Course Name: Industrial Wastewater Treatment

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Week – 11

Lecture 4: Treatment of wastewater produced from pharmaceutical industry

Welcome back. So, we are in module 11, lecture 4 and we are talking about the treatment of wastewater produced from the pharmaceutical industry. So, in this lecture we will be covering the treatment of the antibiotic wastewater, and we will talk about the flow sheet for the treatment of the combined antibiotics and other chemical wastes. We will also talk about the treatment of the synthetic drug wastewater, and we will talk about the flow sheet for the treatment of the waste from a large synthetic drug plant and then we will also talk about the effluent standards for the pharmaceutical industries. As we have already talked about that what are the sources of the wastewater which are generated from various production of the antibiotics as well as the production of the synthetic drugs and what are their characteristics in the previous classes. So, today we will be going to discuss about the treatment of the wastewater which are produced from the antibiotic industries as well as from the synthetic drug industries.

So, this lecture will basically focus on the conventional methods which are used for the treatment of the antibiotic wastewater as well as the synthetic drug wastewater. So, like many other industries pharmaceutical industry also produces a wide variety of products. So, we can have a number of the pharmaceuticals being produced in a large pharmaceutical industry and these products may use a number of inorganic as well as organic materials as raw materials as well as these materials may be of synthetic or vegetable or of animal origin. So, some of the pharmaceutical industries so they may not discharge liquid waste at all for example some of the industries may be dealing only with the manufacture of the solid pharmaceuticals.

So, in that case it is possible that they may not discharge any liquid waste at all whereas in some industries it is possible that very small, but highly concentrated liquid waste may be charged by the industries. Similarly, there can be other industries in which highly alkaline and toxic liquid waste may be produced similarly there can be industries in which certain acidic waste may be produced and so it is very difficult to generalize the characteristics of the pharmaceutical wastewater and that is why it is very difficult to provide a generalized treatment process for a pharmaceutical wastewater. So, it will depend upon the characteristics of the wastewater. So, we have to evaluate that what are the pollutants which are present in the wastewater and based on that characteristics we have to decide that what are the treatment methods that can be adopted so that we can get rid of these pollutants which otherwise can cause lot of damage to the environment if they are released without any treatment. In case of the antibiotic industries the wastewater is discharged into the stream directly.

So, in case of the antibiotic industries if the wastewater is discharged directly to the industries so it can impart an objectionable order, color as well as taste to the receiving water and it can make the water unfit for the drinking water supplies as well as it can make it can render it unfit for various domestic uses also. Similarly, the water will also become unfit for the industrial purposes and the water will be imparted toxicity by the pharmaceuticals which are present in the wastewater. So, they can create toxicity in the water, and which can adversely affect the aquatic flora and fauna. So, the wastewater which is being generated from the antibiotic industries so it cannot be discharged directly into the municipal sewer until unless the sewage treatment plant where it is going so it is properly designed so that it can handle wide varying and concentrated wastes which are coming from the antibiotic manufacture plants. So, it has also been reported that the penciling waste is found to have an effort disturbing effect on the process occurring in within the sludge digestion tank.

So, it is possible that the sewage treatment plant which is treating the municipal sewage so the efficiency of that sewage treatment plant may also go down because of the pharmaceuticals which are adversely impacting the microbes which are causing the reduction in the BOD loads. So, the first and the foremost treatment of the antibiotic wastewater starts from the plant itself. So, during the process a number of organic solvents were used for example, amyl acetate was used in the penciling production, butyl alcohol is also used in the Oreomycin production. So, they should be recovered first of all. So, that the BOD load which is there in the wastewater so that can be reduced because of these organic solvents.

Similarly, it can also reduce the toxic effects in the wastewater, and it will also be beneficial from the economic viewpoint because the organic solvents are quite costly. So, if we are recovering these organic solvents so they can be reused in the process of the antibiotic production. So, antibiotic wastewater if we take it to a settling tank so they can neither be clarified nor they can be chemically coagulated so that the BOD can be reduced. As most of the constituents which are causing BOD in the wastewater, so they appear in the solution, so they are not in the colloidal or in the suspended form. So that's why the clarification or chemical coagulation does not reduce the BOD values very much.

So, that's why the BOD load is not reduced because of the addition of the coagulants or because of the clarification process. So, anaerobic digestion here it may result in a very very good reduction in the BOD. So, if we take the wastewater to the anaerobic digestion process first of all so it may lead to the reduction in the BOD of the antibiotic wastewater. So, in this process when you are taking the wastewater to the anaerobic digestion process the inflow of the wastewater must be controlled and inflow should never exceed 5 percent of the capacity of the digester so that the efficiency of the anaerobic digestion is maintained, and the contents of the digester should also be mixed continuously and slowly so that the anaerobic digestion proceeds at its full efficiency. So, aeration of the waste which is seeded by the microorganisms can also be used for the treatment of the antibiotic wastewater.

So, here if we seed the wastewater with the domestic sewage or if we take the microbes which are available in the garden soil, so it leads to the reduction in the BOD if we are using the aeration process. But their formation of the sludge is very small in this case because of the very low concentration of the colloidal as well as the fine particles and aeration followed by the biological treatment of the diluted sewage. So, we can use the dilution by using the municipal wastewater. So, the aeration followed by the biological treatment can also lead to the reduction in the BOD. So, here in this case the antibiotic wastewater must be diluted by the municipal wastewater and then by using trickling filter we can get a very good reduction in the BOD values.

The colored effluent which are coming out from the trickling filter so it can be decolorized by the chlorination as the color in the antibiotic wastewater may not be reduced by using the trickling filter. So, after the trickling filter process we can take the wastewater to the chlorination so that the color removal can take place. For example, here a wastewater produced from the large pharmaceutical complex in India which is producing antibiotics which is producing vitamin C, symbiotics and fine chemicals and it contains very high acidity. For example, the acidity may be nearly 700 milliamps per liter as calcium carbonate. So, here the wastewater was treated in two stages.

In the first stage the equalization of the wastewater is done. So, the wastewater is taken to an equalization tank where the wastewater flow is equalized. After the equalization we can take the wastewater to the neutralization tank where the lime is added so that the acidity which is present that can be neutralized and then the wastewater is clarified. So, clarification is generally done in an anaerobic digester. So, a glycemic digester may be used for the digestion of this wastewater which is already having which is already free from the acidity and this results in the BOD reduction of nearly 28 to 57 percent.

So, after the first stage is over then in the second stage we can use conventional biological processes for example, we can use the activated sludge process, we can use oxidation ditch. So, after the anaerobic digestion we can take it to the aerated process where the ASP or oxidation ditch, so they are capable of removal of very high values of BOD. So, nearly 70 to 80 percent reduction in the BOD has been observed if this treatment chain is followed. So, here we are using the active discharge process, or we are using the oxidation ditch. So, these are the parameters that basically we need to maintain.

For example, here the organic loading rate in kgs of BOD per kg of MLSS per day. So, it should be between 0.1 to 0.5 for the oxidation ditch whereas, for the activated sludge process it should be maintained between 0.3 to 0.7. The MLSS concentration in the oxidation ditch should be maintained between 3000 to 4000 milligrams per liter whereas, the activated sludge process it should be maintained between 1500 to 2500 milligrams per liter. The aeration time required in the oxidation ditch is high it is nearly 22 hours whereas, in the ASP it is maintained between 6 to 8 hours. So, we can see here the flow sheet for the treatment of the combined antibiotics under the chemical waste. So, here we can see that the combined factory effluent, which is coming from the pharmaceutical industry so, this is taken first of all to an equalization tank where the flow is equalized because the wastewater may be generated intermittent form. So, after the equalization is done so, then the wastewater is taken to the neutralization process where the lime may be added so, that the pH values which are very low in case of this combined factory effluent so, it can be neutralized.

After this neutralization is done so, it is taken to a glyatis ester which is anaerobic digester. So, here the sludge which is formed because the reaction with the lime so, it settles down as well as the digestion of this wastewater may also proceed anaerobically which can lead to the reduction in the BOD nearly 28 percent to 56 percent reduction in the BOD can take place from here. And in this case the sludge may be withdrawn, and the sludge may be taken to the sludge drying beds for the further disposal. The effluent from the glyatis ester may be taken to a sump and then later on it is taken to an active discharge process where basically the further reduction in the BOD may take place. So, it is reported that nearly 80 percent of the BOD may be reduced by using this combination.

And here after this process the effluent goes to the secondary settling tank where again the sludge may be settled down, the sludge may be recirculated for the active discharge process and some of the sludge basically that is wasted so, that can be taken to the sludge drying beds for the further disposal. So, after the treatment of the antibiotic wastewater by using these conventional methods, we can now discuss about the treatment of the synthetic drug wastewater. Synthetic drug plants they also utilize a number of organic as well as inorganic chemicals and these chemicals are produced in a variety of drugs which are produced in different sections of the plant. So, here also we are producing a different type of drugs which uses different type of salts which uses different type of chemicals and there can be different sections of the plant. So, it can be generated from each section so, it may vary.

So, the volume and composition of the wastewater will also vary similarly to vary within from plant to plant also vary from the same plant from section to section also because we are using different raw materials because we are using a number of different processes for the production of the synthetic drugs. So, that is why the typical plant cannot be considered in a synthetic drug industry. So, it will depend upon the process that we are using, or it will also depend upon the type of the drug that we are producing it will also depend upon the process that we are following for the production of the drug. So, the wastewater characteristics will depend upon the type of the drug that we are manufacturing. So, in general the wastewater may be characterized by the high BOD and COD values, but here in this case it is having a highest COD is to BOD ratio.

So, this means that the biodegradability of the wastewater which is produced from the synthetic drug manufacture. So, it is highly non-biodegradable in nature. It may also contain very high toxicity because of number of chemicals that we use, number of solvents that we use. So, the wastewater can be either alkaline or highly acidic in nature and here we find that wastewater may contain a very negligible amount of set level solids as a fraction of the total solids content. The wastewater which arrives from the production of the sedatives. So, it may also contain toxic constituent like potassium cyanide. So, the cyanide will be coming into the wastewater which needs to be treated properly before it is discharged into the environment. Similarly, the alkaline waste may also originate from the manufacture of the sulfur drugs and vitamin B1 and there can be number of organic intermediates which basically may give rise to the acidic waste because it contains lot of organic as well as inorganic acids during the manufacture of the certain synthetic drugs. So, now these synthetic drugs basically have a very great pollution potential, and it has got a diverse characteristic which is coming out from the different section of the plants. So, it is very important that we should plan the treatment of the synthetic drug waste undergoing careful study and complete characterization of the wastewater which is arriving from each section.

We should know that what are the characteristics of the wastewater that is coming out from different section and ultimately, we know that what are the constituents present in the wastewater then we can plan that what can be the treatment methods that can be used for a specific pollutant which is present in the pharmaceutical wastewater. Here in this case when you go for the treatment segregation and equalization it can improve the overall treatment efficiency, and it can also reduce the cost of the treatment. So, if we segregate the different type of waste here which contains a toxic constituents like cyanide for example, we have talked about the sedative plants. So, the potassium cyanide is used. So, cyanide may be coming into the wastewater.

So, it is very important that such type of waste which is acidic in nature which is either containing the toxic constituents. So, they need to be segregated, and they need to be first of all treated. Similarly, the wastewater may also contain very high COD by BOD ratio. So, it is very important before we go for the biological treatment we should also do the lab scale studies so that we can find out that which microbes or which acclimatized microbes can be used for the treatment of this such type of waste water which is having a very high COD to BOD ratio and that is why it is very important that the lab scale studies be performed before we go for the pilot scale or large scale utilization of the biological methods for pharmaceutical waste water. So, the acidic waste which contain toxic elements like cyanide as well as it may contain lot of offensive order producing compounds like aromatic compounds.

So, they should be first of all segregated and they should be treated separately so that the efficiency of the treatment may also be increased. Similarly, the cost of the treatment may also be reduced and first of all this acidic waste may be neutralized by the lime so that the pH basically may be increased and then the order producing compounds so they can be destroyed by using the chlorination process. The compounds which are producing the order, and they are not basically destroyed by the chlorination so they can also be treated by heating it in a furnace so that these compounds basically may be destroyed so that the order which is being generated from the wastewater so it can be reduced. So, now this segregated cyanide wastewater which is acidic in nature after it is neutralized so then basically, we can treat it by using the ferrous salts. So, the cyanides they are converted into the non-toxic complex compounds so they make the complex with the ferrous salts so they will be converted to ferricyanides which is basically which can be precipitated out and then basically we can get a wastewater which is free from cyanide.

So, lime may also be added along with the ferrous salts so that we can adjust the pH to the effective range. So, because we know that for the precipitation of the ferricyanide proper pH it may be required and in the acidic condition it is not possible that the ferricyanide may precipitate so that is why it is very very important that the lime may be added and then basically the precipitation by using the ferrous sulphate may be conducted. So, here the cyanide will first of all react with the ferrous ions so that it can form ferricyanide ions and later on it can convert to the blue ferricyanide precipitate and this precipitate can basically be removed from the wastewater and then basically we can get rid of the cyanide present in the wastewater. So, this method is quite simple in operation it is low in cost as well as it is non-toxic in nature. Cyanide waste can also be oxidized by using chlorine.

So, this is always done in the alkaline conditions, and this process is also known as the alkaline chlorination. So, alkaline chlorination can be used for getting rid of the cyanide. So, here we can have two stage process. So, first of all the free and the weak acid dissociable cyanide is converted to the cyanogen chlorides that is CNCl by using either chlorine gas or we can use the hypochlorite so that basically we can convert the cyanide into the cyanogen chloride as well as it can also be converted to cyanate, and this is always conducted at a pH nearly 10.5 to 11.5. So, the wastewater should be alkaline and that is why this process is known as the alkaline chlorination. So, here the chlorine can react first of all to cyanide, and it can form cyanogen chloride, and this reaction is quite rapid. Similarly, when we are adding hypochlorite ions so in that case hypochlorite ions may react with the cyanide, and it can directly form the cyanate here CNO minus and basically this reaction is also quite rapid in nature and in stage 1b the CNCl is hydrolyzed to cyanate. So, here in case of when we are adding chlorine to it, so it is converted to cyanogen chloride, so the cyanogen chloride is hydrolyzed further to produce cyanate in this case. So, you can see that the hydrolysis of the CNCl produces CNO minus which is cyanate, and this reaction may take nearly 15 minutes to be completed.

After the cyanate is formed then the hydrolysis of the cyanate in the presence of excess chlorine so it may result in the formation of ammonia and carbonate and then we can get rid of the cyanide from the pharmaceutical wastewater and this reaction may take nearly 1 to 1.5 hours to complete. So, this is known as the alkaline chlorination and alkaline chlorination can be used for the pharmaceutical wastewater which contains cyanide in its. The cyanide containing wastewater may also be treated biologically. So, we employ a two-stage process where we go for the anaerobic stage which is followed by aerobic stage so that the cyanide basically it can be removed by using this biological treatment.

So, the microbes which are used so they must be acclimatized to such type of cyanide containing water so that they can assimilate as well as the cyanide may also be removed during the anaerobic digestion as well as the aerobic stage where basically it can also get adsorbed to the sludge which is being generated from these processes. The waste which are other than the acidic waste, so it is found to be ineffective in the BOD and COD reductions. So, here in this case we employ the acclimatized microorganisms, and it has been found to be very effective when we are treating the wastewater by using the microbes which are already acclimatized to such type of pharmaceutical wastewater. But before we go to the treatment of the wastewater by using the acclimatized microbes, we must dilute it so that the treatment can become effective. So, this dilution can be done by using the municipal wastewater.

So, we can dilute the wastewater the pharmaceutical wastewater by adding the municipal wastewater to it and such type of composite waste can be treated by using the acclimatized microorganism even if the large amount of toxic elements is present in the composite wastewater. For example, here the wastewater which is generated from a pharmaceutical complex which is located at Bangalore. So, it is producing the synthetic drugs like Dexedrine, Eskazine, Tetraphosphates, iodex, furasin etc. So, this wastewater it contains many toxic compounds, and it was diluted by using domestic sewage and the acclimatized microbes are used so that we can treat such type of composite wastewater. And this wastewater was found to be having a very high CODs to BOD ratio and the pH was found to be in the acidic range.

So, you can see here that these were the parameters when we have mixed the pharmaceutical wastewater which is coming out from the synthetic drug plants and the municipal wastewater which is coming out from the nearby residential campus. So, the total solids was in the range of 1180 to 1242 milligrams per liter in which the volatile solids concentration was higher in comparison to the fixed solids and the set level solids concentration was very low as we have already discussed and the pH was between 6.5 to 7 and the acidity was 25 to 55 milligrams per liter calcium carbonate and the 5 day BOD was nearly 475 to 567 milligrams per liter the COD was very high nearly 4680 to 6800 and the COD by BOD ratio was also high. So, this indicates that the base that we are getting is having a low biodegradability in this case. Similarly, the chloride values may range between 54 to 102 milligrams per liter, nitrogen was nearly 28 to 32 milligrams per liter, the phosphate was in the range of 2 to 5.5 milligrams per liter and the BOD is to nitrogen is to phosphorus ratio was in 100 is to 5.6 to 6.5 nitrogen is to 0.42 to 1.04 phosphorus. So, we can see here that the phosphorus basically may be low as compared to the standard BOD is to N is to P ratio. So, this type of combined wastewater so, it can be treated by using the extended aeration method and it has been found that nearly 95 percent reduction in COD and 88 percent reduction in the BOD was achieved by using the extended aeration process. So, in such an extended aeration process the loading was nearly 0.075 kgs of BOD per kg of MLSS per day. MLSS concentration was maintained between 5000 milligrams per liter and the MCRT that is Mean Cell Residence Time, or the sludge age was maintained to be nearly 50 days to achieve a 95 percent reduction in the COD and 88 percent reduction in the BOD.

Similarly, a case study from the large synthetic drug plant located at Hardabad in India. So, it can also be discussed here. For example, this plant produces the synthetic drugs which contains analgesics, antipyretics, anthelmintics, anti-filarial, anti-tuberculosis, diuretics, hypnotics, sulfas, vitamins etc. and number of other organic intermediates. So, different sections were found to discharge different type of wastewater and nearly 70 chemicals they have identified like organic as well as inorganic toxic materials were present in the wastewater.

So, in this wastewater the acidic waste was treated separately, and the remaining sections were treated by using the biological methods. So, the acidic waste was first of all utilized by using lime and so that the pH may be maintained to nearly 7. After the neutralization process the sludge that is generated from this process, so it is dried for nearly 5 to 6 days and the sludge was separated and later on this sludge basically was disposed of safely and the neutralized filtrate which was coming out from the neutralization process. So, this may contain a high amount of sulfanilic acid which is nearly 75 percent, which was present in the raw wastewater, but because it is highly biodegradable in nature so it can be directly discharged into the sewer. So, just after the neutralization process and the separation of the sludge we can discharge the process the acidic wastewater which was coming from the synthetic drug wastewater plant directly to the sewers.

Whereas the wastewater which was coming out from the other sections was diluted first of all with the domestic waste water and then it was treated in the two stage bio filters and before and by undergoing the pretreatment by using bar screens, grid chambers and the primary clarifiers. So, the effluent of the secondary clarifier is further treated by a number of oxidation ponds and later on once the BOD, COD as well as the other parameters so they comply to the effluent discharge standards so then it is discharged into the sewers. So, the wastewater that is coming out from the other sections so it can be treated by using the biological treatment process after it is diluted 14 times by using the municipal wastewater as well as we use acclimatized microbes for the treatment process. It has been found in the laboratory biological aerobic reactor that if a loading of 0.29 kgs of BOD per kg of MLVSS and this MLVSS concentration of nearly 3500 milligrams per litre and HRT of 8 hours may lead to the reduction of nearly 90 percent of the BOD and in such experiment it was found that the yield coefficient was nearly 0.56 whereas the decay coefficient for the microbes was nearly 0.12 per day and the mean cell residence time or the sludge age for such process was maintained to be nearly 25 days. So, in the case where we are diluting the pharmaceutical waste water by using the municipal waste water so there is no need of nitrogen supplementation as per the requisite BOD is to N is to P ratio whereas the phosphorus may be required to be added because the phosphorus content may be low as per the BOD is to N is to P ratio and the phosphorus at the rate of 0.84 kg per 100 kg of BOD needs to be added so that the microbial degradation can take place. So, we can see here that in the large synthetic waste drug producing plant the acidic waste basically is treated separately so this may be taken to a neutralization tank where the lime may be added and after which the sludge is separated and the sludge is taken to the sludge drying beds and which is taken to the landfill after the sludge has been dried and this the effluent from here from this process so it can be taken to a balancing tank and later on after this process this can be discharged to the sewer as we can see that the effluent may contain a very highly biodegradable waste water.

So, the waste from the rest of the industry so this is treated by using biological method for example here the wastewater which is coming out from the condenser so it can be taken to a balancing tank and later on it can be taken to a junction box. Similarly, the waste which is coming out from the rest of the section so it can be directly taken to the junction box whereas the domestic sewage which is coming from the residential areas so it is first of all taking to a primary clarifier and the effluent from the primary clarifier so it can be taken to the junction box and the sludge generated from the primary clarifier it can be taken to the registers and then after the digestion process it can be taken to the sludge drying bed where basically the dried sludge may be used as a manure whereas the effluent which is coming out from the digestion process so this may be taken to discharge directly to the sewers. So, here the waste water which is coming out from the other processes for example from the condensers from the residential section as well as from the primary clarifier of the municipal waste water treatment. So, this is first of all taking to the junction box where we add phosphoric acid to it so that the phosphorous which is less as per the BOD is to N is to P ratio so that basically can be sufficed and later on, we can take it to a two-stage biofilter where we can see that we take it to the primary biofilter. So, recycle the wastewater so that we can enhance removal efficiency from here and later on from the primary stage biofilter it can be taken to our secondary biofilter and here we can basically take the waste water to the oxidation ponds and later on after the treatment by the oxidation pond it can be discharged to the sewers.

So, now these are the apparent standards which are prescribed by the central pollution control board and in this case the wastewater which is coming out from the bulk drug and formulation which from the pharmaceutical industries. So, here the compulsory parameters there are two types of parameters here one is the compulsory parameters which are monitored regularly as well as they are applicable for all type of pharmaceutical industries. So, the pH should be maintained between 6 to 8.5, the BOD at 3 days and 27 degrees centigrade it should be less than 30 milligrams per liter, the COD value should not exceed 250 milligrams per liter, the total suspended solids should not exceed 100 milligrams per liter, the oil and grease should not exceed 10 milligrams per liter and the ammonical nitrogen should not exceed 100 milligrams per liter and here the toxicity test may also be performed that is the bio-acid test should indicate that nearly 90 percent survival of fish must take place after 96 hours in 100 percent effluent that is coming out from the waste water. So, when the fishes they are subjected to 100 percent effluent, and they are subjected to 96 hours to it.

So, nearly 90 percent of the fish present in the bio-acid test so they should survive. Whereas there can be some additional parameters also which needs to be also monitored. So, if we are using benzene, xylene, methylene chloride, chlorobenzene during the process so they should be monitored they are coming out in effluent or not. For example, it should the benzene should not exceed 0.1 milligrams per liter, the xylene should not exceed 0.12 milligrams per liter, the methylene chloride should not exceed 0.9 milligrams per liter as well as the chlorobenzene should not exceed 0.2 milligrams per liter. So, these additional parameters it depends upon the state pollution control board, and it will also depend upon the type of process that the pharmaceutical industries are using so that they can ascertain that whether these parameters will be present in the wastewater or not and they need to be monitored or not. So, the phosphate basically should not exceed 5 milligrams per liter, sulfides should not exceed 2 milligrams per liter in this case, a phenolic compound should not exceed 1 milligrams per liter, the zinc should not exceed 5 milligrams per liter, copper should not exceed 3 milligrams per liter, the total chromium should not exceed 2 milligrams per liter and in which hexavalent chromium should never exceed 0.1 milligrams per liter and the cyanide if it is present in the waste water so it should not exceed 0.1 milligrams per liter, arsenic should not exceed 0.2 milligrams per liter, mercury should not exceed 0.01 milligrams per liter and the lead should not exceed 0.1 milligrams per liter. The sodium absorption ratio should be less than 26 and it is applicable when we are discharging the wastewater on the land. We stop here and these are the references that we have used for the preparation of this lecture.

So, thank you.