Environmental Chemistry and Microbiology
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Module - 5
Lecture - 24
Chlorine Chemistry and Disinfection (Part-B)

Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We both are from Civil Engineering Department, IIT Kharagpur. We have divided this course into 2 parts. The first part is Environmental Chemistry. It will covered by me. The second part is Environmental Microbiology. It will be taught by Professor Sudha Goel. This is my fifth module. In my first module, I have discussed about the acids, bases and salts. In the second module, I have discussed about the chemical equilibrium. In the third module, I have discussed about the chemical kinetics. In the fourth module, I have talked about the catalysts. In this fifth module, I will discuss about the chlorine chemistry and disinfection. I started it in lecture number twenty third. This is twenty fourth lecture. This is Part B.

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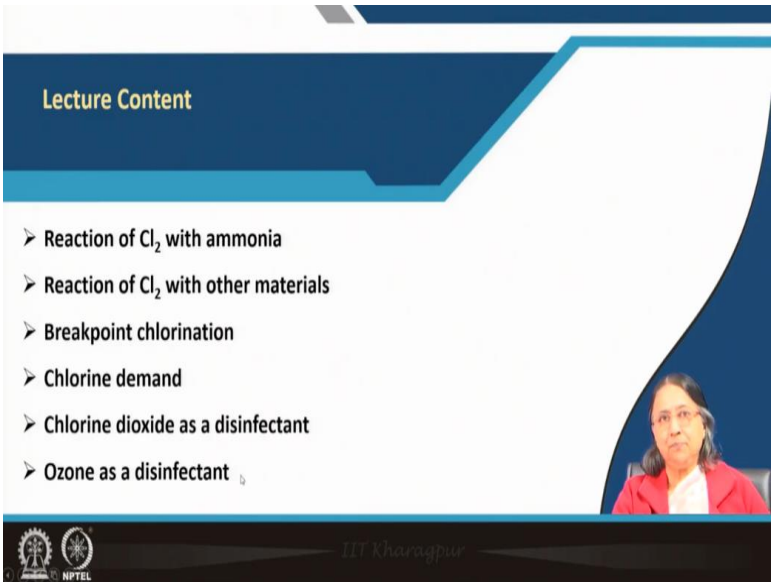

In this lecture, I will cover the reaction of chlorine with ammonia, reaction of chlorine with other materials, breakpoint chlorination, chlorine demand, chlorine dioxide as a disinfectant, ozone as a disinfectant. I have already told you that the chlorine is a very good and widely applied disinfecting agent. I already told you the history that how it started and got

developed. I also discussed about the chemistry of the chlorine and how it is forming the hypochlorous acid and the hypochlorites.

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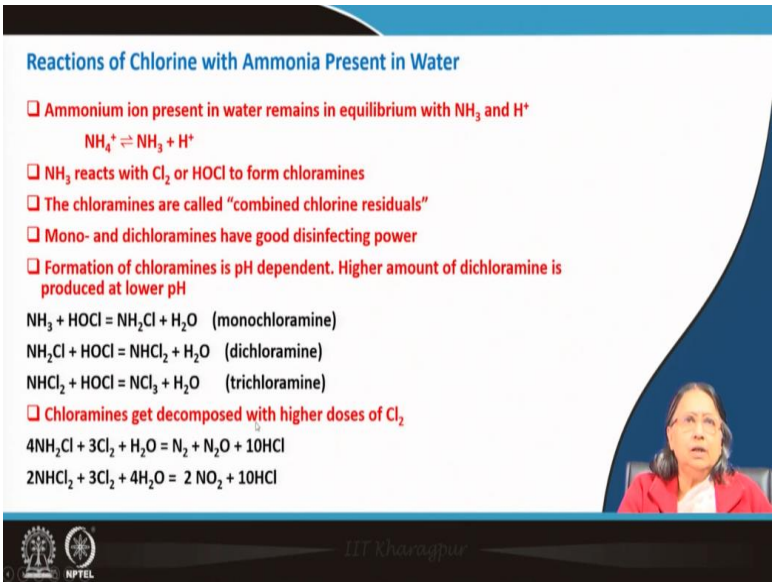

Now, I will show you the reactions of chlorine with other things which is naturally present in water. I already told you that in nitrogen cycle ammonia is produced from the degradation of organic matter (say for example, protein molecules). Ammonium ion present in water remains in equilibrium with ammonia and H^+ as shown in (1):

$NH_4^+ \leftrightharpoons NH_3 + H^+$ ……(1)

NH_3 reacts with chlorine or HOCl to form the chloramines. I have shown you the reactions in the last slide. The chloramines are called combined chlorine residuals. Chlorine, HOCl and OCl^- are called free chlorine or free chlorine residuals. But the chloramines which are produced by the reaction of ammonia with HOCl or chlorine are called the combined chlorine residuals. Mono and dichloramines have good disinfecting property, but not that good as that of the free chlorine residuals. Formation of chloramines are also pH dependent. You have already seen that in chlorine chemistry and also here also you will see that pH has a great role. Higher amount of dichloramine is produced at lower pH. The reactions are shown in the last slide. Firstly, NH_3 reacts with HOCl to give monochloramine. Since there is only one chlorine atom so it is called monochloramine. And here further reaction it gives the dichloro and then trichloramine. Trichloramine is a very toxic substance. Mainly monochloramine and dichloramine are formed. If you increase the dose of chlorine, then what will happen? These chloramines also will be oxidized as shown in (2) and (3).

$4NH_2Cl + 3Cl_2 + H_2O = N_2 + N_2O + 10HCl$ ……..(2)

$2NHCl_2 + 3Cl_2 + 4H_2O = 2NO_2 + 10HCl$ ……....(3)

You see that in (2), nitrogen has been oxidized from -3 to 0 and in (4) it is oxidized from -3 to +4.

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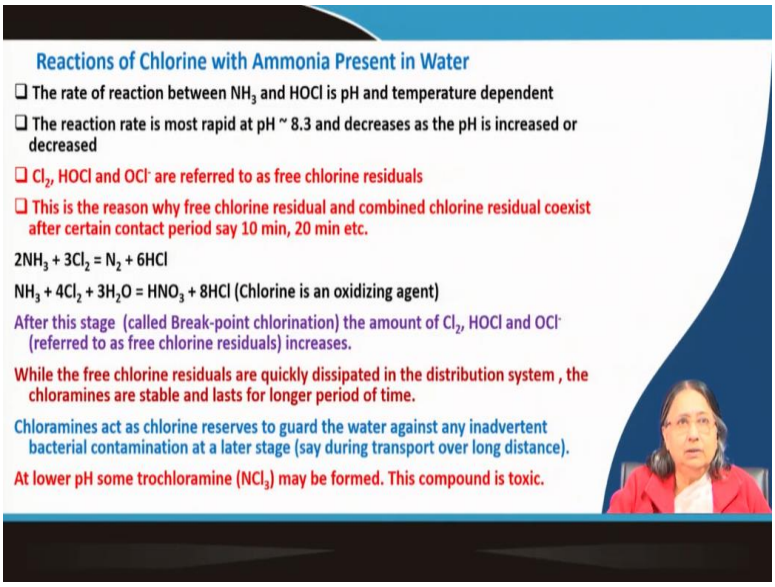

The rate of reaction between ammonia and HOCl is pH and temperature dependent. The reaction rate is most rapid at pH 8.3 and decreases as the pH is increased or decreased. So, at a certain pH, the rate is maximum. But if you increase or decrease the pH, it will become slower.

Now, chlorine, HOCl and OCl^- are called free chlorine residuals. This is the reason why free chlorine, residual and combined chlorine residual coexist after certain contact period, say 10 minute or 20 minute. So, if you allow the chlorine to react for some time and if there is the ammonia present in it (which is very common) then what you will see? You will see that some chloramines have been formed. At higher doses of chlorine following reactions take place:

$2NH_3+3Cl_2=N_2+6HCl$…….(4)

$NH_3+4Cl_2+3H_2O=HNO_3+8HCl$……..(5)

So, chlorine here (in (4) and (5)) is acting as the oxidising agent. One property is that free chlorine residuals are better disinfecting agent. But combined chlorine residuals also have the disinfecting power, but it is weaker compared to the free chlorine residuals. Free chlorine residuals are quickly dissipated in the distribution system. But the chloramines are stable and can stay for long periods. So, when you disinfect, in some place, you do the treatment and then you have to transport the water from that place to some other place. During the passage, you have to protect the water. So, if the chloramines are present there, then it can protect the water during transport. This is an advantage of the chloramines. Sometimes to protect the

water from outside, ammonia is also added in little amount. So, chloramines are in that sense good. It can protect during transport also. At lower pH some trichloramines may be formed. This compound is toxic. So we should maintain the condition such a way that these things are not formed.

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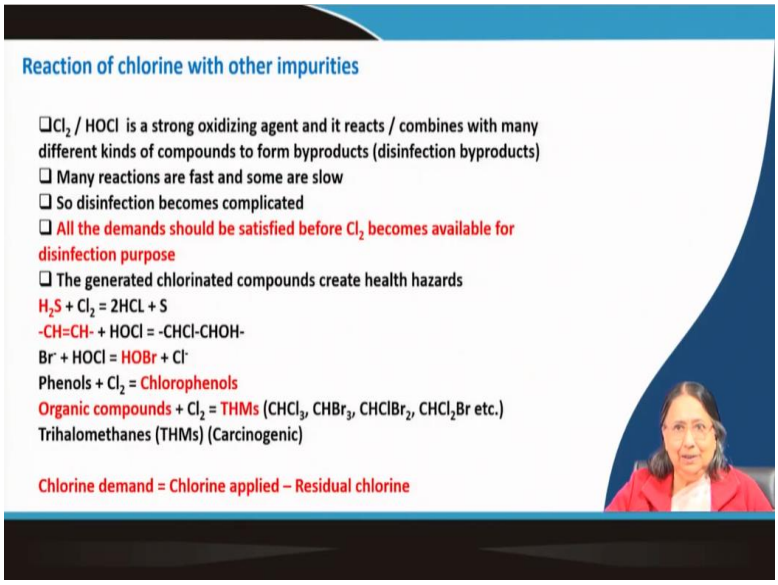

Not only the ammonia, but also other things may be present in the water. What are they and how they react with the chlorine? That is also important. Chlorine and HOCl are strong oxidising agents and they react and combine with many other different kinds of compounds. The products are called disinfection byproduct (DBP). Some of the reactions are fast, some of the reactions are slow. During disinfection, if so many reactions are going on, then it becomes complicated, right. We are using chlorine for disinfection. But chlorine is consumed by some other materials for doing some other reactions. So, this is the demand. Unless the demand is met, we will not get the free chlorine to kill the bacteria. So, after meeting demand of these compounds, we will get the chlorine for disinfection. So, what are those compounds? The generated chlorinated compounds create health hazards. So, we have to consider all those things. Say for example, in groundwater H_2S is present or some sulphide salts are present, because water is leaching through the some sulphide bearing rocks. So, H_2S gas can react with chlorine to form HCl and sulphur. There may be some compounds containing double bond (unsaturated compounds). We know that in a double bond, something can be added. So, HOCl can be added in the double bond as shown in (6).

-CH=CH- + HOCl = -CHCl-CHOH-……(6)

You know, seawater can contain bromide. So, at many places, bromide concentration may be there in water. So, when you disinfect that type of water, then HOBr is formed (hypobromous

acid). Now, HOBr is also good disinfecting agent, but it contains bromine. Bromine is not a very good substance. In some countries I have seen, in the swimming pools, HOBr is used. They have disinfecting property. But at the same time, bromine is there. So, we are not very confident about it.

Many water may contain phenolic compounds or phenols. So, for them, chlorine can add up to the benzene ring of the phenol. So, in the benzene ring, chlorine can replace the hydrogen atoms and it can form the chlorophenols. It is dangerously toxic substance. It can have bitter taste and bad smell also. So, they are not very good substance for our health.

Humic substances, are very common in water. Humic substances are very stable compounds, but they can react with chlorine to form a special group of compounds which are known as trihalomethane (THM). THMs are carcinogenic. Even though they are produced in very low concentrations (ppm or ppb level) yet, if we drink that water continuously, then at least some amount is going within us. So, it may produce cancer. Do you know how this name THM has come? You can see that in compounds like chloroform, bromoform, dibromo chloroform, dichloro monobromo chloroform there are 3 halogen atoms. It is a derivative actually. If you think about methane, it is CH_4. In all THMs, 3 hydrogen atoms are replaced by three halogen atoms. We should not allow these types of compounds to be formed in our drinking water system.

I told you about chlorine demand. Chlorine demand is the difference of chlorine applied and residual chlorine. So, demand should be met first. After that you will get the free chlorine.

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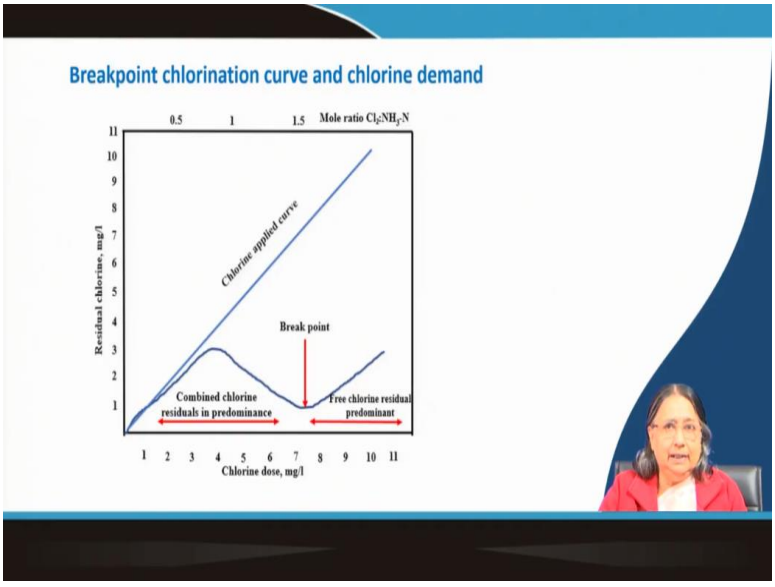

The curve shown in the last slide is very important curve. It shows breakpoint chlorination curve and chlorine demand. Along the ordinate chlorine residual is shown and along abscissa

chlorine dose is presented. Experimentally we can get this curve. We apply the chlorine at different doses. We keep it for some time (i.e., contact time). After that we measure the residual chlorine. Then we plot it against the dose. Now, if it is distilled water, there is no demand. Then whatever chlorine we apply, it will remain as residual chlorine. Then we will get a straight line inclined at 45°. But if it is a normal sample water where say for example ammonia is present then we will get a different type of curve shown in the last slide. It is increasing first, then decreasing and then again increasing. The increasing portion indicates formation of chloramines and decreasing portion indicates destruction of chloramines. At the point where decreasing portion ends, there demand is met. The minima at that point is called the breakpoint. After that, when you increase the dose you will get the free chlorine residuals. It will be parallel to the 45° line. You have to apply dose at least up to this breakpoint. Then everything will be destroyed. Then a little bit extra is kept, so that some free chlorine residuals are there in the water, which will take care of the killing of the microorganism. It is the disinfection. In the last slide mole ratio of chlorine and ammonia nitrogen is also shown as wastewater there may be ammonia nitrogen may be present in different quantity.

For a particular sample we do not know how much chlorine we should apply. If we add too much chlorine that is also not good as chlorine is also not good for health. Sometimes we can feel a chlorine smell in the tap water. It means they have added chlorine in a larger quantity, which is not required. To know how much chlorine, you should add for a particular sample water, you have to do some experiment. We have to know about the breakpoint chlorination curve and chlorine demand. Then we can apply the proper dose.

What are the different types of chlorine you can use? We can use chlorine gas, chlorine water, hypochlorite. Bleaching powder ($Ca(OCl)_2$) is also a source of hypochlorite. But how much the does we should apply, that we have to know. So, how will we know? We can know by doing experiments. We should also note the contact time.

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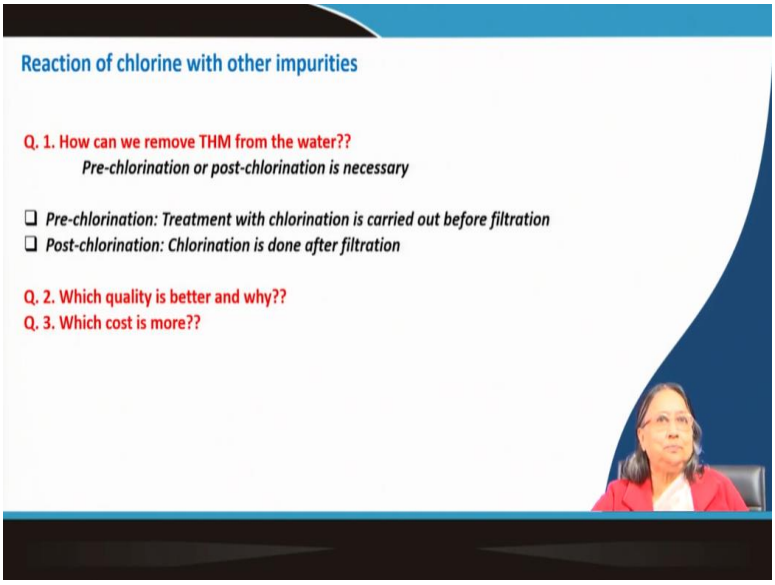

How can we remove THM? I told you that THM formation is very dangerous for us. We can do 2 things. There are 2 options. One thing is pre-chlorination and another thing is post-chlorination. Pre-chlorination is treatment with chlorine carried out before filtration. It means, first we do the chlorination, then we filter the water. Why filtering? Because through filtering you can remove the THM, that formed THM. So, this is called pre-chlorination. Then what is post-chlorination? Here chlorination is done after filtration. First we remove the organic materials. Then we do the chlorination. Both way it is possible. But there are some advantages and disadvantages. If we do chlorination first, then all the organic matters are there. So, we need more chlorine. Then we can remove the formed products through filtration. If we do filtration first, then we do the chlorination, then less chlorine is required. So, in the first case, the cost will be more, because more chlorine is required. What about the quality? Which one's quality is better and why? Think about it.

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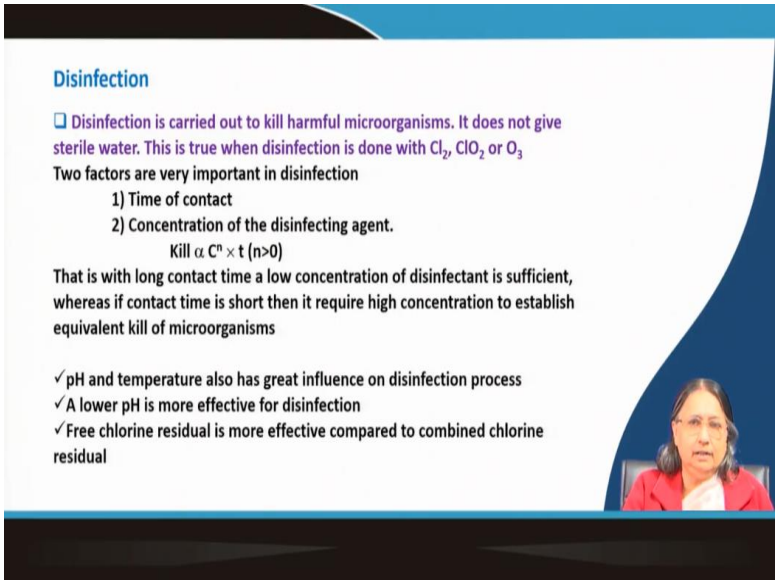

Now, we will see two important things about disinfection. One thing is how much disinfectant I am using and how much time I am keeping. Say for example, I used to go to restaurant, long time back with zeoline bottle. Say for example, they give me one glass of water. I am very thirsty. I want to drink it as soon as possible. Then what I will do? I will add more drops, say for example, 5 drops. I will keep for little time, maybe 5 minutes is enough and then I will drink. But if I am not that thirsty, I may not use 5 drops. I may use 2 drops. I can keep it for a longer period of time, say for example 10 minutes. Then I can drink. So, contact time is important and also the concentration. Kill is expressed as:

Kill $\alpha(\text{Concentration})^n \times t$…….(7)

Disinfection is carried out to kill the harmful microorganism. But it does not give us sterile water which is needed for the operation theatres and for other purposes. So, it is not killing all types of bacteria. But it is only killing the pathogenic bacteria. This is true when disinfection is done with chlorine, chlorine dioxide or ozone. Chlorine dioxide and ozone are other disinfectants. Ozone is used in developed countries. Chlorine dioxide has not been much attempted. Some research has to be done. But chlorine is most widely used. In our country also, we are using chlorine. I already explained to you contact time and concentration and depending upon our need we can vary them. pH and temperature also have great influence. Lower pH is more effective for disinfection. But we usually do it at around 7 to 8 and free chlorine residual is more effective compared to combined chlorine residual. During transport, combined chlorine residual is important because it can protect the water.

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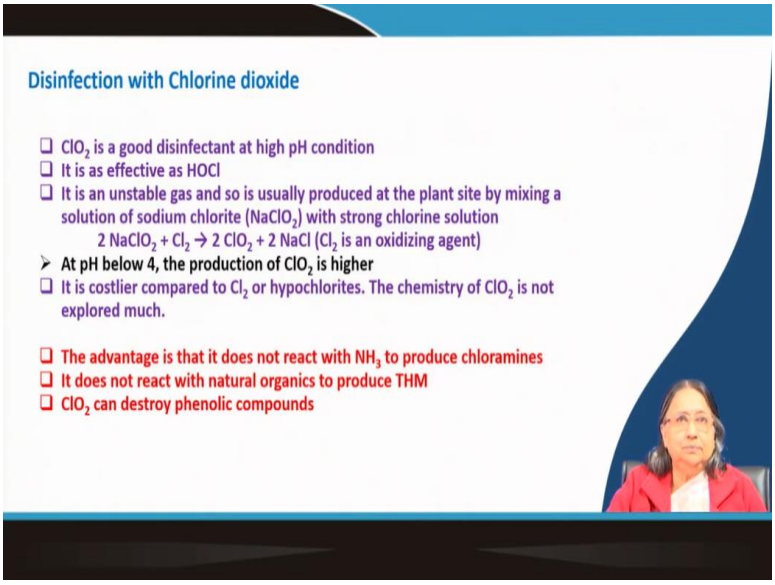

Now, let us come to disinfection with chlorine dioxide (ClO_2). Chlorine dioxide is a very good disinfectant at higher pH condition. It is as effective as HOCl. It is an unstable gas. This is not solid like a $Ca(OCl)_2$ or NaOCl. Solid is better as you can carry from one place to another place. But if it is liquid, still it is okay. But if it is a gas, you cannot carry it. So, this is a disadvantage for chlorine dioxide. It is an unstable gas and it has to be produced on the site itself. This is a great disadvantage. It is produced by mixing a solution of sodium chlorite ($NaClO_2$) with strong chlorine solution. At pH below 4, the production of ClO_2 is higher. It is costlier compared to chlorine or hypochlorite. The chemistry of ClO_2 is not explored much. We are not very confident about this material till now. The advantage is that it does not react with NH_3 to produce chloramine. Hence, chloramine is not produced. It does not react with natural organics. So it does not produce THMs. In case of chlorine you have seen that chlorophenols are formed. But here you see the ClO_2 can destroy phenolic compounds. So, this is a good thing. So, there are advantages and disadvantages.

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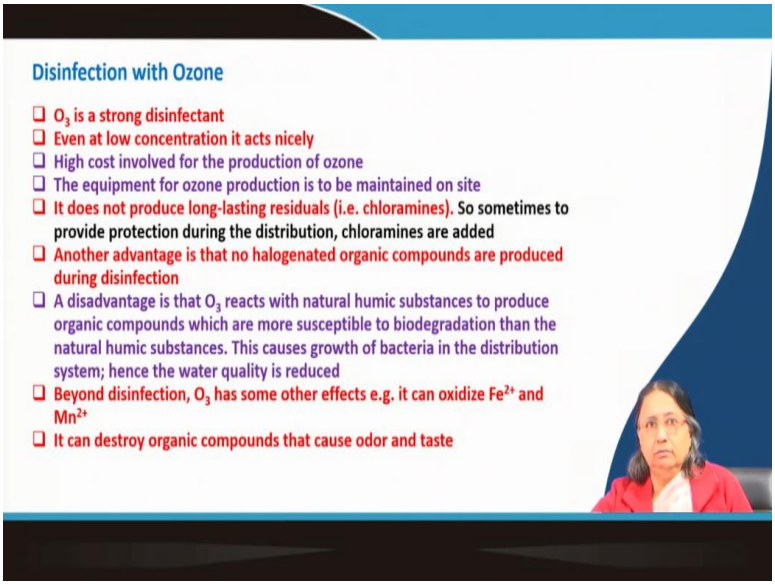

Now, let us come to the disinfection with ozone. Ozone is also widely used nowadays in advanced countries. It is very strong disinfectant. Even at low concentration, it acts nicely. It involves high cost, because ozone production is very difficult. The equipment which is required for ozone production needs to be maintained on the site itself. It does not produce long lasting residual. Another advantage for ozone is that halogenated organic compounds are produced during disinfection. A disadvantage is that ozone reacts with natural humic substances to produce organic compounds which are more susceptible to biodegradation. Maybe THMs are not produced, but some compounds are produced which are susceptible to biodegradation. Then what will happen? It will cause the growth of bacteria. When bacteria will grow in the distribution system, water quality will be reduced. So, that is a disadvantage with this ozone. Beyond disinfection, ozone has some other effects. It can remove the odour. It can oxidise Mn^{2+}, Fe^{2+} which sometimes is present in many water. When it is oxidised, it can be precipitated also as oxide. It can destroy organic compounds that causes odour and taste. So, water quality will be better when it is all these types of compounds are destroyed. So, ozone is also a good possibility, but it is costly.

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As a reference, I can tell Sawyer, McCarty, the same book. You can read.

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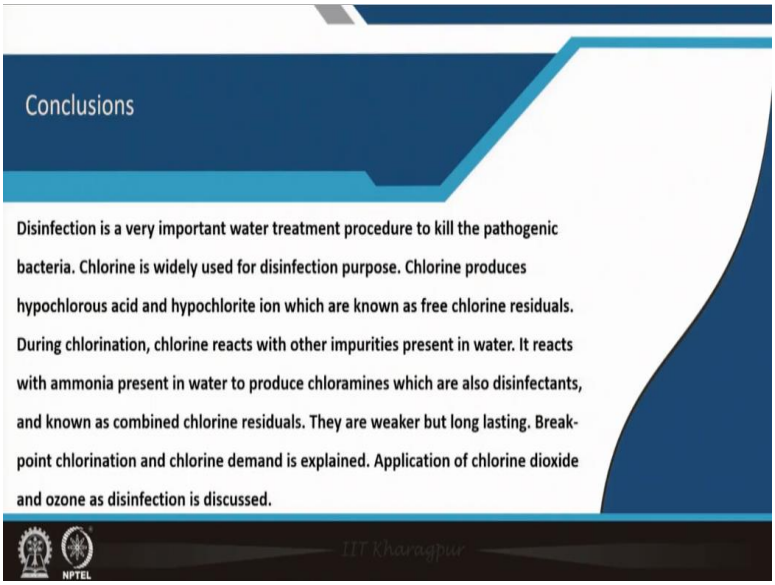

And as conclusion, I can tell for this lecture that disinfection is a very important water treatment procedure to kill the pathogenic bacteria. Chlorine is widely used for disinfection purpose. Chlorine produces hypochlorous acid and hypochlorite ion which are known as free chlorine residuals. During chlorination, chlorine reacts with other impurities present in water. It reacts with ammonia present in water to produce chloramines which are also disinfectants and known as combined chlorine residuals. They are weaker but long lasting. Breakpoint chlorination and chlorine demand is explained. Application of chlorine dioxide and ozone as disinfectant is also explained. Thank you very much.