Course Name: Industrial Wastewater Treatment

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Lecture 5: Treatment of wastewater produced from Textile and Dye and Fertilizers

So, welcome back. We are in module 9, lecture 5 and we are discussing the treatment of the wastewater produced from textile and dye and fertilizer industries. So, in this lecture we are discussing about the fertilizer plant. So, today we will be discussing about the fertilizers which are phosphatic in nature. So, we will talk about the phosphate fertilizers plants as well as we will also talk about the complex fertilizer plant which produces both nitrogenous as well as the phosphate fertilizers. So, the topics covered in this lecture will be on the manufacturing process for the phosphate fertilizers.

So, we will be talking about the manufacturing of the phosphoric acid, the single super phosphate fertilizers, the triple super phosphate fertilizers in this lecture and similarly we will talk about the complex fertilizers. So, we will talk about the manufacture of the mono and diammonium phosphate fertilizers, we will talk about the wastewater which is generated from the fertilizer plants which are complex in nature that is they are producing both the type of fertilizers like the nitrogenous fertilizers as well as the phosphatic fertilizers and then we will talk about the impacts of the wastewater discharge on the receiving streams and we will talk about the treatment of the fertilizers wastewater and lastly we will talk about the fluent standards for the fertilizer industries. So, when we talk about the phosphate fertilizer plant, so this phosphate fertilizer industry is considered as one of the most polluting industries in the sense because here when we talk about the phosphate fertilizers, so it is generally produced from the ores which contains phosphorus and these ores which contains phosphorus, so they may also contain lot of calcium and fluoride also along with it. So, it is possible that during the manufacturing process lot of fluoride may go into the wastewater as well as in the emissions.

So, it has been found in the previous times that the fertilizer industries which are producing phosphate fertilizers, so they were introducing lot of fluoride into the environment by basically production of the hydrofluoric acid as well as the hydrogen fluoride as well as the hydrofluoric acid. So, this fluoride may be going into the water as well as it has also gone into the air emissions also. So, it has basically concentrated into the soil as well as in the crops. So, lot of cattles basically they died because of the high concentration of the fluoride into it, similarly the people who are drinking that water as well as the people who are drinking who are taking those crops, so they also basically got affected by the high concentration of fluoride. So, fluoride is generally the pollutant which has to be there if it is present in the water, so it should be between 1 to 1.5 milligrams per liter because fluoride is required by the body also, but excess fluoride may also cause lot of problems. For example, if the fluoride is less than 1 milligram per liter, so the children basically can have the dental caries or there can be cavity problems in the teeth because of the low levels of the fluoride. So, we generally go for the fluoridation of the water whereas if the fluoride it increases beyond 1.5 milligrams per liter, so then it can also cause lot of bone deformation for example it can cause skeletal fluorosis. So, here the phosphate fertilizers may be single super phosphate fertilizer or the triple super phosphate fertilizers.

So, when we talk of the single super phosphate fertilizers, so they are a mixture of the monocalcium phosphates and gypsum. So, they contain nearly 16 to 22 percent of the phosphorus pentoxide and the triple super phosphate contains nearly 46 percent of the phosphorus pentoxide in it. So, the first and the foremost step in the production of the phosphate fertilizers is the production of the phosphoric acid. So, the phosphoric acid may be produced by dissolving the phosphate rock into the sulfuric acid. So, we can see here that this phosphate rock which contains fluoride as well as the calcium here, so it when reacts with the sulfuric acid, so it may produce lot of gypsum that is there as a sludge, and it may produce the hydrogen fluoride, and it will then produce the phosphoric acid also right.

So, then after the reaction is over, so then we these calcium sulfate crystals which are formed, so they are basically allowed to grow to the adequate size and we know that the calcium sulfate it also basically dries very slowly and here it is basically provided some time so that it can grow in the size and later on this can be separated out from the phosphoric acid by filtration process. And then we concentrate the phosphoric acid to the desired level by using certain evaporation mechanisms. So, if we see the flow diagram for the manufacture of the phosphoric acid, so we can see here that the phosphoric rock may be first of all grinded and crushed and then basically it may be taken to the dilute sulfuric acid and then after this dilute sulfuric acid, we pass it through a strong sulfuric acid and the reaction between the phosphoric rock and the strong sulfuric acid it happens and this basically may result in the formation of lot of fluoride like for example the size of the calcium sulfate it grows, so then we take it for the filtration process where we use vacuum pan filters and then whatever the gypsum is produced, so that may be taken after the settling, so this may be taken for the further use or further disposal. Whereas the filtered water which contains lot of phosphoric acid, so this may be taken to the vacuum evaporation, so that we can concentrate the phosphoric acid which is produced and then later on basically it is taken to the settling tank where we get the phosphoric acid nearly 54 percent in concentration and after the settling we go for the extraction where we use number of solvents like n-butanol or iso-butanol and later on we separate out these solvents from here and we can basically go for the solvent recovery process. So, that is how the formation of production of the phosphoric acid may take place.

So, here we can see that the condensates may contain a lot of fluoride into it, right. So, for example, we are having the wash waters, we are having the scrubbing waters, so these waters may contain a lot of fluoride content into it. So, now we can see the reaction where the phosphate rock or the ore is basically reacted with the sulfuric acid, and it can lead to the formation of the single sulfur phosphate and the calcium sulfate is also generated as the sludge and the hydrogen fluoride will also be generated as a by-product. So, this ground phosphate is first of all taken into a continuous action double conical mixture where the sulfuric acid which is having a 75 percent of concentration is fed to the mixture. So, for phosphate slurry it is formed, so it basically crystallized and because of the low solubility of the calcium sulfate and then the aging of the super phosphate is done and then basically we convert it into the crystalline form of the monocalcium phosphate and which leads to the formation of the single super phosphates either in the powder form or in the granular form.

So, if we talk about the manufacture of the single super phosphate fertilizer, so this is the flow diagram that shows us that how the single super phosphate fertilizer can be made. So, we take the phosphate rock for the crushing, grinding and screening later on we dilute it and then basically we take it to the acid relation mixture. After this mixing it with the 75 percent of the sulfuric acid we take it to the reaction then where the formation of the single super phosphate fertilizer may take place and later on after the crystallization process, we take it to the belt conveyor and then we store the single super phosphate that is formed for certain weeks. For example, here we take around 2 to 6 weeks for aging and after the aging the granules that are formed so that basically can be bagged and then it can be delivered. It can also be basically taken to the granulation process where these particles basically may form the granules.

After the granulation we can take it to the screens and then after the screening process we can cool this thing and then we can pack the single super phosphate granules for the for the delivery. So, when we are going to manufacture the triple super phosphate fertilizer so in that case we go for higher concentration of the super phosphate. For example, here we concentrate it so that we can get nearly 45 to 46 percent of the available phosphorus pentoxide. So, the triple super phosphate is manufactured by the action of the phosphoric acid on the phosphate rock. So, in the previous that is the single super phosphate we have used the sulfuric acid whereas in case of the triple super phosphate we use phosphoric acid into it so that the concentration of the phosphorus pentoxide can be increased.

So, you can see here that the phosphate rock first of all reacts with the phosphoric acid and it will produce the triple super phosphate, and it can also produce the hydrogen fluoride as a byproduct. So, which can go into the emission. So, this process is simpler to that of the single super phosphate production. So, here basically we take the pulverized phosphate rock, and it is mixed with the phosphoric acid and here we use the two-stage reactor for the reaction and the resultant slurry which is formed. So, now it is taken to the granulator after the granulation is done then basically, we cool and store and then we bag or pack the triple super phosphate fertilizer that is formed and then it can be sent for the delivery process.

So, we can see here that this diagram shows us the flow diagram for the manufacture of the triple super phosphate. So, we can take the phosphate rock here we can go for the crushing, grinding and screening process and then we add the phosphoric acid into the two-stage reaction chamber where basically the hydrogen fluoride as well as the fluorosilicic acid. So, this may come out in as the emission and then basically we take it to the granulation chamber where the granules of the triple super phosphates they may form and once the granulation is done. So, then we take pass it through the screen. So, that we can get the desired size and then we cool the granules that we have formed and then later on these granules can be stored and packed for the further delivery.

So, after the discussion on the phosphate fertilizers we can now discuss about the complex fertilizers where we can have different type of combination of the ammonia of the nitrogenous as well as the phosphate fertilizers. For example, we can have the two types of ammonium phosphate that can be formed. So, we can have the mono ammonium phosphates, or we can have the diammonium phosphate production in the complex fertilizer plants. So, the mono ammonium phosphate is made by reacting the ammonia with phosphoric acid and later on we go for the centrifuging process and then drying in a rotary dryer and whereas the dry ammonium phosphate requires a two stage reaction system and so that we can prevent the loss of the ammonia from here and the process is more or less similar to that of the mono ammonium phosphate. And after the granulation is done it is basically followed by the drying process then after the drying the granules which are formed so they can be packed, and they can be delivered to the desired destination.

We can see here the flow diagram for the ammonium phosphate manufacturing plant. So, we can have the ammonia here, we can have phosphoric acid and the cooling water. So, this is taken to the reaction chamber where the reaction between the ammonia and phosphoric acid takes place, and this may result in the formation of the ammonium phosphate. And once the ammonium phosphate is done so then we take it to the granulation and the drying process, later on we take it to the cooling process, after the cooling we take it to the screening process and then basically we can take it to the grinding process so that the bigger particles which are there so they can be grind to the finer particles and later on after the screening process we take the granules to the coating and then we take to the storage and later on we can pack and then we can deliver it to the desired destination. So, the base water characteristics which are coming out from the complex fertilizer plant so they may contain the number of the processing chemicals, they may contain the ammonia phosphoric acid etcetera, they may also contain urea, ammonium sulfate, ammonium phosphate etc. which are coming out from the manufacture of both the nitrogenous as well as the phosphatic fertilizers as well as the combination of the nitrogenous and phosphates fertilizers.

So, we can also find the oil-bearing waste coming out from the compressors right, we can also find that the cooling waters, the wash waters, thus from the scrubbing towers for the purification of gas so they basically also form the part of the wastewater. So, the wastewater may also contain lot of toxic substances as you have already discussed that it may contain arsenic, it may contain monoethanol amine, it may contain potassium carbonate, it may contain di-ethanol amine etc. So, which are used in the nitrogenous fertilizer plants for the purification or for the separation of the carbon dioxide during the process of the ammonia formation. Similarly, the phosphate fertilizer may also contain a number of compounds into it for example, the wastewater that is generated may contain the carbonic acid, it may contain hydrofluoric acid, it may contain fluorocellulosic acid, it may contain fluorides, it may contain phosphates, it may contain suspended solids, it may have a low pH value. So, as well as there can be certain alkaline and acidic wastes again getting generated because if we are using the water for the boiler feed so it may be required that it is passed through the anion and the cation exchanger so it may result in the formation of the alkaline as well as the acidic waste.

So, we may also find lot of toxic elements for example, chromates, zincs which are used for the topology and control, and I think we have already discussed this thing that if we are using quaternary ammonium compounds so these compounds may be eliminated, and they may not form the part of the wastewater. Similarly, if we are using the waste water generated from the cocoon plants so it may contain lot of other pollutants also for example, the phenol and cyanide which come from the poking of the coal so that may basically come into the waste water here and the phenol and cyanide we find as a very toxic pollutants which comes into the waste water if we are using ammonia which is coming from the cocoon plants. So, now this is the composition of the wastewater, which is generated from the complex fertilizers for example, here the pH may be between 7.5 to 9.5. Similarly, the total solids may be around 5400 milligrams per liter we can have the ammonia nitrogen around 700 milligrams per liter we can have the urea nitrogen also which is nearly 600 milligrams per liter we can have the phosphate coming out in the waste water nearly 75 milligrams per liter we can have fluoride which we already discussed which is coming out from the phosphate fertilizers plants so this is nearly 15 milligrams per liter and the arsenic is nearly 1.5 milligram per liter which may come from the separation of the carbon dioxide from the natural gas. So, now there can be number of impacts of the wastewater getting discharged into the receiving streams without any treatment. So, these pollutants which are present we just now discussed so all these pollutants are highly hazardous or we can say they are highly toxic in nature and they can have adverse effects on the stream ecosystems for example, the acids and alkalis if they are directly put into the water without treatment so they can disrupt the aquatic life similarly the arsenic, fluorides and ammonium salts so they can be highly toxic to the fishes. Similarly, amines which are formed so they also can exert a very high oxygen demand as well as they can also basically exert the chlorine demand for example, we have seen that when the chlorine is added so these amines basically may form chloramines so they may demand chlorine and similarly the salt which is present in the waste water so it may render the receiving streams unfit for the drinking water as well as it may also reduce its usage in the industrial purposes.

Similarly, the nitrogen and the other nutrients which are present in the wastewater for example, nitrogen is there the phosphorus is there so it may basically increase the growth of the aquatic plants in the streams, and it will also lead to a problem which is called eutrophication. So, it may increase the content of the phosphorus as well as it may increase the content of the nitrogen into the lakes or the water bodies. So, this may lead to the blooming of the algae in the lakes or the water bodies and this basically may lead to the eutrophication and this may lead to the natural death of the lakes slowly and slowly because of the eutrophication process. So, now let us discuss about the treatment of the wastewater that is generated from the complex fertilizer plants. So, the major pollutants may include oil, it may include arsenic, it may include ammonia, it may include urea, it may include phosphate, it may include fluoride.

So, these are the major pollutants which are generally found in the wastewater which is coming out from the complex fertilizer plants. So, oil which is present so it can be removed in a gravity separator. So, we know that the oil is light so it basically it can float on the surface whereas, the water basically may will settle down and it can be taken out from the bottom and the oil from the top can be skimmed and that is how the oil can be removed from the wastewater. And similarly, the arsenic which is there in the wastewater so that steam may be segregated first of all and that steam may be taken to the concentration ponds or evaporation ponds and after this whatever the solid waste is generated which may contain high amount of arsenic into it. So, that may be safely disposed of or that may be basically taken to the engineered landfill site where basically it can be safely disposed off.

And similarly, the phosphate and the fluoride bearing waste, so they are also segregated, and they are treated by using lime. So, they are coagulated by addition of the lime and then later on when this phosphate and fluoride basically waste this has been removed from the wastewater. So, the clarified effluent may still contain some amount of phosphate and fertilizers. So, this can be diluted by mixing it with the other wastes. So, when we want to remove the phosphate and the fluoride from the wastewater which is mainly generated from the phosphate fertilizers so industries.

So, this may be done by using a two-stage liming process where we take the wastewater to the first reaction where the lime is added so that we can bring the pH which is very low. So, we can bring the pH to around 3 to 4 and this may reduce the fluoride concentration to nearly 20 to 25 milligrams per liter and the phosphorus concentration can also be reduced to nearly 50 to 60 milligrams per liter. And when we are adding lime to it so the calcium fluoride may precipitate out and this may be settled out. Now, this is treated again with lime so that we can now raise the pH to nearly 6 to 7 in the second stage. So, the fluoride and phosphorus concentration after the second stage may reduce to nearly 10 milligrams per liter.

So, then the water which is there so which will contain the sludge because generation precipitation so this basically may be clarified and then it can be released to the receiving stream after dilution with the other waste waters. So, when we are using two-stage fluoride removal process so here this lime precipitation may also be followed by the alum polyelectrolytes population sedimentation. So, it is found to be very efficient. We are removing the fluoride by using the lime precipitation process.So, the alum polyelectrolyte population may help in this case, and we can get a maximum precipitation of the fluoride with the lime it occurs at a pH which is nearly greater than or equal to 12 whereas the optimum coagulation for the alum polyelectrolytes so it may occur at a pH of nearly 6 to 7.

So, now there can be other treatment alternatives which can basically treat the ammonia bearing waste for example we are having a high concentration of ammonia which are coming out from the wastewater generated from the nitrogenous fertilizer manufacture. So, they may be taken to the steam stripping, they may be taken to the air stripping towers and this may also be taken to lagoons after the pH adjustment, or it can be passed through the biological nitrification and denitrification process. So, we want to get rid of the ammonia which is present in the wastewater which is getting generated from the nitrogenous fertilizer manufacture. So, these processes may be used. For example, when we talk of the steam stripping, so it has been found that the ammonia removal from the fertilizer waste is not economical and it has proved to be quite uneconomical in the sense.

So, the removal by the steam stripping may not be used frequently. However, the air stripping towers so it has been found to be highly beneficial when we are basically packing the stripping tower with the redwood sticks. So, in that case the removal of ammonia has found to be highly efficient. Similarly, it has also been found that the removal of ammonia by lagooning the wastewater so it has basically given a very good results as it has been indicated by the study conducted by Niri and here the reduction in the ammonia content by retaining the wastewater in earthen tank which may be around 1 meter deep and then we can put this wastewater for a retention time of nearly day or 2 and after the pretreatment of the waste by lime so that we can increase the pH to around 11. So, it has been done so that the whatever the ammonium compounds are there so they may be converted to ammonia gas as at high pH values.

So, we may find higher amount of ammonium ions converting to ammonia gas and later on this ammonia content can be reduced as the gas basically goes away from the from the lagoon. So, that is why it is very essential that we increase the pH so that we can go for either for the stripping or we can also go for the lagooning also. However, it has been found that the if the wastewater contains urea also so then there is no reduction of the urea content is observed during the lagooning process. So, however if we can provide a longer retention time and we allow the urea to decompose or to convert into ammonia then it is possible that the ammonia may be removed as well as the urea basically can be converted to ammonia and then later on it can be removed from the system. We can also treat the ammonia by using the biological methods for example we can go for the process of nitrification as well as the denitrification process.

So, in the nitrification process under the aerobic conditions we convert the ammonia to nitrite and nitrate and this nitrate basically is then taken to the denitrification process where we use anaerobic processes, and we use denitrifiers basically bacteria which can convert this nitrate into the gaseous nitrogen and nitrogen oxide, and this may be released to the atmosphere under the anaerobic conditions. So, denitrification when it is done so it may require certain carbonaceous matter into the reactors. So, it is essential that we add carbonaceous material to the reactor and in all the cases for example here we are talking about the removal by using biological methods. So, the ammonia removal may take place, but however the urea removal may not take place. So, the urea removal can only take place when we convert the urea into the ammonia and later on, we can treat it by using different methods.

So, now we talk about the treatment of the wastewater effluent that is getting generated from a complex fertilizer plant. So, we can see here that the ammonia plant is there. So, in the ammonia plant we can have the waste generated which is coming out from the absorption tower which may contain monoethanolamine as well as the arsenic bearing waste. So, this arsenic bearing waste may take into an evaporation pond where the arsenic may be concentrated and this arsenic basically later on can be disposed of safely and the oil bearing waste may also come from the compressors. So, this oil-bearing waste may be taken to the oil separator and after the oil separator this wastewater which is generated.

So, this may be taken to as the effluent for the disposal. Similarly, the waste from the ammonia plant and from the urea plants the ammonia and urea may be generated. So, this ammonia and urea may be taken to the biological process. For example, we can take it to the nitrification process so that we can convert the ammonia to nitrate and after the nitrification process is over then we take it to the denitrification tank and we add a carbon source here so that the denitrification process can proceed and in that case the nitrate is converted into nitrogen gas and then it is basically we get rid of the nitrogen ammonia from the system and later on after the denitrification process later on after the denitrification process the waste may be discharged as the effluent. Similarly, the other plants which are there for example, we can have boiler plants, we can have the ammonium sulfate plant, we can have sulfuric acid plant, we can have demineralizers.

So, from here the waste that is generated so that may not be containing very high toxic elements so that may be discharged directly to the effluent. Whereas, if we talk of the phosphate fertilizer plants so we are basically we are having phosphate phosphoric acid plant or we are having the di-ammonium phosphate plant. So, here we take the effluent to the two-stage liming process. So, we take it to a chalkboard first of all and then we add in a other mixing tank we add lime to it and after this process the sludge is settled down. So, after the settlement of the sludge so lot of calcium as lot of phosphorous as well as the fluoride so that may basically get separated out in the form of the sludge and after the effluent is clarified so then it may contain very less amount of phosphorous as well as the fluoride.

So, then can be mixed with the other effluents and then it can be basically discharged to the environment. So, let us talk about the effluent standards which have been set up by the Central Pollution Control Board. So, if we talk about the wastewater which is coming out after the treatment in the nitrogenous fertilizer plants which are producing ammonia which is producing calcium, ammonia, nitrate or producing ammonium nitrate fertilizers. So, in that case the pH should not exceed from 6.5 to 8.5. Similarly, the spinach solids concentration should also not increase 100 milligrams per liter, the oil and grease should not be more than 10 milligrams per liter, the ammoniacal nitrogen should also be less than 50 milligrams per liter, the total general nitrogen as nitrogen it should not exceed 75 milligrams per liter, the pre-ammonical nitrogen as nitrogen so it should not exceed 2 milligrams per liter. Whereas, if we are using the ammonia from the cocoon plants in that case the cyanide concentration should also not increase more than 0.1 milligrams per liter. And the nitrate nitrogen as nitrogen so it should not increase 10 milligram per liter in the urea plant whereas other than urea plant it should not increase more than 20 milligrams per liter. So, then there are standards for the straight phosphatic fertilizer plants where the phosphate fertilizers are only produced.

So, in that case the pH it should be between 6.5 to 8.5, the suspended solids should not exceed 100 milligram per liter, the oil and grease should not exceed 10 milligrams per liter, the fluoride should not exceed 10 milligrams per liter and the dissolved phosphate as phosphorous it should not increase 5 milligrams per liter. So, now if we talk about the effluent standards for the complex fertilizer plant, we are producing NP or NPK fertilizers. So, in that case the effluent standards as prescribed by the central pollution control board so it says that the pH basically should lie between 6.5 to 8.5 for the treated effluents and similarly the suspended solids should not exceed 100 milligrams per liter, the oil and grease should not exceed 10 milligrams per liter, the am housing nitrogen should not exceed 50 milligrams per liter, the total toxic nitrogen should also not increase 75 milligram per liter, the free ammonical nitrogen in the affluent, in the treated effluent it should not exceed 4 milligrams per liter, similarly the nitrate nitrogen should not exceed 20 milligrams per liter as dissolved phosphate as phosphorous should not exceed five milligrams per liter and the fluoride should not exceed 10 milligrams per liter and it has been also prescribed by the central pollution control board that the chromium salt should not be used in the cooling tower as the LED side and similarly the effluents must also be regularly analyzed for the vanadium as well as the arsenic at least once in a year so that and the report should be submitted to the concerned SPCB or the CPCB or the pollution control committee so that we can ensure that these toxic constituents are not going into the wastewater.

So, this ends our lecture on the treatment on the wastewater generation and the treatment of the wastewater which is getting generated from the fertilizer industries. So, we stop here. So, these are the references that we have used for the preparation of this lecture.

Thank you.