency by sedimentation for removal of total suspended solids is nearly 70 to 80 percent, but in case of dissolved air flotation we may be able to achieve nearly 95 percent removal of the total suspended solids. So, after the physical treatment we can go for the biological treatment of the wastewater which is generated from the pulp and paper mills for example, we can go for the waste stabilization ponds. So, if we are having no dirt of the area or large area is available, so in that case we can go for the treatment of the pulp and paper mill effluent by using the stabilization ponds and it has been found that the waste stabilization ponds in such cases may be the cheapest means of the treatment.

So, here we provide generally a depth of 0.9 to 1.5 meters for the treatment, and we provide a very high HRT values that is nearly 12 to 30 days for the removal of the 85 percent of BOD right and which can be achieved up to a loading rate of nearly 56 kgs of BOD per

hectare per day. So, we can also go for erected lagoons. So, these erected lagoons, so they are we can say the improved form of the stabilization ponds in the sense that we require a lesser area also, we can go for the increased loading also and we can also meet the stringent effluent discharge criteria also in this case.

So, we provide a certain aerator here and in these aerators, we provide oxygen from outside which can basically improve the efficiency of the ponds. So, here in case of the lagoons the efficiency is higher than we see in case of the waste stabilization ponds. So, here we find that generally we use mechanical surface aerators because it is possible that because of presence of the fine particles if we are going for the diffuse aeration. So, it may clog the pores of the diffusers. So, that is why the mechanical surface aerators are generally used in the erected lagoons, and it has been found that the BOD reduction of 50 to 95 percent can be achieved at a retention time of 30 to 20 days and we provide a loading rate of nearly 670 to 3040 kg of BOD per hectare per day in case of the erected lagoons.

However, in India the erected lagoons are used when the influent BOD is moderate that is when we are having the partial recovery of the chemicals from the black liquor. So, then after which the wastewater that is generated that may be subjected to the treatment by using erected lagoons or these erected lagoons may also be used as a polishing device. It has also been reported that the HRT of nearly 5 days can result in the 90 percent reduction of the BOD in case of the erected lagoons. So, here the pulp and paper effluents, so they may not contain necessary nutrients which are required for the bacterial growth. For example, the BOD to N is to P ratio of nearly 100 is to 5 is to 1 needs to be maintained so that the bacteria can grow, and the treatment of the wastewater can happen.

So, in that case because the nutrients are lacking in case of the effluent generated from the pulp and paper mills. So, in that case we have to add nitrogen and phosphorous in form of urea or ammonia or phosphoric acid so that this ratio is maintained. And it is also possible that the nutrient addition may not be required also if we are providing a larger retention time for example, if we are providing more than 10 to 15 days of the retention time so in that case the nutrient addition may also be not required. And similarly, we can also find that in the aerobic lagoon nearly 70 percent of the removal of adsorbable organic halides can happen by the aerobic lagoon's treatment. So, we can also go for anaerobic lagoon.

So, here we have we can use additional supplementation of the nutrients and then we can go for the anaerobic process, and we can treat the segregated strong waste also as well as we can treat the combined waste also by using the anaerobic lagoons. So, it has been found that if we are having a BOD loading of nearly 0.048 kgs per cubic meter per day and retention time of 20 days it can result in the removal of nearly 72.5 percent removal of BOD. Similarly, another case reported that nearly 77.5 percent removal of BOD at a retention time of 6 to 8 days and a loading of 0.017 kgs of BOD per cubic meter per day. So, after the anaerobic lagoon it is necessary that we employ aerated lagoons also so that

the effluent quality may be enhanced, and we can get a very high-quality effluent in that way because anaerobic lagoons may result in a number of reduced products which needs to be oxidized before we discharge the effluent to the receiving water bodies. And it has been found that for such cases when we are using the aerated lagoons after the anaerobic lagoons, so a detention time of 7 days is adequate. So, we can also go for the activated stress process for the treatment of the wastewater produced from pulp and paper mills and it has been found to be most satisfactory and most sophisticated systems for the treatment and here again we use the surface aerator instead of the porous diffusers because we have already talked about that the pores of the diffusers basically may be blocked because of the very very fine particles which are present in the base water and that is why in the aeration tank we generally employ the surface aerators.

And it has also been reported that nearly 80 to 90 percent removal of the BOD can happen when we are having a loading rate of 0.2 to 0.3 kg of BOD per kg of MLSS and we provide a detention time of 3 to 9 hours and the MLSS concentration maintained in the aeration tank is nearly 2000 to 4000 milligram per liter the recirculation ratio is between 0.3 to 0.5 and we provide the nutrient supplementation so in that case we can get a very high BOD removal up to 80 to 90 percent.

So, we know that the fine fibers they are not biodegradable in nature so they and they will also not settle down easily so this we have to keep in mind while we are going for the treatment in the secondary settling tank. So, trickling filter can also be used for the treatment however its use is highly limited because it is possible that the clogging of the media with the fibrous materials is present in the pulp and paper mill up to end so this may lead to the choking of the filters very fast and it has also been found that if we are using a very high rate filters also so in that case also the BOD removal was only found to be nearly 40 to 50 percent. So, that is why the trickling filters are not used, or they are having very limited use for the treatment of pulp and paper wastewater. So, here we can see a flow diagram for the treatment of the pulp and paper mill. So, here we find that the black liquor that is coming so this may have a flow of nearly 44 percent and the BOD of load of 80 percent.

So, this is first taken to the lime treatment after the lime treatment it is taken to a clarifier where the sludge is separated out then it is taken to the cooling towers where certain nutrients are added and then it is taken to a anaerobic lagoon and the BOD reduction that is observed for the retention time of 25 days is nearly 92 percent after which it is taken to the aerated lagoon where retention time is kept nearly 15 days and further 87 percent of BOD is removed and then this waste water may be added with the waste water which is coming out from the other processes after certain treatment. So, here for example when we talk of the other wastewater which are not coming from the digester section so they may be passed through the grid chamber so that the heavier particles can be separated out and then it is taken to the clarifier. After the clarifiers calcium hypochlorite may be added which

can result in the color reduction, it can result in the BOD reduction of 92 percent, and it can also result in the and we provide a retention time of 25 days in the stabilization tank for this reaction to happen. After which the wastewater which is generated so it is mixed with the wastewater coming from the treatment of the black liquor and then it is taken to an aerated lagoon where we provide a retention time of 3 days and then we can meet the effluent quality standards. So, the lagooning can also be done for example when we are having very small mills so in that case the black liquor may not be treated separately then it can be stored in a lagoon and then later on when the things are favorable or basically, we find that the concentration has reduced, or the treatment has been done so it can be discharged during the monsoon seasons.

Some soils are also capable in removal of the color from the waste so here the waste may be stored in such type of soil and so that the color which is there in the wastewater so it can be absorbed by the soil, and this will also depend upon the cation exchange capacity of the soil. So, the land treatment method may be employed but you also see that the soil the toxicity is not induced in the soil or infertility basically of the soil also not happens. We can also go for the disposal that is the treated effluent can be utilized for the irrigation, and it has been found that it can be very useful for the crops like maize, paddy, jowar and kenaf and the yield basically has also been found to be at par to the yield coming from the conventional irrigation practices. For example, it has been done for wheat and sugarcane by NEERI and it has been reported that the treated pulp mill effluents can be used for the irrigation purposes. So, in addition to the conventional systems we can also go for other treatment systems also. For example, we can have chemical oxidants like ozone and photocatalysis or we can have ozone plus UV. So, it can be useful in removal of the COD, TOC and color. Ozone alone has been reported to for the removal of 90 percent of EDTA and AOX and nearly 80 percent of the COD. But however, these processes may be costly, and it is required to see the economics of the treatment that whether these processes need to be used, or we can go for the other processes. Similarly, we can also go for the membrane processes where it has been found that 90 percent of color, total suspended solids and AOX can be removed by using this process.

But again, this process may prove to be costly because of the fouling of the membranes because we know that there may be number of fine particles present in the wastewater. So, these may choke the membranes, and it can increase the cost of the treatment. Similarly, the softwood effluents when we are using, so in that case the choking of the membranes may be very fast. So, now in the in nutshell we can say that the activated stress process can be useful for the removal of AOX below 50 percent. So, they can remove BOD around 95 percent, the COD removal may be around 70 percent in such cases.

And it has also been found that the ASP is also quite effective in the removal of chlorinated phenolics and over 75 percent of the chlorinated phenolics compounds. So, they may be removed by the using the active stress process. So, if we talk about the aerated lagoons, so

they are efficient in removal of BOD nearly 95 percent, COD removal is 60 to 70 percent only, the AOX removal is 50 percent and the very high removal of the chlorinated phenols that is nearly 85 percent has been reported by the aerated lagoons. Anaerobic contact filters are also found to be removed the BOD and COD and nearly 90 percent of the BOD can be removed, and 65 percent of the COD can be removed in most of the cases. And USB can also be used for the removal of the BOD, nearly 80 percent of the BOD and the nearly 50 to 80 percent of COD can be removed by using the up flow anaerobic sludge blankets.

And so, we can see that both anaerobic as well as aerobic systems, so they are feasible for the treatment of the pulp and paper wastewater. However, when we are using the bleaching craft effluents, so they may be less suitable for the anaerobic processes because the chlorine present in the bleaching effluents, so they may be toxic to the anaerobic bacteria. And the anaerobic treatment of high strength wastewater, it requires the treatment because it contains very high as well COD. So, it is possible that after the anaerobic treatment, so if the COD removal is not very high, so in that case you have to go for the further treatment. So, now we can use a combination of the anaerobic processes followed by the aerobic process.

So, we see that this is the one of the most efficient processes where we are going first of all for the anaerobic process, then later on we are going for the aerobic process. So, it has the advantages of both the processes of the treatment, and this may result in a higher quality of the effluent also. Similarly, when you talk of the chlorinated phenolic compounds or absorbable organic halides, so this can be removed by adsorption process, this can be removed by ozonation process, this can be removed by the membrane filtration process. Suppose we find that by using the aerobic process and anaerobic process, we are not able to remove these compounds. So, in that case we can go further for the processes like adsorption, ozonation and membrane filtration.

Two or more physicochemical processes can also be combined when we see that the toxic pollutants are not removed from the wastewater which is generated from the pulp and paper mills. And it is also beneficial that we first of all go for the physicochemical treatment and later on we can go for the biological treatment. So, we can optimize these processes that is the combination of physicochemical and the biological process, so that it can provide a long-term solution for the pulp and paper mill effluent treatment. So, it is necessary that we go for the more and more research in this area, so that we can combine these processes, and we can get a very highly efficient solution for the treatment of the pulp and paper wastewater. So, now we can see that there are certain effluent standards for example, when we treat the pulp and paper mill effluent, so we have to comply to certain norms, so that we can discharge this wastewater into the environment.

For example, if we when we talk of a large pulp and paper industry which is having a capacity above 24000 metric ton per annum, so in that case we find that the pH of the

effluent should be between 7 to 8.5. The BOD of the wastewater for measured for 3 days at 27 degrees centigrade, it should be nearly 30 milligrams per liter, the COD should be 350 milligrams per liter, the suspended solid should be nearly 500 milligrams per liter. And for the absorbable organic halogens or halides, so it has been found that this should not be more than 1 kgs per ton of the product and it has been implemented since March 2008. So, we have to also see in addition to the BOD and COD that what are the AOS values coming out in the effluent.

Similarly, when we talk about the small pulp and paper industries, so we see that when we are discharging the waste water into the inland surface water after the treatment, so it should have a pH between 5.5 to 9, it should have suspended solids of 100, the BOD should not exceed 30 milligrams per liter, the pH of the waste water if we are disposing it on the land, so it should be between 5.5 to 9, suspended solids should not increase 100 milligram per liter, the BOD should not be beyond 100 milligram per liter and here the sodium absorption ratio which is very much required for the fertility of the soil should not be go beyond the 26. Similarly, the values of AOS in case of the small pulp and paper industries, so it should not increase 2 kgs per ton of the paper produced and this is effective from the from March 2006. So, we stop here, and these are the references that we have used for preparation of this lecture.

Thank you.