Physico-Chemical Processes for Wastewater Treatment

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Lecture 37

Ion-Exchange - I

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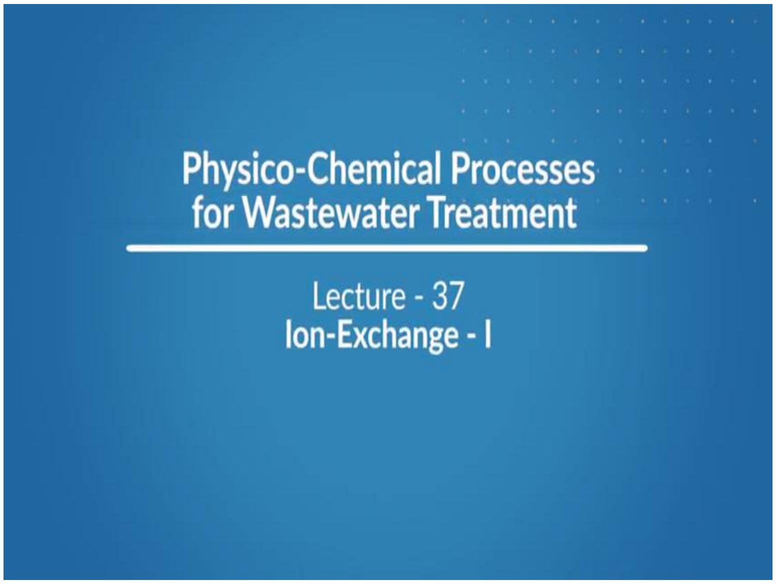

Physico-Chemical Processes for Wastewater Treatment

Lecture - 37
Ion-Exchange - I

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. So, in the previous lectures, we studied different unit operations which can be used for treatment of water and wastewater and we started with flow utilization basin followed by aeration then we studied coagulation, flocculation, settling followed by filtration then adsorption.

So, similarly in the similar to adsorption there is another operation which is very common in water or wastewater treatment which is called as ion-exchange. Previously we understood during the water quality analysis section, that a number of ions are undesirable and these ions may be toxic may not be toxic, some of the non-toxic ions include like magnesium, calcium, sodium, all those parameters which are not desirable for various designated uses.

So, like, we do not desire hardness to be present. So, calcium and magnesium ions are never desired to be present in the water if the water has to be used for industrial applications, including like steam generation. So, we want the calcium magnesium to be removed. Similarly, many places we want that sodium to be removed. In addition, there are a number of ions which may be toxic in nature like cadmium, arsenic, all those materials.

So, we can also remove these toxic ions using ion-exchange method. So, ion-exchange method can be used to remove hardness by removing the calcium magnesium ions. Also, it can be used for removing various toxic ions also. And as the word shows whenever we are doing ion-exchange, so one of the ions will be adsorbed and another ion will be released.

So, we have to cross check all those conditions, whether the resin that we are using or the ion-exchange material that we are using is good enough, the exchanged ion is within the permissible limit these things we have to cross check.

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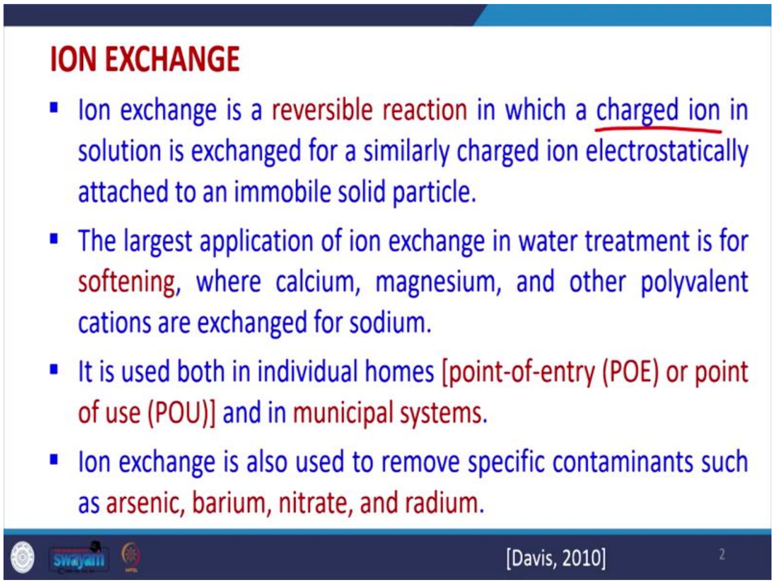

ION EXCHANGE

- Ion exchange is a reversible reaction in which a charged ion in solution is exchanged for a similarly charged ion electrostatically attached to an immobile solid particle.
- The largest application of ion exchange in water treatment is for softening, where calcium, magnesium, and other polyvalent cations are exchanged for sodium.
- It is used both in individual homes [point-of-entry (POE) or point of use (POU)] and in municipal systems.
- Ion exchange is also used to remove specific contaminants such as arsenic, barium, nitrate, and radium.

[Davis, 2010]

Now, it is an exchange is like a reversible reaction in which a charged ion in the solution. So, that charged ion may be any of the undesired material, so that may be calcium magnesium that can be any toxic material and that is exchanged for a similarly charged ion, which is already electrostatically attached to an immobile solid particles. So, this undesirable charged ion is exchange by not that much undesirable charged ion, which is already there on the immobile solid particles, so we exchange that ion.

So, this is, ion-exchange process is used in the water treatment very commonly, for softening, for, where calcium, magnesium and other polyvalent cations are exchanged for the, by exchanging with sodium. So, this is very, very common. Ion-exchange type of unit operations maybe from very small scale to very big scale.

So, they can be used in the individual homes, they can be used in the municipal systems, they can be of very, very big size and they can be, already told they can be used in the very small scale at the individual homes also. Ion-exchange can be used to remove some specific contaminants such as arsenic, barium, nitrate, radium, etc. So, this is also possible using ion-exchange.

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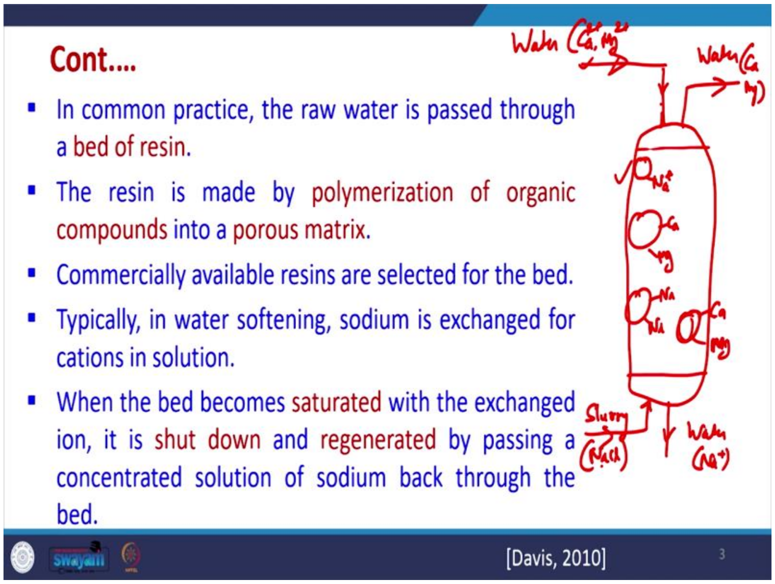

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- In common practice, the raw water is passed through a bed of resin.
- The resin is made by polymerization of organic compounds into a porous matrix.
- Commercially available resins are selected for the bed.
- Typically, in water softening, sodium is exchanged for cations in solution.
- When the bed becomes saturated with the exchanged ion, it is shut down and regenerated by passing a concentrated solution of sodium back through the bed.

[Davis, 2010]

So, in common practice, what is done is that, suppose, we have this bed is there. So, we will be having a bed, packed-bed similar to the adsorption. So, suppose this is the bed and we have some water which is coming and that water is there and that water is containing suppose calcium, magnesium, etc. So, this is there. So, calcium Ca2 plus, Mg2 plus will be there.

Now, in this packed-bed it will contain a resin or some material which will be having, suppose this is the resin and this is having sodium. So, this will be having Na plus. Now, when the water will go through this packed-bed actually the water which is coming out. Now, the water will contain more amount of Na but it will not be containing calcium and magnesium.

So, the bed will get exhausted and the bed will now contain calcium, it may contain magnesium, but Na will be exchanged. So, this is how it works. And after some time, when all the resins will get exhausted. So, that means each of the resin will not contain any sodium. So, again there will be only calcium, magnesium and this particular thing will be immobile. So, that is there. So, after some time what is in done, the backwashing is done or the regeneration of the bed is done.

So, how it is done? So, in place of that, now in the backwashing condition or regeneration condition a slurry or a slurry containing NaCl will be sent. Now, this NaCl, this everything will be replaced, so Ca will be coming out in the backwash condition the water which will be coming out after some time it will contain very high amount of calcium and magnesium, but this Na will replace the Ca and Mg.

So, again the original condition where a lot of Na is there and the resin will be there and that is the whole bed will be regenerated and that can be used in the next cycle. So, this is how it works. So, in common practice the raw water is passed through the bed of the resin. The resin is made up of like polymerized organic compounds and they are formed into a porous matrix.

Now, there are commercially available resins which may be there depending upon the concentration of calcium magnesium of any other ion that has to be exchanged. So, we have to cross check that. Typically in water softening, sodium is exchanged for cation. So, we generally will be having sodium-based resin. So, when the bid becomes saturated with the exchanged ion, so that means all the resins, Na has been replaced by calcium and magnesium.

So, under that condition, this bed is regenerated by passing a concentrated solution of sodium back through the bed. So, this is there. So, and thus we can regenerate the bed and we can use the bed further.

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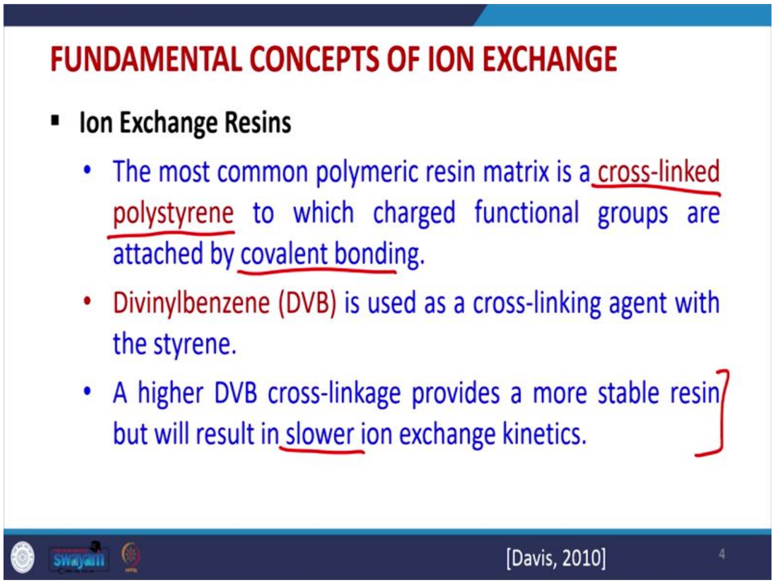

FUNDAMENTAL CONCEPTS OF ION EXCHANGE

- **Ion Exchange Resins**
  - The most common polymeric resin matrix is a cross-linked polystyrene to which charged functional groups are attached by covalent bonding.
  - Divinylbenzene (DVB) is used as a cross-linking agent with the styrene.
  - A higher DVB cross-linkage provides a more stable resin but will result in slower ion exchange kinetics.

[Davis, 2010]

Now, there are some fundamental concepts for ion-exchange. So, one of the most important thing is ion-exchange resin. So, which type of ion-exchange resin has to be used or which type of, that depends upon the ions that have to be exchanged. So, the most common polymeric resin metrix is like a cross-linked polystyrene to which different charged functional groups are attached by covalent bonding.

So, we can manipulate this. And a little bit while creating this resin matrix or producing this resin matrix. And then like Divinylbenzene is used as a cross-linking agent with the styrene. A higher DVB cross-linked material provides a more stable resin, but it may result in slower ion-exchange kinetics.

So, that has to be cross checked that how much cross-linking we have to do, because we do not, if the kinetics is slow, so that means we will be requiring a bigger bed for treatment of same flow rate of water. So, we have to cross check that how much cross linking has to be done. Though the, this resin will be more stable, but these things we have to cross check. So, that is why we had to carry experiments at the lab scale also for determining all these parameters.

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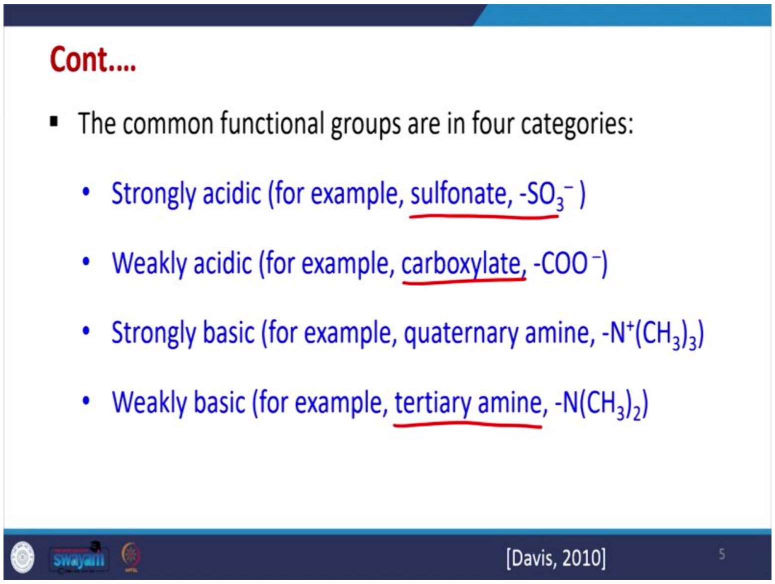

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- The common functional groups are in four categories:
  - Strongly acidic (for example, sulfonate, $-SO_3^-$)
  - Weakly acidic (for example, carboxylate, $-COO^-$)
  - Strongly basic (for example, quaternary amine, $-N^+(CH_3)_3$)
  - Weakly basic (for example, tertiary amine, $-N(CH_3)_2$)

[Davis, 2010]

Now, there are a number of functional groups, which are possible and all the functional groups can be categorized into four different categories. So, like strongly acidic. So, in this case the example is of like sulfonate functioning maybe there, then weakly acidic where carboxylate functional group may be present. Strongly basic or weekly basic, so strongly basic quaternary amine, in the weekly basic case we have tertiary amine.

So, we have resin on which different functionalities can be there and this we can decide beforehand. Depending upon our requirement, the ions to be exchanged, the concentration of ion which is there and the kinetics also because we have to cross check with respect to kinetics that how much time it will take for exchange to happen. So, that is there.

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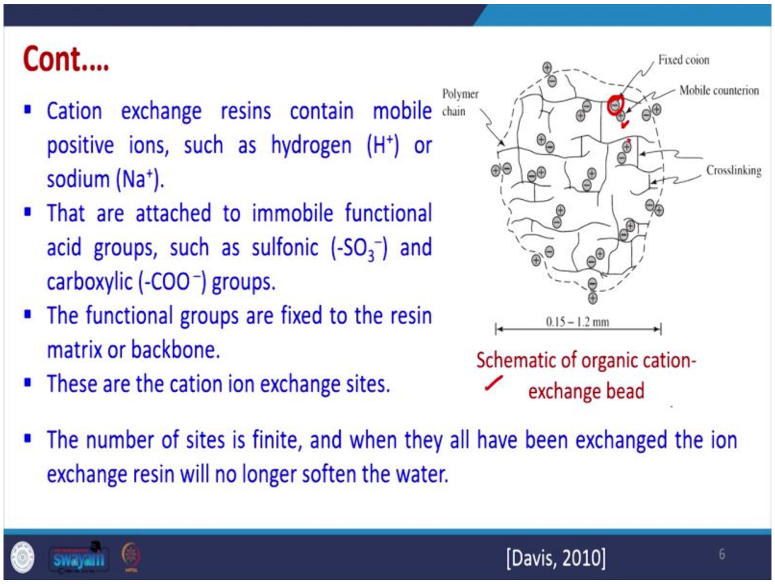

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- Cation exchange resins contain mobile positive ions, such as hydrogen (H^+) or sodium (Na^+).
- That are attached to immobile functional acid groups, such as sulfonic ($-SO_3^-$) and carboxylic ($-COO^-$) groups.
- The functional groups are fixed to the resin matrix or backbone.
- These are the cation ion exchange sites.
- The number of sites is finite, and when they all have been exchanged the ion exchange resin will no longer soften the water.

Schematic of organic cation-exchange bead

[Davis, 2010]

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Now, cation exchange resins contain mobile positive ions such as hydrogen or sodium. So, they are attached to the immobile functional acidic groups such as sulfonic or carboxylic group. So, this plus charge will be always be attached to this minus charge. Now, the functional groups are fixed to the resin matrix or the backbone. So, this is there. And these are the cation ion-exchange sites.

So, these sites where the functionalities are there, they are called as sites, cation exchange sites. The number of sites is always finite, when, but we desire the number of sites to be highest possible. So, this is there. So, and when all the resins have been exchanged, so, will the, this resin cannot be used further and it has to be regenerated, the way it has been told earlier. So, depending upon the regeneration solution may be different depending upon the ion which is getting exchanged or what is the actual original immobile functional group which is there. So, that will depend upon that also.

So, whether it is weakly acidic, highly acidic, all those things are very, very important parameters when understanding these ion-exchange resin. So, we can see here the cross-linking is there. So, higher the cross-linking stability will be higher, but kinetics will be slow. So, this is the fixed anion, which will be fixed, but this is the mobile counter ion, which can be exchanged. So, it is possible to exchange these ions and these can be regenerated also. So, this is there. So, this is how the, this is the schematic of organic cation exchange bead which is there.

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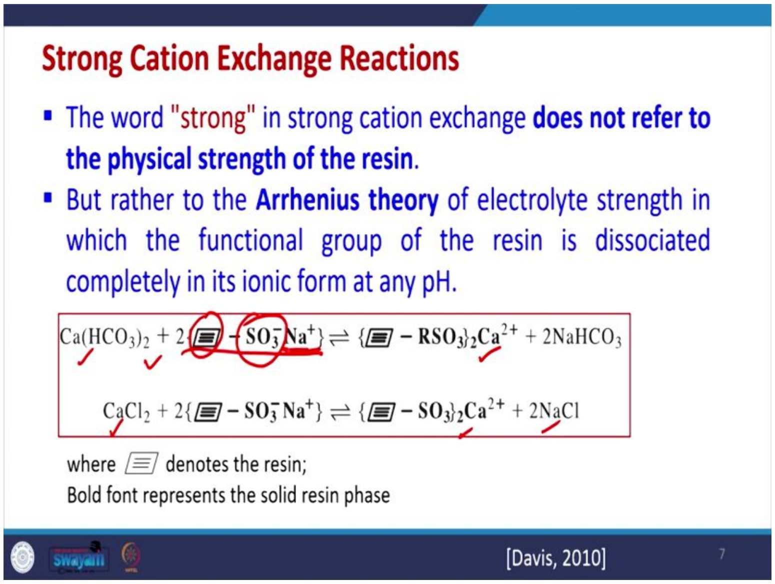

Strong Cation Exchange Reactions

- The word "strong" in strong cation exchange **does not refer to the physical strength of the resin.**
- But rather to the **Arrhenius theory** of electrolyte strength in which the functional group of the resin is dissociated completely in its ionic form at any pH.

$$Ca(HCO_3)_2 + 2\{\boxed{\equiv} - \mathbf{SO_3^-} Na^+\} \rightleftharpoons \{\boxed{\equiv} - \mathbf{RSO_3}\}_2\mathbf{Ca}^{2+} + 2NaHCO_3$$

$$CaCl_2 + 2\{\boxed{\equiv} - \mathbf{SO_3^-} \mathbf{Na^+}\} \rightleftharpoons \{\boxed{\equiv} - \mathbf{SO_3}\}_2\mathbf{Ca}^{2+} + 2NaCl$$

where $\boxed{\equiv}$ denotes the resin;
Bold font represents the solid resin phase

[Davis, 2010]

Now, going further there are strong cation exchange reactions which are possible. So, strong here does not mean that the physical strength of the resin, here it means that with respect to functional group. So, rather to the, like what type of functional groups are there and whether the cation exchange how much cation exchange is possible, we can, can we replace all the cations or not. So, all these things are there.

So, it depends upon the electrolyte strength in which the functional group of the resin is dissociated completely in its ionic form. So, this is there suppose. So, this is the resin you can see here. And here the calcium is there in the, calcium carbonate is there. So, we can see here that it is replacing. Similarly, it is replacing the calcium chloride also in this case, so both are possible. This particular sign denotes the resin.

So, this is the total resin matrix and in this case this is the fixed anion and this is the section which can be replaced. So, this is strong cation exchange reactions are possible under that condition.

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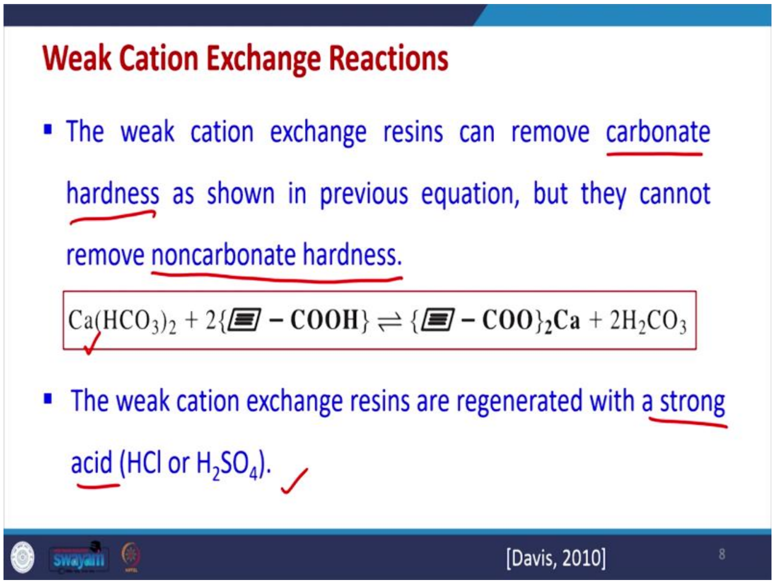

Weak Cation Exchange Reactions

- The weak cation exchange resins can remove carbonate hardness as shown in previous equation, but they cannot remove noncarbonate hardness.

$$\boxed{Ca(HCO_3)_2 + 2\{▤ - \mathbf{COOH}\} \rightleftharpoons \{▤ - \mathbf{COO}\}_2\mathbf{Ca} + 2H_2CO_3}$$

- The weak cation exchange resins are regenerated with a strong acid (HCl or H_2SO_4).

[Davis, 2010]

There are weak cation exchange reactions are also possible. So, under that condition the resins are able to remove the carbonate hardness. So, calcium from carbonate hardness can be removed, but they cannot remove the calcium from non-carbonate hardness. So, they can only perform this particular first reaction, they cannot perform the second reaction under the simple weak cation exchange regions which are there. So, and they can be easily be, but these can be easily be regenerated by using a strong acid. So, this is possible. So, there are different types of possibilities of ion-exchange also within different ion-exchange resins.

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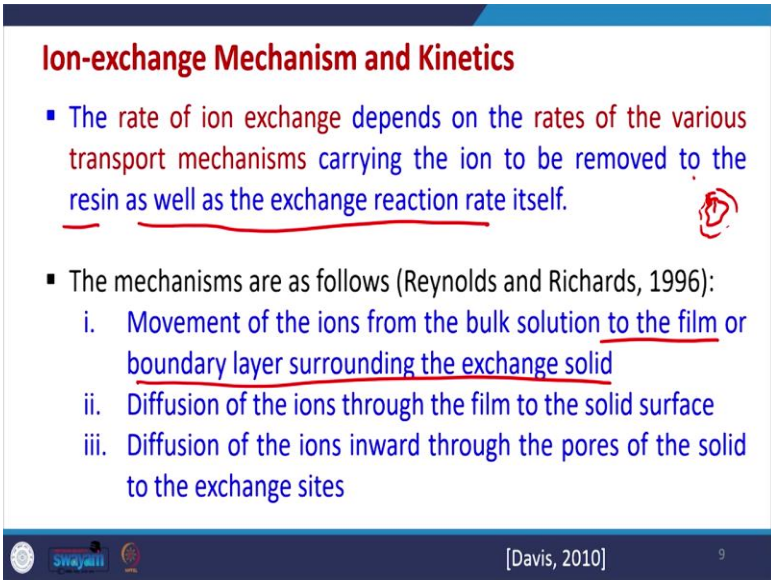

Ion-exchange Mechanism and Kinetics

- The rate of ion exchange depends on the rates of the various transport mechanisms carrying the ion to be removed to the resin as well as the exchange reaction rate itself.
- The mechanisms are as follows (Reynolds and Richards, 1996):
  1. Movement of the ions from the bulk solution to the film or boundary layer surrounding the exchange solid
  2. Diffusion of the ions through the film to the solid surface
  3. Diffusion of the ions inward through the pores of the solid to the exchange sites

[Davis, 2010]

Now, what are the different ion-exchange mechanism and kinetics? So, the rate of ion exchange depends upon the rates of various transport mechanisms, which get carried out in the bed. And depending upon the ion to be removed, and how the ion moves towards the resin and how quickly or how faster the ion-exchange reaction takes place. So, a number of parameters are there. Now, there are different steps within the mechanism.

So, how the ion-exchange mechanism works it is shown here. Now, we always want each of these steps to be fastest possible. So, this is whatever is desirable. So, as in the adsorption case, here also the first step is the movement of the ions from the bulk solution to the film which is, or the boundary layer which is surrounding the exchange solid. So, always the bead which is there it will always contain some liquid film.

So, the movement of ion from here up to the liquid film, so, this is the first step. Now, the diffusion of ions through the film to the solid surface. So, here how quickly the ions diffuse across the film. So, this is there, this is the second step diffusion of ions through the film. Then diffusion of ions inward through the pores of the solid to the exchange site. So, this is the third step, that how quickly within the solid the pores which are there, so, how quickly the ion moves through those pores inside into the exchange resin. So, that we have to see.

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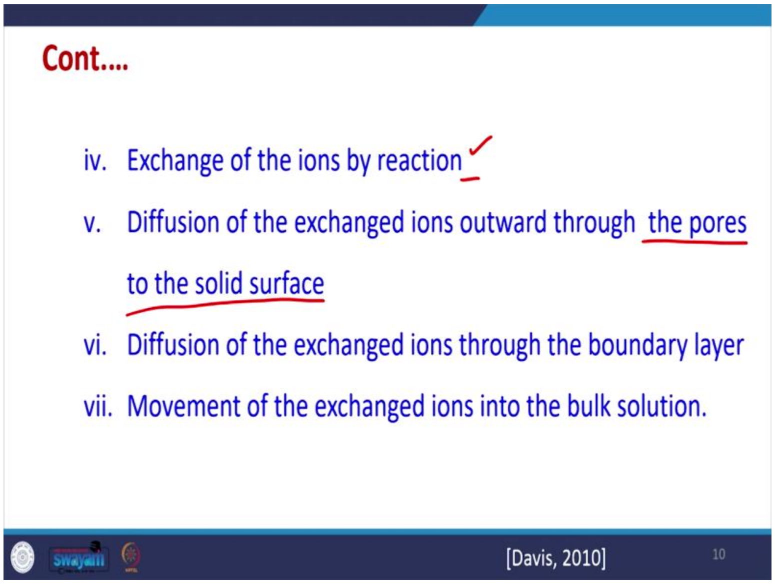

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iv. Exchange of the ions by reaction ✓

v. Diffusion of the exchanged ions outward through the pores to the solid surface

vi. Diffusion of the exchanged ions through the boundary layer

vii. Movement of the exchanged ions into the bulk solution.

[Davis, 2010]

Then exchange of the ions by the reaction. So, there will be some exchange reaction will be taking place that may be strong that may be weak. And how quickly this exchange reaction take place. So, this is also very important. Now, in the adsorption case generally here the conditions stop, but for ion-exchange, there are more steps because the exchanged ion will come out through the pores of the solid surface.

So, we have to see that the exchanged ions should come out through the pores of the solid surface, then diffusion of the exchange ion through again the boundary layer are filled and movement of the exchange ion into the bulk solution. So, these are the different steps. Now, here whether depending upon the molecular size of the exchanged ion. So, here Na plus or Ca2 plus what type of ions have to be exchanged, we cross check.

So, pores are very important, none of the places the pore diffusion should be controlling, we always desire the exchange of ion should be the rate controlling step or it should be the slowest step and we always want this slowest step to be the fastest possible and we desire the cross-linking in such a manner that the pore diffusion should never be a rate controlling step.

Also, the flow rate of the water to be treated through the bed can decide or help in deciding whether the, what will be the thickness of the boundary layer. So, we do not want the thickness of the boundary layer to be big so that this step or the second step is never the rate controlling step. And similarly, we can, through the flow rate we can decide, minimize the resistance with respect to the first step and the last step.

So, these are the various mechanism steps within the ion-exchange. And the overall thing is that we do not want any of these steps to be slowest. We want this step to be the controlling and within this step we want it to be the faster, because this we can manipulate or we can decide while deciding the resin itself and all other steps the resistances we can minimize by properly deciding the operating parameters with respect to treatment.

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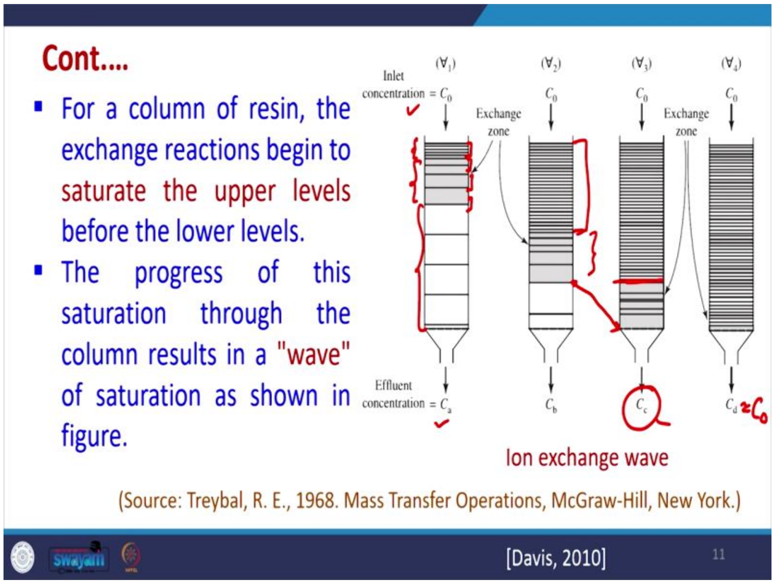

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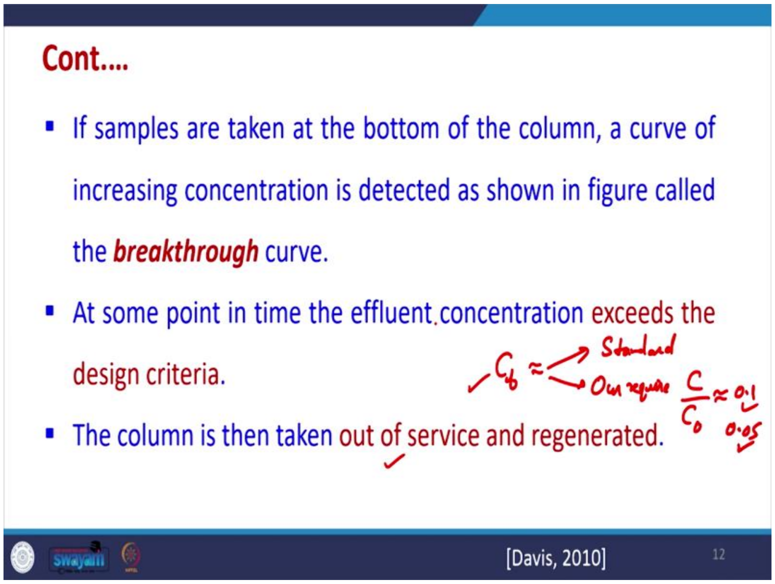
- For a column of resin, the exchange reactions begin to saturate the upper levels before the lower levels.
- The progress of this saturation through the column results in a "wave" of saturation as shown in figure.

Ion exchange wave

(Source: Treybal, R. E., 1968. Mass Transfer Operations, McGraw-Hill, New York.)

[Davis, 2010]



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- If samples are taken at the bottom of the column, a curve of increasing concentration is detected as shown in figure called the ***breakthrough*** curve.
- At some point in time the effluent concentration exceeds the design criteria.
- The column is then taken out of service and regenerated.

$C_b \approx$ Standard
Our requirement $\frac{C}{C_0} \approx 0.1$
0.05

[Davis, 2010]

Now, for a column of resin, the exchange reactions begins to saturate the upper levels first before the, so suppose the flow rate is from the top. So, initially this zone will be utilized then this zone then this zone. So, we can see here the moment this is like mass transfer zone in the adsorption. So, in the effluent concentration is coming out Ca here and inlet concentration is C0.

Here, only this section of bed has been fully utilized, this section of bed is being used and this section of bed is not used at all till now, after some time the exchange, this is the exhausted bed. And this is the bed in which the removal is happening and this is unutilized bed. As soon as it will reach a point like here this section has been utilized and this particular section reaches the outer end of the border, outer end of the bed or the last section of the bed.

So, under that condition the concentration which will be coming out, it will be now moving towards the initial concentration range and after some time this Cd when whole of the bed will get exhausted it will become equal to C0. So, that means, no further cation exchange is happening and we have to cross check, we have to regenerate the bed. So, this is there. So, this is called the wave, the progress of the saturation wave through the column results in a wave of saturation as shown in the figure. And we always want to model this.

And second thing is that we want to, we want, it is always desirable to reach this concentration maximum time delay possible. So, we want this concentration to be reached in very long duration. And before that a very large amount of water should have been treated, so this is desirable. If the samples are taken at the bottom of the column and a curve of the increasing concentration is detected as shown in figure.

So, this is called breakthrough curve. And this is similar to the curve that we have studied for adsorption. So, this is like adsorption breakthrough curve here we have ion-exchange breakthrough curve. At some point in the time the effluent concentration will exceed the design criteria. So, the design criteria could be like with respect to what application we are going. So, sometimes that design criteria, the final concentration or the breakthrough concentration will be set by the standards.

So, suppose any arsenic has to be removed. So, under that condition, we will always desire that the arsenic should be within the drinking water standard. So, that means Cb will be the concentration as decided by the standard. Sometimes it is possible that we may have to treat the water in the second stage. So, we may decide the value of C, C by C0 depending upon our requirement. So, like it may be 0.1, it may be 0.05.

So, this we may decide. And that design criteria also suppose, we have to go for calcium and magnesium ion removal. So, under that condition if the water has to be used suppose for steam generation. So, there will be a certain maximum limit with respect to calcium and magnesium which can be used for steam generation without any scaling in the pipelines. So, under those conditions, we have a set value which is as per our requirement.

So, we can always desire the breakthrough concentration and depending upon that we will come to know that whether the column is out of service and then we have to regenerate the column before actually we can use the water for the run.

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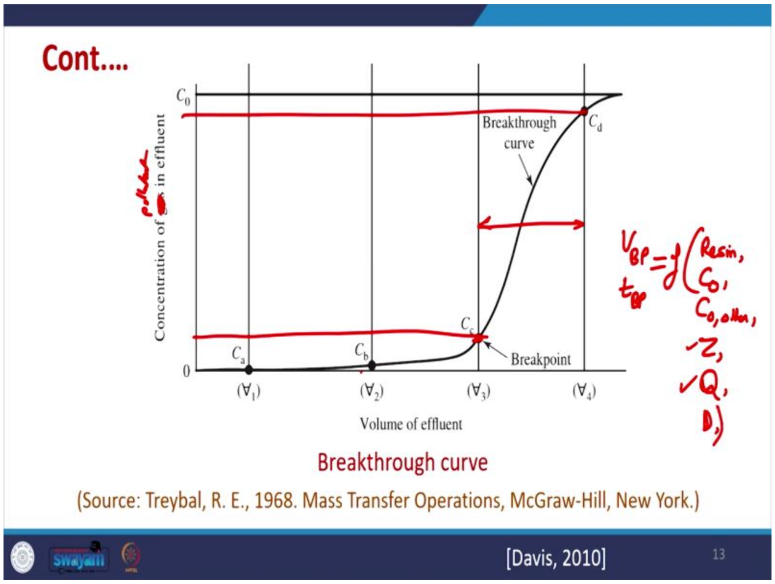

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Breakthrough curve

(Source: Treybal, R. E., 1968. Mass Transfer Operations, McGraw-Hill, New York.)

[Davis, 2010]

Now, so, this is the type of curve that will come out. Suppose the concentration of gas is there or concentration of any pollutant in the effluent has to be cross checked. So, like in the initial case, so, Ca, Cb, Cc, Cd. So, this is there the same as Ca, Cb, Cc, Cd. So, this is the breakthrough time and that breakthrough time can be decided depending upon a number of parameters. And similarly Cd where we have actually reached the C0 concentration it is. So, this time up to this time the bed is totally exhausted, but one main point is this not this and, but we can always want this Cd and Cc to be same and the bed to be exhausted at the same time.

Now, as we studied earlier, that time of breakthrough, this time which is there or the volume treated at breakthrough. So, if I can write volume treated at breakthrough or time for breakthrough this is a function of a number of variables. And what are those variables? So, we have to decide, first, the first variable is the resin itself that what type of resin we are going to use.

So, this is very, very important consideration that once we decide okay, this is the resin that we are going to use, then based upon that we can perform these small scale tests in the lab. And from that, we can decide a number of parameters under which we can predict tentatively and then we can carry out some confirmation experiment, etc. So, resin is first parameter, then it will be the concentration of different ions that has to be exchanged.

So, we have to cross check that what are the different concentration of ions in the water that has to be treated and that depends. Also, the concentration of other ions it may be possible that it will depend upon the other ions for which we are not exchanging and what are their affinity towards the ion which will be exchanged. So, suppose Na has to be exchanged and the Na from the resin is coming out in the water and the water is having good affinity for that.

So, the kinetics will improve very tremendous, so we can use the smaller bid for same treatment of water. So, concentration of the ions that have to be exchanged. Concentration of other ions that is also important and their affinity with respect to different ions. Then, in addition to that, the height of the bed is very important that how much is the height of the bed. So, it will depend upon that condition also, it will depend upon the flow rate of the bed and the particle size of the resins also.

It is possible that flow rate diameter are the parameters on which this volume at breakthrough and the time at breakthrough will be dependent. So, we can carry out a number of experiments, we can use the model similar to the adsorption packed bed and we can predict the breakthrough time. And depending upon that model that we have developed, we can decide that okay what flow rate we are going to use, what height, what diameter, so that we can maximize the exchange usage rate, resin usage rate.

We want all the resin to be used properly. And we want the breakthrough time or volume at the breakthrough time to be highest possible. So, this way we can do this. So, whatever is the theory, some of the models with respect to adsorption packed-bed can be used in the ion-exchange bed also and we can develop a similar theory or approach for design of ion-exchange resin packed-beds. So, this is there.

And we will try to continue this and understand the different features of ion-exchange resins in the next lectures onwards. And we will try to know that what is the exchange capacity, what is the separation factor, how to use them. And there are a number of other thing that we must understand with respect to ion-exchange resin. As well as how it works in the bed itself.

So, all these theories and other things we will try to understand in the next lecture. So, we will continue with the ion exchange resin later on. Thank you very much.