Water and Waste Water Treatment

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Module No # 11
Lecture No # 52
Adsorption Isotherms

Hello everyone, we have been looking at adsorption, we are changing the phase of a set of compounds and what are you are going to look at is removal of multiple compounds of interest by adsorption. And you want to change phase, one phase is water we do not want it to be in the aqueous phase and you want to remove it and adsorb it on to another surface which is the activated carbon. The example, that we are looking at or the media of interest that we are considering.

Here I want to be able to understand how much use and if I use the certain amount of certain characteristics and certain surface area, what will be the final concentration of my effluent if the influent concentration is this? Here we have to look at the surface area, the concentration of the relevant solids in that particular volume. How much volume of water is going to come in contact?

And more important concentration initially and after equilibrium has been reached or it is going through the relevant system. Let us look at these aspects.

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$q \propto C$

Adsorption isotherms

We are going to look at adsorption isotherms which to understand the relationship between the q, the concentration of the relevant adsorbate on the adsorbent. And how it relates to concentration of the adsorbate in the water? Let us look at this.

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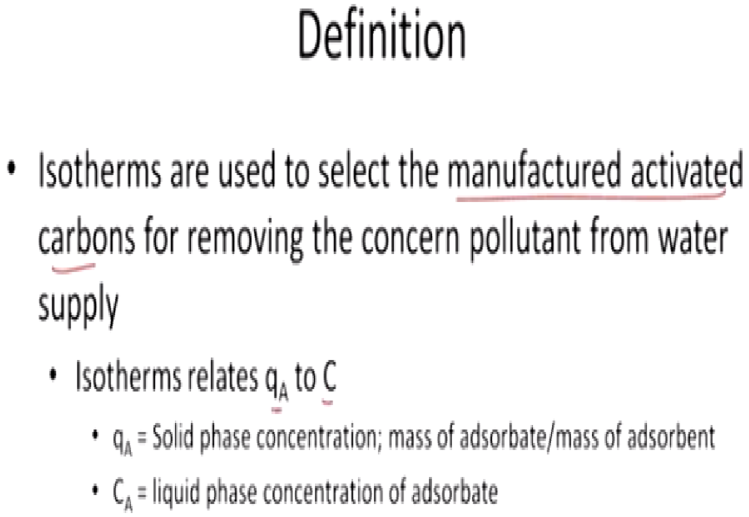

Definition

- Isotherms are used to select the manufactured activated carbons for removing the concern pollutant from water supply
  - Isotherms relates q_A to C
    - q_A = Solid phase concentration; mass of adsorbate/mass of adsorbent
    - C_A = liquid phase concentration of adsorbate

Isotherms are used to select the manufactured activated carbon and so forth. Isotherms relate q to C and this is something I already mentioned.

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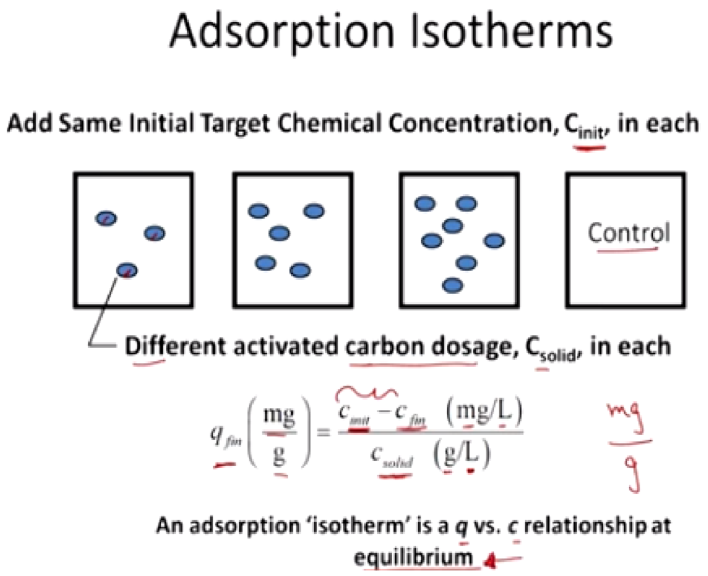

Adsorption Isotherms

Add Same Initial Target Chemical Concentration, C_{init}, in each

Different activated carbon dosage, C_{solid}, in each

$$q_{fin}\left(\frac{mg}{g}\right)=\frac{c_{init}-c_{fin}\ (mg/L)}{c_{solid}\ (g/L)} \qquad \frac{mg}{g}$$

An adsorption 'isotherm' is a *q* vs. *c* relationship at equilibrium

What do we have? How do I get this particular q? Add the same initial target chemical concentration in each of them. And different activated carbon dosages in each so the compound of interest C initial, the concentration of the compound of interest initially is the same but the dosage is different you see relatively less, more media and then one control. after 6 days or depending upon the kind of compound 4 days or such.

You are going to mix it and then let it reach equilibrium and then you are going to check this, what is this q? q final it is milligram per gram units, let us see how it comes. In a numerator you have going to have C initial. Concentration of the adsorbate initially and after equilibrium has been reached, so that is the relevant concentration by concentration of the relevant solid, grams per liter.

Milligrams per liter by grams per liter so then you are going to end up having milligrams of the compound adsorbed per gram of the relevant solid. And then adsorption isotherm is a q versus c relationship more importantly this is always at equilibrium keep in mind at equilibrium. Equilibrium is a state when the system has gone to the furthest extent possible or has been allowed to reach the furthest extent possible at the given temperature and pressure. It gives you an idea about how far the system can travel, layman's terms.

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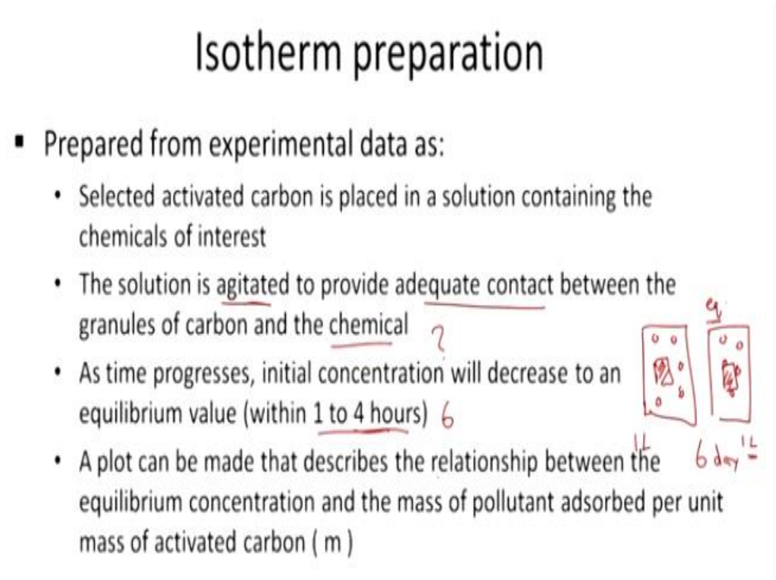

Isotherm preparation

- Prepared from experimental data as:
  - Selected activated carbon is placed in a solution containing the chemicals of interest
  - The solution is agitated to provide adequate contact between the granules of carbon and the chemical
  - As time progresses, initial concentration will decrease to an equilibrium value (within 1 to 4 hours)
  - A plot can be made that describes the relationship between the equilibrium concentration and the mass of pollutant adsorbed per unit mass of activated carbon (m)

Isotherms preparation, we will look at particular set of data later prepared from experimental data. Selected activated carbon is placed in a solution as we just talked about containing the chemical of interest. The solution is well mixed to provide contact between the granules of carbon and the relevant adsorbate or the chemical. The time depends 4 hours or 6 days, it depends upon the type of compounds.

Initial concentration will decrease, why will this concentration decrease? Initially if this is my media, well the media is never going to have such flats surfaces, I am just using that because I am poor at drawing. This is the compound so after sometime what will happen after equilibrium, 6 days or 4 hours or such? This is my media and some of the relevant compound will be adsorbed 1, 2, 3.

2 moles in the water while 3 moles are absorbed, this is after 6 days so equilibrium has been reached that is what we are assuming. The initial concentration is decreasing now earlier there were 5 moles per one liter of water. Here there are only 2 moles per 1 liter of water because 3 moles are adsorbed onto the relevant solid. That is something to keep in mind, initial concentration will decrease to an equilibrium value. And then you can plot it and get the relevant relationship and we will look at this.

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Types of isotherms

Types of isotherms, there are different relationships depending upon the types of compounds, the mode of adsorption. We will look at the most simplest one which is rarely used.

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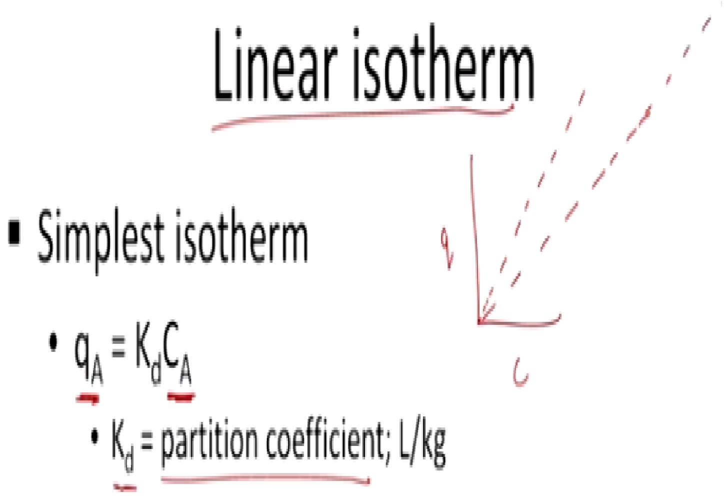

Linear isotherm

- Simplest isotherm
  - $q_A = K_d C_A$
    - K_d = partition coefficient; L/kg

This is the linear isotherm, q is linearly dependent upon the concentration of the compound in the water. It is the partition coefficient, K_d is the partitioning coefficient. But here it says more or less like if this is very high, even q will be very high. But that is never going to happen why is that? Because your media has at the end of the day certain properties, certain limited surface area.

It is not as if you keep increasing the concentration the q also is going to increase. If this is C and q, this is the reasonable but it is never going to be like this. It is not that slope it is not going to be end up looking like this. Because there you have thresholds so this is rarely used.

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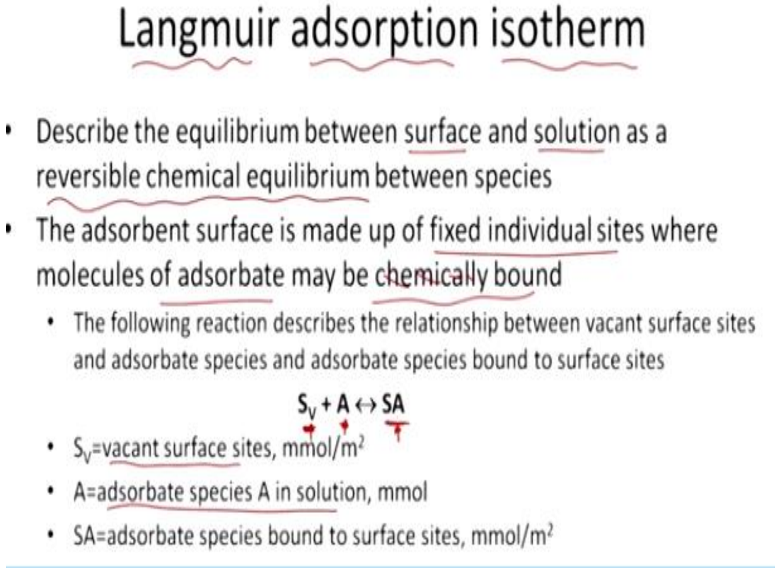

Langmuir adsorption isotherm

- Describe the equilibrium between surface and solution as a reversible chemical equilibrium between species
- The adsorbent surface is made up of fixed individual sites where molecules of adsorbate may be chemically bound
  - The following reaction describes the relationship between vacant surface sites and adsorbate species and adsorbate species bound to surface sites

$$S_V + A \leftrightarrow SA$$

  - S_V=vacant surface sites, mmol/m^2
  - A=adsorbate species A in solution, mmol
  - SA=adsorbate species bound to surface sites, mmol/m^2

And here we are going to now move on to looking at Langmuir adsorption isotherm. Here we are going to assume that there are limited number of sites and there is equilibrium between the compound, the sites available for adsorption and the adsorbed sites. That is what we are going to look at, so equilibrium between surface and solution and we are assuming that it is a reversible chemical equilibrium between these species.

The species are the surface and the relevant compound, the adsorbent surface is made up of fixed individual sites. We have a limited number of individual sites where the adsorbate can be chemical bounded or it can be bound if not chemically bound. Here we have this is the site, this is i think the compound and this is the area, let us look at the relevant nomenclature.

And this is the relevant bond site, let us see compound being adsorbed onto your relevant site, let us look at the nomenclature. This is the vacant site, Sv is the vacant site, milli moles per meter square, adsorbate species in solution this is the concentration in the aqueous phase this is the vacant sites available per meter square. And this is the sites that have been adsorbed. Adsorbed species bound to surface so there is equilibrium between this, so it can go one way or the other, that is something to keep in mind.

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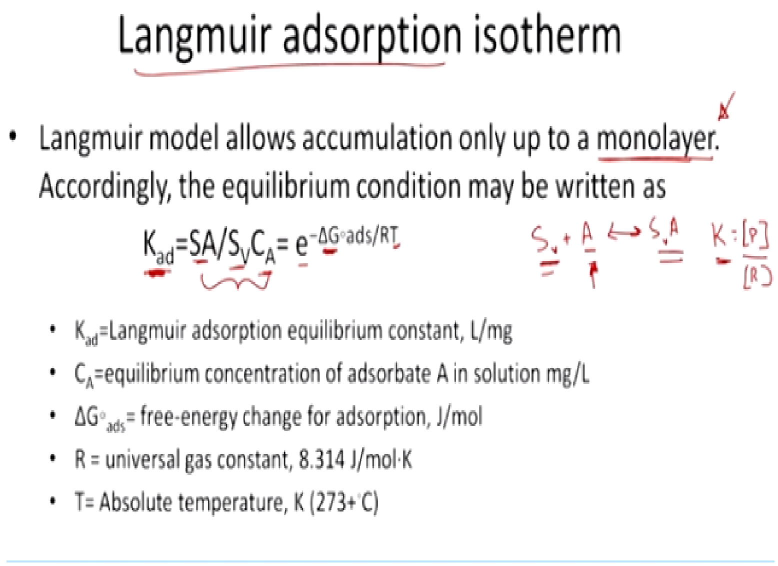

Langmuir adsorption isotherm

- Langmuir model allows accumulation only up to a monolayer. Accordingly, the equilibrium condition may be written as

$$K_{ad}=SA/S_VC_A= e^{-\Delta G^{\circ}ads/RT}$$

$$S_v + A \leftrightarrow S_vA \qquad K:\frac{[P]}{[R]}$$

  - K_{ad}=Langmuir adsorption equilibrium constant, L/mg
  - C_A=equilibrium concentration of adsorbate A in solution mg/L
  - ΔG°_{ads}= free-energy change for adsorption, J/mol
  - R = universal gas constant, 8.314 J/mol·K
  - T= Absolute temperature, K (273+°C)

Langmuir adsorption isotherm, so let us take this forth, so we are looking at this Langmuir adsorption. And one fundamental aspect about this is we are assuming that we are only going to have one layer or mono layer of adsorption. This is my site and once all these sites have been taken up that is it you are not going to have other layers. That is one aspect because as you saw or as we discussed with respect to physical adsorption where Vander Waals forces of attraction are relevant especially in the context of granular activated carbon.

You can have different layers, it is not only going to be mono layer, it is relevant over larger or longer distances. That is one aspect to keep in mind, we will come back to that. Equilibrium condition can be written so we have that Sv vacant sites plus the relevant compounds being in equilibrium with the adsorbed sites. If this is the equilibrium constant, K that is going to be equal to products by the reactants.

That is what we have products which is the Sa by Sv, number of vacant adsorb sites into the concentration of A. And that ΔG, this is pretty, this is something that of equilibrium relationship K and ΔG^0. We are concerned mostly with this but now you can see the effect of temperature as you increase or decrease the temperature, you can see how K will be affected and thus this equilibrium between Sva and Sv that is something to keep in mind.

What do we have here? K_{ad} is the Langmuir adsorption equilibrium constant, C_A as I mentioned is the concentration of A in the relevant solution, ΔG^0 is the free energy change for adsorption R and T, this is something that I have let me see how I can use this to get it done.

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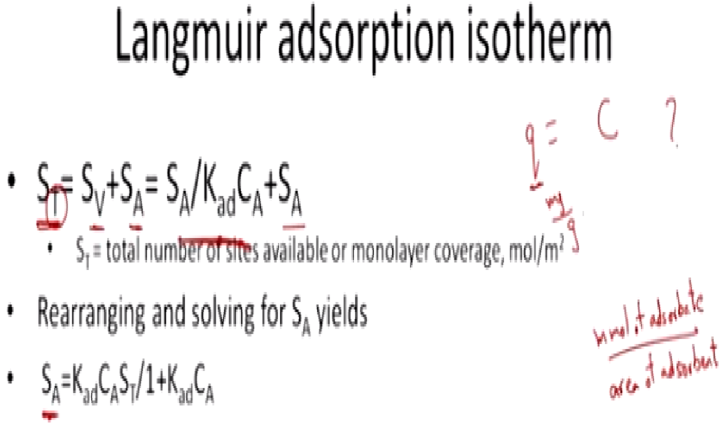

Langmuir adsorption isotherm

- $S_T = S_V + S_A = S_A/K_{ad}C_A + S_A$
    - S_T = total number of sites available or monolayer coverage, mol/m^2
- Rearranging and solving for S_A yields
- $S_A = K_{ad}C_AS_T/1 + K_{ad}C_A$

$q = C$?

mg/g

$\frac{\text{mmol of adsorbate}}{\text{area of adsorbent}}$

But I want to be able to get a relationship where I end up with q and C, how do I do that? For that I will use the relevant assumption that S total. There are fixed number of total sites, some are vacant, some are adsorbed Sv + Sa, so some are adsorbed and Sv we know that we can get it from the relationship here, we can get that relationship here and now we can write it in these terms.

S_T is equal to total number of sites available or mono layer coverage, rearranging we are going to get this particular term. But this is in milli moles or moles per meter square but here my units are milligram of the adsorbate per gram of the adsorbent. Let us see how we will go from here to there, one is here it is area milli mole of adsorbate or my compound per area of adsorbent.

But I want to have milli gram of adsorbate per gram of adsorbent, so how do I do that? One is molecular weight of the adsorbate and the other one is area per mass of the adsorbate. I have to multiply it with that.

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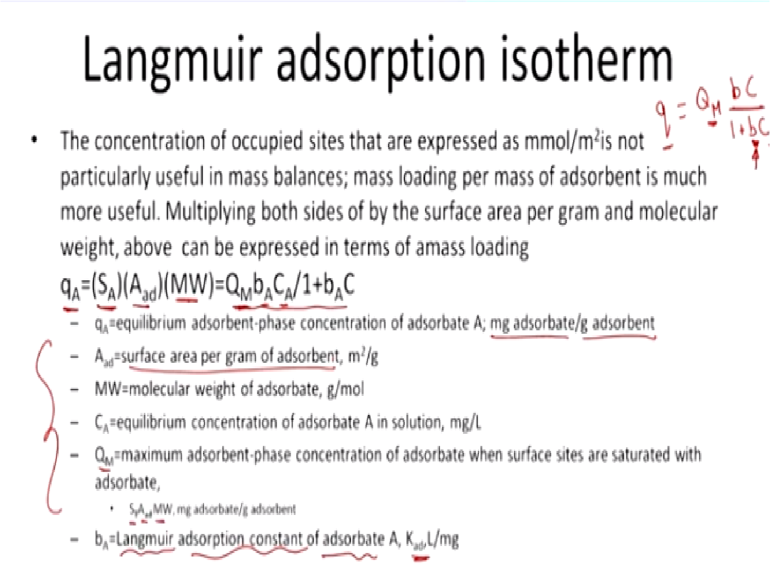

Langmuir adsorption isotherm

$q = Q_M \frac{bC}{1+bC}$

- The concentration of occupied sites that are expressed as mmol/$m^2$is not particularly useful in mass balances; mass loading per mass of adsorbent is much more useful. Multiplying both sides of by the surface area per gram and molecular weight, above can be expressed in terms of amass loading
  $q_A=(S_A)(A_{ad})(MW)=Q_M b_A C_A/1+b_A C$
  - q_A=equilibrium adsorbent-phase concentration of adsorbate A; mg adsorbate/g adsorbent
  - A_{ad}=surface area per gram of adsorbent, m^2/g
  - MW=molecular weight of adsorbate, g/mol
  - C_A=equilibrium concentration of adsorbate A in solution, mg/L
  - Q_M=maximum adsorbent-phase concentration of adsorbate when surface sites are saturated with adsorbate,
    - $S_T A_{ad}$MW, mg adsorbate/g adsorbent
  - b_A=Langmuir adsorption constant of adsorbate A, K_{ad},L/mg

How do I get q? This is what I had earlier, moles per liter square by multiplying with Ad which is meter square per gram and molecular weight which is grams per moles, I will end up with milli grams per gram, milli gram of adsorbate per gram of adsorbent. That is what we discussed earlier so then this is going to end up like this and q max, q is equal to q max. it depends upon S total where I have that you have S total and I multiply it with my particular area and molecular weight.

I will end up getting q max, so that is what I have so I ended up with q max and relevant terms, b A is nothing but this K and C is the concentration of the compound at equilibrium. What do I have? I have q is equal to q max there is a certain limit, it is a maximum, it is limited by a particular threshold b into concentration of the compound in the water at equilibrium +1 by b C, b is also K.

Please note that the key aspects are we are having a relationship between q and C and here we have equilibrium constant or which we are calling as Langmuir adsorption constant of adsorbate. This is a function of 2 aspects both the adsorbate and the adsorbent. That is something to keep in mind and it is also going to have a q maximum. That is what we have here and these are the general aspects which we already discussed as i mentioned q maximum s total area of adsorption or surface area per gram of adsorbent.

Surface area available per gram of adsorbent into molecular weight of your adsorbate, that is something we looked at.

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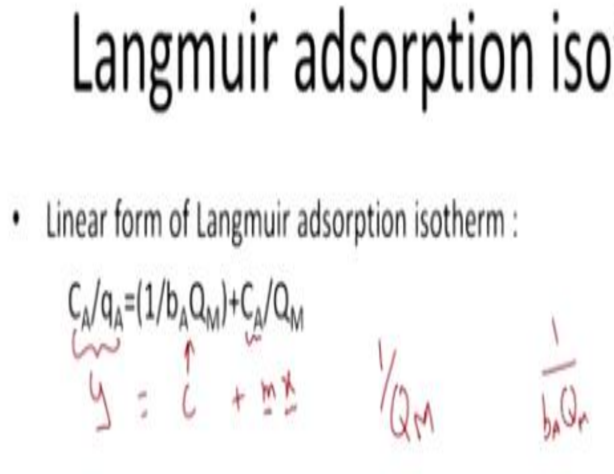

Langmuir adsorption isotherm

- Linear form of Langmuir adsorption isotherm :

$C_A/q_A=(1/b_AQ_M)+C_A/Q_M$

$y = c + mx$ $\quad 1/Q_M \quad \frac{1}{b_AQ_A}$

Linear form of Langmuir adsorption isotherm, sometimes I want to see the linear form so that I can fit the data relatively easily. if I play around with the variables this is what I end up with as you can see if this is y is equal to mx+ C, this is my intercept m or x, CA is my x. m, the slope is 1 by Q M and my intercept is 1 by bA Q_M, that is something to keep in mind.

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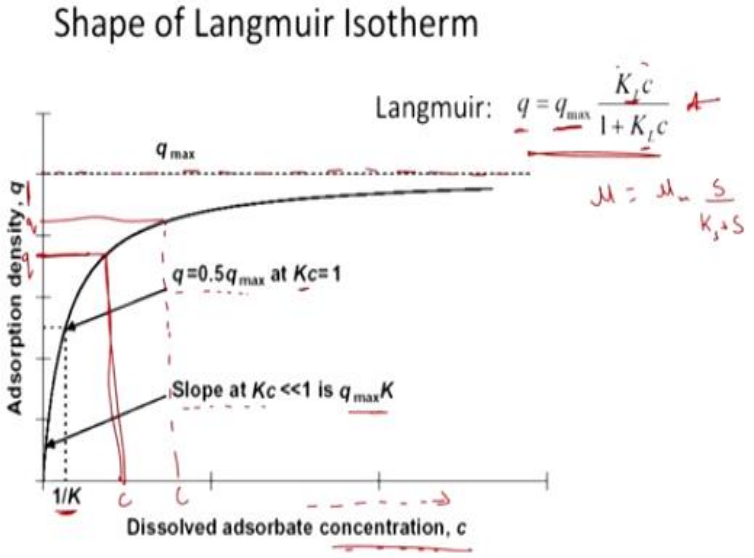

Shape of Langmuir Isotherm

Langmuir: $q = q_{max}\frac{K_L c}{1+K_L c}$

$\mu = \mu_m \frac{S}{K_s+S}$

Let us look at the shape of this Langmuir isotherm, q is equal to q max into B c by 1 + B c. Note that different people are using different nomenclature but one aspect is you are always going to have a maximum and the relevant coefficient here adsorption constant. This is the q max as you can see there is going to be a maximum so that something to keep in mind, on the y axis you have q, on the x axis you have the dissolved adsorbate concentration at equilibrium.

At 1 by k if you think of it, this is like our mono kinetics where you have mu is equal to mu max into s by k s + s and so forth. You can look at the relationship and so forth. But here similarly we have the relevant setup at 1 by k q equal to 0.5 q max at kc is equal to 1, k into c is equal to 1. If k into c = 1 you see that q = q max by 2.

That is something to keep in mind and slope when Kc is far less than 1 is q max K when Kc is far less than 1 is q max to k that you can see from the relevant relationship. This is how the Langmuir isotherm is going to look like it going to approach it maximum at the later so here even though you are increasing the concentration, what do you see here? Let us compare this at a particular C value, this is the relevant case at a particular series, a particular queue.

And even here you can see the relevant efficiency of removal both at higher and lower concentration, that is something to keep in mind.

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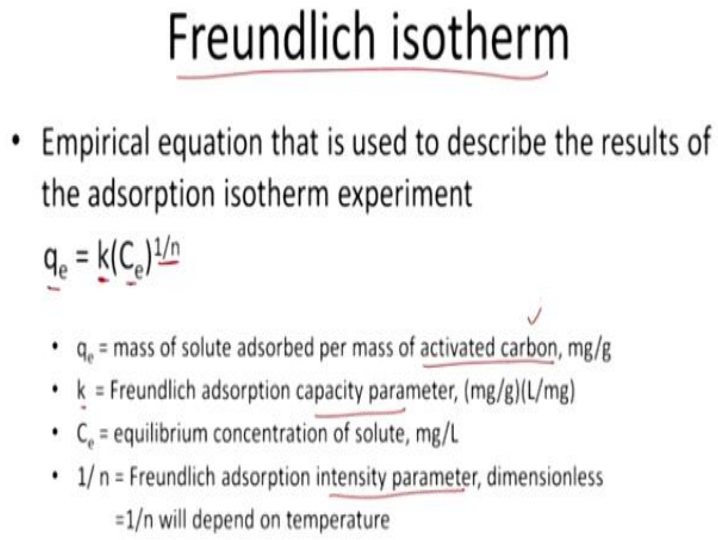

Freundlich isotherm

- Empirical equation that is used to describe the results of the adsorption isotherm experiment

$$q_e = k(C_e)^{1/n}$$

  - q_e = mass of solute adsorbed per mass of activated carbon, mg/g
  - k = Freundlich adsorption capacity parameter, (mg/g)(L/mg)
  - C_e = equilibrium concentration of solute, mg/L
  - 1/ n = Freundlich adsorption intensity parameter, dimensionless
    - =1/n will depend on temperature

Freundlich isotherm, let us see so we were looking at Langmuir until now Langmuir where we have a threshold and another aspect, is it is mono layer. But we know that especially with granular activated carbon where you have hydrophobic compound being adsorbed onto the media and the key aspect is that we have the Vander Waal forces of attraction which do not limit the adsorption to only layer but multiple layers.

And thus, we see that rather than Langmuir for the relevant granular activated relevant adsorption, Freundlich isotherm is relative more or a better fit. It is an empirical equation that is used to describe the results of adsorption isotherm especially for granular activated carbon. q = K the capacity and the Ce, 1 by n here, people sometimes people use n. You have to look at it before you look at the relevant units or applications.

This will give you an idea about the intensity, K will give you an idea about the capacity. qe is equal to mass of the solute adsorbed per adsorbent. And k is the Freundlich absorption capacity parameter and Ce is the equilibrium concentration of solute. And 1 by n is Freundlich adsorption intensity parameter as I mentioned which is dimensionless.

But some people use m so you have to look at that. This is a pretty good fit or typically explains the adsorption on the activated carbon pretty well, that is something to keep in mind.

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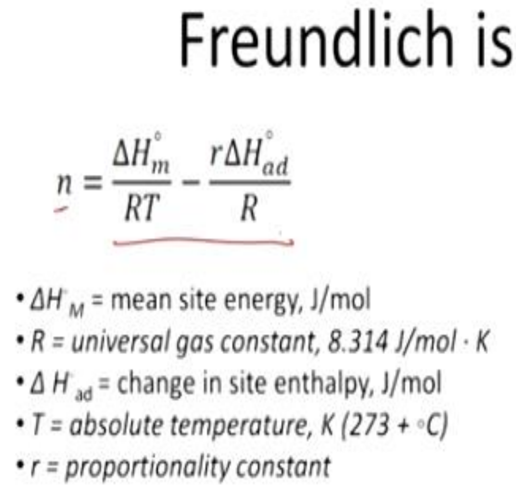

Freundlich isotherm

$$\underline{n} = \underline{\frac{\Delta H_m^{\circ}}{RT} - \frac{r\Delta H_{ad}^{\circ}}{R}}$$

- ΔH_M = mean site energy, J/mol
- R = universal gas constant, 8.314 J/mol · K
- ΔH_{ad} = change in site enthalpy, J/mol
- T = absolute temperature, K (273 + °C)
- r = proportionality constant

And this n will depend upon temperature as you can see here enthalpy, we will not go into that in detail here. One aspect is n will depend upon temperature that is something to keep in mind.

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Freundlich isotherm

$q = K C^{1/n}$

- The linear form of the Freundlich equation:
  - $\log(q_e) = \log(k) + (1/n)\log C_e$

$y = C + m x$

Freundlich isotherm linear form, I have q = k C to the power of 1 by n. If I take the logarithm y = mx + c.

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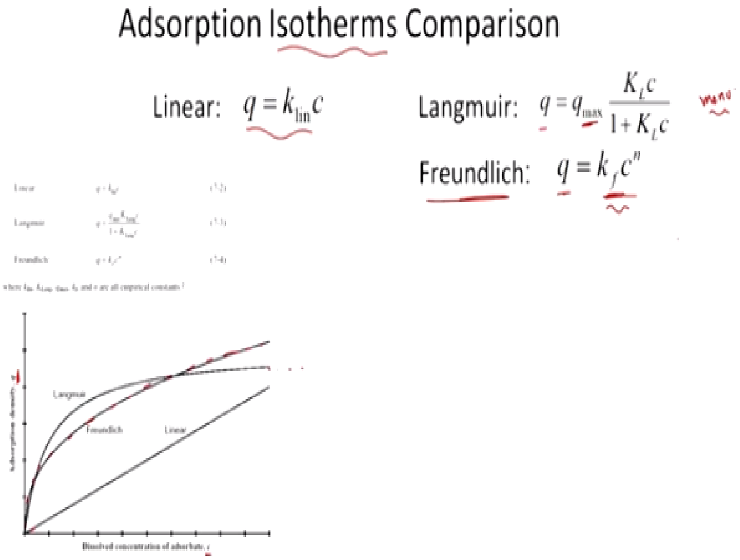

Adsorption Isotherms Comparison

Linear: $q = k_{\text{lin}} c$

Langmuir: $q = q_{\max}\dfrac{K_L c}{1 + K_L c}$ mono

Freundlich: $q = k_f c^n$

Here we have a comparison of the different kinds of isotherms, we have looked at adsorption isotherms linear rarely used but you see the relationship between q the concentration adsorbed on to the adsorbent. And C the concentration of the compound in the aqueous phase. But it can be different phases too so linear it is increasing linearly and then q with a q max where is that?

Langmuir, so you see it quickly reaches a q max saturation and q with respect to Freundlich, you see the different profile out here, key aspect is q max and mono layer, here it allows for heterogeneous adsorption and thus different layers, that is something to keep in mind let us move on.

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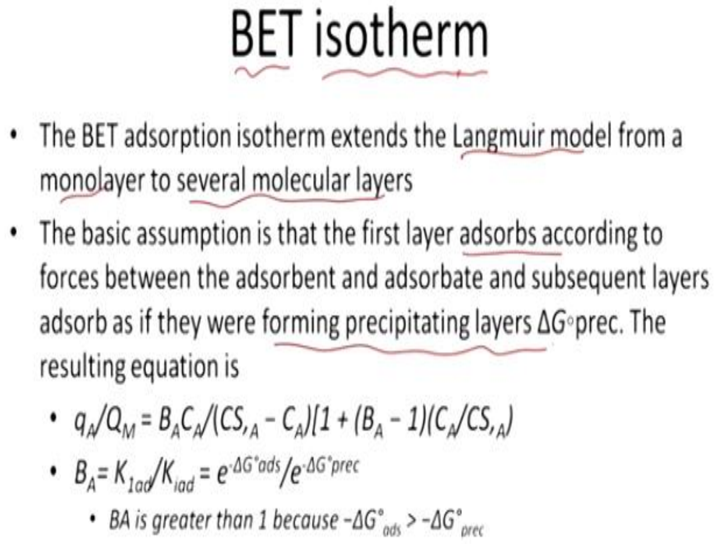

BET isotherm

- The BET adsorption isotherm extends the Langmuir model from a monolayer to several molecular layers
- The basic assumption is that the first layer adsorbs according to forces between the adsorbent and adsorbate and subsequent layers adsorb as if they were forming precipitating layers ΔG°prec. The resulting equation is
  - $q_A/Q_M = B_A C_A/(CS,_A - C_A)[1 + (B_A - 1)(C_A/CS,_A)$
  - $B_A = K_{1ad}/K_{iad} = e^{-\Delta G^\circ ads}/e^{-\Delta G^\circ prec}$
    - BA is greater than 1 because $-\Delta G^\circ_{ads} > -\Delta G^\circ_{prec}$

We have another isotherm, we will just look at this, look at the overview the Langmuir is going to be looking at or consume only one-layer, mono layer. This BET isotherm takes it further it is going to allow for different layer of adsorption. Here we are going to use the basis from Langmuir and you are going to say there is one. And then once that is filled up you are going to have another layer and typically if the first one is assumed to be adsorption, the other one is precipitation.

The only thing is here we are going to allow for multiple layers, to several molecular layers. Langmuir is for mono layer, this one is for several molecular layers. Here we are saying the first layer adsorbs and subsequent layers adsorb as if they were forming precipitating layers that is the relevant aspect. Relevant equation we are not going to mug up anything you just need to be aware of it.

But key aspect is this allows for several layers not just mono layers. You have the different variables, you can look at those.

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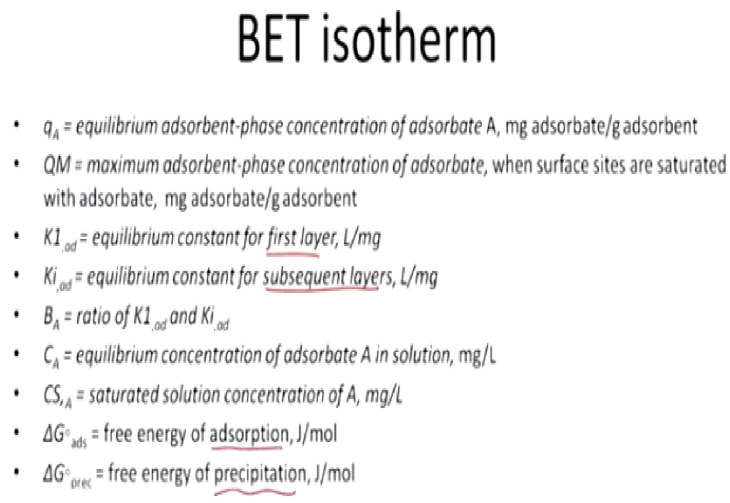

BET isotherm

- q_A = equilibrium adsorbent-phase concentration of adsorbate A, mg adsorbate/g adsorbent
- QM = maximum adsorbent-phase concentration of adsorbate, when surface sites are saturated with adsorbate, mg adsorbate/g adsorbent
- $K1_{,ad}$ = equilibrium constant for first layer, L/mg
- $Ki_{,ad}$ = equilibrium constant for subsequent layers, L/mg
- B_A = ratio of $K1_{,ad}$ and $Ki_{,ad}$
- C_A = equilibrium concentration of adsorbate A in solution, mg/L
- $CS_{,A}$ = saturated solution concentration of A, mg/L
- $\Delta G°_{ads}$ = free energy of adsorption, J/mol
- $\Delta G°_{prec}$ = free energy of precipitation, J/mol

We have the more or less the same terms, q maximum equilibrium constant for the first layer, we had that earlier but now we also have one for different layers and here we have to keep in mind that the first layer adsorption and the other layers we are assuming that to be precipitation.

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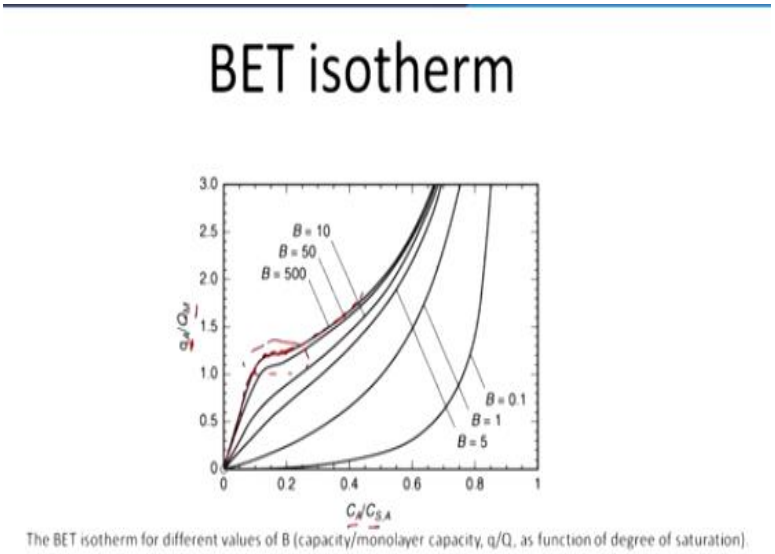

BET isotherm

The BET isotherm for different values of B (capacity/monolayer capacity, q/Q, as function of degree of saturation).

Here in this picture, you can see that relatively clearly so here why is this flat occurring here? The first layer has been saturated and after this first layer has been saturated then you are going to have adsorption on the other layers. That is what you see out here, q as a function of q maximum and C A by CSA. This plateau or such that you see here because the first layer has been saturated.

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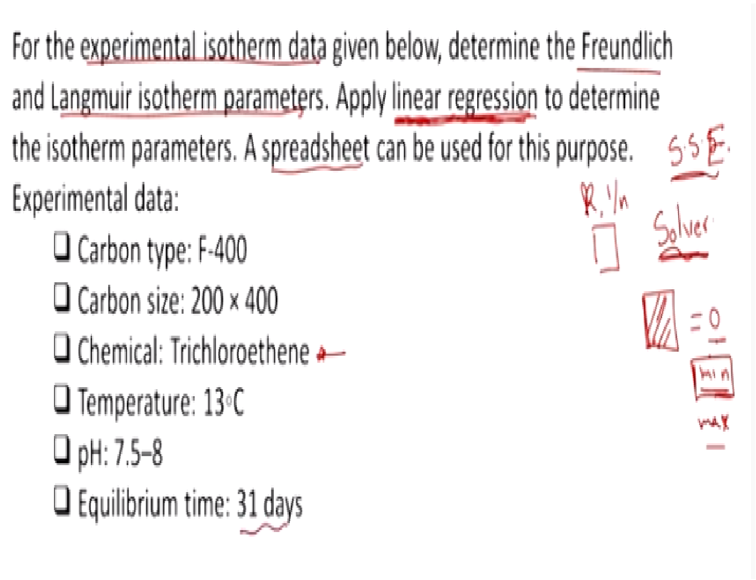

For the experimental isotherm data given below, determine the Freundlich and Langmuir isotherm parameters. Apply linear regression to determine the isotherm parameters. A spreadsheet can be used for this purpose.

Experimental data:

- ❑ Carbon type: F-400
- ❑ Carbon size: 200 × 400
- ❑ Chemical: Trichloroethene
- ❑ Temperature: 13°C
- ❑ pH: 7.5–8
- ❑ Equilibrium time: 31 days

Let us move on and look at relevant data and look at an example. We have some experimental isotherm data, determine the Freundlich and Langmuir isotherm parameters. First, I want to find the parameters and then apply linear regression, I told you how to go about it, typically looking at sum of squared errors. You can do this in excel by setting the cells and calculating the sum of squared errors and minimizing the sum of squared errors by using a tool called solver.

This will let you to change a particular cell to either 0 or to minimum or to maximum, how will you change this to come to 0, minimum or maximum? By changing another cell. Here sum of squared errors as to be minimum, so I will say that this cell of interest has to be minimum and what can you change? You can change my parameters of interest, my parameters of instant interest are k and 1 by n.

You can do this in excel using solver but people use the built-in functions but that would not typically solve your purpose in the long term. Linear regression to determine the isotherm parameters but for ease of calculation or analysis, the question ask you to look at first linearize the relevant equation and then apply regression. Spreadsheet meaning excel can be used. What is the data?

We have different carbon type, the chemical trichloroethane, temperature pH and so forth. Equilibrium time, so considerable time has been given so we are assuming equilibrium has been achieved and this is the key aspect we have.

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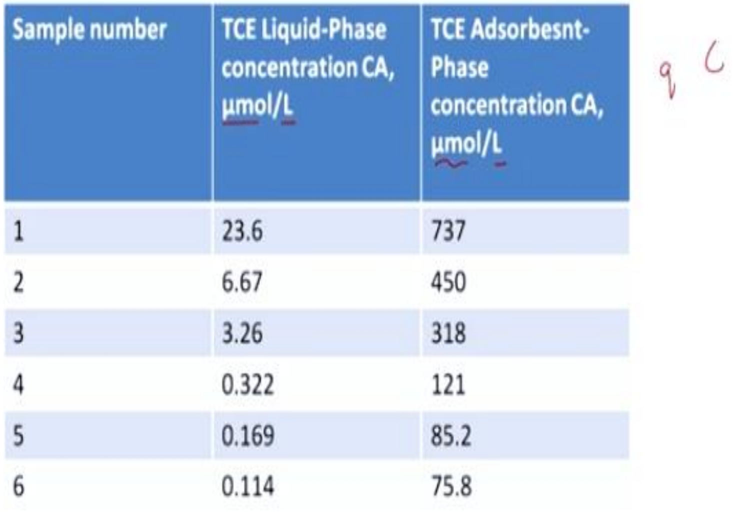

Sample number	TCE Liquid-Phase concentration CA, µmol/L	TCE Adsorbesnt-Phase concentration CA, µmol/L
1	23.6	737
2	6.67	450
3	3.26	318
4	0.322	121
5	0.169	85.2
6	0.114	75.8

TCE, liquid phase concentration micromoles per liter, TCE adsorbent phase concentration micro moles per liter, this is the adsorbent phase this is the liquid phase concentration. You have the relevant values out here. Then you can play around with it and calculate q and C, well some are already given indirectly.

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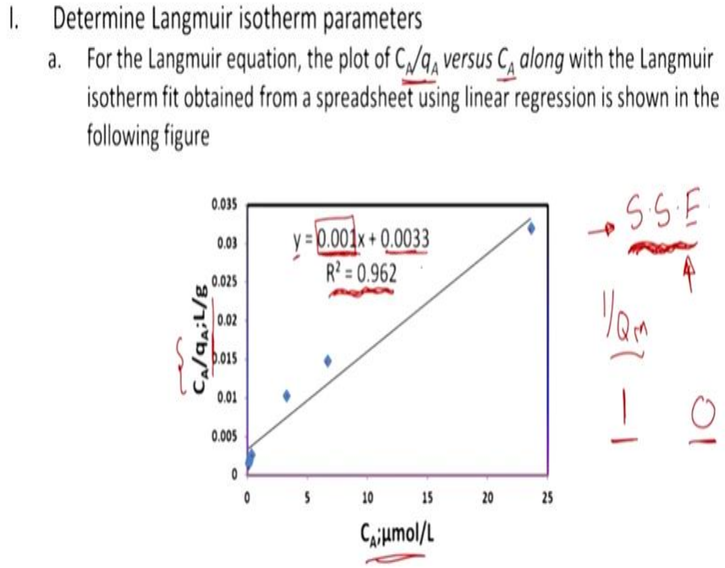

I. Determine Langmuir isotherm parameters

a. For the Langmuir equation, the plot of C_A/q_A *versus* C_A *along* with the Langmuir isotherm fit obtained from a spreadsheet using linear regression is shown in the following figure

For the Langmuir isotherm, we are going to linearize it, there was a particular way to linearize it. Here you have C A by q A as the Y and CA here as X and this way you can linearize it. You saw the relevant equation there. And then I am going to plot the data, all here my TA used the excel and asked it to fit it directly. But I urge you to learn how to use the sum of squared errors at this point when we are at this point, the TA will give a link to look at or understand how to calculate.

Or try to find best fit by minimizing this sum of squared errors, so here we have this y, this is y = mx + C. But if you look at the relevant variables I think this particular slope was 1 by QM so let us see.

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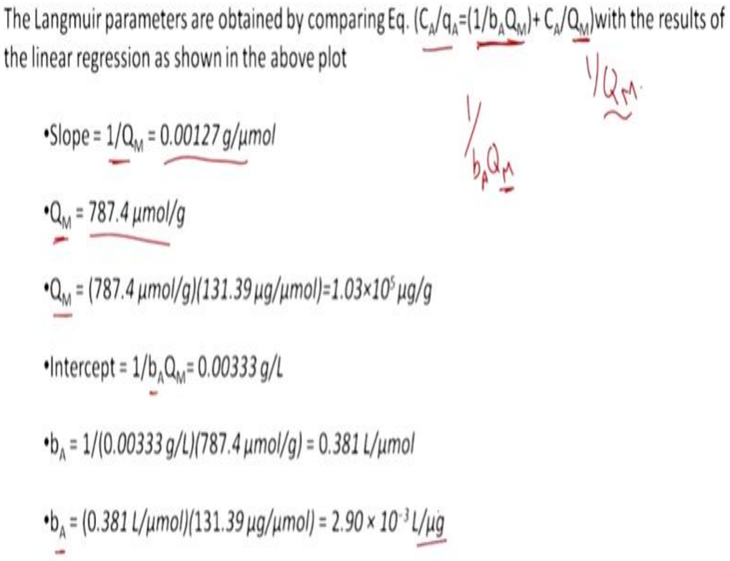

The Langmuir parameters are obtained by comparing Eq. ($C_A/q_A=(1/b_AQ_M)+C_A/Q_M$)with the results of the linear regression as shown in the above plot

$1/Q_M$

$1/b_AQ_M$

- Slope = $1/Q_M = 0.00127\ g/\mu mol$
- $Q_M = 787.4\ \mu mol/g$
- $Q_M = (787.4\ \mu mol/g)(131.39\ \mu g/\mu mol)=1.03\times10^5\ \mu g/g$
- Intercept = $1/b_AQ_M= 0.00333\ g/L$
- $b_A = 1/(0.00333\ g/L)(787.4\ \mu mol/g) = 0.381\ L/\mu mol$
- $b_A = (0.381\ L/\mu mol)(131.39\ \mu g/\mu mol) = 2.90\times10^{-3}\ L/\mu g$

1 by Q_M, this is the linear relationship, this is the intercept, 1 / Q_M is the slope. Slope is 1 / Q_M, from that I can calculate Q_M. And then I know the intercept is this but here note that you are having the rounded off values, so that will give you considerable error but R square, another aspect here, R square will give you an idea about how good or how well the data is explained by this model compared to the using just the average.

If R square is 1 that means it is very well explained or perfectly explained if it is 0 it is very poorly explained. It is also going to take into account the sum of squared errors. R square of 0.96 is good by not remarkably great. R square of 0.96 is good but I would suggest that you look at sum of squared errors. But that might not be good to look at when you are using different kinds of equations here.

We will stick with R square for now so Q_M, we already have Q_M and I know the intercept which is 1 / (b_AQ_M), I already know Q_M, now I can calculate b_A. And that is what we are going to do, here we are going to calculate b A. I am not talking in detail about the relevant units, you can play around with the units and figure out how to get that done?

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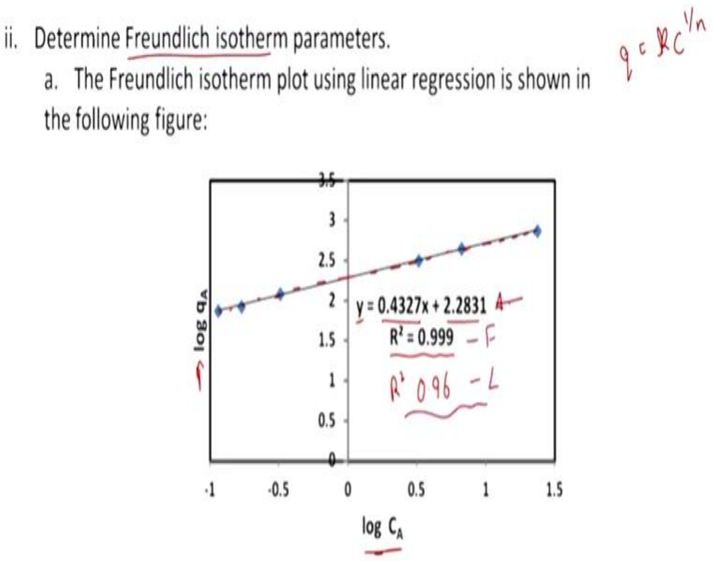

ii. Determine Freundlich isotherm parameters.

a. The Freundlich isotherm plot using linear regression is shown in the following figure:

$q = KC^{1/n}$

And then Freundlich was what now? q = k into C to the power of 1 / n, if you take the logarithm you will linearize that. Here log q on the y axis and log C on x axis, q and C A you have that from your relevant experimental data and then TA fit the relevant model. And when he fitted it and we see that R square is now much better earlier it was I think 0.96 now it is 0.99 and it is y = mx + C.

Here with relatively simplistic analysis, we are saying that the Freundlich isotherm is doing better at explaining the data compared to the Langmuir one. And now let us go about calculating the relevant constant here.

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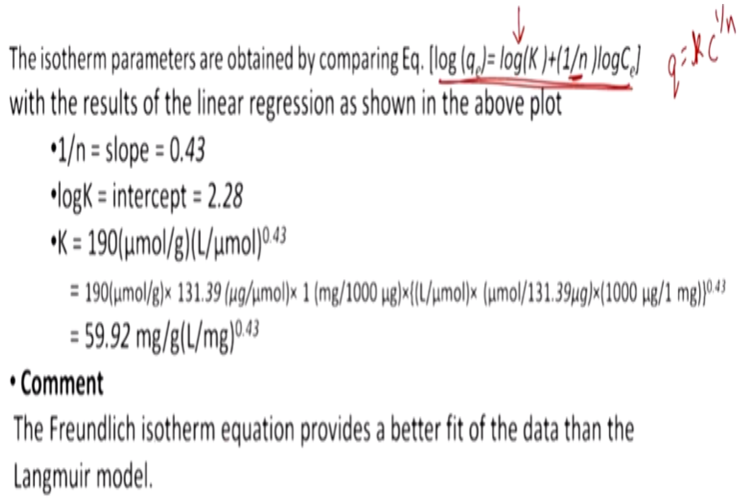

The isotherm parameters are obtained by comparing Eq. [$\log(q_e) = \log(K) + (1/n)\log C_e$] with the results of the linear regression as shown in the above plot

- $1/n$ = slope = 0.43
- $\log K$ = intercept = 2.28
- $K = 190(\mu mol/g)(L/\mu mol)^{0.43}$

  $= 190(\mu mol/g) \times 131.39\ (\mu g/\mu mol) \times 1\ (mg/1000\ \mu g) \times \{(L/\mu mol) \times (\mu mol/131.39\mu g) \times (1000\ \mu g/1\ mg)\}^{0.43}$

  $= 59.92\ mg/g(L/mg)^{0.43}$

- **Comment**

The Freundlich isotherm equation provides a better fit of the data than the Langmuir model.

Let us see what we have. This is the linearized one, earlier it was q = k into C to the power of 1 by n, now by taking logarithm, you linearize the relevant equation, so what is the slope? y = mx + C, this is the slope 1 by n from that I am going to get that and intercept is log k, that is what we have out here, from that I can calculate the relevant variables. This is what we have discussed from, Freundlich isotherm provides a better fit.

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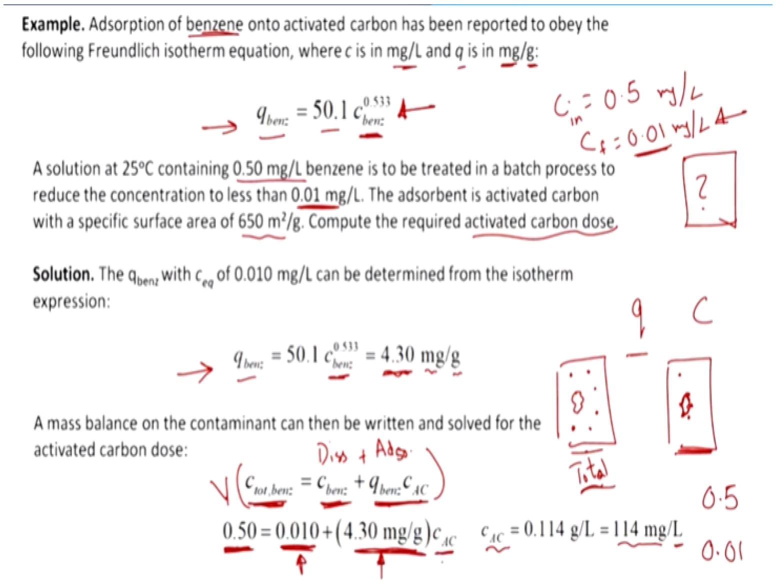

Example. Adsorption of benzene onto activated carbon has been reported to obey the following Freundlich isotherm equation, where *c* is in mg/L and *q* is in mg/g:

$$q_{benz} = 50.1\, c_{benz}^{0.533}$$

A solution at 25°C containing 0.50 mg/L benzene is to be treated in a batch process to reduce the concentration to less than 0.01 mg/L. The adsorbent is activated carbon with a specific surface area of 650 m²/g. Compute the required activated carbon dose.

Solution. The q_{benz} with c_{eq} of 0.010 mg/L can be determined from the isotherm expression:

$$q_{benz} = 50.1\, c_{benz}^{0.533} = 4.30\ mg/g$$

A mass balance on the contaminant can then be written and solved for the activated carbon dose:

$$V\left(c_{tot,benz} = c_{benz} + q_{benz}c_{AC}\right)$$

$$0.50 = 0.010 + (4.30\ mg/g)c_{AC} \qquad c_{AC} = 0.114\ g/L = 114\ mg/L$$

And then another example, here we have Freundlich information for a particular compound, what is this compound? It is for benzene. Adsorption of benzene onto activated carbon has been reported to obey the following Freundlich isotherm equation where C is concentration of benzene in the aqueous phase in milligrams per liter. And q is the concentration of benzene in milligrams adsorbed onto gram of the activated carbon.

This is what we have, so 25 degrees centigrade and all that fine and 0.5 milligrams per benzene is to be treated, this is the initial concentration. Initial concentration is 0.5, C initial is 0.5 milligram per liter. In a batch process, main aspect of batch process is to reduce the concentration to less than 0.01. C final has to be 0.01 milligram per liter.

The adsorbent is activated carbon with specific surface area of 650 meter square per gram, compute the required activated carbon dose. Here we just looked at general aspect, here what is it that we have? This is the final that I want and I want to know how much activated carbon I have to put in this particular solution per liter, what is the relationship? I know that this is already the relationship.

Let us use that here, this 0.01 is the one at equilibrium this C final will be the one at equilibrium or after equilibrium has been reached. In this relationship this C benzene is going to be equal to 0.01. When I plug in 0.01 looks like I will end up with q the equilibrium one that is going to be our q which is going to be in equilibrium with the C. At equilibrium is going to be 4.3 milligrams of benzene per gram of the activated carbon.

One aspect to notice that earlier this is activated carbon and this is benzene initially 1, 2, 3, 4, 5, 6 and then later. I have only one in the solution and 1, 2, 3, 4, 5 moles are absorbed onto the activated carbon. But the total moles or total mass is still the same, the total mass is still 6 or total number of moles per volume is still 6 here. Total number of moles is that because it is a batch process, the total mass is conserved there.

C total benzene will be equal to the benzene in the aqueous phase and benzene adsorbed onto the relevant activated carbon. Initial one is 0.5 this is per unit volume that is why concentration is working out if I multiply with volume, it will be per or with respect to mass, that is something to keep in mind, so 0.5 is the initial one and in what phases is that? One phase is still in water, 0.01 milligram per liter which is the final one.

And the other one is that it is also present onto the media and I know that it is going to be at 4.30 milligram per gram. And here I am going to have concentration of the activated carbon required from the equation. I see that I need to add 114 milligrams per liter of the particular solution to be able to bring down my benzene concentration from 0.5 milligrams to 0.01 milligram per gram, that is something to keep in mind.

2 aspects; we calculated q from the particular Freundlich isotherm and then we understood that the total moles or total mass is going to be the same when I am going to consider both the dissolved and the adsorbed phase. Initially everything is dissolved so that is why it is C total benzene and then afterwards some is dissolved and some is adsorbed, dissolved one is 0.01 and this is with respect to the adsorbed one and from that I can get the concentration of the activated carbon.

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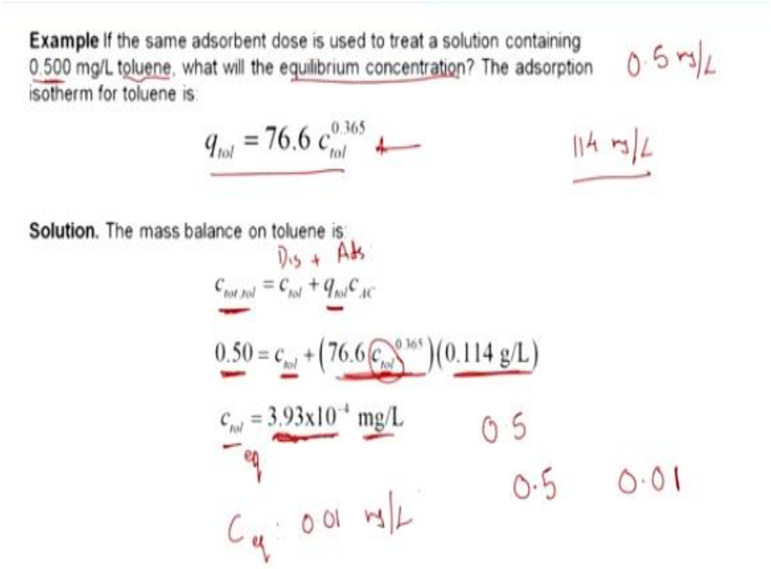

Example If the same adsorbent dose is used to treat a solution containing 0.500 mg/L toluene, what will the equilibrium concentration? The adsorption isotherm for toluene is:

0.5 mg/L

$$q_{tol} = 76.6\, c_{tol}^{0.365}$$

114 mg/L

Solution. The mass balance on toluene is:

Dis + Ads

$$c_{tot,tol} = c_{tol} + q_{tol} c_{AC}$$

$$0.50 = c_{tol} + \left(76.6\, c_{tol}^{0.365}\right)(0.114\ \text{g/L})$$

$$c_{tol} = 3.93\text{x}10^{-4}\ \text{mg/L}$$

eq

0 5

0.5 0.01

C_{eq} : 0.01 mg/L

Let me move on, so another example if the adsorbent dose is still the same meaning it is 114 milligram per liter is still used to treat a solution containing initially 0.5 milligram per liter of toluene, another hydrophobic compound benzene 2 relatively hydrophobic compound, what will be the equilibrium concentration? Here they are not asking us how much activated carbon to use but they are saying this is the amount of activated carbon that you have or the mass per volume of the solution that you have.

And if my toluene is there instead of benzene at this concentration, what is the final one going to be at equilibrium? The absorption isotherm for this particular toluene is also given, as I mentioned the isotherm will depend upon both the adsorbate and the adsorbent, that is why you see a different relationship here, mass balance so this is total before adsorption, everything is only dissolved afterwards it is some of it is dissolved and some of it is adsorbed.

This is per unit volume that is why this particular concentration terms are can be used here. Typically, we look at the mass so 0.5, everything is present in the dissolved 0.5 milligrams of toluene per liter. I want to know what is the concentration at equilibrium. And I also know q already, q is given out here and this C is that the concentration of toluene adsorbed onto the activated carbon is going to be dependent upon the concentration of toluene which is in equilibrium in the solution.

And the concentration of activated carbon it is 114 milligram per liter so from that I get the concentration of toluene at equilibrium or the final to be 3.93 into 10 power -4. You see that 3.93 into 10 power -4 milligram per liter at the same dose initial one was 0.5. But for benzene you saw that even though initial was 0.5 the final was only 0.01, you know that toluene has seems to be relatively more hydrophobic than benzene and thus it wants to leave the water and will be strongly adsorbed onto your particular activated carbon.

That is one aspect to note here, you see that the final concentration is pretty much less than the C equilibrium, when you had only benzene I think that was 0.01 milligram per liter, that is something to keep in mind.

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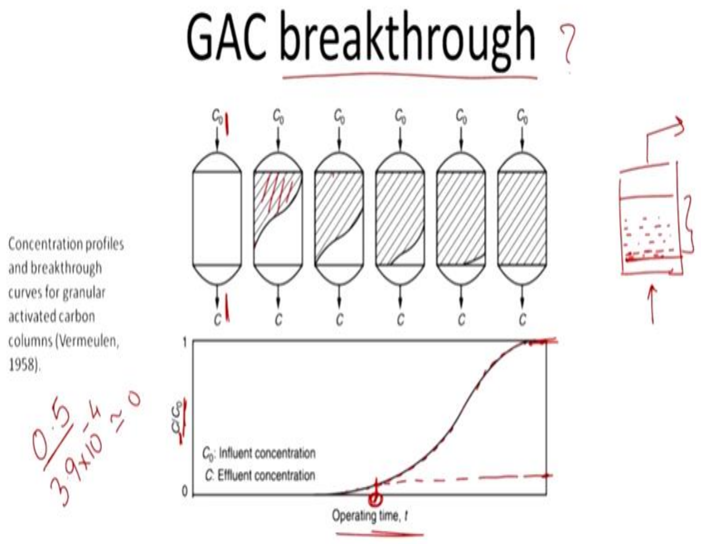

GAC breakthrough ?

Concentration profiles and breakthrough curves for granular activated carbon columns (Vermeulen, 1958).

$\frac{0.5}{3.9 \times 10^{-4}} \simeq 0$

Granular activated carbon breakthrough, what is this breakthrough? Here this was a batch process, we are looking at a batch process but in waste water or a water treatment plant you are going to have water flowing continuously. You cannot have batch process there; it is going to be a continuous flow system typically a plug flow if I may say so. You are going to have the kind of system that we looked at in the figure.

You are going to have these activated carbon systems up flow or down flow depending upon it let us see here. I have up flow and here is my mass transfer zone so initially most of the compounds will be adsorbed in this zone itself, later the zone is going to go up and up, what do I mean by that? Here I have the polluted water, this here I have the treated water. And in this graph, we are going to look at operating time on the x axis and C by C naught, C is the effluent concentration, C naught is the initial concentration.

Initially what is the profile going to look like? Nothing in the effluent, everything is being adsorbed, think of toluene earlier. Even though I have 0.5 initially it was I think something like 3.9 into 10 power -4 milligram per liter in the effluent, that is the equilibrium concentration. It is more or less equal to 0, C by C naught is almost equal to 0.

But over time what happens most of the sites on this particular activated carbon are going to be adsorbed, there are no more free sites for it to be adsorbed upon. Also note that in water you are not going to have just toluene you will have other organic carbon or organic compounds which will also absorb onto your particular activated carbon, you will also have this competing adsorbate that is something to keep in mind.

Over time you are going to have this particular activated carbon being exhausted that is term that I am using. Here you are going to start having or seeing that the effluent concentration is going to increase and after certain time the effluent and influent concentration is going to be almost the same. You will have to decide what is your acceptable concentration is, something like this at this level. That if that is that level then this is the breakthrough time.

GAC breakthrough, let us see when your effluent concentration is exceeding your objective or final concentration that you want to have. That is what we have.

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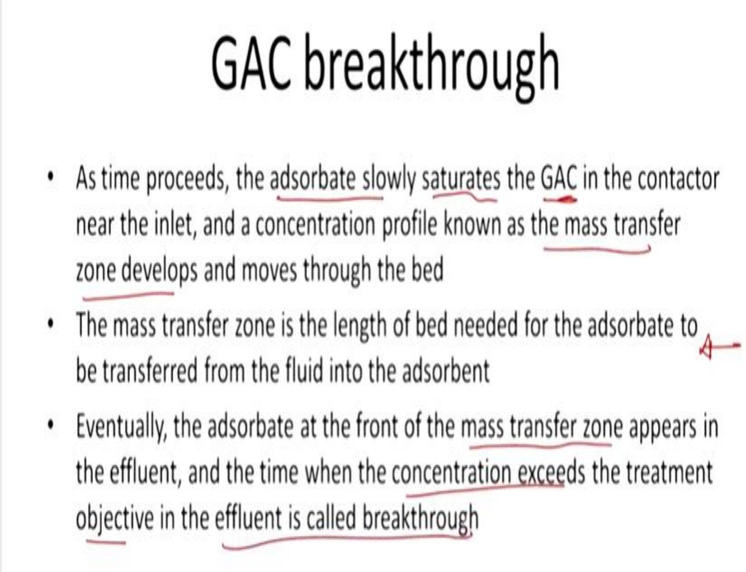

GAC breakthrough

- As time proceeds, the adsorbate slowly saturates the GAC in the contactor near the inlet, and a concentration profile known as the mass transfer zone develops and moves through the bed
- The mass transfer zone is the length of bed needed for the adsorbate to be transferred from the fluid into the adsorbent
- Eventually, the adsorbate at the front of the mass transfer zone appears in the effluent, and the time when the concentration exceeds the treatment objective in the effluent is called breakthrough

Time proceeds, adsorbate slowly saturates or is exhausted, saturates the GAC and a concentration profile known as the mass transfer zone develops, we looked at the mass transfer zone and moves through the bed, the mass transfer zone is the length of the bed needed for the adsorbate to be transferred from the fluid into the adsorbent. This is something to keep in mind.

Mass transfer zone is the length of the bed needed for the adsorbate to be transferred from the fluid into the adsorbate. And eventually though what is going to happen? The front of the mass transfer zone appears in the effluent that is what you have, front of the mass transfer zone appears in the effluent, that is what you see our here. And then you are going to see the concentration of your effluent increasing.

And the time when the concentration exceeds the treatment objective, this is what we discussed, the effluent is called breakthrough. We say that the GAC or the system has achieved breakthrough.

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Ion Exchange

And in the next session we are going to start talking about ion exchange, so there it is ion exchange, it is not just Vander Waals force of attraction. But with that i will end today’s session but key aspect is we are having media so that we can remove relatively hydrophobic compounds from the water and what is the media that is typically used in water or waste water treatment for this purpose of adsorption of organic compounds? It is granular activated carbon. With that i will end today’s session, thank you.