Physico-Chemical Processes for Wastewater Treatment Professor V. C. Srivastava Department of Chemical Engineering Indian Institute of Technology Roorkee Lecture - 13 Aeration - II

Good day everyone and welcome to this lecture on treatment of water and wastewater by physical chemical method. So, we will continue with the aeration section on how the aeration helps in the removal of gases and some partial treatment of other iron and manganese which are present in the water. So, till now, what we have done is that we tried to study the basics of aeration and that basic was trying to find out what is the solubility of any gas in the water how it can be calculated. So, in the previous class that we determined that okay the aeration for aeration, the solubility of gases in the water can be found out using the Henry's constant.

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Solubility of gases in water
Problem ¹⁶
The particle pressure of O_2 in the atmosphere is 0.21 atm. Find the concentration of O_2 in water (in mg O_2 /liter of water) at 20°C & 5°C.
Given that for oxygen, Henry's constant (H) is equal to 4.3×10^4 atm at 20 °C, Δ H=1.45×10 ³ kcal/kmol, and b=7.11.
Given that: $p_A = 0.21$ atm, H = 4.3×10^4 atm at 20 °C
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Now, continuing further, we will try to solve some problem today and also understand other important basics with respect to how the aeration rate varies and how it is dependent. So, we will continue with the same. So, solubility of gases in water will try to solve some problems. So, in the problem one, it is given that the partial pressure of oxygen in the atmosphere is 0.21 atmosphere. So, we know very well, approximately 21 percent is the oxygen in terms of mole percent in the atmosphere.

Now, we assume if we assume ideal gas law, so that means at 1 atmosphere the partial pressure of oxygen in the atmosphere is around 0.21 atmosphere, so, we are approximating, but it will really help. Now, what we have to do is that we have to find out the concentration of oxygen in water in milligram of oxygen per litre of water at 20 degrees centigrade, as well as at 5 degrees centigrade.

So, if this is asked and for any other suppose in place of oxygen, we have H_2S or any other gas. So, we want to find out the concentration. So, what we should look for is that, what is the what are the values of Henry's constant and with respect to temperature, there was a equation which was given in the previous class, so, that what is the empirical constant values with respect to Henry's constant relationship with respect to variation temperature.

So, that we have to look for Henry's constant value at some temperature and also, we have to look for the value of b and delta H which was given. So, this is there. So, if we find out for oxygen we will be finding out Henry's constant is given by this 4.3 into 10 raise to 4 atmosphere and at 20 degrees centigrade and delta H is 1.45 into 10 raise to 3 kilo calorie per kilo mole and b is equal to 7.11 which is dimensionless. Now, so, already we know these things, so, what we have to do is that we have to find out the concentration of oxygen in water.

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So, we have already derived this formula, if you have to find out in milligram per litre. So, this was the formula partial pressure of oxygen into molecular weight of oxygen into 10 raise to 6

divided by Henry's constant and this Henry's constant should be in whatever unit this partial pressure is there. So, this is there if partial pressure unit is in kilo pascal or in pascal or in kilo bar et cetera we have to this H should also be in the same unit.

So, this is there so, far the present case P is given as 2.1 atmosphere. So, we are using the this also is in atmosphere. So, this is there so, if we put all the values we will be finding out that the concentration of oxygen in water at 20 degrees centigrade is around 8.6821. In fact, if we actually means or it will be coming out around 9 so, 9. Some places it is nine 9, 9.1, 8.9. So, this is the actual value which is there and that variation is because the water contains other things as well.

It is not pure water so it will it has certain amount of carbon dioxide also it is a different pH water so it is not a pure water. So, that is why this variation is there, but we are tentatively getting the same value at 20 degrees centigrade. So, this is we can easily calculate. Now, the second step is that we have to calculate the value of oxygen concentration in the water at 5 degrees centigrade. So, for doing this, we now required this H value at 5 degrees centigrade,

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Solution	
Now calculating Henrys' constant at 5 °C	
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$\log H_{s^{\circ}c} = \frac{-1.45 \times 10^{3}}{1.987 \times (273)} + 7.11 \implies H_{s^{\circ}c} = 30650.64 \text{ atm}$	
C_{o_2} (in mg/L) = $\frac{0.21 \times 32 \times 10^6}{(30650.64 \times 18)}$ = 12.17 mg O ₂ /liter of water at 5°C.	
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So, we need to calculate this H value at 5 degrees centigrade, this is calculated using this equation which was given earlier also and using this the H comes out like this. So, we can see there is a enormous increase the log H is this and H plus value is this and from this value if we find out it will become 12.17 milligram of oxygen per litre of water at 5 degrees centigrade. So,

this way we can find out the concentration at any other temperature also. Now, continuing with the same problem.

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Now, suppose, there is a second problem if a groundwater contains H_2S gas and the concentration of H_2S as gas in the groundwater is 2 milligram per litre. And these may be very true you may have heard that many times people die as soon as they enter any sewerage system. So, this happens and so, people die because of some gases and that gases maybe H_2S also and because and also methane so in the sewer lines were interceptors and other things are there for cleaning when people are going inside actually already some methane formation has already taken place.

So, amount of methane which is already dissolved in the sewer is very high and because the already concentration is high and that interceptor or that place it is closed. So, that gas comes out and occupies the space about that water air interface and when the any person goes there, actually, he suddenly gets or he respirators in that atmosphere and since oxygen is not there only methane, H2S, ammonia et cetera are there. So, they have a problem.

So, the question is framed from that aspect. So, a groundwater contains H_2S is at concentration 2 milligram per litre, determine the concentration of H_2S is in the headspace of a closed tank containing the groundwater at 23 degrees centigrade given that H_2S the Henry's constant is equal to 5.15 into 10 raise to 2 atmosphere at 20 degrees centigrade. So, this is there.

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So, what we do is that we again use the same formula. Now, we want to we have to use the opposite way, we have to find out the partial pressure of the gas, so we just do the opposite and put all the values so we will be finding at. The partial pressure of H_2S is 5.453 into 10 raise to minus 4 atmosphere and which is actually in terms of PPM by volume it is equal to 545 PPM and at this is much higher concentration than desirable.

So, even if 2 milligram per litre of H_2S is in the water emits enough H_2S gas in the atmosphere, if it is closed confined environment where the PPM value is way beyond the standards which are there. So, we can understand from there that how why people die when they suddenly go inside the any sewer line or other place we call for cleaning et cetera. So, we should always take out the gas first, then enter into that sewer line, otherwise the issues may happen. So, this question clearly tells this. (Refer Slide Time: 09:12)



Now, going further, we have already solved this now, concentration here the partial pressure is solved and partial pressure can further be converted into the concentration. So, concentration will come out like a 0.77 milligram per litre which is not very high it seems, but in terms of PPM, it seems very high and beyond the concentration limits which have been set by the central pollution control board et cetera.

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Now, if this question is then that the Henry's law constant for some gases at 298 kelvin is given below at 1 atmosphere suppose so, these are the values for different gases which are given. Now what we have to find out these type of questions are generally asked in the exam et cetera. So, arrange the gases in the increasing order of their solubility, as you mean that the partial pressure of the all the gases is same.

So, this is like asking the question that we have already discussed previously. So, already we have discussed that the solubility concentration of any component in form or gas in the water is directly proportional to the partial pressure and inversely proportional to the Henry's constant and since Henry's constant is given here and it is, so, what we have to look is that, which whichever gas has lowest Henry's constant its solubility will be higher, because the partial pressure is given same.

But if so, we can easily tell that that the lowest concentration will be this so, it will be like in this order N_2 will be lowest followed by H_2 , followed by O_2 and followed by CO_2 . So, this will be the order in which solubility will be there. Now, there is another thing which is very important. So, in this way, we may presume that amount of CO_2 dissolved in the water is higher than oxygen, no, it is not possible in the atmospheric condition, because the partial pressure of oxygen.

So, we have to cross check with respect to partial pressure. So, remember for partial pressure for partial pressure of oxygen is 0.21, but the actual amount of CO_2 which is there, so, if we assumed

500 PPM also, so, the partial pressure of CO_2 is much much lower than the partial pressure of oxygen. So, both partial pressure and Henry's constant both should be taken together for understanding this. So, this is very very important. There is another important aspect of this is that that many times we have to calculate that how much amount of methane is getting generated in various treatment processes.

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So, suppose, we have a anaerobic treatment process and which is there and somehow the gases are coming out from here and if we assumed a tentatively know the composition or otherwise also so, how much amount is calculated what is done is that, this gas is actually dispersed inside a system where inverted cap is there and now, this when the gas actually goes inside this water, so, this cap goes up and by measuring the distance and already knowing the diameter, we can tentatively find out that, how much gas has collected inside this inverted cap.

And now, since water will be there, and water will be having certain solubility, so, that solubility we can calculate. So, we can tentatively calculate the amount of gas which has been produced by already we know the amount of water which is there. So, what are what is the solubility of that gas in the water so, that we can find it and also the in the headspace using the partial pressure condition we can find out.

And through that we can calculate back and it will give an approximate idea that how much amount of gas in terms of moles et cetera has been formed during this anaerobic digestion or anything. So, it the it has a lot of uses in the wastewater treatment and other places as well. Now, going further we have till now understood the solubility of gas and how we can find out.

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Now, going further with respect to theory of aeration. Now, in the aeration what happens it is like a gas liquid mass transfer process in which the transfer of gas is taking place. So, and that transfer will depend upon there are two phases. So, one is gas phase another is liquid phase. Now, in the aeration we want the gas to go inside the liquid take out all other gases out or opposite way it by some mechanical aeration or something is being done.

Rate of change of concentration is a function of this driving force:

$$\frac{dy}{dx} = f(p) = f(C_s - C)$$

C_S=Saturated concentration at the gas-liquid interface;

C=Concentration in the bulk of the liquid

So, we want the gases inside the liquid to come out. So, there are two driving force for mass transfer gas liquid mass transfer during aeration process one is the driving force inside the gas phase. So, what is the partial pressure of that gas depending upon that that gas will go inside the liquid or not that will depend. Second is the concentration gradient, the concentration gradient is like CS minus C and that in this case the CS is that saturation concentration of the gas at the gas

liquid interface. So, this is same as the solubility of gas whatever is the maximum solubility of gas at that temperature. So, CS is that one thing that we have derived till now. Now, what is the concentration of the gas in the bulk of the liquid.

This is very important than the difference between CS and C gives the driving force with respect to movement or rate of movement of the particular gas inside the water or particular gas moving out of the water, so, both things are very important. So, this dy by dx is like rate of movement or change of concentration of that gas. So, that is dependent in the gas phase with respect to partial pressure and in the liquid phase with respect to this concentration gradient. So, this is there and this is very very important consideration.

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Now, there is a term which is called as oxygen transfer rate and during oxygen transfer or any other gas transfer there are certain aspects in the water treatment we are always interested in oxygen. So, we will be discussing now onwards mostly on oxygen transfer rate, what are the mass transfer resistances with respect to movement of oxygen inside the liquid.

So, these aspects we are going to study in detail. So, oxygen transfer rate is very important parameter for understanding many things like how the pollutant or VOCs removal in aeration take place. So, any aeration of type of systems, how the pollutant or VOCs or gases removal will happen, this will be dependent upon this OTR value.

So, this is there, second thing is that during studies in bio reactors or in activated sludge process, the growth behaviour of microorganisms that is dependent upon this oxygen transfer rate, if the oxygen transfer rate is not there, any microbial species or plant culture will not grow. So, their growth actually depends upon this oxygen transfer rate.

So, in the aeration unit only the it helps in the pollutant or VOCs removal in the bioreactors it helps in the growth of the microbial system in the activated sludge process, it helps in the pollutant removal as well as in the growth of the microbial species which are present inside that activated sludge process.

Now, during any oxygen transfer, there are certain mass transfer resistance or oxygen transfer resistances encountered for the transfer of oxygen. So, suppose we have a this reactor is there and we have something like here, this is the interface and then we have we want to transfer the oxygen from this point to this point and so, what are the resistances.

So, as per the chemical engineering mass transfer theories, which are there any liquid gas interface always has a film. So, it depends upon the mass transfer theory that we are applying. So, we are right now considering the film two film theory to under two film theory, any interface always has two films, one film on the gas side and one film on the liquid side. So, there will be a gas film which will be there, so this gas film will be there at this interface and similarly, there will be a liquid film will be there at the interface.

So, this will be there. So, the first resistance will be the movement of this of this gas molecule at the surface of this, so this is like bulk movement. So, there is not much of the problem because under various conditions generally the pressure is high. So, movement of the gas from the bulk of the liquid to the gas film top of the gas film is always very quick and it will be there.

After that molecule has to move across that film. So, this is the gas film resistance will be which will be there between the bulk gas. So, this is bulk gas and then this is the gas liquid interface. So, this film which is there that will offer a gas film resistance. After that there will be interfacial resistance at the gas film gas liquid interface and again there will be a liquid film resistance between the interface and the bulk liquid phase. So, this is like bulk liquid phase. So, that resistance will be there. So, these are the three major resistances, which are there and these are true for aeration type of units.

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But there will be another will be there that we will discuss now in the next slide. But if we have a biological system, so, for any biological system along with the interface and two films, which are there, there will always be a microorganism is there, so, that microorganisms will also be surrounded by a film and that microorganisms if we blow out the figure, actually, this microorganism's maybe something like this.

So, they have may have pores inside and this is true also for catalyst also says there are many resistance, so liquid phase resistance for transfer of oxygen to the liquid film surrounding the microbial cell or microorganisms, then we have to check that means the gas will move from here to here, then that liquid film resistance around the cell, this will be there.

Then intracellular resistance, which will be inside that that particular microbial flock, so, that will also offer a resistance. And that may be true for a catalyst also, then resistance due to there will be some rate of conjunction of that oxygen insight in particular in the bioreactor. So, how quickly the microorganisms are taking that oxygen.

So, depending upon that, there will be a resistance. So, these are the various resistances which are there in any aeration and these resistances actually resist the transfer of any gas inside the liquid. So, which are there now for better understanding all these steps which are there. So, we will not be considering these steps most of these steps for aeration, we are only considering that only aeration is there, no other microorganisms et cetera there. So, we are neglecting that

resistances and we are only considering that gas film resistance as well as the liquid film resistance.

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So, under that can determine the oxygen transfer across that gas liquid interface can be given by this equation. Now, in this equation, it is also called as OTR or Oxygen Transfer Rate. So, in this case, it is proportional to the concentration gradient in the gas phase. So, concentration in the gas phase divided by H minus concentration of the in the liquid sorry this is concentration at the interface and this is concentration in the bulk liquid.

Similarly, in the there will be a we can write in terms of this also in terms of gas phase it is written here. And then we can write in terms of partial pressure also. So, this way in this equation KLa is called overall gas liquid mass transfer coefficient. So, this is a combined term, which is most often used for determining the oxygen transfer rate and this is so, because we can always find the concentration in the bulk liquid, we can find out the concentration saturation condition also using Henry's law or otherwise.

So, through that we can find out the KLa. So, if KLa is known we can find out the what is the maximum possible oxygen transfer rate. So, this is possible and through that we can perform a lot of calculation individually KL individual is called liquid film coefficient and a is called the interfacial area per unit volume.

Now, KL which is the liquid film coefficient can also be found out using this formula and it is like the ratio of liquid diffusivity to the thickness of the film. And similarly, the interfacial area per unit volume can be calculated like this also this is using this formula. So, but generally what we do is that we try to find out KLa separately and this is used for finding out the oxygen transfer rates and any other condition. Now, other parameters are defined here that COG is the oxygen concentration in the gas phase.

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H is the Henry's constant CO2 L is the oxygen concentration in the liquid phase. Similarly, CO2 GL is the oxygen concentration at the gas liquid interface and LO2 is the maximum oxygen solubility so that we have already calculated earlier. Now, PO2 G and PO2 L are the oxygen partial pressure in the gas phase and in the liquid phase respectively. So, this is there. Now, what is the importance of overall gas liquid mass transfer coefficient. So, this is the most important parameter in the aeration, if we do not know KLa we cannot find it out or we cannot design the system itself. So, this is the most important parameter.



So, overall the oxygen mass transfer rate can be described by means of KLa. So, if KLa is known, we can always find out the OTR Oxygen Transfer Rate or oxygen mass transfer. So, these can be found out this is the most important design parameter because individually KL and a are difficult to measure under real conditions.

So, KL individually which was given it's very difficult to know because we do not know the thickness. And surface area actual available and volume at the interface is also very difficult. So, a KL is very difficult to find out a is also difficult to measure under real conditions. So, that is

why because in the in the actual condition, it is possible then place of a clear face we have a bubble which is there.

So, what is the size of bubbles, so, we do not know the surface area. So, a cannot be found out. So, there are many problems with respect KL and a so KLa together is finding out the oxygen transfer that KLa impart the design and operation impacts the design and operations of bioreactor and all the scale up methods which are actually devised or given in the literature of for scaling a bioreactor for scaling up aeration units, et cetera all are based upon this KLa, which is like overall gas liquid mass transfer coefficient.

Now, in this case, the one question which may be asked is that why not we are trying to find out using the actually this will this Kg. So, using the gas phase mass transfer coefficient why only liquid phase. Because the liquid phase mass transfer resistance with respect to gas transfer is much much higher than the gas phase, mass transfer resistance.

So, we only concentrate on the liquid phase mass transfer resistance KLa and that actually gives a more idea it can be if the KLa value is not available, otherwise, KLa is generally can be found out using various methods and that we will discuss later on. And KLa has a lot of it can be affected by a number of parameters inside the aeration unit.

And what is done is that that KLa values far common type of gases are reported at certain temperatures. Now, common type of gases means we report generally gas and water system both. So, it is possible that in place of gas suppose we have for oxygen water system is there. So, it is possible that KLa for this system is reported.

Now, any other place suppose we required this system any other system where in place of water we have ethanol or something like this. So, for this there are empirical equations which are given based upon the KLa for O_2 water system and those equations are used for finding out any other gas liquid system and KLa for that gas liquid system and also we can account for the effect of temperature also. So, this is there these things will learn in the next lecture. So, we end right now with overall gas liquid mass transfer coefficient. We will continue with the basics and also perform some calculations on the KLa in the next lecture. Thank you.