Course: Adsorption Science and Technology: Fundamentals and Applications

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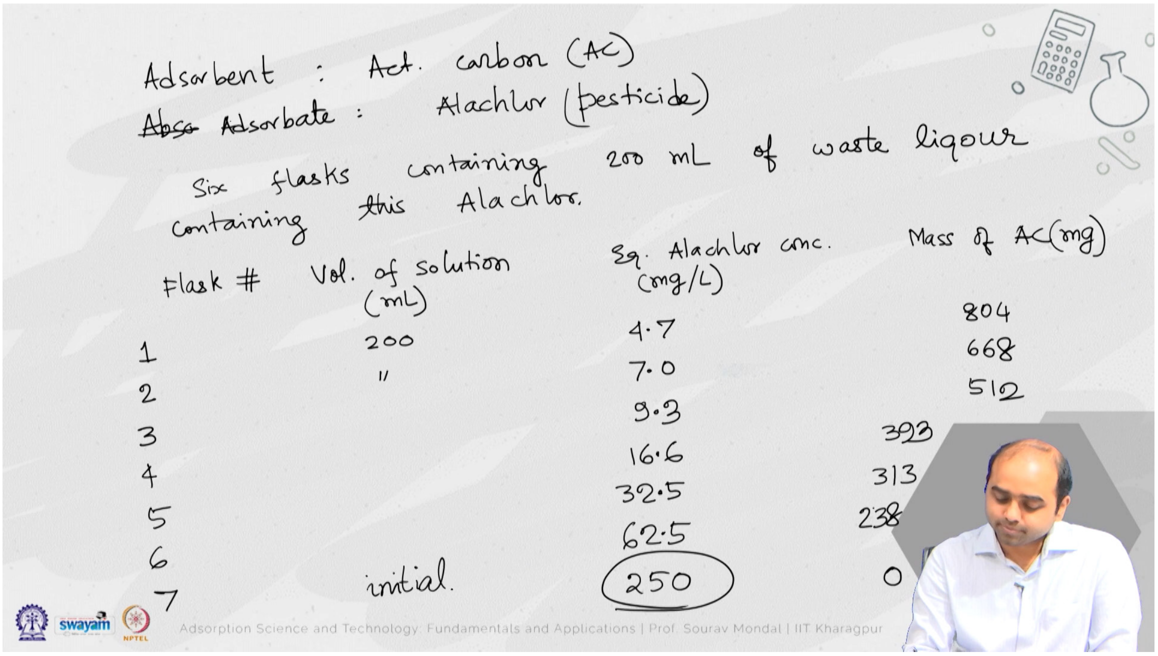
Week 02

Lecture 9 | Equilibrium Modelling – II

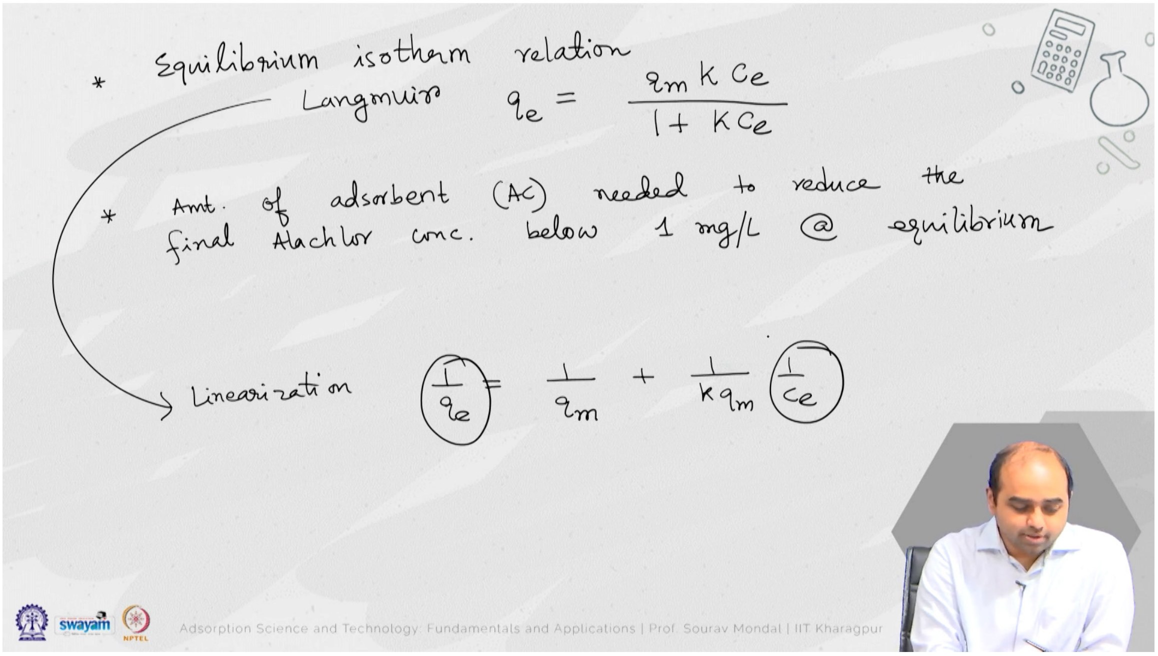
Hello everyone, welcome to this class on equilibrium modelling. Now, equilibrium theories are based on the isotherm profiles as we have already seen in the previous lectures about the Langmuir isotherm, the Freundlich isotherm and there are several others different different isotherms and in the last lecture we actually solved out worked out some problem related to this equilibrium modeling of this process. Now, in this lecture too, we will I mean it is a continuation of the equilibrium model we will try to work out another one or two more problems in this direction. And, we will see that how the isotherm models can be you know fit or developed from the experimental data and how this model can be used to predict the equilibrium concentration or other way round to work out how much of the adsorbent would be needed to achieve or to attain a target value of the solute concentration in the final treated solution. So, again we will take a this example of an you know this waste water or a water treatment solution. So, we say that let us have this adsorbent as the activated carbon which is added or which is used to remove a adsorbate, is one of the pesticides. Alachlor is a popular you know pesticide chemical which is very hazardous in the carbon cycle of the environment. So, we try to use this activated carbon to purify or to remove alachlor from this solution. So, let us say we have you know 6 flask or 6 containers containing 200 ml or a fixed volume of this waste liquor containing this alachlor. So, let us list down the conditions.

So, let us say we have I will list down the equilibrium alachlor concentration in milligrams per liter and mass of activated carbon, in milligrams that is added to each flask. So, let us say the first flask the all the flask has a volume of 200 ml in the first flask we add 804 milligrams of activated carbon and that produces an equilibrium alachlor concentration of 4.7. Similarly, in the other flask the volume is same and we achieve up you know 7 with equilibrium concentration of 9.3. Similarly, for the third case on adding sorry. 512 milligrams the alachlor concentration turns out to be 9.3. So, as you can understand at the mass of the carbon or the mass of the adsorbent is reduced the equilibrium concentration increases because you do not have sufficient amount of the adsorbent to actually you know to remove or to take up this alachlor from the pesticides or remove this alachlor. Similarly, the next one fourth one, we have this as little bit less amount.



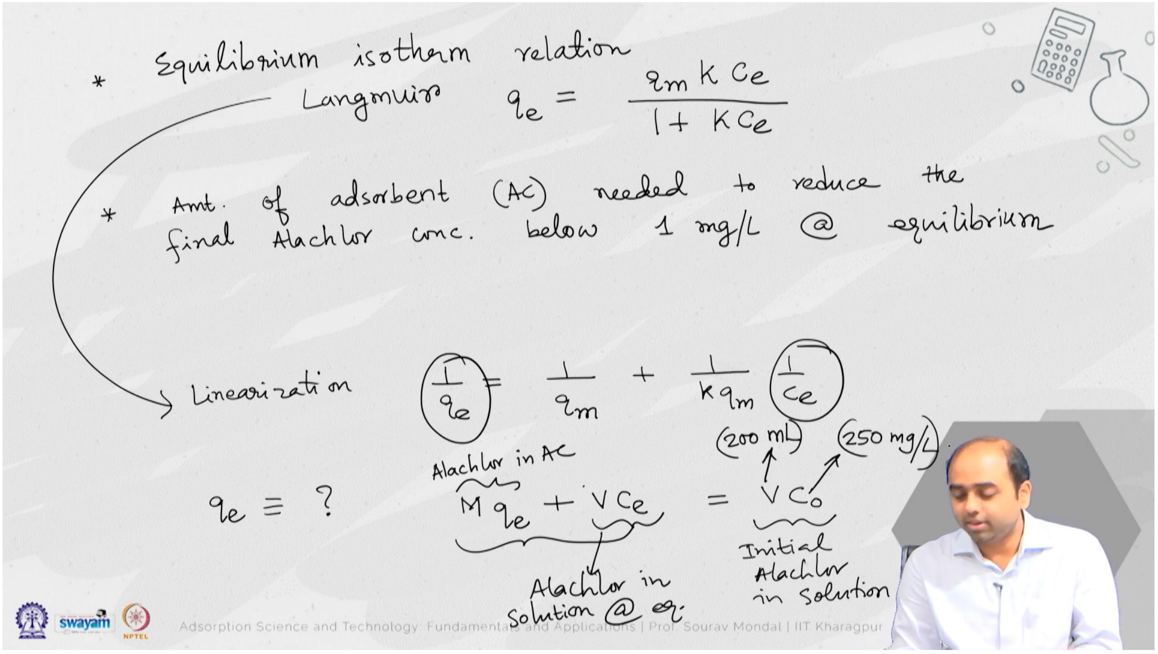
Then we have fifth one in all of these cases the volume of the solution is same we further reduce the adsorbent concentration. Sixth one the this is further reduced this um amount of the adsorbent and naturally the equilibrium concentration is increased. Now, there is one more condition ah that if we do not add any adsorbent. So, the adsorbent is 0 the alachlor concentration is 250. So, this last one this last row represents that 250 milligram of alachlor 250 milligram per liter concentration of alachlor is actually the alachlor concentration that is present in the liquor.

So, this can be this value is actually can be treated as the initial concentration of the adsorbate. Right? because after this is the concentration that you get without adding any adsorbent. So, naturally this is the case where the concentration of the alachlor is present in the solution and of course, after adding adsorbent when you measure the concentrations you get different levels of the equilibrium concentration by adding different amounts of the adsorbent. So, now the first step so with this this is like a small experiment that is done to find out ah the you know amount of as find out the alachlor equilibrium concentration. So, from here the first question is to work out the equilibrium isotherm concentration.



So, we are looking for a Langmuir type model. Of course, you can use the Freundlich model also. So, the Langmuir model is given by this. So where K and qm are the constants qe represents the equilibrium concentration of the adsorbate in the adsorbent and C represents the equilibrium concentration of the adsorbate in the solution phase. This is what is already known to you, qm and k are the two constants k is the equilibrium constant and qm is the maximum capacity of the adsorbate that can be taken up by this adsorbent now this is the first part so we have to work out what would be this constant and the second part of this question is the problem would be to estimate the amount of adsorbent or essentially in this case activated carbon needed to reduce the final alachlor concentration below 1 milligram per liter at equilibrium.

Because if you note in the problem where we have added different amounts of the adsorbent the minimum equilibrium concentration that is attained is 4.7 milligram per liter even after adding 800 milligrams around 800 milligrams of activated carbon. So, the idea is that what would be to filter or to let us say to treat 200 ml of the solution what would be the amount of adsorbent that is needed. So, that the final equilibrium concentration reaches 1 milligram per liter which is around the discharge or the environmental disposable limit for this alachlor concentration. Now, the first work out the first part we have to find out you know the values of qe and Ce from the available data.

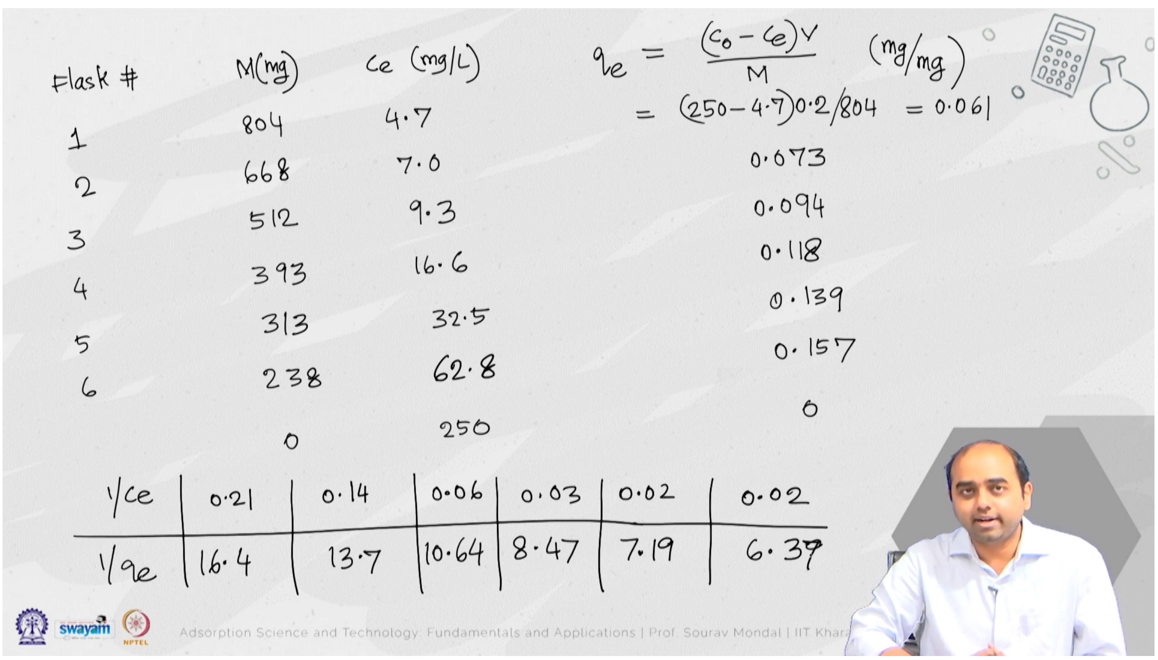


So, this Langmuir isotherm on linearization takes the form of 1 by qe as. So, we have to do a regression of this 1 by qe with 1 by c and the slope will give us k into qm and intercept would give us the constants of q m right. So, this this value of q e would be obtained in terms of milligrams of alachlor with per milligram of the this carbon or gram of the carbon. And the unit of K would be like the inverse of the concentration liter per milligram. So now we have this so now the task is to work out what would be the amount of Ce values are already known to us.

It is these values which is present these are essentially the Ce values these are essentially the Ce values this is the m values mass of the adsorbent and this is the volume of the solution in each case. So, to find out the Ce values or the concentration in the adsorbate phase Ce we have to I mean this is something we have to find it out from the qe from each case then only we can make a plot of 1 by q e versus 1 by Ce. So, to find out the Ce values we can use the mass balance relation. So, the amount that is adsorbed right by the by the this adsorbent that is m into q e plus the amount that is present in the solution at equilibrium that is V into Ce So, this is the total amount of alachlor. So, this is the amount present in you know allochlor in activated carbon, this is the amount of alachlor or this adsorbate in solution at equilibrium right.

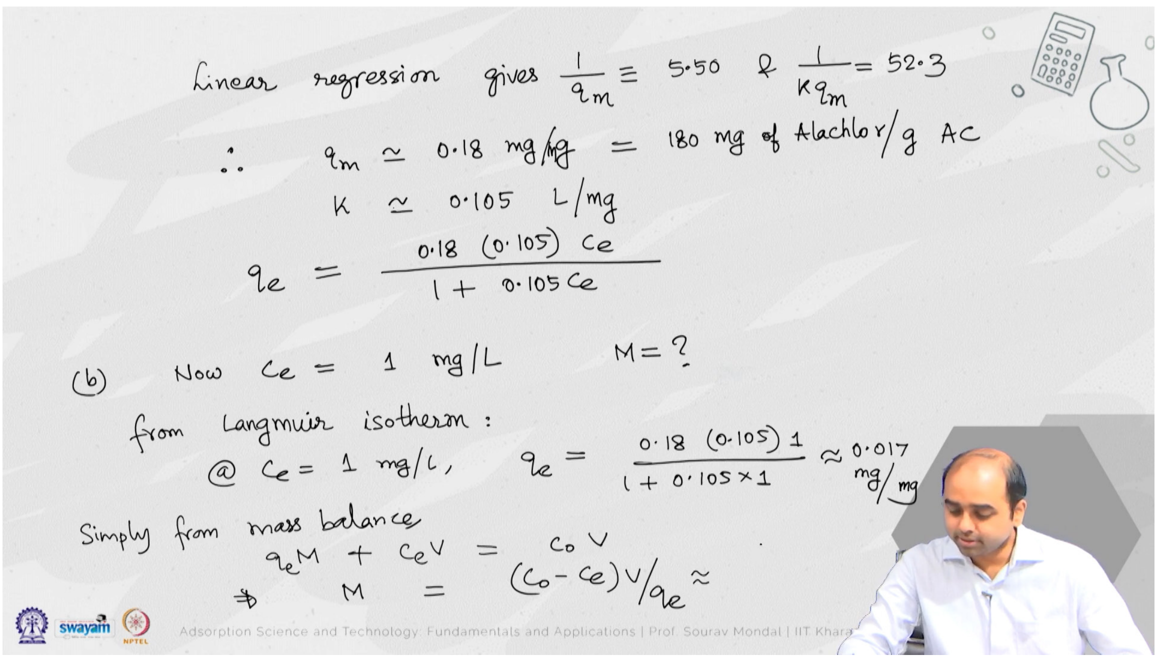
So, this is after the equilibrium has happened. So, the amount that is up taken by the activated carbon is m into qe, qe is the concentration of this adsorbate in the adsorbent phase and Ce is the equilibrium concentration in the solution phase. This would be equal to the initial concentration of this alachlor this initial alachlor in solution. So, this volume

V is 200 milliliters C0 is 250 this is 250 milligrams per liter and this is 200 ml. So, this fraction is constant for all the case. So, the initial amount of the alachlor is 250 cross this 0.2 that is the amount or the milligrams of alachlor that is present in all the case and with addition of different amounts of adsorbent the equilibrium concentration is reduced. So, from there we can work out what would be the qe values in this case. So, let us try to work this out. Then we have the mass of the adsorbent the volume is fixed for all cases so we do not write that value Ce values we will write this is the amount of adsorbent that is added and then from there what would be the value of qe which is nothing but C0 minus Ce into V divided by the amount of the adsorbent and this will be getting in terms of milligram per milligram of the adsorbent. So, for the flask 1 around 800 milligrams of activated carbon was used and the concentration equilibrium concentration 4.7. So, if you work out the numbers this turns out to be this is 250 milligrams, this is multiplied with 0.2 liters divided by 804. So, this is 0.061. Similarly, for second case, we can work out all these numbers.



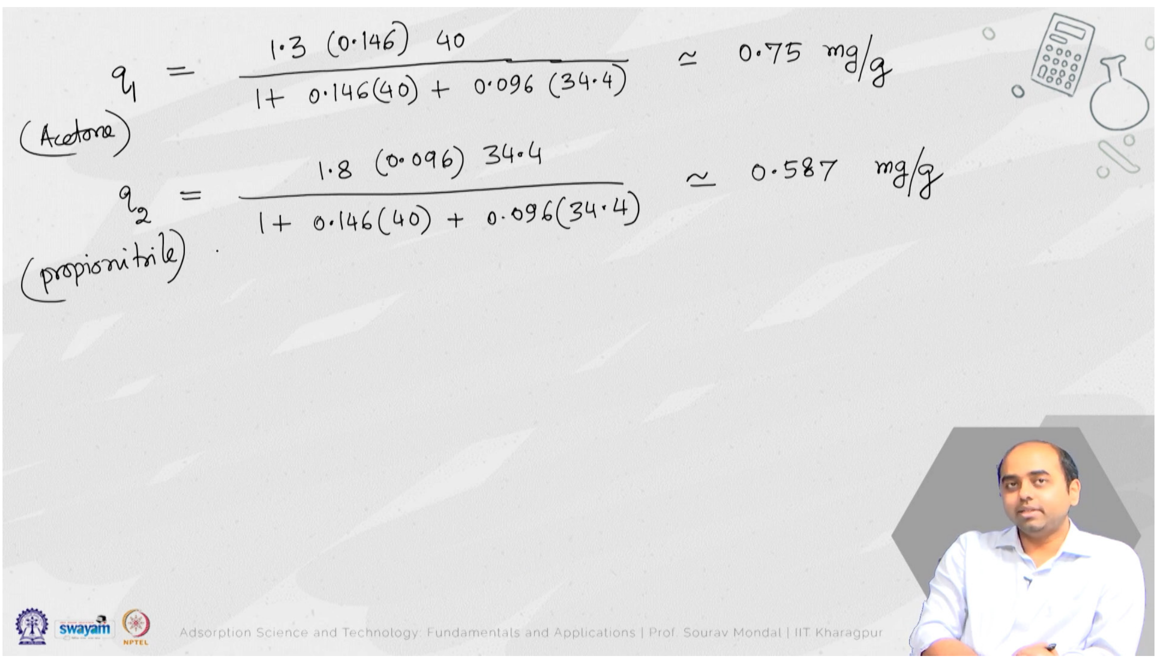
And as you see the amount of adsorbent is increasing sorry decreasing the amount that is up taken is increasing. The qe values are increasing because the system is getting pushed more and more towards the equally towards that maximum limiting capacity as the concentration of alachlor is fixed in all the gases. This is just working out all the numbers and finally, when you have 0 adsorbent the equilibrium concentration is 250 and the qe value is 0. Now, from here you can work out what would be the values of 1 by Ce and 1 by qe values. So, the qe 1 by qe values are calculated as obtained from inverting these values that we have calculated. So, this number is 62.8. So, if you see or if you work out the different calculations. So, this is what roughly the value looks something like this.

Now, if you do a linear regression either you can draw these points in a, in a graph sheet and try to draw a best fit line of 1 by Ce with respect to 1 by qe then from there you can work out the slope and intercept. Alternatively you can do linear regression and you can do this summation of the error residuals to as to find out the optimized value of these two linear regression coefficients and the linear regression value gives you. 1 by qm which is the intercept as 5.50 and 1 by k into qm which is the slope as 52.3. So, from there you can work out that qm is approximately 0.18 milligram per gram and this constant is 0.105 liters per milligram. So, this is equal to 180 milligram per gram of the adsorbent. So, this is milligrams of alachlor per gram of the activated carbon. So, this suggest that now we can construct I mean this Langmuir isotherm looks as this and this is completing the first part. So, the second part of this is problem this part b which talks about that now Ce is set to 1 milligram per liter. So, in this case we have to work out what would be the mass of the adsorbent right.

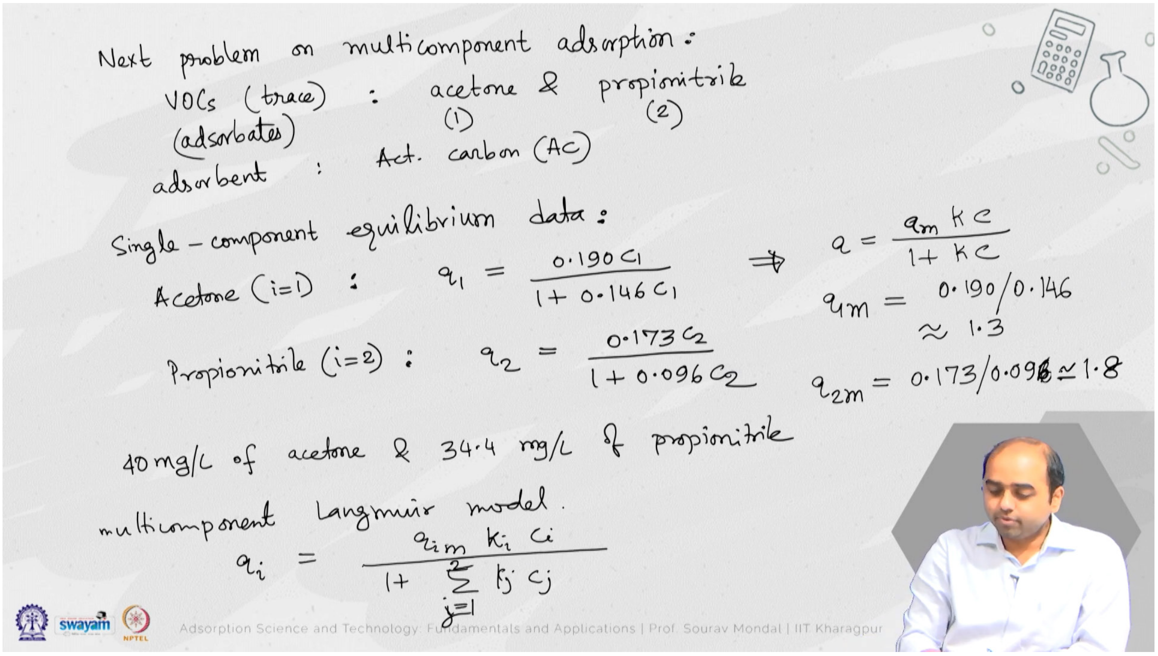


So, from this exercise we can I mean from this Langmuir isotherm. So, we can work out from Langmuir isotherm we can work out that at this equilibrium concentration at Ce is equal to 1 milligram per liter what would be the value of qe. And this is around 0.017 milligram per milligram of the activated carbon. Now simply from mass balance. We can say that the amount that is removed or this you know initial concentration or the initial whatever is there is equal to the final equilibrium concentration plus the amount that is up taken by the adsorbent. So, from that theory itself we can work out that the amount that is up taken and the amount that is present in the solution at equilibrium is equal to the amount that is present initially. So, from here we can work out that M, the requirement of M stands out something like this and roughly if you work out the numbers. So, this is 250 this is 1 this is 0.2 and this is 0.017 this turns out to around 2930 milligrams. So, we see that to reach a value of. To reach a value of 1 milligram per liter the amount of the adsorbent that is needed in this case is around 2.9 grams of the activated carbon to filter out 200 milliliter of you know 2 milliliter of the waste liquor containing 250 milligrams of alachlor and to bring down the concentration up to 1 milligram per liter at equilibrium.

So, now we move to the next problem. So, the next problem we try to use a competitive or a multi component adsorption model. So, two volatile organic matters, is present in trace amount right. So, these are acetone and propionitrile is present in a aqueous stream and they are to be removed using activated carbon. So, this are these are the adsorbates and the adsorbent is activated carbon. Now you are provided with the single phase or single component equilibrium data for both.



So, for acetone let us say acetone we call it as species 1 and propiononitrile we call it as species 2. So, for species 1 acetone the Langmuir isotherm is given as. So these are the individual Langmuir isotherms for these two solutes. And now it is asked that in a so, these these data this Linear isotherm data for these two cases is actually obtained from their individual you know isotherm experiments. And now it is asked that when you have a mixture of solution containing let us say 40 milligram per liter of this acetone and 34.4 milligram per liter of propionitrile. Then what would be their equilibrium values can that be obtained and can that be compared. So, now this is this is a problem where you have a binary solute system or two solute system and their individual capacities are known to us. So, we have to use the multi component Langmuir model in this case. So, which is q i if you recall q i m a i c i divided by 1 plus the summation of all the species present in the solution. So, in this case it would be 1 to 2 as we have only 2 species in this case.



So, now from this case as we see there is a 2 this 2 type of equation two constants that we have and the numerator and the numerator is essentially nothing but so this if you recast into the form of q is equal to q m a c by 1 plus k c then we can work out that q 1 m is equal to 0.190 by 0.146. So that turns out to be around 1.3 similarly q2m is 0.173096 and that turns out to be around 1.8. Now, we have worked out the values of Q m for these two individual cases. Now, these can be coupled together. So, now, you know the Ki values K1 K2 values q m 1 and q m 2 values.

So, now, we can use the multi component model. So, now, to work out q1 we will use this theory of multi component. So, 1.3 multiplied with 0.146 and now we have for the first case 40 milligram per liter. So, this is for the acetone case and in the numerator we will be summing up k into c k1 into c 1 plus k 2 into c 2. So, where the effect of the concentration of the other species will also come in the picture. So, this is the value of qe in this I mean q1e in this case. Similarly, for q2 you will be getting in the same way as 1 plus k1. So, the denominator in both case is same. So, comparing these two values this is the top one is for acetone and the bottom one is for propionitrile. You can see that the uptake of propionitrile is comparatively less than acetone and interestingly in this case it is it is different from their single component uptake values because if you put the uptake values or if you compare their single component uptake values at 40 and respectively at 34.4 you will see that the values are larger. But in the case of the competitive multicomponent system or when there is a mixture as you know there is competition of the sites for by the other molecule to adsorb the same species the relative values decreases. So, I hope all of you have followed this lecture and found it useful. Thank you and we will start this next lecture on kinetics of the adsorption. Thank you.