Course Name: Industrial Wastewater Treatment

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Lecture 4: Treatment of wastewater produced from Textile and Dye and Fertilizers

So, welcome back. We are in module 9, lecture 4 and we are discussing the treatment of wastewater produced from textile and dye and fertilizer industries. So, in this lecture today we will cover about the fertilizer industries. We will talk about the manufacturing processes which are used for the nitrogenous fertilizers. We will also talk about the wastewater which is generated from the nitrogenous fertilizer plants. So, the fertilizer industry is a form of secondary chemical production.

This means that we are producing the fertilizers by a combination of other chemicals and these chemicals may be used for the production of fertilizers which contain number of nutrients which are required for the soil. For example, the nitrogen, the phosphorus and the potassium. So, if the soil is deficient in these nutrients, then it can be used for enhancing the productivity of the soil and the crop. So, here we can have different type of fertilizers that we can use.

For example, we can have the nitrogenous fertilizers, we can have the potassium fertilizers, we can have the phosphorus fertilizers. Either these fertilizers can be made separately, or these fertilizers can be made in a single complex and that is why it is known as the complex fertilizer plants and otherwise we call it as a nitrogenous fertilizer plant or we call it as a phosphorus, phosphatic fertilizer plant. So, the fertilizer that we require, so they may be natural for example, we may produce the fertilizers by composting process and this composting process and also add nutrients to the soil and we call that as a natural fertilizer. Whereas, when we use chemicals so that we can produce a different type of salts of nitrogen, phosphorus and the potassium and that can be added to the soil which can be absorbed by the soil and their concentration increases in the soil which enhances the fertility of the end the productivity of the soil. So, as per the chemical composition the fertilizers can be categorized into three main groups.

One is the phosphatic fertilizers which contains phosphorus as the base element and which is expressed by the presence of phosphorus pentoxide percentage for example, the super phosphates for example, single super phosphates fertilizers that we use, similarly the tri super phosphate fertilizers that we use. So, these types of fertilizers are made in a specific industry which is called the phosphate fertilizer plant. Whereas the nitrogen fertilizers they contain the nitrogen as the base element and the which is expressed in terms of nitrogen percentage for example, we can have the production of urea here, we can have the

production of ammonium sulfate, ammonium nitrate and ammonium chloride. So, these fertilizers may be added to the soil so that we can enhance the productivity of the soil. Similarly, potassium fertilizers they contain potassium as the base element, and it is expressed by the percentage of potassium oxide present in the fertilizer.

So, then we can have the complex fertilizers for example, we can have the combination of nitrogen phosphates and potassium for example, we can have the fertilizers like ammonium phosphate, or we can have the fertilizers like ammonium sulfate phosphate. So, these are the examples of the complex fertilizers which are made in a single plant and these plants basically produce the nitrogenous fertilizers also these plants produce the phosphate fertilizers also as well as they produce the combination of the fertilizers. So, the potassium fertilizers generally it involves the mining process only and the potassium chloride is mined in this case, and it is benefited, and it can be directly used without any chemical processing. So, that is why the potassium fertilizers are generally they do not require the large processes industrial processes and that is why we are not going to discuss the potassium fertilizers in this lecture, and we will talk about the nitrogenous fertilizers as well as the phosphatic fertilizers in this lecture. We will focus on the nitrogenous fertilizers as well as the phosphorous fertilizers in this lecture.

So, when we talk of the nitrogenous fertilizers manufacturing process so in that case the ammonia is the main raw material. So, generally the ammonia is first of all produced and then basically it can be used for the production of other chemicals for example, we are using the ammonium chloride, or we are using the ammonium sulfate. So, then basically the ammonia is the base chemical that we use for the production of these type of fertilizers. So, ammonia can be produced by the synthesis of the nitrogen and hydrogen. So, this process is known as the Haber's process and here the nitrogen and hydrogen may fuse to form the ammonia.

So, hydrogen can be generated either by steam reforming of the natural gas or it can also be produced by the electrolysis of the water whereas, nitrogen is either produced from the air liquefaction or it can also be produced by the combustion of the natural gas. So, ammonia that we are using so this can also be available as a byproduct from the coke oven plants. So, that also can be used, but we have to look that the contaminants that are present in the coke oven wastewater and they can impart the toxicity to the wastewater generated from nitrogenous fertilizer plants which are using ammonia which is available from the coke oven plants. So, let us first of all discuss the manufacturing process for ammonia. So, in case of the production of ammonia the natural gas is taken, and it is desulfurized by adsorbing the H2S gas on the surface of zinc oxide or active carbon.

So, here the desulfurization process is first of all followed then followed by the catalytic steam reforming where basically we mix it with the superheated steam that is up to 500 to 600 degrees centigrade. So, the natural gas after desulfurization process it enters the

primary reformer, and it passes over the nickel catalyst. So, it is converted to hydrogen, carbon monoxide and carbon dioxide gas and the gas leaving the primary reformer may now enter into the secondary reformer where the hydrogen, nitrogen, carbon monoxide, carbon dioxide and water may be produced and where basically the natural gas may also be cooled up to 360 degree centigrade and by passing it through the waste heat boilers before it is sent to a carbon monoxide shift plant. In the carbon monoxide shift we generally convert the carbon monoxide to carbon dioxide by using iron oxide catalyst or we also use the chromium oxide initiators. So, the carbon dioxide which is formed is then removed by using chemical or physical adsorption processes.

For example, here we can have the chemical absorption by using monoethanol amine, MEA. Similarly, we can also use diethanol amine that is AMDEA whereas we can also use the hot potassium carbonate solutions so that we can absorb the carbon dioxide which is present in the natural gas and this can be then removed from the system and then later on this carbon dioxide can be purified and then it can be used for the manufacture of the urea in the further processes. Similarly, we can also use number of physical solvents for example, we can use glycol dimethyl ethers, or we can also use propylene carbonate in this case. So, then we take this gas to the catalytic methanation, and we use a nickel catalyst for the methanation process. Now, for the ammonia synthesis we take the gas from the methanator it is then compressed and then it enters the converter which contains iron catalyst so that it can form ammonia here.

So, ammonia gas from the converter is then condensed so it gets converted to the liquid form it is then flushed so that whatever the other gases which are there so they may be pushed out from the liquid and then the liquid ammonia can either be stored in a pressure storage or basically it can be stored in an atmospheric double insulated refrigerated tank. So, this is a flow diagram which shows that how ammonium refracting can be done. So, you can see here that the natural gas basically passes through the adsorbent like zinc oxide activated carbon and the catalyst like cobalt oxide or molybdenum oxide or zinc oxide and then basically here in the desulfurizer it is desulfurized so that basically the H2S and the VOCs so they can be removed from the natural gas. And then we take this gas to the primary steam reforming where the nickel catalyst is used. After the primary steam reforming we take the gas to the secondary steam reforming where again the nickel catalyst is used and we pass hot compressed air here also and in the primary steam reforming we pass steam and then later on this gas the temperature is reduced by passing it through the waste heat boilers where the heat is exchanged and the gas is cooled and then we take it to a CO shift converter here basically the CO is converted to the carbon dioxide and then we take it to a separator where basically the carbon dioxide is separated from the gas where basically we use the solvents like potassium carbonate, MEA or MDEA so these are used so that we can separate out the carbon dioxide gas and then later on we can purify it and the solvents regenerated from here so they can be recycled.

Similarly, the wastewater may be generated from the secondary steam reforming, and we can also take the gas to the secondary steam reforming and then we can separate out the gas from the primary steam reforming also. And after the CO2 separation the gas is taken to a methanator where the methanation is done and here we may find that the methane emission basically takes place and lot of heat is also generated and this methanation may be done in presence of the nickel catalyst. And after the methanation process we take it to the ammonia converter where basically this ammonia is formed and then this ammonia basically may be taken to the waste heat boilers and this waste heat boilers basically cools it and then basically the ammonia gets converted to the liquid form and this liquid form ammonia can then be refrigerated or stored. So, they may basically form certain wastewater here similarly we can also get the ammonia basically getting entered into the wastewater from this process. So, we can see here that the equation that is nitrogen and three molecules of hydrogen so when they combine so they form two molecules of ammonia. So after this when the liquid ammonia is formed so then it is taken for the manufacture of the urea. So here we take the liquid ammonia from the storage tank and we take it to the urea plant and then basically it is preheated and the temperature may be decreased to around 10 degree centigrade and here the ammonia and carbon dioxide so they are fed through the synthesis section so that we can have a molar ratio of nearly 2 for ammonia is 2 carbon dioxide and then basically here the urea may form in addition to that where the carbonate is formed and the dehydration of the carbonate may result in the formation of the urea and the urea reactor basically the most of the condensate carbonate so it is converted to urea and water. So, this reaction mixture which contains urea as well as the carbonate, so it is then basically distributed over the stripper tubes. So the carbon dioxide is then introduced in the opposite direction in the stripper tube and the basically the further urea formation may take place here and urea carbonate solution which is leaving the stripper is sprayed on the bed of the ball rings in the rectifying column and then basically this urea may be taken to the flash tank where basically the concentration of the urea in the storage tank may be around 70 to 80 percent. After this we take the solution to further concentration and we basically prepare a melt which may contain around 98 percent of the urea by using evaporation under vacuum conditions and this urea melt is then pumped and it is taken to the prilling towers and the prints are received on the conveyors and they are transported to the bagging sections we can have the powder of the urea formed and this may be packaged and then it may be sent for the delivery.

So, we can see here the flow diagram for the urea manufacture so, we are having the liquid ammonia here which is passed into a high pressure condensers and similarly we are also providing the pure carbon dioxide which is also coming from the recycling or from the purification of the carbon dioxide that we have taken out during the CO shift process after adsorption in the solvents and then basically this is taken to the reactors and in the reactor the liquid ammonia and the carbon dioxide so they may combine and they will form urea and carbon dioxide so we can see here that carbon dioxide and ammonia when they

combine so they first of all form the carbamate and this carbamate then basically dehydrate and then it forms the ultimately the urea. So, after this process we pass the solution which contains carbonate as well as the urea on the stripping towers where basically we are having the counter current of carbon dioxide being sent here and later on we take it for the rectification process and then we take it to the flash tank where the concentration of urea basically is increased to nearly 75% and then we take it to the vacuum evaporation where the concentration of the urea may be around 98% and then we take it for the prilling or granulation process and then from the prilling and granulation process we take it to the cooling and screening and then basically we take it to the coating and finally for the delivery. Similarly, the condensate that is collected from the vacuum evaporation so it may basically be adsorbed first of all adsorption process is there and then basically we can hydrolyze it so that we can basically strip it with the presence of urea or carbonate from here. So, now in nutshell when we talk about the nitrogenous fertilizer plants and so every plant has ammonia production unit into it. So, the ammonia is the base chemical that we use for manufacture of all other fertilizers here so the ammonia will be present in all the nitrogenous fertilizers.

So, a reactor is now required till the synthetic ammonia will be reacted with the other chemicals so that we can produce the final product for example if you want to produce ammonium chloride, we want to produce ammonium sulfate so then basically we have to choose a chemical so that we can convert the ammonia into that final product. So and then plants may also have certain auxiliary units so that we can produce whatever the chemicals we are basically using it here for example you may use sulfuric acid you may use nitric acid also so if we talk about the urea manufacture in nutshell so we are having the production of the synthesis gas which can be produced from the carbonation material by passing steam or air into it and it forms a mixture of hydrogen and carbon monoxide so this is known as the synthesis gas and later on we basically pass it over a nickel catalyst so that we can convert the CO into the oxygen and carbon dioxide and later we separate and purify the carbon dioxide gas and we remove the residual carbon monoxide from the gas mixture and then we take it for the manufacture of the ammonia by reacting the hydrogen and nitrogen over a catalyst and the synthesis of urea by treating the ammonia with the carbon dioxide so this is done at high temperature and high pressure so this results in the synthesis of the urea when we talk about the process of manufacture of the ammonia so we can divide into three parts for example we can have gasification we can have the gas separation and then we can have the production of ammonia here for example here the naphtha or the natural gas basically may be steam reformed and here we pass air as well as the steam and it basically forms the CO hydrogen and carbon dioxide then again it is passed into a shift conversion where the CO is converted to carbon dioxide in presence of air in steam and then basically the gas that contains now carbon dioxide hydrogen and nitrogen so it is passed through a gas absorption tower here so this gas absorption tower will have the solvents like mono-ethanol amine, potassium carbonate or arsenic basically may be

there then the carbon dioxide may be absorbed right and this carbon dioxide later on it can be purified and then it can be used for the urea manufacture whereas the gas which from which the carbon dioxide has been removed so this is now taken to the methanator where the steam is passed and now this gas may contain nitrogen hydrogen and some amount of CO and later on basically this from the methanator the methane is formed and as well as the nitrogen and hydrogen are there so this methane that is formed so this can be used as a fuel and then basically here we can have in the compressors we can have some leakage which will contribute to the wastewater in this case similarly when we take it to the cooling so in that case the boiler blow down so it will impart to the wastewater in this case similarly when it is passed through the ejector so here also some amount of ammonia can be leaked in this case and this may form the part of the wastewater so then it is taken to a storage tank which is also called the Horton sphere where the ammonia is stored right and then the liquid ammonia can then be used for the manufacture of the urea and we can also recover the ammonia which may be leaking from these areas. Similarly here when we are going for the recycling of the carbon dioxide obviously when we are going for the purification of the carbon dioxide so in that case it is possible that there can be some losses coming in the water and this basically monoethanol amine as well as the potassium carbonate as well as arsenic may find their way into the wastewater so these are the some of the sources of the wastewater that may enter during the manufacture of the ammonia plant. We can take the carbon dioxide as well as liquid ammonia here and then basically the formation of the urea takes place in this autoclave and then basically the urea which is formed so it is now taken through the filters right it is then condensed basically and then it is taken through the filters its concentration may be enhanced and then basically here we can find that some of the leakage may result in the urea and ammonia finding their way into the wastewater similarly the filter wash it may also contain some amount of urea the vacuum when then we take it to the vacuum crystallizer so that we can basically crystallize the urea that is formed so that it can be basically powdered and here the condenser water may also contain a lot of ammonia into it and later on we take it to the centrifuge and then basically these crystals which are formed so they are then dried and they are remelted then we take it to the prilling towers and finally the powder form of the ammonia is produced so we can see that the urea dust may also be generated during the prilling process and then basically the product finally is now packed and then it is delivered to the desired destination. So, now let us talk about the manufacturing process for ammonium sulfate so we can have the ammonia if the ammonia is coming out from the other plants for example we have already talked about that if the ammonia is coming from the cocoon plants then it is required that the carbon dioxide may be produced separately so that we can produce urea out of it and here the ammonium sulfate may be produced by reacting the anhydrous ammonia with the sulfuric acid so ammonium sulfate may also be produced from the gypsum so gypsum is generally produced from the phosphate fertilizer plants and this gypsum or calcium sulfate sludge that is generated in the phosphate fertilizer plants so that also can be used for the production

of the ammonium sulfate and similarly here in this process the calcium sulfate is reacted with the ammonium carbonate solution so that we can produce the ammonium sulfate out of it instead of sulfuric acid.

So, now the reaction of ammonia and sulfuric acid may take place and react the gaseous ammonia and the concentrated sulfuric acid and we take nearly 98.5 percent weight by weight of sulfuric acid and they are introduced into a evaporator crystallizer which is operating under vacuum so that the crystallization of the ammonium sulfate may take place and later on the crystals of the ammonium sulfate so they may be dried and then they can be packed and delivered. So, we can see the process flow diagram for the ammonium sulfate manufacture and we can see here that the liquid ammonia is passed into a evaporator so where the evaporation basically happens and then basically we also introduce steam here and then it is taken to the reactor where the sulfuric acid the concentrated sulfuric acid may be added and this is reactor as well as the crystallizer so the crystals of the ammonia may form so here we find that the ammonia may come out as in the wastewater. Now after the crystallization process it is basically taken for the filtration process where again the wastewater may be generated, and this wastewater may contain ammonium sulfate into it. So, after the filtration process it is taken for the dehydration and drying so we use air steam which is heated and then basically which is used for the dehydration as it is drying of the granules of the crystals which are formed and here also we find that the wastewater generation may take place and it may contain some amount of ammonium sulfate into it and then basically after the drying process the crystals which are formed so they basically are taken for the bagging for the packing and for the delivery further.

So, after the ammonium sulfate production we can also go for the production of the ammonium nitrate for example here when the ammonia is reacted with the nitric acid so then we can produce the ammonium nitrate. So, in this case the nitric acid may either be produced in the same plant where we can oxidize the ammonia and then we can convert this into the nitric acid. So, this nitric acid, which is produced, or we can also take the nitric acid from outside also whereas it will be beneficial that the nitric acid may produce in the same plants so because we are producing the ammonia here so this ammonia and the nitric acid so then when they react, so this basically forms the ammonium nitrate. So anhydrous liquid ammonia is evaporated first of all in an evaporator and using the cooling water and here the stoichiometric quantities of the nitric acid which is having a concentration of nearly 55 percent weight by weight and the gaseous ammonia, so they are introduced and by an automatic ratio controller to a neutralizer so where the reaction between the ammonia as well as the nitric acid takes place. So, after this process this ammonium nitrate solution which is formed which is coming out from the neutralizer so this may be taken to the storage but if we are manufacturing the solid ammonium nitrate so then it may be concentrated by evaporation process.

So, then evaporation to concentrate ammonium nitrate may be done so that we can produce the solid ammonium nitrate and then basically we can also mix here some filling materials so that we can reduce the nitrogen content from 35 percent to 33.5 percent and these filling materials are nearly added which are nearly four percent by weight of the total ammonium nitrate and this is generally powdered limestone or dolomite or even kaolin can be used as a filling material so this will reduce the content of the nitrogen by filling it by these materials and after this we can take the concentrate to the filling or granulation process and later on the granules which are formed so as they are dried they are screened so that we can have the specific sizes and then it is definitely finally cooled and later on it can be packed and delivered. So we can see here that the manufacturing process for the ammonium nitrate so here we can see that the liquid ammonia is basically taken first of all to the evaporation tank and then basically it is taken to the tank where basically the neutralization and the reaction is going on where nitric acid is added so after the reaction of the nitric acid and the ammonia so the ammonium nitrate may be formed and this may be neutralized further and later on we can take it to the flash evaporation so that whatever the impurities which are there so they may be evaporated out and later on we can take it to the storage tank where this liquid ammonium nitrate may be stored and further we take it to the secondary operation if we are going to produce a certain solid out of it so then we take it for the secondary operation and then we mix it after this secondary operation we mix it by using dolomite, kaolin or the limestone as the filler material and then we later on take it either we can produce the granules from it or we can also take it to the pilling towers and then later on it can basically be dried, screened, cooled and then we can form the powder form of the ammonium nitrate in such cases so then it can be taken to the for the packaging for the delivery process. So calcium nitrate may also be formed here for example if we dissolve the calcium carbonate that is the limestone we reacted with the nitric acid so this may produce the calcium nitrate for example you can see this reaction that is when calcium carbonate and the nitric acid so they combine so they can form the calcium nitrate fertilizer and the limestone which is there it is first of all taken to the dissolving tower and nitric acid is fed at the bottom of this dissolving tower and so that the calcium nitrate is formed and then this calcium nitrate which is formed so it is taken to the settling tank. So, after the settling the excess acid which is present so it may be neutralized with ammonia and the fertilizer is now produced in the liquid state.

So we can see here that the limestone is first of all taken to the dissolving tower and the nitric acid may be added from the bottom and here the formation of the calcium nitrate may take place and later on we can settle it out so that the calcium carbonate can be separated out and after this settling process we take it to the nucleation process with ammonia and after the nucleation process we can basically take the ammonium nitrate so we can take it for the mixing where basically we can adjust the nitrogen content into it and we can get the liquid waste spills here so here basically the some amount of the calcium nitrate may come into the waste water and other chemicals which are using similarly then the packaging after

the production of the liquid calcium nitrate we can take it to the packaging in the barrels and then basically it can be delivered to the requisite destination. So, the wastewater generation from the nitrogenous fertilizer plant so it may contain mainly ammonia right so there will be lot of nitrogenous compounds present in the wastewater so in the effluent we can have the ammonical nitrogen present as well as we can also have the urea nitrogen present when we talk about the wastewater which are getting generated from the nitrogenous fertilizer plants. So, most of the contamination it comes from the production of the ammonia itself so we can see that lot of chemicals we use during the production of ammonia so they all come into the wastewater and so the wastewater will be characteristically high in the ammonia content it will have the suspended solids into it, and it will also have carbon monate when you produce urea. So, these effluents may have high pH, and they may require the pH adjustment also for example after the pH adjustment we may also go for the settling process. So, now when you talk about the wastes which are coming out from the nitrogenous fertilizer plant so it may contain lot of processing chemicals for example if you are using sulfuric acid so that will come into the waste water we are using nitric acid so that may also find its way into the waste water similarly the final products like urea ammonium sulfate ammonium phosphate that we produce so these all chemicals these all fertilizers they find their way into the waste water.

So, in addition to the pollutants which are present in the waste water we can also have the oil bearing waste which are coming out from the compressor house these compressor house are basically installed in the ammonia and the urea plants so here the cooling tower basically wash may also basically which is coming from the scrubbing towers so that may also add to the waste water similarly the so in addition to the above we can also have the oil bearing waste which are coming out from the compressor house which are installed in ammonia and the urea plants and some portion of the waste water may also come from the cooling water and the wash water which are arising from the scrubbing towers which are used for the purification of the gases so they also basically joins the waste water stream here similarly the waste water which are coming from the scrubbing towers may also contain lot of toxic substances for example we have already seen that we are using arsenic or monoethanolamine, potassium carbonate, diethanolamine so these chemicals may also find their way in the waste water and these are highly hazardous and toxic waste which may form the part of the nitrogenous fertilizer up to it. So we can have the acidic as well as the alkaline waste so they may be generated from the water treatment plant for example when we are going to produce the deionized water so in that case the number of cation anion exchangers and cation exchangers may be applied so that we can provide it to the boiler feed water so here also we can have the generation of either the alkaline waste or the acidic waste which is generated from the concentrates which are produced from the effluents of these anion exchangers. Similarly, we can also find lot of toxic elements like chromates zinc etc. which may be used for the corrosion control right but if we are using non-chromate technology for the corrosion control for example if we use quaternary

ammonium compounds so they can eliminate the toxic compounds like chromates or zinc into the wastewater. Similarly, we may also find certain additional pollutants like phenol and cyanide so these phenol and cyanides may be present when we are using the ammonia from the cocoon plant. So, the cocoon plants generate the wastewater which contains very high amount of phenols as well as the cyanides these pollutants will also find their way in the wastewater which are coming out from the nitrogenous fertilizer plant if they are using the ammonia which is produced from the cocoon plants.

So, we stop here, and we will be discussing about the phosphate fertilizers and the complex fertilizers in our next class, and we will also talk about the wastewater treatment which is coming out from the complex fertilizer plants, so these are the references that we have used for the preparation of this lecture.

Thank you.