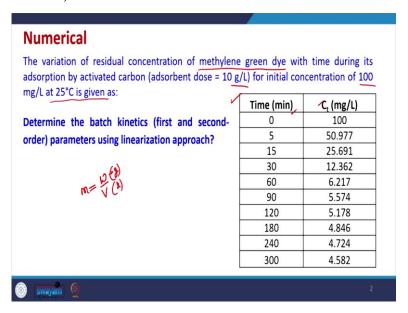
Physico-Chemical Processes for Wastewater Treatment
Professor V C Srivastava
Department of Chemical Engineering
Indian Institute of Technology Roorkee
Lecture 34
Adsorption IV

Good day everyone and welcome to these lectures which we are continuing on adsorption which is used in the, as a Physico-Chemical process for water or wastewater treatment. So, it is one of the unit operation which is used commonly. So, in the previous lectures, we started studying regarding that adsorption kinetics and we found that how to acquire the data for adsorption kinetics in a lab using the actual wastewater and how to get the basic data with respect to time versus the adsorption capacity, and that data can be fitted to various types of kinetic models.

So, the basic thing is that, if any of the model is well fitted that means, all the assumptions which are there with respect to that model can be represented over all the basic mechanism can be represented by that assumptions which are there for that model. Second thing is that, we can use the fitted parametric values to represent the adsorption kinetic by that model.

And further that whole equation can be used in the design of continuous adsorption unit also. So, this is there. So, we will continue in the previous lecture, we studied how to acquire the data. Now, we will try to analyze how to use the data for actually fitting any of the first-order, second-order models etcetera. So, and we will be using a simple linearization approach also, nonlinear kinetics can also be used for solving So, any of the approach can be used.

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So, the data which is given here that the variation of residual concentration of one dye, which is methylene green dye with time during its adsorption by activated carbon for initial concentration of 100 milligram per liter at 25 degrees centigrade is given in this table, so this is there. So, in the previous lecture, we have already found out that we get the data only time versus Ct. So, certainly the large number of beakers etcetera may have been used, and they were kept in the same incubator shaker for these times, which are given.

Now, each of the beaker contained 100 milligram per liter of methylene green dye and in each of the beaker adsorbent dose of 10 gram per liter has been given. So, that means, here we are directly giving the value of 10 gram per liter directly adsorbent dose, so adsorbent dose if it is represented by m. So, it will become like it is actually W by V where W is in how much gram of how much mass has been used. So, it may be having a unit of gram and V generally it will be 50 ml, 100 ml something like this, but we can always convert this thing into liter. So, m is represented as the adsorbent dose in gram per liter. So, directly 10 gram per liter has been given here. Now, we have to find out the pseudo-first-order and pseudo-second-order kinetic parametric values and how to represent the model.

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Co (mg/L) /	Dose (g/L)	T (min)	Ç /	9, (mg/g)	q _e (mg/g)
100	10	0	100	0	0
100	10	5	50.977 ~51	4.9023	4.9023
100	10	15	25.691	7.4309	7,4309
100	10	30	12.362	8.7638	8.7638
100	10	60	6.217	9.3783	9.3783
100	10	90	5.574	9.4426	9,4426
100	10	120	5.178	9.4822	9.4822
100	10	180	4.846	9.5154	9.5154
100	10	240	4.724	9.5276	9.5276
100	10	300	4.582	9.5418	9.5418

Now, first we have to calculate, use this data for calculation. So, concentration is fixed in each of the beaker it is 100 milligram dose is also fixed 10 gram per liter already given. Now, the time has been given 0, 5, 15, 30, 60, 90, 120, 240 and 300 minutes up to which the different beakers were kept in the incubator shaker at 25 degrees centigrade and after some time these were the values which were obtained.

Now, what we do is that from this we can get the qt value and generally these are not highly accurate only up to 50, 25 is enough. So, we can still determine the value from this expression which was given in the previous lecture also C0 upon Ct W by V. And this can also be given a C0 minus Ct upon m, and where m is the adsorbent dose, so, this is like m.

So, for the first case like 50 So, we can always find out 100 minus 50, suppose I am taking only 50, so 100 minus 50 upon 10. So, it will be around 50 by 10, So that means around 5. So, this is what is there 4.9021 so, because it is actually equal to 51. So, this is the case of 51 it will be 49 divided by 10 so, that way it is 4.9 so, this is the value. So, this way we can determine the qt.

Now, there are two approaches, one approach is to find out the quevalues, generally this the last data which is there, so, because we see here the concentration is not changing much after the, after some time. So, that means, the quevalue the equilibrium value experimental is virtually 9.55 maybe, so, this will be the maximum adsorption capacity which is possible at equilibrium condition for these sets of parameters. So, this is there.

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			1st Order Kinetics			2 nd Order Kinetics		
Co (mg/L)	Dose (g/L)	T (min)	q, Cal (mg/g)	kf 🦯	qt (Cal)	q Cal (mg/g)	k,	qt (Cal)
100	10	0	0	0	0	0	0	0
100	10	5	9.444	0.146	4.902	9.805	0.020	4.902
100	10	15	9.444	0.146	8.394	9.805	0.020	7.354
100	10	30	9.444	0.146	9.327	9.805	0.020	8.404
100	10	60	9.444	0.146	9.443	9.805	0.020	9.051
100	10	90	9.444	0.146	9.444	9.805	0.020	9.289
100	10	120	9.444	0.146	9.444	9.805	0.020	9.413
100	10	180	9.444	0.146	9.444	9.805	0.020	9.540
100	10	240	9.444	0.146	9.444	9.805	0.020	9.605
100	10	300	9.444	0.146	9.444	9.805	0.020	9.644
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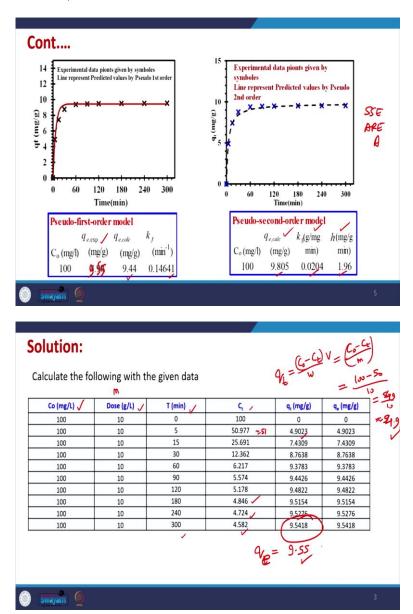
Now in the second step we have to use this data for fitting. So, already we have performed the calculation. So, what we can do is that we can use any nonlinear approach for finding out the parameters of Kf. So, under that approach, we can always use any of the regression techniques for solving this. And second approach is to use the linearization approach to solve. So, both any of the approach can be used, we can always linearize the first-order model and second-order model, we can use the nonlinear approach and directly go for regression and fit using the regression fit and in that case, what we do is that we minimize the sum of the square of errors.

So, any of the error functions can be used. So, like this is sum of squares of errors. So, that is possible SSE and this SSE can be represented by something like this. So, qt calculated minus qt experimental divided by qt experimental. And okay, so no, we do not for if we divide so, it will become average of error. So, for square of error we do not divide we just we can directly use this expression for finding out and we have to sum for all the data sets from 1 to n. Similarly, there is another function which can be used, which is called average relative error.

So, that function can be also be used. So, under that condition, what we do is that in the average relative error it will be like this 1 by n summation i used to 1 to n and then we can use the expression like qt calculated minus qt experimental divided by qt experimental and we can take the mod of this so, that the minus and any negative error and positive error do not cancel each other. So, we can find out average relative error also called as ARE. So, we can

use different types of error functions and minimize those error functions with respect to such a manner that we can find out that kf and the calculated values of qe. So, this is possible.

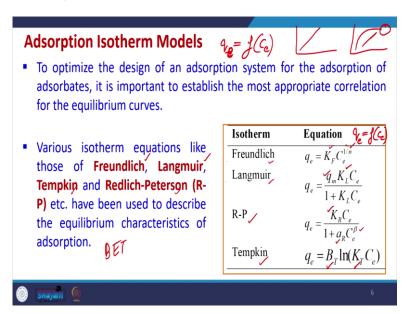
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And we can later on use these values to again get the fitting like this. So, if we represent the data this is qt versus time, so, it will be given by this experimental data points. Now, in the actual case we found that the actual experimental value is around 9.55, the qe values. So, it is actually wrongly written it is 9.55. So, this is the experimental value and as per the model fitting pseudo-first-order we are finding the qe calculated value is 9.44 and the Kf value is here. Now, in the second order the qe calculated value is 9.8. And the ks is this and Hs is the.

So, what we cross-check is the, any of the error functions SSE, which one is minimum for so, here we can directly use any of these parametric values or here also you can see the fits of both the models, the pseudo-first-order, pseudo-second-order fitting is also given here. So, we can use any of these approaches to find out the values of the rate constant.

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Now, going further along with the adsorption kinetics, adsorption isotherm models are also very, very important. And this is so because we always try to see that what is the maximum adsorption capacity which is possible and what is the maximum adsorption capacity with respect to some equilibrium residual concentration. See, we always to find out in chemical engineering and in particular in mass transfer, we need to have some equilibrium data points, then only we can find out whether with respect to the at that temperature, how much will be the equilibrium data points.

And then we draw operating lines and other things. So, like for you know, Henry's law, so, as per Henry's law, it is the equilibrium data is generally relation linear, because we consider only dilute concentration, if higher concentration is there, the curve maybe like this. So, operating line, like maybe like this, we can decide the operating line ourselves, and based upon that, we can find out the length, height, diameter, etcetera of the actual pack bed. So, this is possible.

So, without equilibrium data, we can never design a system, this is first thing. So, we require equilibrium data for any unit operation to design and if it is mass transfer control. So, this is possible. So, we require these isotherm models, which actually represent the equilibrium data

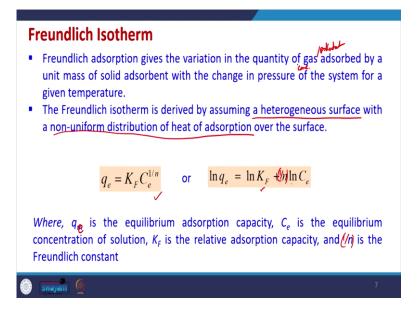
at that temperature to, so, this is there to optimize and design any adsorption system for adsorption of adsorb, it is important to establish the most appropriate correlation for equilibrium curve.

So, this is there to optimize the design of any system this is very important. So, various types of equations like Freundlich, Langmuir, Tempkin, Redlich-Peterson, multiple, more than 30 type of isotherm equations are available, and BET is also one of them. we will discuss that in detail later on. So, some of the common isotherm equations are like this Freundlich, Langmuir, Redlich-Peterson, Tempkin.

And any isotherm equation is actually represented by qe, q equilibrium at equilibrium what is the adsorption capacity and it is always a function of residual concentration of the pollutant in the solution. So, all these equations are actually qe, which are function of Ce and these functions, which are there are the parameters that we have to find out like for Freundlich Kf 1 by n this is 1.

So, these are two parameter models we can see here a Freundlich, Langmuir, because they have only two unknowns. So, qm and Kl. Similarly, Tempkin also Bt and Kt. So, we have two these are these Freundlich language and Tempkin are two-parameter models. Redlich-Peterson whereas, it is three-parameter model because we have three terms Kr aR and beta. So, three unknowns are there. So, we can have a large number of equation models and any of these can be used to represent the adsorption isotherm or equilibrium curve data.

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The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform

distribution of heat of adsorption over the surface:

$$q_e = K_F C_e^{1/n}$$

$$\ln q_e = \ln K_F + n \ln C_e$$

Where, qe is the equilibrium adsorption capacity, Ce is the equilibrium concentration of

solution, K_F is the relative adsorption capacity, and 1/n is the Freundlich constant.

Now, going further because Freundlich and Langmuir are most commonly used. The simple

two-parameter model equations so we will try to discuss Freundlich and Langmuir little

more. So, Freundlich isotherm gives the variation in the quantity of gas are pollutant

adsorbed by a unit mass of solid adsorbent with the change in the pressure oblique

concentration. So, this is the concentration of the system for a given temperature.

Now, the Freundlich isotherm is derived by assuming a heterogeneous surface, the one of the

first assumption is that it assumes the adsorbent to be a heterogeneous surface with non-

uniform distribution of heat of adsorption over the surface. So, this is one of the basic

assumption which is there for Freundlich isotherm and this is represented by this expression

exact derivation can be looked into the original paper.

Now, this equation can be linearized using this approach, so, we can take log on both sides.

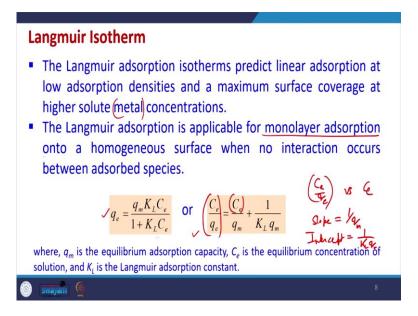
So, ln qe is equal to ln Kf, n into lnCe. So, what does it tell? So, here the qm is the sorry, qe is

the equilibrium adsorption capacities, Ce is the equilibrium concentration of solution. Kf is

the relative adsorption capacity Kf and n or 1 by n we can here it will become 1 by n, 1 by n

is the Freundlich constant that we need to determine. So, the this is there.

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The Langmuir adsorption is applicable for monolayer adsorption onto a homogeneous surface when no interaction occurs between adsorbed species

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \, q_m}$$

where, q_m is the equilibrium adsorption capacity, C_e is the equilibrium concentration of solution, and K_L is the Langmuir adsorption constant.

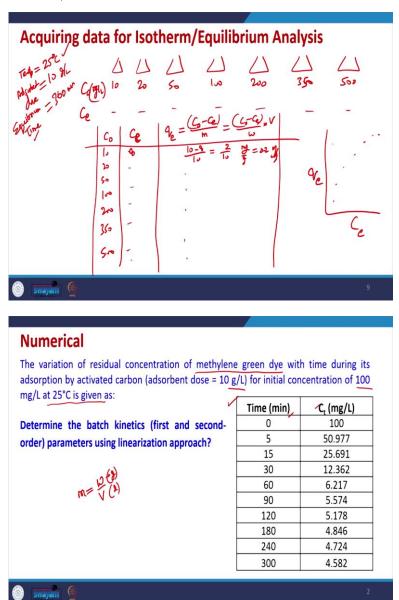
Now, going further, there is another model which is most commonly used it is called Langmuir isotherm. So, Langmuir isotherm or adsorption isotherm, predict linear adsorption at low adsorption densities and a maximum surface coverage at higher metal concentrations are higher solute concentration. So, it can be any of these. So, this is the assumption, now, it is applicable for monolayer adsorption. So, in the Langmuir, we assume a monolayer adsorption only. So, that means, it is only applicable for chemisorption system because they have a monolayer adsorption. So, this is there.

Now, this can be represented by this equation qe is equal to qm Kl Ce 1 plus Kl Ce and this can be linearized also using this equation, the good thing is that we have Ce known, we have qe known and we can plot a Ce by qe, qe versus Ce equation. In fact, this equation can be converted into many linear equations. So, this is there and once this is known, the slope will

be equal to 1 by qm, and intercept will be equal to 1 by Kl qm and since qm will be known from slope we can determine the Kl value also. So, this is there.

So, Kl and qm are the Langmuir constants, qm is very important because it represents the maximum monolayer coverage which is possible. So, this is like a maximum adsorption capacity of any adsorbent with respect to any adsorbate. So, this we can determine.

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Now, how to find out or acquire the data for isotherm or equilibrium analysis. So, as we have done earlier will again discuss this with respect to kinetics. So, in this there is a difference, difference is that, that we again take lots of beakers. So, we have lot many beakers which are taken and for acquiring this data and again since beakers are, we have fixed certain

parameters, so, one of the fixed parameters could be temperature, suppose it is 25 degrees centigrade.

And then in addition to that, we again fix the adsorbent dose or mass also. So, like adsorbent dose will be fixed. So, we have two possibilities. One is that to vary the adsorbent dose and keep the concentration constant. Second approach, which is more commonly used in the experimental case is that we vary the concentrations. So, each of the concentrations will be different.

So, like starting from 10. So, if each of the 10 milligrams per liter 20, 50, 100, 200, 350 maybe, 500. Everything is a milligram per liter. Now, adsorbent dose we fix suppose 10 grams per liter. So, each will be having 10 milligram per liter. Now, there is a difference with equilibrium time so, from the equilibrium data curve sorry kinetic data curve, we try to get the what is the time which will be sufficient for equilibrium to attain.

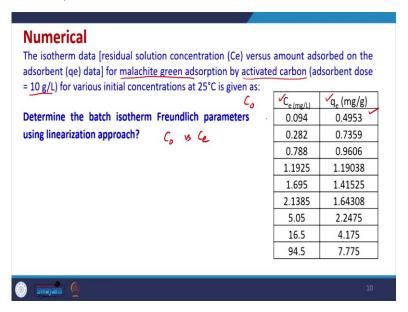
So, like in the previous, if we take the previous problem, we find that around 300 minute equilibrium is attached. So, we take any time more than 300 minutes. So, we can take maybe 360 minutes and we will fix the time. So, that will be equilibrium time. So, after this time. So each of the beaker will be kept for this much time in the incubator shaker at 25 degrees centigrade. And after that the adsorbent will be separated out. And from the supernatant, we will try to measure the residual concentration and we determine here the residual concentration which is at equilibrium because we have given enough time for equilibrium to attain.

And we will try to find out each of the equilibrium data which is there. So, this will be like this actual data will look like this that we have C0. And because that there is no factor of time, So C0 will be there 10, 20, 50, 100, 200, 350, 500 then we have residual concentration which is there. So, each of the residual concentrations will be known. And after that we determine that qe. So, this is like Ce this is concentration at equilibrium and then qe, qe can be determined as C0 minus Ce upon m or as previously we can find out is C0 minus Ce w into V. So, any of the formula can be used for finding out these values.

So, for first case suppose the equilibrium concentration is 8. So, this will be 10 minus 8 upon 10 because we have already used 10 gram per liter. So, this will be 2 upon 10 milligram per gram or 0.2 milligram per gram. So, similarly, we can find out each and we can draw a graph

like que versus Ce. So, this is called as adsorption isotherm at 25 degrees centigrade for one concentration solution. So, this is how we try to find out the graph.

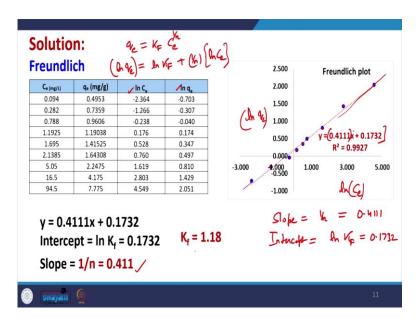
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Now, let us try to solve some problems to better understand this. So, here a numerical is given isotherm data is given where the residual solute solution concentration versus amount adsorbed on the adsorbent qe data is given for a dye which is malachite green adsorption by activated carbon and adsorbent dose again for simplicity has been taken as 10 grams per liter.

And these are the various concentrations, various for various residual directly equilibrium concentration and the quevalue is given, here the in place of C0 directly this value is given, now it is possible that in some of the questions only C0 versus Ce data is given. So, from that data you have to calculate the questions of the thin is the, so here directly Ce versus que data is given. Now, we have to find out the Freundlich and Langmuir parameters using a nonlinear or linearization approach.

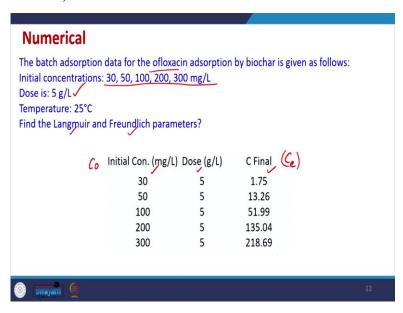
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So, suppose we have to find out for Freundlich. So Freundlich equation already we found out, the Freundlich equation is qe is equal to Kf Ce raise to 1 by n and it is a linear form is ln qe is equal to ln Kf plus 1 by n ln Ce. So, this equation is there. So, we can plot a curve of, ln qe versus ln Ce. So, what we do is that we have to check that we have to determine the ln Ce and ln qe. So, ln qe will be on the y axis and then ln Ce will be on the x axis and we can plot this and from the plot, the slope will be equal to, in from the equation the slope will be equal to 1 by n and the intercept will be equal to ln Kf.

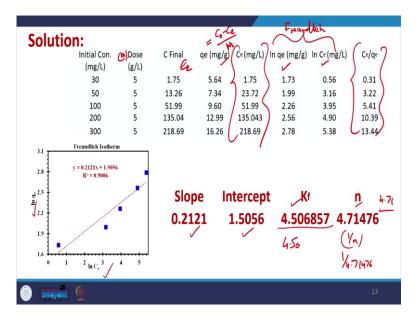
So, both we can determine. So, this is what is the Ce qe is known. So, we determine ln Ce ln qe, all the parameters are determined here. Now, we plot this by these points you can see here. All these points are there, and we fit a equation on these points. So, this equation is given by this, the R square value is 0.9927. So, fitting is good and we can use, so the intercept is 0., the slope is sorry 0.4111 and the intercept is 0.1732. So, we can see here, so, slope is equal to 1 by n 0.411 and intercept is this from this we can find out the Kf value. So, through this we can find out the both the parameters Kf and 1 by n.

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Similarly, we can find out these another equation which is given here. Here in place of directly given the Ce versus final data here initial concentration is given, dose is 5 gram per liter and final concentration which has been found is given here. And the dose is 5 grams per liter. So, we have difference we have in place of directly getting the Ce versus qe data, we have the initial concentration that means C0 versus Ce data is available here. Now, what we can do is we have to find out the Langmuir and Freundlich parameters for this ofloxacin adsorption by biochar.

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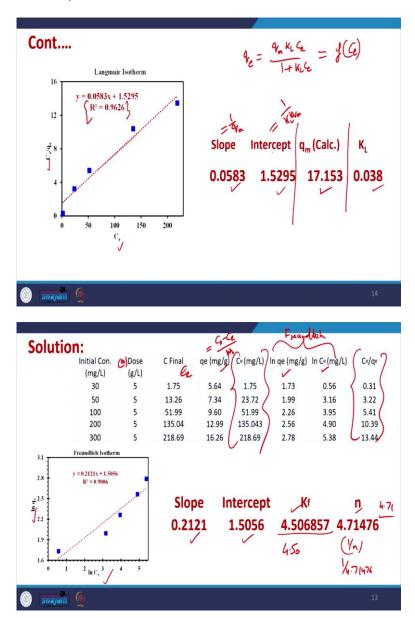


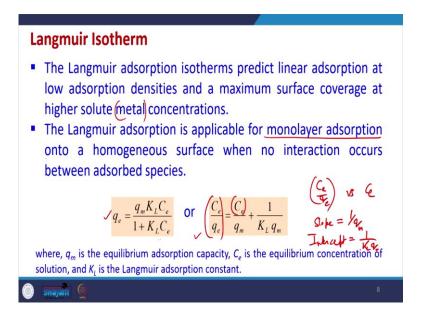
So, if we find out, so initial concentration is there, this dose is there q final or Ce is given, So we can find out this qe is equal to C0 minus Ce upon dose or we can call it M, so the

adsorbent dose is like M. So, qe has been found out Ce already known. So what we do is ln qe ln Ce, we determine and similarly, we can determine Ce by qe also, because we will use this column versus this column for finding out Langmuir parameters. And these two columns will be used for finding out Freundlich parameters.

We can perform the calculation directly. So, from here, if you plot In qe versus In Ce, the slope will be 0.2121 and intercept is 0.15056. So Kf and n can be found out or 1 by n can also be found out which will be equal to 1 by 4.71476. So, these number of digits are not essential, we can only keep up to a certain 4.50 is enough, the parametric value of 4.7 value, so we can always reduce to significant digits only for calculation sake it is given here.

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Now, similarly, we can plot the Ce by qe versus Ce data. So that here and Ce by qe versus Ce data, and we can here you can see here the plotting has been done. They have been linearized. So slope is 0.0583 and intercept is given. So once this is there, for Langmuir equation of this type, we know the slope is equal to 1 by qm and intercept is equal to 1 by Kl qm. So this slope is for this case, this slope is equal to 1 by qm and this is intercept is equal to 1 by Kl qm. So qm, we can take 1 divided by 0.0583, so this will be the answer and once qm is known, and intercept is known, we can determine the Kl value.

So through these equations, we can find out different parameters, and then we can start using this equation. So we can represent the data. What we have to do is that we should cross check what is the value of R square. So we can see here, the R square is better for Langmuir isotherm. So that means for this ofloxacin removal case, we should use the equation this qe equal to qm Kl Ce, 1 plus Kl Ce this expression and we can put these values in this equation and whatever is the final equation as a function of Ce, we can represent this data by this Langmuir equation. And this Langmuir, this data can be later on we use for plotting the equilibrium data on the curve or it can be used for designing the system later on.

So, that will be study later. So, these are Langmuir and Freundlich isotherms are the most common isotherm and to in today's lecture, we tried to understand how they can be determined. So, through this will end this lecture, in the next lecture, we will try to understand another important isotherm equation which is called as BET equation Brunauer–Emmett–Teller.

And that isotherm equation can be used in one of the apparatuses to find out the actual porosity parameters. So, different surface area, pore size all those things can be determined using the BET equation using the nitrogen adsorption data. So, this is there. So, we will continue further in the next lecture. Thank you very much.