## Physico-Chemical Processes for Wastewater Treatment Professor V.C Srivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture 54 Disinfection - III

So, good day everyone and welcome to these lectures on disinfection that we have been continuing since last two lecture for water treatment, and through disinfection, we are able to remove various types of pathogens out of water, before we can use the water for drinking or for other uses. Now, we have learned that different types of chlorine compounds are used for disinfection. So, along with the chlorine, we can use ozone, we can use ultraviolet radiation and some other types of compounds as well for disinfection.

So, in the previous two lectures, we studied the chemistry of the chlorine in the water as well as its reaction with the ammonia and other nitrogenous compounds. We also studied half-reactions or redox half-reactions via which we can calculate the oxidizing power of different chlorine compounds. And thus, we can compare different chlorine compounds with respect to their potential for oxidizing different types of pathogens in the water, as well as other organic compounds. So, going further, we will try to learn the mechanism of disinfection of these compounds and how they work?

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Mechanisms of Disinfection

The mode of action by which disinfectants inactivate or kill microorganisms is dependent on a large number of variables.

This brief overview is limited to some of the common water disinfectants and two broad classes of microorganisms:

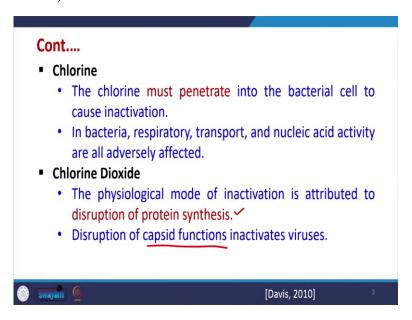
Bacteria

Viruses

So, the mode of action by which disinfection inactivate or kill microorganism, this depends upon a number of variables. So, for and this will also depend upon the type of microorganism which is present. So, we can classify these type of microorganisms into two broad categories,

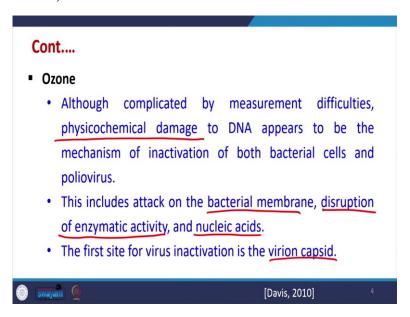
either bacteria or virus. So, we will be limiting this discussion with respect to these bacteria or virus.

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Now, the chlorine if it is added, so, chlorine will penetrate into the bacterial cell and thus, it will inactivate that bacteria, so, this is there. The in bacteria, the respiratory transport and nucleic acid activity all get affected when chlorine penetrates via its bacterial cell, so thus it inactivate the bacteria, so, this way it is able to inactivate the bacteria and its potential for pathogens, etc, is a totally removed. Now, chlorine dioxide, the physiological mood of inactivation of this is due to the disruption of the protein synthesis which is carried out so, it disrupts this protein synthesis capability. And because of that, the viruses or bacteria get inactivated. Now, disruption of capsid functions also inactivate with the viruses.

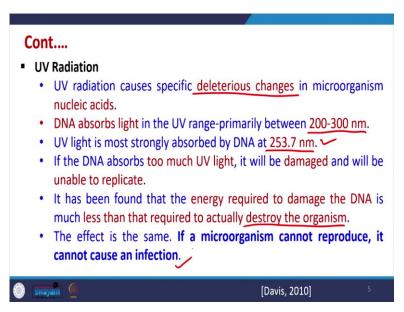
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Going further for ozone, so, although it is complicated to measure the difficulty, how it works? But it is understood that the physiochemical damage is caused by ozone to the DNA. And because of that, the inactivation of both bacteria and viruses occurs. So, it will react with the bacteria or virus, and it will cause a lot of physicochemical damage.

And overall it totally inactivate these bacteria and viruses. And this includes attack on the bacterial membrane, disruption of its enzymatic activity, and the nucleic acids as well. The first site for virus case the first site for virus inactivation is it's virion capsid. So, similar to the other chlorine chemical site, via this mechanism inactivate the viruses.

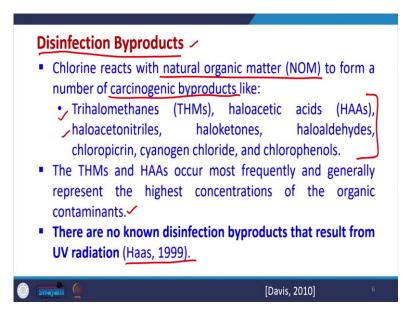
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Now, for the ultraviolet radiation, how the, what is the mechanism by which it inactivate different bacteria and viruses is discussed here. So, UV radiation will cause specific changes in the microorganisms in particular in nucleic acids. So, like DNA it will absorb light in their UV range primarily in that range of 200 to 300 nanometer and it will get absorbed this if the UV light is in this range and in particular at around 254 nanometer, so it will be strongly absorbed by the DNA and if DNA absorbs this UV light, so it will get damaged and will not be able to replicate.

So, this is the mechanism of inactivation which is there and it has been found that energy required which is required to damage the DNA it much less than that required for actual destruction of the organism itself. So, these 254 nanometers is one other critical wavelength which has been reported in the literature and if a microorganism cannot reproduce it cannot cause infection as well. So, this is the, this is how UV radiation works.

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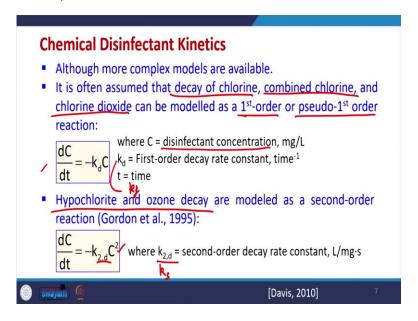
Now, when we are using these types of chemical compounds ozone ultraviolet radiation sector for wastewater disinfection, so, many a times many disinfection byproducts get formed. So, these byproducts may have also a lot of importance that which type of byproducts are getting form and whether they themselves are toxic or not. So, this is important. So, chlorine reacts with natural organic matter to form a number of carcinogenic byproducts. So, that means, these byproducts which are listed here, they are undesirable because they are carcinogenic and these byproducts include trihalomethane, haloacetic acids, haloacetonitriles, haloketones, halo aldehydes, chloropicrin, cyanogen chloride, chlorophenols etc.

So, we do not want these byproducts to be form. So, we had to see that the amount of different chlorine compounds which are used should be very accurate and the most of the matter which is there, both organic matter and pathogens all should be totally oxidized. So, this is very very important, if everything is oxidized, then the formation of these byproducts will be minimal. So, we can use the water there after otherwise it will be very difficult.

The trihalomethanes and halo acetic acids occur they get formed most frequently and they generally represent the highest concentration of the organic contaminants in the water. So, we have to see that we these do not get form otherwise we cannot use the water after disinfection also, there are no unknown disinfectant products that result from UV radiation, it has been but it still with them also if any of the proteins, etc there or some type of nitrogenous compounds are there. So, in general they may be toxic beforehand, but if only partial destruction of theirs occur, so, sometimes we may form some compounds which may be toxic more than the parent compounds themselves. So, that may cause problems.

So, this is again a problem that we have to see that the oxidation should be full. And the minimization of the pathogens along with the organic matter in the water should be full so that we have no intermediate compounds which may have toxicity more than the parents compounds themselves. Now, we will go further and we will try to study the chemical disinfection kinetics and try to understand the kinetics. So, many complex models are available, but we will be concentrating only on simple models.

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Decay of chlorine, combined chlorine, and chlorine dioxide can be modelled as a 1<sup>st</sup>-order or pseudo-1<sup>st</sup> order reaction:

$$\frac{dC}{dt} = -k_dC$$

$$\frac{dC}{dt} = -k_{2,d}C^2$$

where C = disinfectant concentration, mg/L

 $k_d$  = First-order decay rate constant, time<sup>-1</sup>

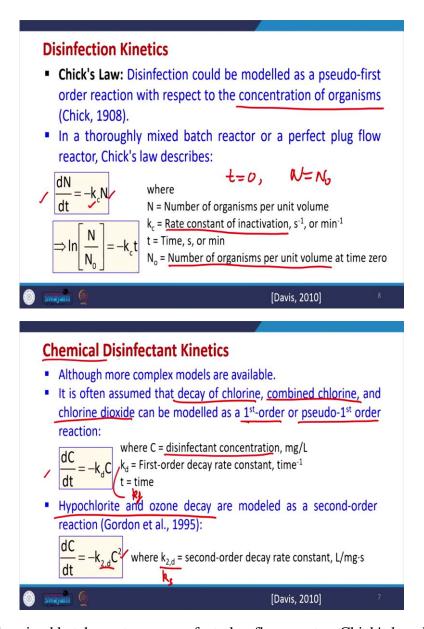
t = time

 $k_{2,d}$  = second-order decay rate constant, L/mg·s

So, like the decay of chlorine, combined chlorine and chlorine dioxide for any of these can be modeled by a simple 1st order or pseudo 1st order reaction which is given here, in this case we assumed that dC by dt is proportional to C or minus dC by dt is proportional to C, where C is the disinfection concentration and Kd is the first decay rate constant.

Similarly, hypochlorite and ozone decay they are modelled as second order reaction and in this case the power with respect to concentration of the disinfected is 2 and here we are assuming second order. So, this is second order decay rate constant. So, this can be named variously sometimes it will be reported at ks and this will be reported as kf, so, any of these nomenclatures may be there. So, but this is how they are model.

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In a thoroughly mixed batch reactor or a perfect plug flow reactor, Chick's law describes:

$$\frac{dN}{dt} = -k_c N$$

$$\Rightarrow \ln \left[ \frac{N}{N_0} \right] = -k_c t$$

where

N = Number of organisms per unit volume

 $k_c = Rate constant of inactivation, s^{-1}, or min^{-1}$ 

t = Time, s, or min

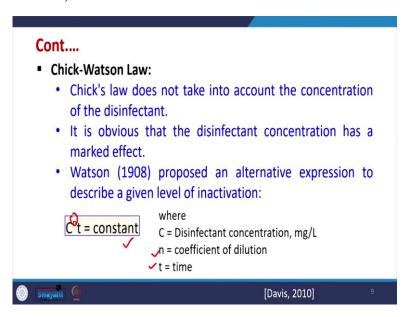
 $N_0$  = Number of organisms per unit volume at time zero

Now, going further Chick's law is there and there in that chick's law is given that disinfection could be modeled as a first-order reaction with respect to concentration of organisms themselves. So, in place of concentration of disinfection, chemical disinfection they have modeled with respect to the concentration of organisms itself.

So, in a thoroughly mixed reactor with are in a perfect plug flow reactor, chick's law describes that the rate of change of concentration of organism is proportional to the concentration of organism itself and this can be modeled as Kc where is the Kc is the rate of constant of inactivation and it is first-order, first-order rate constant of inactivation.

So, and N0 is the number of organisms which are present at time 0 are at the initial condition. So, this is we are integrating assuming at time t is equal to 0, N is equal to N0, where N0 is the number of organisms which are present in the per unit volume at time t equal to 0, so, this is there. So, this is chick's law.

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Watson (1908) proposed an alternative expression to describe a given level of inactivation:

 $C^n t = constant$ 

where

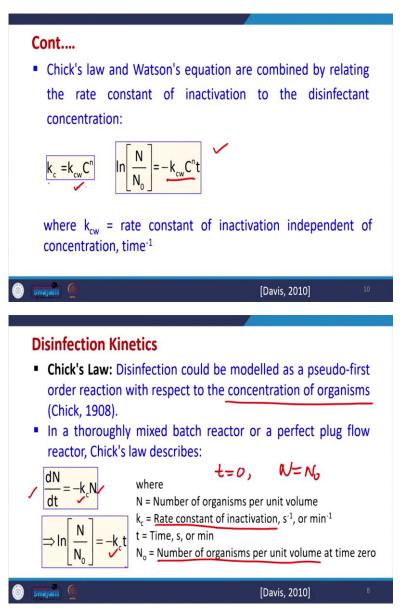
C = Disinfectant concentration, mg/L

n = coefficient of dilution

t = time

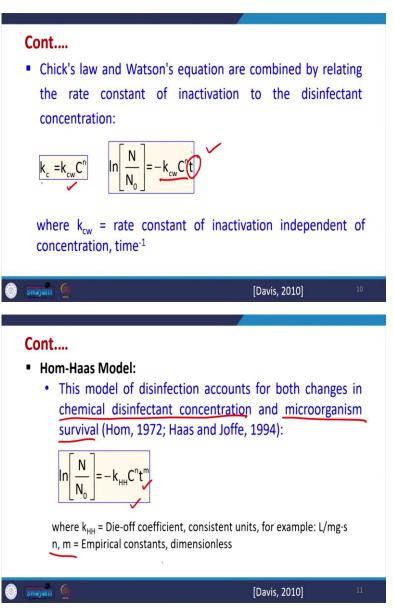
Now, then there is another model which is called as Chick-Watson law and under chick's law, it does not consider the concentration of disinfection. So, and it is obvious that disinfectant concentration has a marked effect. So, Watson proposed an alternative expression to describe the level of inactivation and this is given by this that disinfection concentration and n is the it is raised to n which is n is the coefficient of dilution and t is the time. So, with respect to this, this is constant and through this, this is called Chick's Watson.

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And chick's law and Watson's equations are combined by combine are combined by relating the rate constant of inactivation to the disinfection concentration. So, what is done is that? The kc which was given by chick's lock, this kc is considered to be a function of the concentration of the disinfectant. So, this is kc is equal to kcw C raise to n. So, this way, we have combined that chicks and Watson. So, Kcw is the rate constant of inactivation independent of the concentration, whereas, kc was considered to be dependent upon the concentration of that disinfection, so this is there.

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Hom-Haas Model:

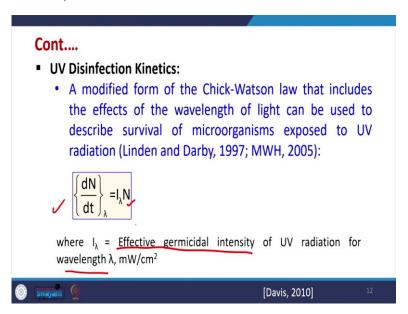
$$\ln \left[ \frac{N}{N_0} \right] = -k_{HH}C^n t^m$$

where  $k_{HH}$  = Die-off coefficient, consistent units, for example: L/mg·s

n, m = Empirical constants, dimensionless

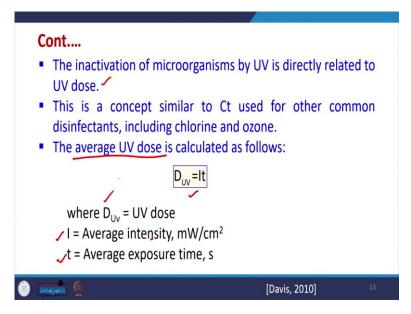
Then there is another model which is called as Hom-Haas model. And this model of disinfection accounts are both changes in the chemical disinfection concentration and the microorganism survival also. So, this is very similar to a chick and Watson but here the t raised to m is there so remember this is different, where here it is only t. So, this is there, and n and m are empirical constants which are there, so, this is there.

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Now, then, UV disinfection kinetics is also there a modified form of Chick-Watson law that includes the effect of wavelength of light that can be used to describe the survival of microorganism which are exposed to UV radiation. So, under that condition the dN by dt is proportional to N, and that proportionality constant is called as effective germicidal intensity of UV radiation with respect to wavelength lambda, and its unit is milliwatt per centimeter square or appropriate units can be used. So, through this we can model the UV disinfection kinetics.

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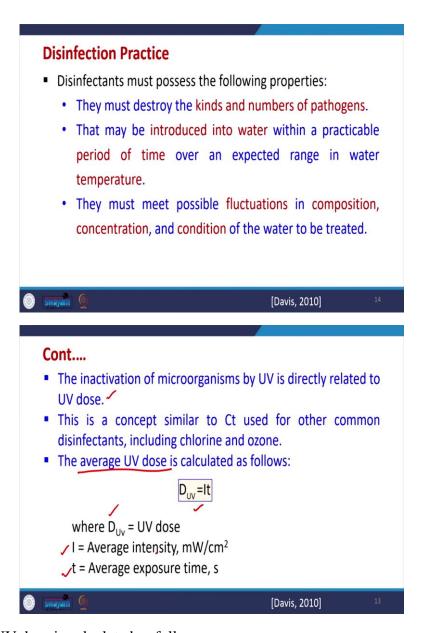
**UV** Disinfection Kinetics

$$\left\{ \frac{dN}{dt} \right\}_{\lambda} = I_{\lambda} N$$

where  $I_{\lambda}\!=\!$  Effective germicidal intensity of UV radiation for wavelength  $\lambda,\,mW/cm^2$ 

The inactivation of microorganism by UV is directly related to UV dose also. Now, this is a concept similar to the concentration of other disinfection including chlorine, ozone etc. So, UV average UV dose is calculated using this expression where I is the average intensity and t is the average exposure time. So, through this we can find out the UV dose which is there. So, this is there.

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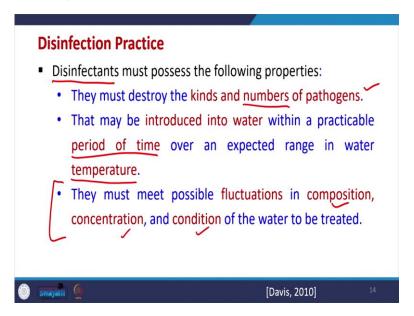
The average UV dose is calculated as follows:

$$D_{UV}$$
=It where  $D_{Uv}$  = UV dose 
$$I = Average intensity, mW/cm^2$$
  $t = Average exposure time, s$ 

Now, these kinetic expression for can be used to model that disinfection how it is occurring in any system or in water and we can report these parameters and through this we can find out, with same different chlorinated compounds, which type of how the water is getting

disinfected? And if we can know this disinfection kinetics, we can design a bigger system also, so the this is possible.

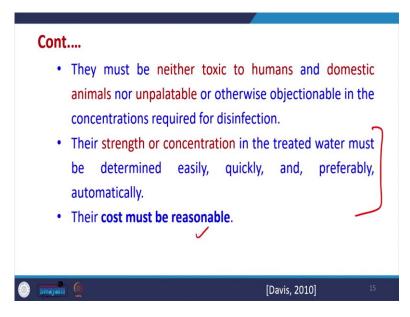
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Now, going further how disinfection is practiced. So, some of these things we are going to discuss in these slides. So, disinfections if we are doing, so disinfectant must possess the following property, they must destroy different kinds and different number of pathogens. So, they this is must. They may be introduce in the water with a practicable period of time over the expected range in the water temperature. So, we can expect the water temperature. So, depending upon that we should know that what is the time required for disinfection to occur and this will come from the disinfection kinetics and under this condition, they must be able to fulfill the variations in composition concentration and conditions of the water.

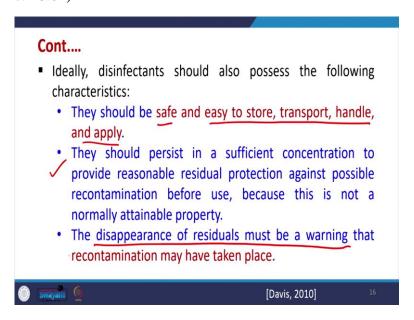
So, all these things should be fulfilled if any fluctuation up to a certain limit happen, still the disinfection should be good enough, so, this is there. And these disinfectants must neither be toxic to human beings or domestic animals or no unpalatable or otherwise objectionable in the concentration required for disinfection.

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There is strength or concentration in the treated water must be determined easily quickly and we should have a proper available data for that, so, this is there. And also, the cost must be reasonable. So, this is another thing. Now, ideally the disinfectants should passes the following characteristics.

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So, they must be safe, easy to store, transport, handle and apply, so, this is there. They should be persist in sufficient concentration to provide residual protection against possible recontamination before use, because this is not a normally attainable properties we have to cross-check this, the disappearance of residuals must be a warning that recontamination may have taken place. So, this is possible. So, this we have to cross-check before using the

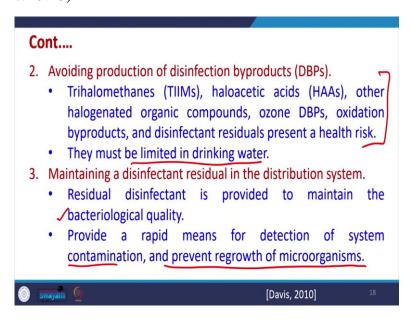
disinfection that there was this particular characteristic and they are able to perform this. Then there are certain regulatory contexts are also there.

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So, selection of appropriate disinfection strategy for water treatment requires a balance of three driving forces. So, providing water free of pathogens. So, there are some 10 regulatory focus that which type of thing we have to remove whether it is coliform bacteria, then what are the plate counts, then different types of cysts and then other types of viruses, etc. So, how much they have to be removed? What are their regulatory requirements are there?

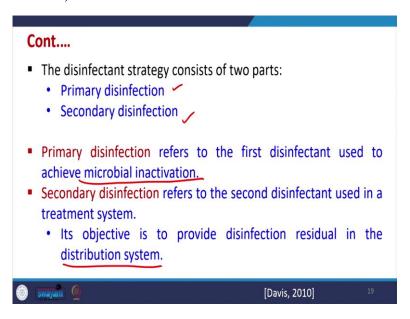
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The second thing is that avoid production of disinfectant byproducts, So, earlier we have seen that these materials they are highly carcinogenic. So, they must be limited in the drinking water, so we have to see that the disinfectant that you are using, they must not produce the byproducts which fall into this category. If they are producing they must be within certain limits, so, this is there.

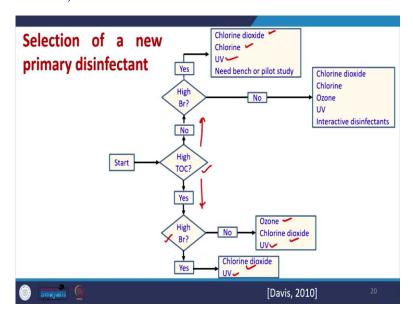
Also, we have to see that we have to maintain a disinfectant residual in the distribution system and this is provided to maintain a particular back to logical quality and provide a rapid means of detection of system contamination and prevent regrowth of microorganisms, while distribution of water is being done. So, this also has to be seen. So, these three conditions we have to meet while using various types of disinfectants.

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Now, disinfectant strategy in particular consists of two different sections, one is called primary disinfection and another is called secondary disinfection. So, in the primary disinfection, it is used for microbial inactivation. And in the secondary disinfection it refers to the disinfection which is used in the treatment system. And its objective is to provide disinfection residual in the distribution system where while transporting the water, no recontamination should occur.

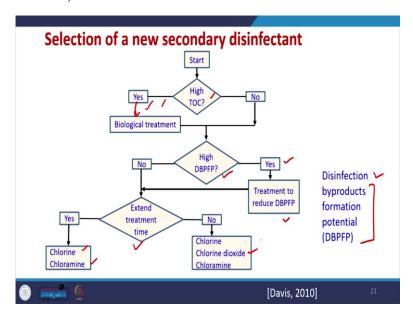
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So, this is a strategy which is given here a generic strategy for a selection of new disinfectant for treatment of some particular wastewater. So, we have to characterize the wastewater first, after all the treatment has been done already. And then we can use this strategy to select a primary disinfectant. So, we will start with the checking that whether the water contains TOC or not. If high TOC is there, we will adopt this method, no TOC will go like this.

After TOC we checked the bromide concentration, if it is high we can go for chlorine dioxide and UV if it is no then we can go for ozone, chlorine dioxide or UV. So, we can adopt any of these. So, except for ozone the strategies are similar. If again no TOC is there is still a bromide concentration is high we have to go for chlorine dioxide chlorine UV or we may require some pilot scale studies before using any of these and if no bromine is present, we can still adopt these techniques, but pilot scale studies etc may not be required.

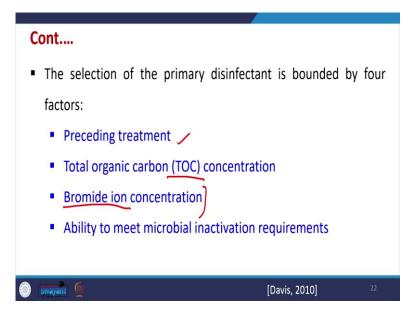
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Similarly, for secondary disinfectant, if high TOC is there that means we have to go back and remove that and if no, so we have to see that if it is coming maybe some biological treatment or we have to cross-check that whether these disinfectant byproducts are there or not. So, we have to see that these disinfectant byproduct formation potential in water is there, if TOC is high, we have to go for biological treatment and then come back. And if no, we can directly go for checking these DBPFP and check whether if this potential is there we have to reduce this potential otherwise, we can go directly to extend that treatment time.

And after that, we can if the treatment extended treatment time is required or not depending upon that we can use chlorine or chloramine or chlorine dioxide also. So, any of these strategies may be adopted. So, this is only symbolic only we can have on own idea with respect to selecting the different types of primary or secondary disinfectant and those is very important parameter and for that we may have to perform initial batch studies beforehand in the lab before actually selecting and so, this way we can adopt these strategies for disinfection.

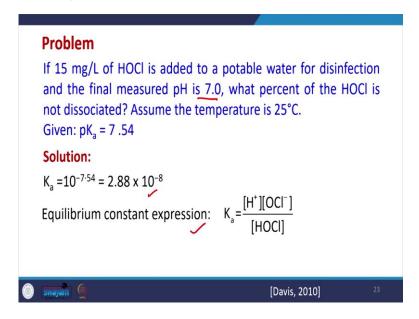
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Now, the selection of primary disinfectant is certainly bounded by the preceding treatment. So, that tells us whether TOC concentration is there or not. If at that also depends upon the bromide concentration generally it will not be there that much. And also, then we cross-check that what is the ability of the that particular compound that we are selecting as a disinfectant to meet the microbial inactivation requirements.

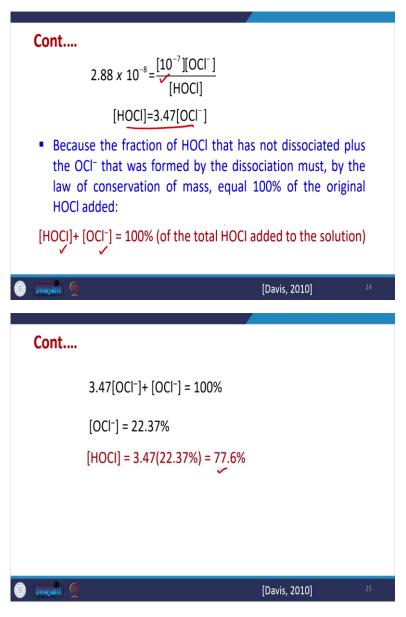
So, after doing this, we can perform the disinfection we can select the disinfectant in such a manner and its dose etc we can determine from the by performing the lab scale experiments, etc., so, this is there. Now, going further. We will try to some solve one or two problems before ending this disinfection section.

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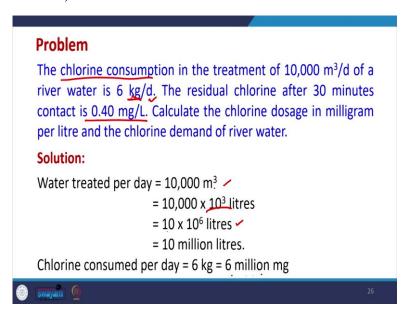
So, if suppose 15 milligram per liter of HOCl is added to a potable water for disinfection and the final measured pH is 7. So, what percentage of HOCl has not dissociated? So, this type of question we did earlier itself, so, this is the k, this is the equilibrium constant already we have done this, then place of pH 6, now, the pH is 7 only difference is there.

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So, for pH 7 this is there, so, we can find out and after because the concentration of total concentration of chlorine will be some of HOCl and OCl minus. So, using this particular equation which is obtained we can calculate and we can see that 77.6 percentage of the HOCl is available at pH 6 it was 97. So, understand with only one unit change the amount of HOCl has decreased from 97 or 99 percent to 77 percent. So, this is a tremendous decrease and we can perform such calculation.

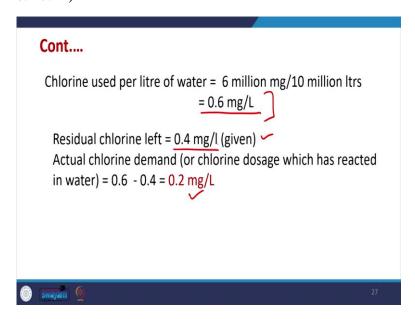
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Then there is this is the second question which is given here, the chlorine consumption in the treatment of 10,000-meter cube per day of river water is six kg per day. So, this is the chlorine consumption which is there for treating 10,000-meter cube of water per day. Now, that residual chlorine after 30-minute contact is 0.4 milligram per liter, so, this is given and this is available.

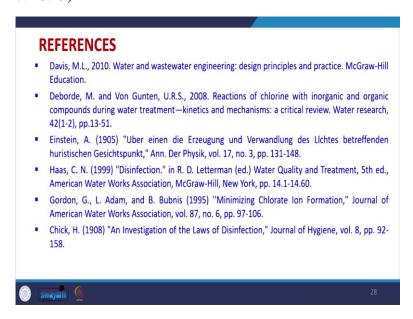
So, calculate the chlorine doses in milligram per liter and the chlorine demand of the river water? The water treated per day is 10,000-meter cube, so, this is equal to 10,000-meter cube into 10 raise to 3 liters, so, it becomes 10 into 10 raise to 6 liters or 10 million liter. Now, chlorine consumed per day is 6 kg is given here. So, 6 million, so, 6 kg is equal to 6 million milligram.

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So, this we are doing so, as to understand what is the chlorine requirement, so chlorine used per liter of water is 0.6 milligram per liter. Now, the residual chlorine left after 30 minutes is given, so, it is 0.4 milligram per liter. So, that means, the actual chlorine demand which is there is only 0.2 milligram per liter, so this is there. So, we have to see that whether we should use this much amount of chlorine or not, this is we can we have to cross-check that whether it is essentially required because the amount of residual chlorine left is high. So, we can cross-check this way.

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So, we have used several references in preparation of these slides with respect to disinfection, you can go and study any of these. Now, we have studied the disinfection in detail in last three lectures including the today, we found that many chlorinated compounds, chlorine related compounds, ozone and UV radiation can be used for a water disinfection and we studied the chemistry of the chlorine with respect to water with ammonia and other nitrogenous compounds.

In addition, we understood the ozone chemistry as well, how ozone is generated, etc. Similarly, we understood the UV radiation and its generation and its uses for disinfection. Remember we have already studied in AOP the photochemical method as well as the ozone treatment method. So, it was already known to us beforehand they can be used for destruction of organic matter as well as for pathogens, now, we understand.

Thereafter we studied the different kinetic expressions are there. So, we can perform the batch data and from that we can use the kinetic expressions to find out the parameters and once we find out the parameters we can use the kinetic expression for actually designing a disinfection reactor, this can be used. And finally, we have tried to learn how to use or select the different types of disinfectant depending upon the total Organic matter bromine concentration, pH, etc., of the water that has to be disinfected. So, this to this we will end this section. So, you can refer to any of these references for. Thank you very much.