Mass Transfer II

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So, in today's lecture, we take up the new unit operation, adsorption. So, first we started with absorption, then we had distillation, then we moved on to extraction, which was the last topic and now, we will take up this new unit operation, adsorption.

Now, you must have noticed, by now, that there is some similarity in all this unit operations. There is a difference, as far as mechanism is concerned of, mechanism of separations for example, we started with absorption. So, we had two phases, liquid vapour and there was one transferring component. Then, we switched to this distillation. There we had two phases liquid and vapor, but, we have two components at least, A B and then, one stream, one we had period A and another stream, we had period B. Then, we started with extractions.

So, there we had three components, A B C and two phases and then, we had separation of these three phases, these three components or distribution of these three components in two phases. So, as far as similarity is concerned, you must have noticed, that there are at least two phases right and then, there is a transferring component, or more than one transferring component.

So, there is a similarity and there is a difference in the mechanism of separations. Now similarly, as far as operation is concerned, you know from the practical point of view, we said that, we can have a continuous contact process or we can have stage wise.

So, here also you know, when we take up this new topic absorptions, you know, we have two phases and there will be a transferring component, or at least one transferring components. We can also have multi components adsorptions, that is also possible.

For this course, for simplicity purpose, we restrict our discussion to single component adsorptions. So, we have two phases, one transferring component, so, there is similarity, alright. There is a difference, the difference will be in the mechanism, what causes adsorptions or the mechanism of separation, here is by adsorptions, not absorption, not by you know miscibility or difference in the solubility as we saw in case of extractions or not by relative volatility, which we saw in case of distillations.

So, adsorptions, we can, if we can recall from your previous knowledge, it is not a new unit operations. For a long time, people used, say activated charcoals carbon, right in water purifications. So, we had waste water or say ground water may be enriched with certain undesirable species, say for example, colour, right. So, charcoal is very good known adsorbent for colour.

So, take waste water; bring in contact with solids like charcoals, coals etcetera. Allow them to give some time. So, we say that there is equilibrium. Like in all the previous unit operations, you have to give some batch time, some equilibrium time, then the two phases now there are in equilibrium. So, the component which is supposed to be transfer from waste water or from ground water or from portable water to the solid surface, it comes to equilibrium, thermodynamic equilibrium.

So, there is a similarity that, we have two phases, say we have liquid or gas in one phase and then we have solid in second phase. So, two phases and then, we have one transferring components. We said that, we can have more than one component. We can have multi multiple components systems.

So, for simplicity, if we have one component, this component gets transfer from liquid or gas to the solid phase. Depending upon the activity, partial pressure concentration in one phase, the system reaches equilibrium. That means, no more this component can be, you know, thrown or can be sent to this solid surface. Solid phase concentration has reached equilibrium with the liquid or gas phase concentrations.

So, we have thermodynamics, very similar to the previous cases y verses x for distillations. For solubility or for absorption, we say solubility verses the partial pressure concentration, in the liquid phase verses gases phase concentrations. We talked of extractions, we had solubility of three different components, different solubilities that causes different extent of distribution into phases.

So, similarly, here we have thermodynamics, which will tell us that given this partial pressure, how much is the amount of solute which is going to be adsorbed, which is going to be update by this.

So, there is a similarity and of course, this is totally new process. Here, we have different mechanism. We will talk about the adsorptions, surface adsorption, we talked about port diffusion, and we will talk about absorption desorptions, etcetera.

So, there is always in all these unit operations, which we had, there is similarity and there is a difference here. Adsorption in the recent times has gain lot of importance. Why because of, you know, may recall in the first lecture also, we said that because of air pollutions environmental concern. So, all this flue gases from power plants, from you know, chemical industries now, the tolerance has gone down, you know, very strict emission rule by e p a, environmental protection agencies or the similar Indian government agencies.

So, now concentration of sulphur dioxide emitted from power plants, cannot exceed more than 500 p p m’s, cannot be more than 200 p p m’s. So, that is norm. So, what are the techniques? One technique already we have discussed, absorptions. That is a very good method. Take this flue gas, bring in contact with the good solvent, water, sulphuric acid and then, you have this mechanism of different solubilities.

So, sulphur dioxide is more soluble in water than say oxygen, nitrogen or air. So, that is mechanism solubility. Adsorption is a very good technique. You bring in contact with the solvent, with the solid adsorbent will call it later and then, there will be uptake of this solid for the sulphur dioxide. So, it is a different unit operations; different mechanism. Recent times, you have seen, may heard of new materials like carbon nanotubes, may be zeolites, carbon molecular sieves.

So, these are new type of adsorbents. Alumina, you know are tailor modified surface functionalize alumina. So, different type of adsorbents you have, solid wave we have, which have come you know, which have been developed in the last one decade or so. So, adsorption has again lot of importance in the last decade, because of this environmental pollutions.

So, we continue with this new unit operation adsorptions and we will have similar approach. Some introductory, you know, slides or lectures then, we will switch to this thermodynamic. Will establish thermodynamic; will have to do some experiments to establish this thermodynamics. Then, we have this batch mode. We will talk about this stages, first stage, second stage, multi stages. Here, we will talk about the pact column breakthrough experiments bases throwing absorptions operations.

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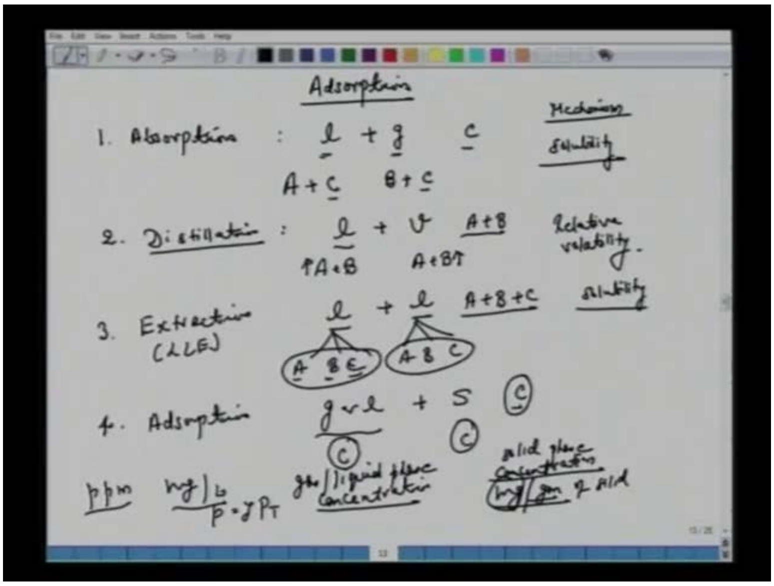

So, let us start, make a note of few, you know, contents we had here. So, we are beginning with new unit operation, which is adsorption. So, let us not note down. We said we started with absorption. So, we have liquid plus gas. So, notice here, two phases and there is a transferring component, let say C.

So, we are talking of say A plus C, water and you know sulphur dioxide and we have this air and C. So, C is a transferring components, but, we have two phases, distillation. So, may be here, we can put some mechanism. So, what is the mechanism of absorption? It is a solid, alright. Distillations, here also we have two phases, liquid plus vapor and here, we are talking of two components, minimum two components, A plus B.

So, liquid phase also has A plus B; vapor phase also has A plus B. Except in one case, A is a larger, other case B is larger. What is the mechanism of separation here in distillation? This is relative volatility.

Then, we have this extraction. Then, we discussed extraction or we call it l l e liquid liquid extraction. Here also, we have two phases, l plus l. So, when we write like this, both are liquids, but, they are immiscible liquids. So, we have two phases; we call them extract and raffinate, etcetera. We had, you know, in principle three components, A plus B plus C.

So, both phases contain all three A B C, A B C. Of course, in different proportions; one became the solute, one became the feed, one became the solvent. We call them one as extract phase; we call one of them as a raffinate phase. What is the mechanism here? Again, it is a difference in solubility distributions.

So, different different mechanism. The one we are going to take up today is adsorption. So, here also we have two phases, gas or liquid. So, one phase and we bring in contact with S solid and here we have one component C. We can have more than one component, but, you know for simplicity, it is one component which is getting transferred, which is getting distributed in this C and C here.

So, we have gas or liquid phase concentration, gas or liquid phase concentration and here we have solid phase concentration, alright. So here, may be, we are talking in terms of milligram per litter. We can also express in terms of partial pressure. So, may be mole fraction into total pressure or we can talk in terms of p p m, part per million

So, this is gas or liquid phase concentrations and what we have here is a solid phase concentrations. How much the C milligram per gram of solid. So, this is your solid phase milligram of C adsorb in the solids.

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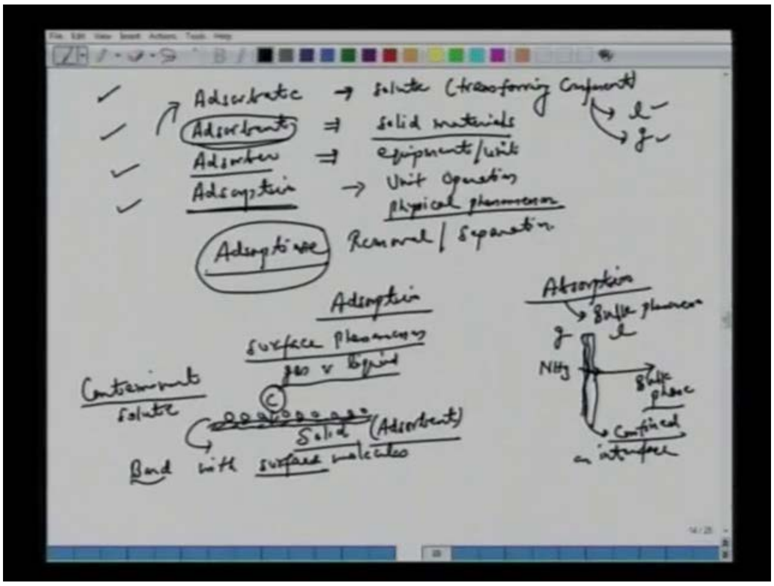

So, talking of this nomenclatures in adsorptions, you know, it is, you have, say the first, you know, very common nomenclatures or terminology we use, adsorbate, adsorbent, absorber, you know of course, we have this adsorption.

So, this adsorption is nothing, but, unit operation. Similar to distillation, extraction, absorption, it is physical phenomenon. It is a physical phenomenon. What is adsorbate? This is a solute, the transferring component. So, the solute gets adsorbed. What is adsorbent? Similar to the solvent, right. So, this would be yours. So then, some, so this adsorbate here, solute which is transferring adsorbent, is your solid material.

So, this solute is dissolve in the liquid or in the gas phase. Aqueous system, for example, or the gases phase, an adsorbent this is solid materials. So, adsorbate is going to be absorbed by this adsorbent or by suitable adsorb. One has to develop this material to adsorb this, just like one has to develop certain solvent to solubilise or to dissolve certain contaminants. Absorber, this is the unit, this is, and it is an equipment. So, it is an equipment, some physical unit, in which, you are going to carry out this adsorption.

So, these are the words, terminology adsorbate, adsorbent, absorber, adsorptions. We say adsorptive remover or adsorptive separations. So, we mean here adsorptive. So here, we mean the same thing that separation is carried or is caused by this adsorption, which is physical phenomenon.

So, let us continue with the topic here adsorptions. But, it is in general, the traditional definition, this is a surface phenomenon. Unlike when we say absorption, which we have discussed as a first unit operation, in this course, this is bulk phenomenon or bulk effect.

So essentially, when we have this gas phase, liquid phase, say ammonia, this gets solubilised on the surface as liquid. Then, it diffuses, moves inward into this bulk phase. In other words, this ammonia does not remain confined does not remain confined in this, on this interface on interface. So, it says absorptions.

When we say adsorption, we say it is a surface phenomenon that means, if you take the solid, which is again our adsorbent here. Will take up an example of, you know, the trimming the some solid, say charcoal. Coals bring in contact with gas or liquid, say air or water, it contains certain solute contaminant, which you want to separate or you want to recover, certain solute which you want to recover from this phase.

So now, this C solute, now, this gets adsorbed. So, when we say adsorb, say that, here this is remains confined on this surface. This would be the very traditional definition for this adsorptions. We will see that, what we are trying to say here, that this molecule makes certain bonds with the surface molecule. There is a bond with surface molecules. This surface is adsorptions.

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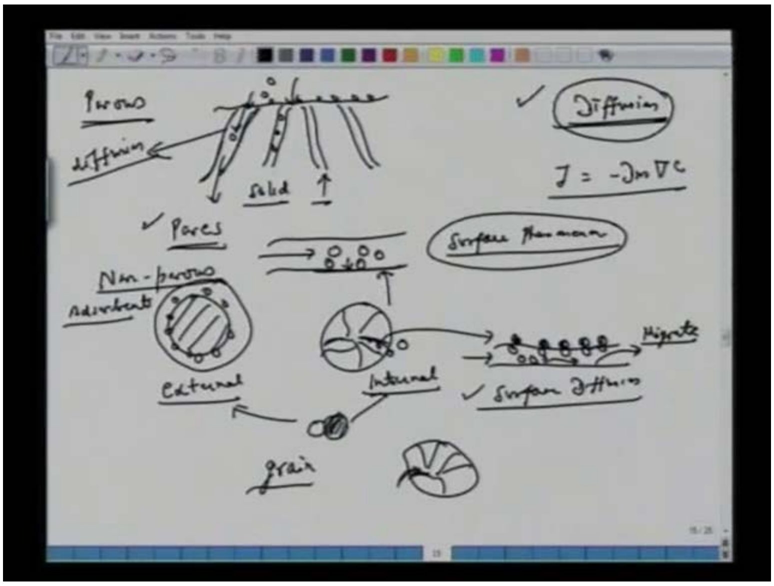

So, when we said that this is a traditional definition for adsorption as a surface phenomenon, what we are trying to say here that there are certain materials, a good number of materials, in fact, most of these materials they are, say, we call it porous, alright. So, let us try to understand what we mean by the surface phenomenon. What do we mean by the absorption, which is a bulk phase.

So now, when the molecule gets in or gets adsorb on the surface, now what happens, these are the porous materials, which has very large pores, very long pores which goes deep inside this solid. Things will be clear, you know, as we continue discussion of these adsorptions. But, for the, try to understand, what we mean by this surface adsorptions or surface phenomenon.

So now, the solute get adsorb, but, there is a convict subtract. So, it diffuses inside. So, there is a solid diffusion. Remember we talked of, you know, molecular diffusion. When we took up this first course on this mass transfer, we talked of diffusion by Flick's law, j equal to minus d m del C gradient.

Now, we are talking of this diffusion within the pores, pores of this. So now, the solute C cc, some are getting adsorb here, on the surface bounded with the surface molecules; some of them were getting diffused inside. But, when they diffuse inside the pores, they still get adsorb or bounded with the surface molecules.

So, that is why we are trying to say, that it is a surface phenomenon. Whether it happens on the surface, so we can have, say theatrical non porous non porous adsorbent, non porous solid. So, here the molecules are getting adsorb on the top surface, because this non porous, there are no conduits like this and no pores like this. But, if you have pores, tracks like this, these molecules, they will diffuse inside, but still, they will get adsorb like this on the surface.

So, whether it happens of the top external surface or it happens in internal surface, internal or it happens external, the molecules are getting bounded on this surface. That is adsorptions. Certain force, certain, you know, interaction between this molecule and the molecule of the solid, whether on the top external or whether inside on the pores.

So, even here these are the pores, these are the molecules of solids with which, this is making a bond. So, you should understand, whether internal or whether external, this is surface phenomenon, alright. Of course, further we are getting into details; we can have, when all kinds of one other effects like surface diffusion, just like we talked of pore diffusion, molecular diffusion right. Molecular diffusion, pore diffusion similarly, we can have surface diffusion.

This adsorb molecule can also migrate on this surface. So, this would be like getting into further details of, you know or maybe we have instead of pores, we can have grains, right. Even you had some course on material science. There are certain defects like, in the materials on which is possible, these are molecules which are adsorb, then migrating, then migrating they are hopping. So, all kinds of mechanism is there in this adsorptions.

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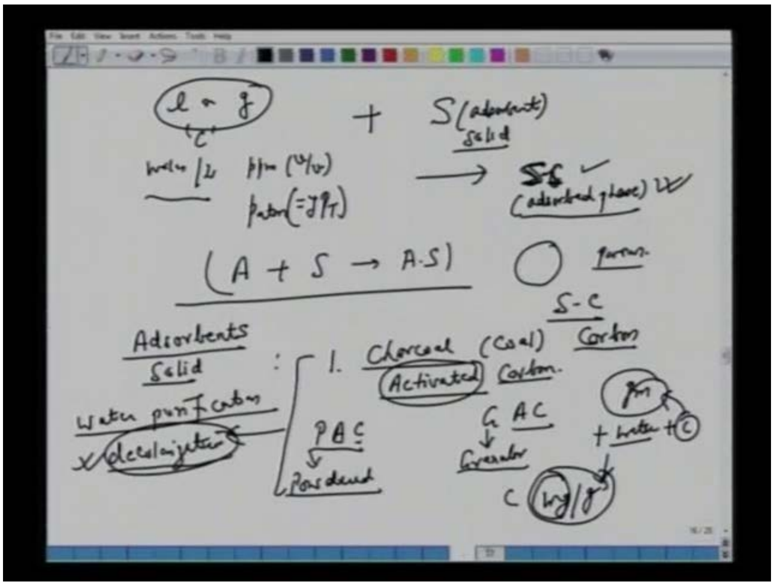

At the end of the day, we are saying that we have liquid or gas. It contains certain solute moles per litre for the liquid. For the gas phase, may be, we like to say p p m part per million volume by volume. May be, we like to say, well the partial pressure is p atmosphere, which means we are talking of mole fraction into total phase liquid or gas containing the C plus S.

So, S is adsorb. We will denote like this. Then we have S dash C. We say adsorb phase. All this actually is a solid phase. So, liquid phase, gas phase, it contain C, bring in contact with solid. Different phase we talk in terms of adsorbed phase, which is nothing but, solid has adsorbed, it has taken up some amount of C. Whether on this surface, if it is a non porous or within this pores, if it is a porous materials, right we have S dash C, a molecule A plus S, we have A dot S.

So, different ways of representing these adsorptions. Now, let us take some few examples. You know, some of you may be familiar, may have come across in some context. So, let us take example of certain adsorbents solid. The first thing, you know, which will occur to us, one must have, you know, we talk about just now this charcoal. It is one of the material, very primitive, gives for a long time in the past several years nothing but, actually coal, alright. For some form of carbon, you know, different carbon has different type of allotropes returning of charcoal. Sometimes, we call it activated carbon, that is a scientific name or you want to bring certain scientific aspect into this, it is a activated carbon. At some point of time, we will discuss what do we mean by activated carbon.

So, charcoal activated carbon, whether they are in p A C form or they are G A C powder. So, they are either in powder form, powder activated carbon or charcoal or we have G A C granular activated charcoal or activated column. So, this one example and it is very extensively used. We gave an example in water purification. Even today, may be different different form, may be different surface modifications, but, is extensively used in very efficiently for water purifications, in particular decolourizations. So, colour can be dice etcetera; can be easily removed by this coal, by the charcoals; very good adsorbent or decolourizations.

So, if we take certain amount of gram of solid, bring in contact with water, alright. This should be able to absorb very large amount of milligram per gram. So, this water contains certain C, certain colour volatile organic compound. It will get adsorb and you can per gram of solid, one can remove very large amount of the C components.

So, C milligram adsorb in one gram of solid. That is the solid phase adsorb phase we talked about. So, charcoal is one example. Another example which should come to your mind is alumina.

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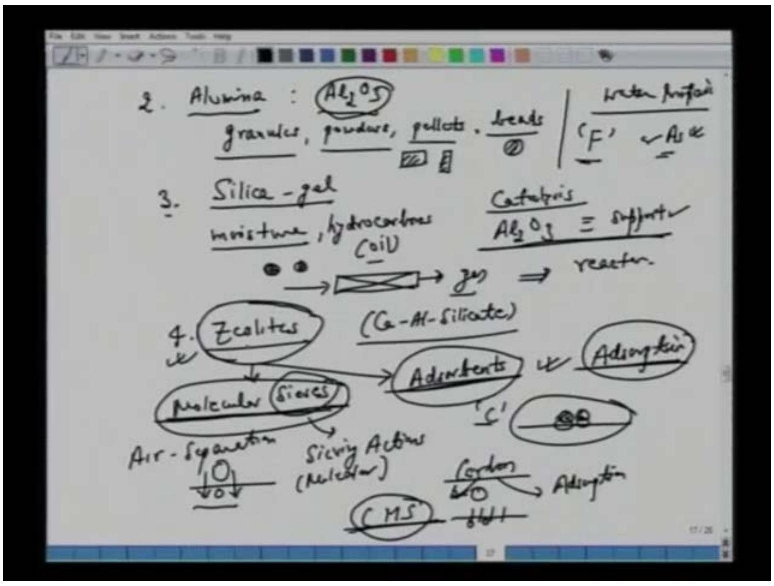

Alumina is also very popular, very old, very common adsorbent used in adsorptions or in separation process. What you mean by alumina? Actually, if this is A l 2 o 3. This is the best, you know, chemical formula for alumina.

The closest of alumina will also have different forms. Alumina will also be in forms of, say, granules; it could be in form of powders or pellets. So, we are talking of certain cylindrical pellets like this. One makes use of very small, one inch, half inch pellets or may be beads. So, we are talking of some spherical beads.

So, different different form, just like g s e, p s e we talk for charcoals; for alumina like pellets beads granules etcetera. It is used very extensively in water purifications, especially to remove fluoride. So, all over part of the country, it has very huge amount of fluoride; are even arsenic. One can make use of this alumina to remove this. Of course, on those who are familiar with catalysis, alumina serves as a good support.

So, may be, time permits will come to this and we will see what we mean by supports. So, these are different applications. But, whether supports or direct application in water purifications, now we have the similar mechanism.

We have some solute, which is getting adsorbed this alumina. Silica gel, this is another common adsorbent, very extensively used to remove moisture. Alumina can also adsorb large amount of moisture or say hydrocarbons or oil.

So, silica gel, you know, we must have seen radius. l o is radius type of beads in purifiers and you have this gaseous stream you packed with this silica gel to remove moisture before this gas is fit to some say chemical reactor.

So, silica gel is also very common adsorbents. Another example which should come to your mind is zeolites. Zeolites have been used very extensively also in the past. Zeolites is nothing but, may be calcium aluminium silicate. This is also very common or very closest molecular formula, chemical formula for zeolites. Zeolites, traditionally zeolites where used as molecular sieves. If you have heard of it, molecular sieves, today zeolites are very extensively used as adsorbents.

So, may be here, we have got an example of material which has two different types of functions. So, same materials, in one context we can use this as a molecular sieves; another context, we can use them as adsorbents, which is what we are discussing in this unit operation, adsorption.

So, we are talking of different mechanism. Same material has the capacity to adsorb or to remove certain solutes. Same materials or may be certain tailoring modifications can act as molecular sieves. So, here molecular sieves again, your, may be in the knowledge from chemical process technology, they were used in very extensively today in air separations.

So, these zeolites, they act as sieve, which means larger molecules will be filtering here and small molecules will make a base. So, it is a sieving action. Here, the mechanism is molecular sieving, sieving actions at molecular level. Here, we talking of adsorbents; mechanism is adsorptions. Bond, they make bonds with this surface molecules.

So, zeolites as we said it has two functions. You know, sometimes use this as molecular sieves; sometimes same material can be used or by some modification, they can be used as adsorbents.

In this context, same if we call by, if we know from your knowledge, from chemical process technology, say it, some same carbon carbon can act as an adsorbent. Just now, we took the example adsorption. Carbon can also be tailor modified to use as C M S, carbon molecular sieves.

So, they exist just like zeolites. Carbon also has a role as carbon molecular sieves. This one can modify the pores of carbon, keep the large molecular side oxygen, allow small molecules to filter through this. That is a sieving actions.

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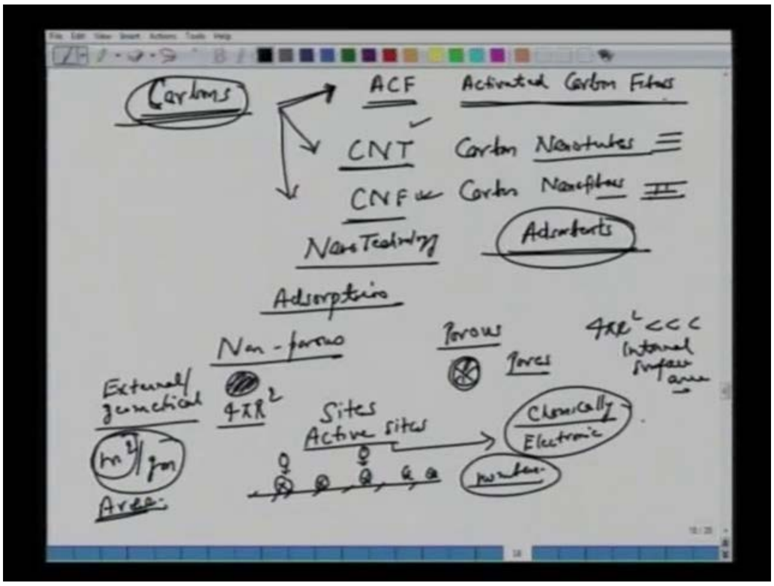

So, these are the examples of, common examples of adsorbents. We will like to still spend some couple of minutes here on carbons. It is very common, very popular. So, we are not talking of charcoals. We are talking about carbons. These days, carbons for your information, we have activated carbon fibre. It is now, it is a relatively newer materials.

Last ten twenty years, we have heard a lot of activate carbons fibres used in so many applications in adsorption and warm interpolations development of certain sensors, activate carbon fibers in materials strength was a composites.

We also have C N T, carbon nanotubes. Talking of nano technology, carbon also made, has made a progress here; carbon nanotubes, carbon nano fibers. carbon nano fibers. So here, we are talking of graphitic. Certain structure, layers of graphty nano fibers may be, there are disordered.

So, the example is, for your knowledge, this carbon has, as old as, may be thousand years old and as new as, may be, you know, current years. Here, we had a lot of work on carbon nanotubes, carbon nanofibers is a part of this nano technology. Here also, this carbon C N T or C N F is used as an adsorbent.

So, lot of R and D works are done, are currently under progress development of C N F, development of C N T, development of a C F as adsorbents. So, these are the examples. Now, let us start getting into the mechanism part or you know, more details, what is happening when we have this adsorptions. So, first we said, generally, we can have non porous adsorbent solid or we can have porous adsorbent.

So, when we say non porous, essentially we are saying that, its external surface or geometrical surface is responsible for adsorptions. On the other hand, when we say porous surface, then we are saying the very huge amounts of pores exist inside, which are responsible for this adsorptions. We are talking of pores, here it is non porous. So, whether non porous or porous, we talk in terms of sites or active sites.

So, we are saying that, it is the surface on which there are sites, which are actives to adsorb these molecules. So, when we say active, this could be active. Of course, one is chemically are very active. So, we are talking in terms of some chemical bonds, electrovalent bonds, covalent bonds they form, they can also be very active electronically. Right

So, these are active sites. Of course, we cannot count the numbers here, but, one way of representing all these active sites or sites for adsorption is meter square per gram. We call it, you know, area, surface area.

So, one gram, how many, what is the area which is responsible for adsorptions. So, nonporous of course, this would be for a spherical, it would be 4 pi R square. For porous, one has this 4 pi R square, will see it is much smaller, much and much smaller than internal surface area.

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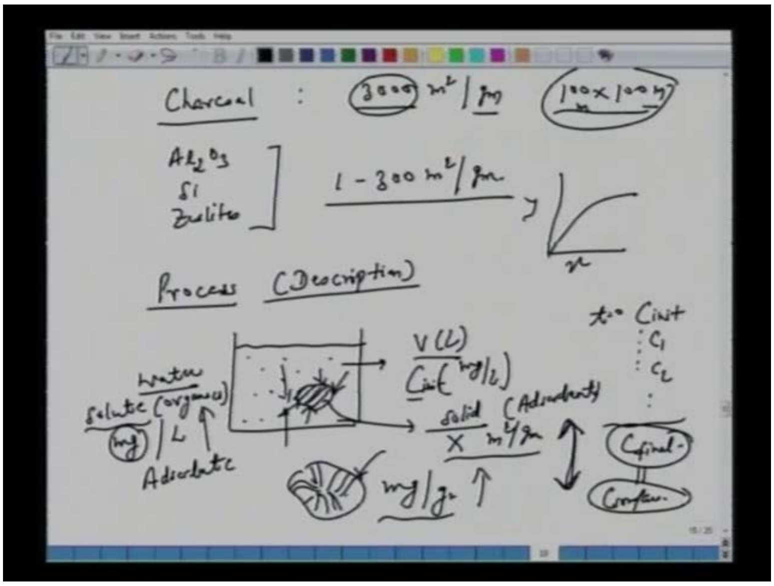

So, what is the good case for charcoal or you know, made of carbons, this area, this could be as high as 3000 meter square per gram. So, one gram of charcoal has 3000 square meter of area responsible for adsorptions. These are on which will have, not all of them, may be some of them active slides.

So, 3000 meter square per gram, right, 100 into 100 nearly that out of magnitudes. You can imagine 100 meter long, 100 width as that much of area has gone into one gram of charcoal. Alumina, we talked, another vary silica, zeolites, they are also have very large surface area. May be, you can say, as low as 1, as high as may be, 300 250 meter square gram.

So, these are, we will come back to this again. We will take in details. We are talking of, now, the surface area which is responsible for adsorptions and how do they adsorb. We talked of chemical bonds; electronic bonds are very active there

Let us discuss the process. Let us have a process discussion. So, what we do, the most simplest example would be take a beaker, and take a water tank. It has water. This water contains say, certain amount of solute, say colour, right or certain organics. Colours dyes are nothing, but, certain organics.

So, it has certain milligrams per litre. So, I have taken say V litre of water; it contains certain solutes. So, the concentration let us say C. So, we will give a name here, C. Some unit here, say it as milligram per litre.

So, liquid phase contains certain organic, which concentration is milligram per unit. I bring in contact solid charcoal. So, this is the adsorbent. This organic is adsorbate. adsorbate Solid charcoal is a adsorbent. So, this has certain properties, meter square per gram, certain X meter square per gram, it has a surface area.

So, I bring in contact. Now, I have this process adsorptions. I start with, let us say C initials n I t. So, this solutes which are there, they will get adsorbed. Not necessarily on the external surface, charcoals are very large porous materials. They have very huge pores.

So this, they will diffuse inside, migrate inside by these pore diffusions. So, I start with certain concentration C, initial t equal to 0. Naturally, it will expect that C concentration of water phase slowly slowly will get down, C 1 C 2 and this solid phase concentrations which will set milligram per gram is going to increase.

So, this will decrease, this will increase till they will be in equilibrium, when we say that C final. Now, this C final has come into equilibrium with C surface milligram. That is the thermodynamics that we want to discuss, the way we discuss in case of absorption, distillation, extractions, we talked of y versus x.

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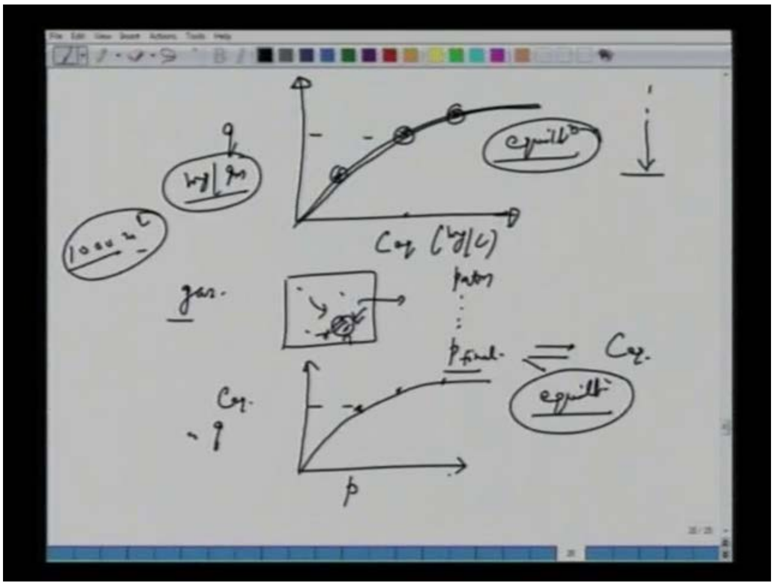

Similarly, we have this equilibrium, which is q, denoted milligram per gram. Here, you have C aqueous phase, which is milligram per litre. Certain final concentrations, like I get one coordinate, it cannot absorb more than this. Adsorption, it has finite capacity. We said that it has 1000 square meter per gram.

One gram has so much of surface area. So, in proportion to this area, is going to adsorb that much milligram, I got one coordinate, I do of some other experiment, I start with different concentration; concentration comes down.

Final concentration, I get different label. So, I connect all this point to have my equilibrium. So, this is the equilibrium we are trying to establish with all the unit operations, absorption, distillation, extractions. Remember the first thing is that, we have to address equilibrium. We have to develop this curve here.

So, this is the experiment, very simple experiment. If you have the liquid phase, you can do this. If you have the gas phase, very similar, we have to take, may be close chambers, take this gas phase.

So, you have certain parts in place p atmosphere. To begin with, bring in contact with the solid sulphur dioxide. Ammonia will get adsorbed or inside partial pressure will decrease. You will reach p final. Corresponding to this p final, they will be in equilibrium; the solid we have C.

One can also plot, given this partial pressure. What coordinate I have got, equilibrium, just C equilibrium or you call it q, 1 point. Start with different partial pressure, you have different points, you connect all these points here, you have another equilibrium.

So, this is what we are supposed to construct or we are suppose to generate or we have to rely, thermodynamic, some physical thermodynamic and data book. So, that is the first thing, thermodynamic equilibrium.

So again, you know, going back to the example, very simple experiment. We are trying to say here that very similar to what we had in all interpretations, absorption, distillation extractions one has to construct, one has to generate this equilibrium data or you have to rely on some previous data, you know, reported in the text book or in some thermodynamics hand book.

So, the experiment is very simple. Initial minus final; whatever is the last change in that concentration, either gas phase or the liquid phase, that material must have gone into the solid surface. You make a simple material balance, to obtain, and to generate such data. Let us do this small computation here.

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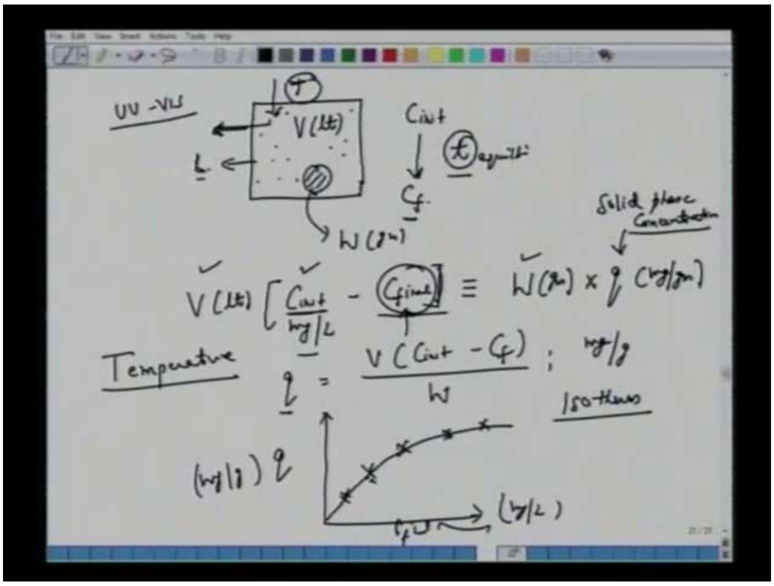

$$V(\text{lt})\left[\underset{\text{mg/L}}{C_{int}} - C_{final}\right] \equiv W(\text{gm}) \times q\ (\text{mg/gm})$$

$$q = \frac{V(C_{int} - C_f)}{W}\ ;\ \text{mg/g}$$

So, we are saying that, we have this volume filled with a liquid, let us say V litre. We started with C initial and after time t, you have reached C final. So, when we say it has reached C final, you must ensure that the concentrations of the solute in this liquid phase is not changing with time, it has reached equilibrium.

So, maybe you have some sensor or you are taking a small amount of solute, very small amount you are sending. So, if it is a colour, may be you are sending into some u, v is some equipment, ultraviolet visible, you know, equipment. It monitors the concentrations, concentration changes, then we have this C F. We say that we have reached equilibrium to do this. Of course, we had this solid. It took that w weight gram.

So, what is the balance here? V litre started with C initial minus C final, which is, say milligram or say moles per litre. So, so much milligrams of solid has gone from this liquid phase to the solid phase and we started with w gram of solid phase. Let us say, now it has concentrations q. So, this is q is often used for solid phase concentration. So, solid phase concentrations, which is here, milligram per gram.

So now, we have p is fixed. Start with C initial, w is fixed here. We monitor C final at the end, after infinitely time, long time, very large time we have reached this number. We calculate this q from here. Q is nothing but, V C initial minus C final over w milligram per gram that is a unit of this q.

Start with different C initial, you get different q and then, we plot this q versus C final. So, this adsorbed phase solid is in equilibrium with this C final; not with C initial. We started with C initial, now, we have reached C final. So, we get one point here. Start with differential C initials, we have different points. We have different points We connect, we have very similar qualitatively data points like this.

We will call it isotherm. Why isotherm because, one has to fix this temperature. So, temperature in this experiment was fixed at t, say 30 degrees centigrade. We did this experiment. We had to put this in some kind of path, where the some thermal static temperature was fixed. We got this point; we changed the C initial. We got different points, construct this, we have this C final milligram per gram; here q and this is your milligram per litre and have this.

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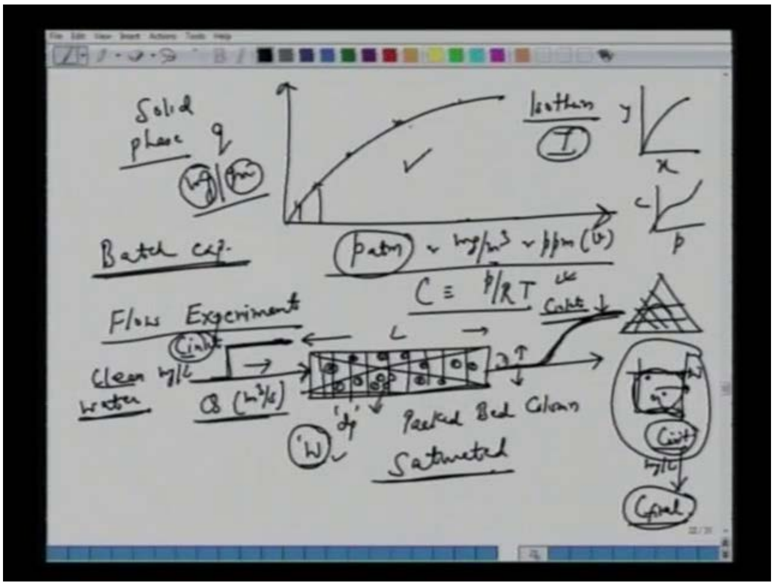

If you do this experiment for the gas phase, may be, you can plot as p partial pressure in atmosphere. Here, we can have q. We can have the similar curve like this, certain data points like this.

This is also known as isotherm. For the gas phase, instead of p atmosphere, may be, you can, one can also plot milligram per cubic meter. So, it is a gas phase. One can also plot parts million volume basis etcetera. So, different ways here. Still, may be, you can keep it milligram per gram.

So, so much, one gram of adsorbent has adsorb, so much milligram of ammonia or sulphur dioxide starting with different different partial pressure, different different concentrations C. May be, you can write p over R t applying ideal gas. So, one can construct this q. So, this is all about batch experiment. For any system, we want to study, we need this is a first thing one has to do.

Just like in case of solubility, remember, we talked of y versus x for distillation. For solubility, partial pressure versus C, some curve like this. For extractions, we talked of equilateral diagram like this. Then we said there is a phase, etcetera.

So, this is also a phase diagram; solid phase and the gaseous phase or the liquid phase. So, this has to be generated, thermodynamically calculated and so, to refer to some home work or if that type of formation is not available, one has to do this experiment. There is another experiment one can also do, flow experiment.

Let us spend time here to understand, improve our concept, what is this flow experiment. So, this was the batch experiment. We did fixed amount of solid in fixed amount of the volume. Flow experiment, what we do, let us say we make a column. So, this is a packed bed, packed bed column, we pack it.

So, we denote by this cross. All it means, there are orders, granules, beads, pellets of all these adsorbents. So, we have acted, it has certain length, it has certain diameter. There is a flow here q, let us say cubic meter per second.

So, we water, simplest example water, pure water. Clean water does not have any solute, flows through this at this constant flow rates. It gets in here and gets out here. This particle, let us say, the size is t p. We have put w amount of solvent.

So, batch experiment, we also put w. Here also, we have put w, right. Except there, the q was 0. There was no flow and everything was closed here. We brought in contact with this, with water. Here, we are bringing in contact with water, except there is a flow in and out at certain time, let us say V for this tracer here.

What is the tracer? This tracer is nothing but, the colour. Just like we said in case of batch experiment, this water contains initially some C initial of colour and dye. Here, we are saying that at certain time, we bring in contact with water.

So, we have injected this, this we injected this colour with this concentration C. Instead of C initial, we have C inlet, same milligram per litre milligram per litre. We have w gram, we have w gram we have those granules, particles of d p, here also we have d p. Here, the flow was constant, sorry the flow was 0 here.

Here, there is a flow continuously in and out. What we will expect that is more important to see what analogy, what is the difference between this batch experiment or the data from the batch experiment. What we have here and what is the, and what between this and what we are going to get here. So, what you will expect, the bed was initially clean, no colour here. Now, you inject this at certain time. For a long time, nothing will come out from this. You take a sample from here. It is a clean bed. Slowly and slowly, this is getting saturated with the colour; there is a advancement. Then, you start saying the bed there is some amount of colour here.

Till after a long time, you will see that or you will also expect at this, we locate entire bed is saturated. Why because, it has a limited capacity. Just like here, it was a equilibrium when C initial got down to C final and after a long time this concentrations does not change. So, that is equilibrium. Here now, there is equilibrium here. What do you will expect that this concentration is now same as C in left, right.

So, in the beginning it is 0. Slowly and slowly it will increase till this level becomes same as this level. Now, the bed has become saturated. No matter how much amount you use, whatever gets in, leaves from here.

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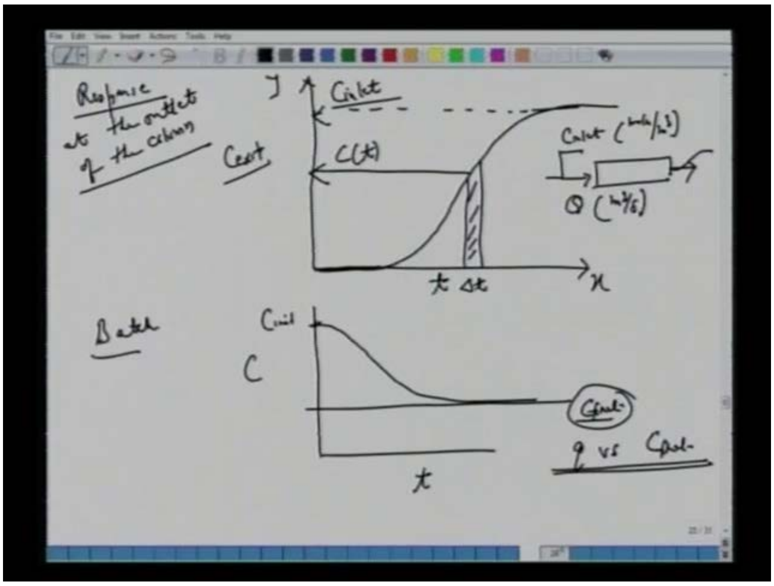

Let us come back to this diagram here. So, this is a response, plotting with response at the outlet, response at the outlet of the column or this packed bed column. What we did in case of batch experiment, there also, you could have monitored the time. With time, how does C concentration changes? So, there is start with C initial, concentration changes, change the decreases till it reaches C final.

Then, we did the calculations, made the material balance to plot q versus C final, alright. What we are doing here is, we also plotting with the time, except we are plotting C exit, C exit what we are monitoring at the exit. So, we said for a long time, you will not see any concentration here. Bed is clean, the wave has not reached at the exit, slowly and slowly this concentration will increase till the bed become saturated and this level has now reached C inlet.

So, we made a material balance and a batch. Here, we should make it balance under flow conditions. How do we make? So, recall this, redraw this packed bed here. We have response like this. Step functions, C inlet and we have this response here, which you have plotted from this x and y. So, at a time t, let us take del t, concentration generally C, of course, it is changing with time. So, let us just make a material balance. So, we have this q cubic meter per second of this water, it flows C inlet, let say moles per litre or per cubic meter.

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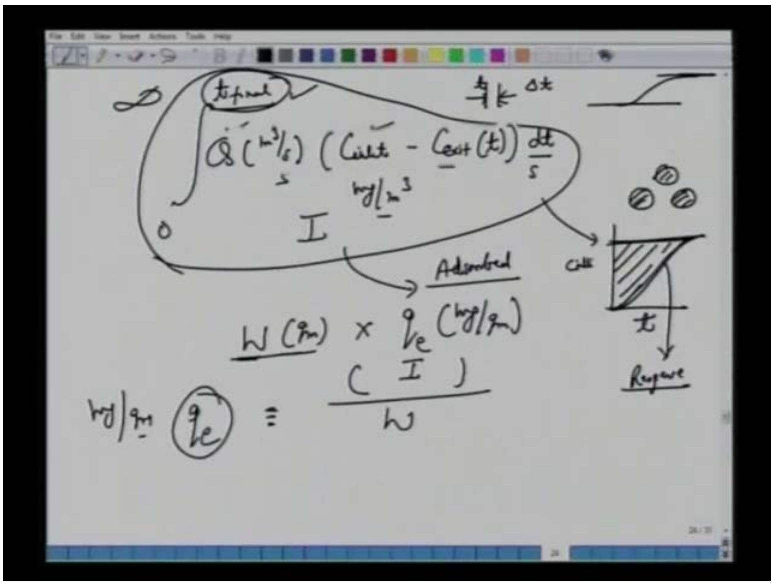

$$\underbrace{\int_{0}^{t_{final}} Q\,(m^3/s)\,(C_{inlet} - C_{exit}(t))\,dt}_{I}$$

$$W\,(gm) \times q_e\,(mg/gm) = (I)$$

$$mg/gm \quad q_e = \frac{(I)}{W}$$

So, what balance we have? At any time q, which is cubic meter per second multiplied by inlet, multiplied by C exit, which is continuously changing with time. So, we are making this balance at t. At a time t, we have taken a differential time of del t, over which to make this balance. So d t, integrate this 0 to t final.

When we say this t final, it is a equilibrium time, after a long time, infinite a long time when the concentration has reached the inlet and does not change. The entire bed is saturated. So, what is this amount here? Entire milligram per cubic meter, this is time here, this is time here per second. So much milligram has adsorb, gone from this liquid phase. So, much amount has adsorbed.

Where it has gone; where it has gone into this solid phase. All this packed bed which contains, so many granules, particles they have adsorbed. What is amount here adsorbed? That is, w totally started with, you have w gram of this charcoals or beets and it is say, capacity is not q. That is a q e, which should have brought at earlier for batch experiment milligram per gram.

So q is fixed, C inlet is fixed, C the time changes; we can calculate, we can do this integrations. This is nothing but, if you be careful this is nothing, but, the area over this C inlet, area over this curve here, it is a response, this is the response.

So, this is the area uptake. You can calculate; you know the way q e. That is what we are looking for. How much amount milligram per gram has been adsorb over this time t. Final or the equilibrium time is at integrations, this i, over this w, that is milligram per gram here.

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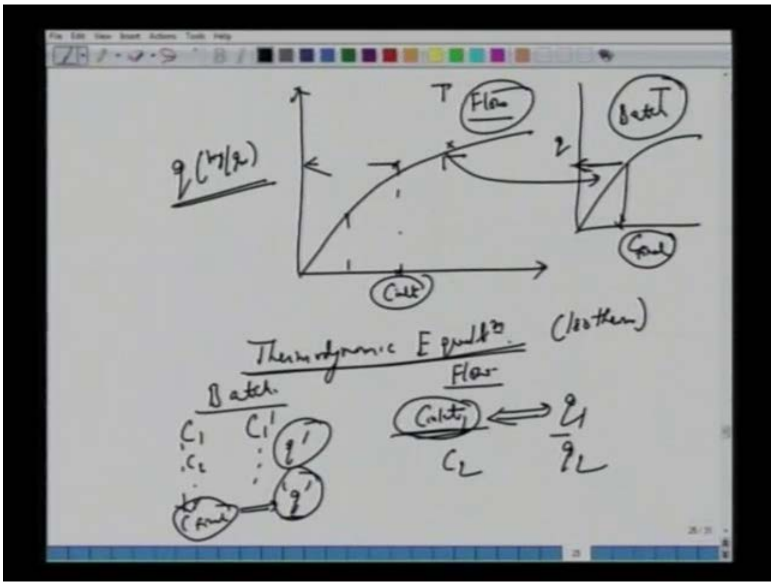

What you will expect that for that conditions, whatever C you have chosen, C inlet, with that C inlet, the q which you have calculated from that area under the curve, this is number data is q milligram per gram. This has to be same as what we have obtained from the batch experiment, where we brought at C final and it has to be the same, because in the batch or whether there is a flow, the material, the adsorbent has come in equilibrium with the solutes.

So, as long as fix the same temperature right, that is the batch experiment or it is a flow experiment, the bed is saturated. It is saturated with the C inlet or here saturated with the C final that is equilibrium. At one data point, change the next experiment, take some other C inlet, take some other experiment C inlet, you plot these two curves is the same one at the same. So, that is because it is we are talking of thermodynamic equilibrium. That is your isotherm, we call it one temperature.

So, whether this is the batch, must understand and batch, we start with C 1 C 2 C 3 decreases, still we have C final. We have this q here equilibrium which we calculate. Flow experiment, we do with C inlet, wait till you have equilibrium, calculate with q. This q versus C inlet must be same as this q versus C final. Change C inlet, you have different q 1 q 2, different concentrations. Change different initial concentrations, C 1 prime, you have different q prime, two one batch experiments. For the flow experiment, must give you the same result, which is your thermodynamic equilibrium. One has to calculate the way we have done it, the simple experiments or one has to relive some literature data. Somebody has already done for it. For different temperature, you will get different isotherms. May be at higher temperature, the capacity decreases, adsorption decreases, some system is possible that higher temperature capacity increases. So, all possible exothermic endothermic will discuss those.

So, todays lecture what we have done, we have introduced this in new unit operations adsorptions. It has liquid, it has one phase. Be in contact with the solid as a transfer this equilibrium and how do we approach. First, we characterize the sample our adsorbents, it could be porous; it could be non porous. One has to do certain experiments, certain analytical techniques and are there to calculate how much is this beet? How much is a surface area meter square per gram? Then, one has to do the thermodynamics, thermo dynamics either batch experiment or flow experiment. Batch experiment is relatively easier to do it, but, it takes a long time right 12 hours, may be 24 hours to reach the equilibrium.

So, one has to do this type of experiment. We establish isotherm. Isotherm is very similar to y versus x for distillations or solubility versus p or Henry's law for absorptions or for equilateral equilateral diagram, where we have this phase diagram for this extraction system.

So, the approach is the same. First establish your thermodynamic then, you make some species balance, mass balance or you talk in terms of stages. First stage absorber, second stage absorber or you have continuous packed bed, you know, different type of contactors.

So, the next class when we meet, we take up this topic for the stage wise for the continuous contactor.