Course Name: Industrial Wastewater Treatment

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Week - 02

Lecture 10: Adsorption Process

Hello everyone, today we are going to study based on the adsorption process. If you recall in our previous lecture, we have discussed about the adsorption process, the concept, the mechanism behind the adsorption of the adsorbate onto the surface of adsorbent. Then we have discussed also the various isotherms, the mass balance analysis. So now how these adsorption isotherms they are developed for that there are various studies to be performed. So in this lecture we will be dealing with the batch study which is carried out for development of isotherm. Then we will be also discussing about the column study which is used to carry out the breakthrough analysis and to design a adsorption column.

So there are various design parameters, so all those design parameters we will be taking one by one in this lecture. So let us discuss about the batch study, why this study is performed. Basically as we have discussed there are various isotherms to develop to determine the various parameters of different isotherm we have to conduct this batch study. So this batch study is performed by taking a fixed amount of sample say 100 to 250 ml in different volumetrical flask, say we have taken 4 to 5 number of flask and then we have to add different amounts of adsorbent starting from say 0.5 gram, 0.6 gram, 0.7 gram like that different doses of the adsorbent in all these flasks. And then after adding the adsorbent into the solution and mix thoroughly in rotary shakers till the equilibrium is achieved. So, equilibrium is basically when the further adsorption does not occur so that condition, we say that is equilibrium conditions and this depends upon the type of adsorbent we are using.

After this equilibrium is achieved then the sample has to be filtered and after filtration this sample has to be taken out from each flask and then it has to be analyzed for that pollutant. So we will be having here the initial concentration say C_0 and then after analysis say if the concentration becomes C_e that is after the equilibrium. So this concentration and the different doses of the adsorbent which is added into the different flask that we have to note down and then we can analyze the various isotherm and their model parameters. So here if we see this is the procedure whatever I have explained so we have to take a definite amount of sample say 100 to 250 ml in each flask and then we have to add different doses of adsorbent into different flask and then it has to be mixed in shakers and after the equilibrium or minimum time allowed for samples to achieve the equilibrium that is normally 7 days for powder activated carbon however this varies from type of the adsorbent. So, at the end of this test period when equilibrium is achieved, we have to take out the samples it has to be filtered and then the amount of adsorbent which is remaining in the solution that has to be measured and the analysis is performed to find out the different isotherm parameters.

So how to find out these isotherm parameters for that we have to plot the isotherm. So here if we see the Langmuir isotherm as in the previous lecture we have seen this Langmuir isotherm the linearized form of this isotherm we can write as $\frac{1}{qe} = \left(\frac{1}{K_A q_m}\right)\frac{1}{Ce} + \frac{1}{q_m}$, where this q_e is basically the adsorption capacity at different equilibrium time and then this K_A is basically the Langmuir isotherm constant and then q_m is basically the maximum adsorption capacity whereas C_e concentration of adsorbate remaining after the equilibrium is achieved. In this equation if we see this is like y this is like m and this if we take as x so we will get y is equal to mx and this if we take as c so this, we will have a straight-line plot so in the form of $y = mx + c$. So here you can see this slope is $1/K_A$ into Qm whereas the intercept we can get by plotting the isotherm curve. So, this if we plot $1/q_e$ onto the y axis and $1/C_e$ onto the x axis as per the isotherm model its linearized form then we will get a straight line and this straight line if we find out the intercept and if we find out the slope of this straight line we can calculate these model parameters.

So here in this if we see this $1/q_e$ this is the equation of the isotherm and in this the intercepts that is 0.01123 so this 0.01123 that will be equal to $1/q_{max}$. So $1/q_{max}$ that will be equal to 0.01123 and the slope that will be equal to $1/K_A \times q_{max}$ that will be equal to 0.44 by using this if we know this $1/q_{max}$ is equal to this so we can find out q_{max} value and similarly in this equation if we put that q_{max} value which is obtained from this relation so we will get the value of Langmuir constant K_A. So this is how we can find out the model parameters by using batch study. The column study is also performed so this column study is performed to find out the design parameter of column so this study is done in a continuous mode whereas the batch study it's in a batch mode. So here what we have to take we have to take the wastewater sample which having certain pollutant having concentration C_0 so which is taken as a adsorbate concentration and from this if we see this tank is connected with the pipeline and one control valve is fitted here so as to control the flow of the wastewater through this pipeline and then this wastewater is allowed to fall into this funnel which is attached with the adsorption column and this column if we see this is the packing of the adsorbent say activated carbon so this will be packed within the column and the water will be allowed to percolate through this column and from the bottom of this the samples will be collected at different point of time at different interval of time and it will be analyzed for its concentration so we will have initial concentration which is there in the this tank and the final concentration at different time interval say at time t say this is equal to C and then we have to plot the breakthrough curve and we can analyze different model parameters. So here how to plot this breakthrough curve how to find out the point of breakthrough and the point of exhaustion so this is done by plotting the breakthrough curve and you can see here this is the normalized concentration this is C/C_0 it means the ratio of the concentration of the adsorbate at any point of time with respect to the initial concentration of adsorbate in the solution so this normalized concentration is plotted for different time interval say t_1, t_2 t_3 till the bed is exhausted so here if we see the breakthrough curve we have got for adsorption study so here how to find out this breakthrough point how to find out the point of exhaustion basically breakthrough point is defined as the point when the concentration of the adsorbate in the effluent comes to around 5%

of the initial concentration of adsorbate in the solution. So, C/C_0 that must be equal to 0.05 so corresponding to C/C_0 we have to draw a horizontal line and then we have to draw a vertical line where it intersect that will be called as the breakthrough time whereas concentration of the adsorbate in the wastewater will be termed as the breakthrough concentration and that is equal to $C/C_0 = 0.05$ then if we further analyze this breakthrough we will get that the 50% of head is exhausted at $C/C_0 = 0.5$. So, there again we can draw a horizontal and vertical line and then we can find out what is the 50% adsorption occurring at that particular time so this time indicates that time at which the 50% of the capacity of your adsorption column will be exhausted. Similarly there is another point of concern that is point of exhaustion so this point of exhaustion at $C/C_0 =$ 0.9-0.95 we should take this as a point of exhaustion and when the $C/C_0 = 1$ it means the concentration of the adsorbate that is coming after the adsorption that is equal to the initial concentration of adsorbate then this point is called as the complete exhaustion of the bed and this is defined as the time of complete exhaustion that is t_e so here this breakthrough study is carried out not only to find out the breakthrough time but it is also carried out to analyze the type of adsorbate its nature what type of adsorption is occurring.

So another important aspect in breakthrough study that is mass transfer zone mass transfer zone basically this is the length of the adsorbent bed where the adsorption is occurring basically this we determined by using this equation which is equal to $H_{mtz} = Z\left[\frac{V_E - V_B}{V_E - 0.5\,(V_E - V_B)}\right]$, where this H_{mtz} indicates the height of the mass transfer zone or the length of the mass transfer zone which will be equal to z where z is the height of the adsorption column and then in bracket there is a $V_E - V_B$ so V_E and V_B they are basically the throughput volume of the water at the point of exhaustion and at the point of breakthrough respectively and using these two parameters we can define what is the height of the mass transfer zone and if we see here the mass transfer zone basically this depends upon the hydraulic loading rate if the hydraulic loading rate is very high in the extreme conditions then the height of the mass transfer zone may be even greater than the height of the adsorption column which means that the adsorbate will not be further removed and the calculation of mass transfer zone is very important to define the height of the column if we further analyze the breakthrough curve so here if we see this is the throughput volume of the water at the point of breakthrough and this is at the point of exhaustion and here this if we see this is normalized concentration in the beginning if this is the height of the mass transfer zone so column has sufficient height where this adsorption process can occur but as soon as the adsorption proceeds the adsorbent bits getting exhausted and height increases and finally the condition arises when the depth of the column is even lesser than the depth of the mass transfer zone so in this condition you see there won't be any adsorption and and this is basically the point of exhaustion of the weight when the $C/C_0 = 1$. So, this height of mass transfer zone is very important to finalize the overall height of the column required for this adsorption process. By analyzing the breakthrough curve we can also determine a very important characteristic of the adsorbate which is presented to the wastewater so here if we see there are one two three four different types of breakthrough curve and in these two cases if we see this $C/C_0 = 0$ for these two curve so it means whatever the adsorbate that is present it is completely adsorbable nature so it will be 100% absorbed if we analyze its end point one is finished at a point $C/C_0<1$ and this curve is the $C/C_0 = 1$ so if the $C/C_0 <1$, what does it mean that the adsorbate concentration is not coming out even after the exhaustion of the bed it means something is being degraded within the adsorption column so this type of curve indicates basically that the adsorbate is also biodegradable or degradable within the column some of the adsorbate is being degraded that's why this $C/C_0 \neq 1$, while if the C/C_0 in this case if it is equal to one it means that is non-biodegradable means whatever is coming into the column the same is coming out of the column it means the adsorbate that is non-biodegradable so the nature of the breakthrough curve we can find out the nature of the adsorbate present into the wastewater so in in these two graphs if we see the $C/C_0 > 0$ so if it is more than zero it means there are certain the adsorbate is not completely adsorbable so some part is adsorbable some part is not adsorbable that's why in the beginning itself there is no complete adsorption and the $C/C_0 > 1$, so this type of curve indicates that the type of adsorbate which is adsorbable also not adsorbable also so this is the different aspects of breakthrough.

So finally using this breakthrough we find out the breakthrough adsorption capacity which is basically 25-50% of the theoretical adsorption capacity and this can be determined by using this formula $(X/m)_b = X_b/m_{GAC} = Q\left(\frac{C_0 - C_b}{2}\right) t_b/m_{GAC}$. So whereas in this if we see the q is basically the flow rate that could be in m^3/day that could be in L/day whereas C_0 that is the initial concentration of adsorbate present in the solution while C_b is the concentration of adsorbate at the time of breakthrough so average of the two $\frac{C_0 - C_b}{2}$ that has to be taken and then it has to be multiplied with the time of breakthrough and then by using this equation we can find out what is the breakthrough adsorption capacity.

Then let us design a granular activated carbon so again we have to perform the mass balance analysis so if we see this is a column so in this column adsorbent is filled and the wastewater inters here at a flow rate of Q having initial concentration C_0 and here this is the same flow will come out and here we have taken that granular activated carbon so if this is condition and say after time t the concentration becomes C_e so for this how to perform the mass balance analysis and then to find out different design parameter of granular activated carbon.

So, here if we see this is the mass balance equation that is the basic equation $Accumulation = inflow - outflow - amount\ absorbe$, in this case the accumulation is 0, ($0 = QC_0t - QC_et - m_{GAC} \times q_e$) and the inflow that is QC_0t means how much amount of adsorbate is getting into the column this is QC_et this gives how much the adsorbate going out of the column and then this is how much adsorbate being absorbed within the adsorbent that is $m_{GAC} \times q_e$ so if we further solve this equation what we will get that is $\frac{m_{GAC}}{Qt} = \frac{C_0 - C_e}{q_e}$, which is defined as the adsorbent usage rate so adsorbent uses rate is basically defined as the amount of adsorbent being used per unit volume of wastewater so this is equal to $\frac{C_0 - C_e}{q_e}$. $C_e = 0$, if we presume that the concentration after the equilibrium becomes very negligible then this adsorbent uses rate means $\frac{m_{GAC}}{Qt} = \frac{C_0}{q_e}$ that can be written as C_0/q_e so this equation we can also use when we neglect the concentration of adsorbate in the solution after the equilibrium so these are the two equations we use to determine the adsorbent usage rate.

Similarly another parameter which is called as the empty bed contact time empty bed contact time is the time for which the adsorbate remain in contact with the adsorbent so this is determined by the volume of the adsorbent bed divided by the flow rate so this volume of the bed if we further write in terms of its area and depth so this will be equal to area of the bed into depth of the bed divided by this the flow rate if we write in terms of velocity of flow then this will be equal to velocity of flow into area of weight so area of bed ($EBCT = \frac{V_b}{Q} = \frac{A_b Db}{v_f A_b} = \frac{Db}{v_f}$) area of bed in the denominator and numerator that will get cancelled and we will have this depth of the bed divided by velocity of flow through the bed. Then another important parameter that we use to determine the total amount of activated carbon required that is activated carbon density as we know this is the ratio of the mass to the volume $\rho_{GAC} = \frac{m_{gac}}{V_b}$, so this is mass of the granular activated carbon filled into the column having its bed volume V_b so by taking the ratio of the two we can find out the density of the activated carbon.

Then we have a specific throughput volume of water treated so this is specific throughput that is defined as the volume of water treated by per gram of the adsorbent used so this is defined as the specific throughput volume which the unit is in m^3/g and this can be determined by this equation $\frac{Q \times t}{m_{GAC}}$, where Q and t is defined as earlier and here if we Q again put in terms of volume of bed so this will $\frac{V_b t}{EBCT \times m_{GAC}}$ that will give you the value of Q and then $\frac{t}{EBCT \times \rho_{GAC}}$. So any of the two equation we can use to find out the specific throughput volume which is basically the amount of volume of water that is being treated per unit volume of adsorbent then similarly we have another form of this we can write this $\frac{V_b t}{EBCT}$ then this m_{GAC} we can replace it $\rho_{GAC} \times V_b$ of the bed so density of granular activated carbon into this vb will give you the mass of granular activated carbon so after substituting this value we get finally the specific throughput volume we can calculate using this another equation that is equation number (vii) and then similarly the carbon usage rate so carbon usage rate that is basically how much carbon is required for treating unit volume of the water or the wastewater so this is a CUR which indicates the carbon usage rate and its unit that is in g/m^3 if we write this is $\frac{m_{GAC}}{Q \times t}$ which is basically the volume of the water so this will give you the carbon uses rate and this if we see this is the inverse of the specific throughput volume, $\frac{1}{Specific\ throughput}$ and then similarly the volume of water treated for a given EBCT time that if we have to calculate so this will be equal to $\frac{Mass\ of\ GAC\ for\ given\ EBCT}{GAC\ usage\ rate}$ so this will give you how much volume of the water can be treated by having a particular time and then similarly we can calculate the bed life so this is basically the $Bed\ life,\ d = \frac{Volume\ of\ water\ treated\ for\ given\ EBCT}{Q}$ if we do we can find out the overall bed life of the activated carbon.

So again if we see the major aspects of design of the granular activated carbon so we see that is contact time, hydraulic loading rate, then depth of the activated carbon and then how many number of units we have to design so a minimum of two parallel carbon contractor unit is designed but in case of there are multiple units so one unit we can keep it as a standby and then rest of the unit will keep on working so as some of the units they required regeneration so one stand by unit is always preferred for this granular activated carbon.

And then this is the type of example which we have to find out Langmuir and Freundlich isotherm coefficients using the test data which is given below so this is basically the mass of the granular activated carbon added so this is 0.00 means nothing is added here 0.001 gram is added then 0.01 gram is added so for different doses of this granular activated carbon there is a c value is given 3.37, 3.27 so like for different doses of this the c value is given whereas the initial concentration of this adsorbate in the solution is given as 3.37 so equilibrium time is obtained after seven days.

so this is calculation table you can see C_0 value is given and here C_e value is given so from this we can calculate C_0 - C_e and then this is the mass of the adsorbent added so this is q_e value we get that is milligram of adsorbate being adsorbed per gram of adsorbent (mg/g) so this C_0 - C_e divided by doses of adsorbent being added so this has to be divided so we will get this data so we have to also calculate this C_e/q_e value so C_e value is given here q_e value we calculated here so find out this C_e/q_e in another column.

Similarly in this case also as per the calculation we have to find out the plot for Freundlich isotherm then plot for Langmuir isotherm. So if we see this is the equation of the straight line plot of Freundlich isotherm this is the equation for straight line plot of Langmuir isotherm so here if we compare the R^2 value of this both of these two models so we see the R^2 value of this Langmuir model is much much better than this R^2 value of Freundlich equation but here if we find out the slope that is $1/q_{max}$ the value comes here this is negative because the trend line if we see that is going downwards so does not meet with the fundamental assumption of Langmuir isotherm and this q_{max} value cannot be negative because of this though the R^2 value of this plot is much higher compared to this R^2 value of Langmuir model but it will not comply with the adoption process because the q_{max} value here what we get from this plot is negative which is not at all possible so we can conclude this isotherm does not comply with the adoption process so in this we see this is the Freundlich isotherm model which implies slope equal to 5.0767 which is equal to 1/n so from this we can find out the value of n and similarly the intercept that is -0.8344 so if we put equal to K_f so K_f value also we can determine equal to 0.1464.

So this is how we can determine the model parameter using different isotherm data and then this is another numerical which deals with the fixed bed column study so here if we read this a fixed bed activated carbon absorber has a fast mass transfer rate and the mass transfer zone is essentially a sharp wave trend assuming the following data applied determine the quantity of carbon required to treat 1000 L/min of flow and also find out its bed life. The given data is this like compound is TCE that is trichloroethylene initial concentration that is 1 mg/L and its final concentration after the equilibrium that is 0.005 mg/L similarly the other data for density of the granular activated carbon is given which is equal to 450 mg/L and then the model parameters like K_f is given so this is Freundlich capacity factor so K_f value is given and also the its intensity parameter 1/n is given equal to 0.62 and then EBCT time is given equal to 10 minutes. So here from the problem we can see this follows the Freundlich isotherm model and the initial concentration and final equilibrium concentration is given so for this we have to find out how much dose of carbon is required and what will be the bed life of the column so first of all we have to find out the GAC usage rate for this TCE so this GAC usage rate that is $\frac{m_{GAC}}{Q \times t}$ so this will be equal to $\frac{C_0 - C_e}{q_e}$ and again if we qe we write equal to its $K_f C_e^{1/n}$ because it follows the Freundlich isotherm so we can write this as qe equal to$K_f C_e^{1/n}$ and now if we put the value of $C_0 - C_e$ so that is 1 milligram equilibrium concentration is very very less so we can neglect this concentration so $C_0 - C_e$ will be equal to C_0 that is 1 mg/L and then this is the K_f value that is given as 28 and then this is C_e value which is given as 0.005 to the power of 1/n so 1/n is also given that is 0.62 so if we put this value in this equation we can find out what is the carbon usage rate that is 0.953g of granular activated carbon is required for treating one liter of flow then we can find out the mass of the carbon required for a given EBCT time so EBCT time here if we note that is 10 minute time so for 10 minute time how much mass of GAC will be there in the bed so this is $V_b \rho_{GAC}$ of the granular activated carbon so this is equal to $EBCT \times Q \times \rho_{GAC}$ as defined earlier so by putting the value here we can find out how much activated carbon dose is required so here EBCT time that is 10 minutes then Q is 1000 L/min and then this is density of the granular activated carbon which is equal to 450 g/L so after calculating we will get this much dose of granular activated carbon is required and then here if we see this is the volume of the water how much volume of the water we can find we can treat within this 10 minute EBCT time so this will be equal to $\frac{mass\ of\ GAC\ for\ given\ EBCT}{GAC\ usage\ rate}$, so GAC usage rate already we have calculated that is 0.953 and this is the amount of adsorbent that we are using we have calculated which is equal to $4.5 \times 10^6 g$ so if we divide these two we get this value that is equal to $4.72 \times 10^6\ L$ or we can say this is 4.72 million liter. Then similarly we can find out how much bed life will be there for the column so this is bed life = $\frac{volume\ of\ water\ treated\ for\ given\ EBCT}{Q}$ so this is the total volume of the water which we have got 4.72 million liter so $4.72 \times 10^6\ L$ divided by its Q which is the flow rate so this is 1000 L/min so if minute we come convert into day so this will be multiplied by 1440 so by converting it into day we get this is the overall bed life for that activated carbon .

So this numerical discuss about the application of those concepts in determining the adsorbent dose determining the bed life then this is another example if we read this is a treated wastewater with a flow rate of 1000 liters the flow rate is given as 1000 L/min is to be treated with the PAC to reduce the concentration of residual organics measured as TOC from 5 to 1 mg/L so initial concentration is 5, 1 mg/l is the equilibrium concentration and then what it says that Freundlich adsorption isotherm parameters were developed as discussed previously assuming the following data applied determine the PAC requirement again the same thing to treat the wastewater flow is already given that is 1000 L/min assuming the following data the data is given so this is mixed of organics C_0 is 5 mg/L, C_e is 1 mg/L, GAC is 450 g/L, K_f is 150, 1/n is 0.5 so we can see quickly so this is PAC dose using following equation we can determine. So this is $\frac{m}{V} = \frac{C_0 - C_e}{q_e}$, qe if we put equal to $K_f Ce^{1/n}$ so in the equation form so $q_e = K_f Ce^{1/n}$ so this by this we can get m/v value so this m/v value came by putting the value $\frac{C_0 - C_e}{K_f Ce^{1/n}}$ so after putting this value we get the value of PAC doses that is equal to 0.0267 g/L and then the Annual cost $=\frac{0.0267\ g/L \times 1000\ L/min \times 1440\ min/d \times 365\ d/yr \times \$0.50/kg}{10^3\ g/kg}$ and then finally we get the total annual cost for this adsorption process that is $7,008/year.

So, these are the references we have followed.

Thank you