Course Name: Industrial Wastewater Treatment
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Lecture 01: Ion Exchange Process

Hello everybody, I welcome all of you to the Module 2, Lecture 1 and the topic of our discussion today will be on ion exchange process. So, the concept covered during this topic will be introduction to the ion exchange process. First of all, we will talk about what is ion exchange, how this ion exchange process happens and what are the materials which are involved during the ion exchange process, what type of material we use so that we can undergo the ion exchange reactions and ion exchange process and the treatment of water or wastewater by using ion exchange materials. Similarly, we will also talk about what are the typical ion exchange reactions that happens when the ion exchange material comes in contact with the water or wastewater which contains the ions which you want to remove. And after that we will talk about the exchange capacity of the ion exchange resins which is a very important term that if you want to design, if you want to find out that what amount of resins we require to remove a particular concentration of a certain ion present in the water or wastewater and what should be the exchange capacity based on which we can decide about how much resin we require.

Similarly, then lastly, we will talk about the total ion exchange capacity versus the operating capacity of the resin and in the end, we will take a very small numerical which will tell you about how to calculate the exchange capacity. So, the ion exchange process is a unit process in which the ions of a given species they are displaced from an insoluble exchange material by ions of different species in the solution. So, here what happens that the material which you are having that is the ion exchange material or we also call it as resin. So, this resin contains certain ions and there are certain ions which are present in the water or wastewater which you want to remove.

So, the ions that are present in water or wastewater they are exchanged by the ions which are present on the resins which is again insoluble exchange material and so it happens that the water or the wastewater is free from the targeted ions that you want to remove. For example, you can see here that the hard water coming here so the hard water is made in contact with the resins which are present on the ion exchange material. So, this ion exchange material contains sodium ions on it and all of you know that the hardness basically is caused by calcium and magnesium ions majorly which are present in the water which you want to treat. So, this is passed through this material, and we see that the ions basically the calcium and magnesium ions they are exchanged by the sodium ions and the water which basically becomes free from these calcium and magnesium ions, and it is then basically laden with sodium ions though, but it becomes soft. So, this is how the ion exchange process works and this process is commonly used in various industrials and scientific and as well as the water treatment and wastewater treatment applications and the ion exchange material that we use is called the ion exchange resins or it is also called ion exchange media and they have an ability to selectively adsorb the ions from the solution and release other ions in exchange as just now explained.

So, in the domestic wastewater softening the sodium ions are replaced by calcium and magnesium ions and thus it can reduce the hardness as just now explained in this example is there and ion exchange materials can be used for number of water and wastewater treatment applications. For example, it can be used for the removal of nitrogen, it can be used for the removal of the heavy metals, it can be used for the removal of totally dissolved solid. So, ion exchange process can be operated in batch mode as well as continuous mode. So, batch processes are the processes where we want to treat the water which is coming out in a very small quantity or the units or the industries where basically the generation of wastewater is small or when we are applying this process in a laboratory scale so then we generally go for a batch process.

In the batch process as you can see that the resins basically, they are put into the container, or we say it as a reactor. So, in this reactor the resins are placed and the solution that we want to treat is placed in this reactor also known as batch reactor and it is continuously stirred. So, whatever the ions basically that we want to remove so when they are removed or when the equilibrium is achieved or when the saturation of the resins takes place so after that we stop the process, and we filter out the resins or the media from the batch reactor and the filtrate that we get is free from the targeted ions. So, that is how the batch process works and these materials which are coming out that is the ion exchange resins or ion exchange media so they are subsequently regenerated and they can be reused and the industries where we are having continuous generation of the water or wastewater so in that case we go for a continuous process where the exchange material is placed in a bed or a packed column and the water which is treated is passed continuously through this column, right. either it can be in the up-flow mode or it can be in the downflow mode the water which contains a certain targeted ion so they are passed through this filter media or basically which is packed with the resins and the targeted ions they are exchanged with the ions which are present on the resin and then we can get the water that is the effluent that is coming out is free from the targeted ions and as soon as the resin capacity is exhausted then the operation is stopped and the column is backwashed so that the suspended solids or the trapped solids which are there, they can be removed from the system and then these resins which are there so they are regenerated. So, regeneration we will talk in the coming lectures.

We can see here that continuous process and the batch process for removal of the hard water, you can see that the ion exchange column is there and the water is being continuously fed into this column and the ion exchange resins so they may contain sodium ions on it here, so this sodium ions basically is exchanged by the calcium and magnesium ions and the water become free from the hard water similarly the hard water can be placed in a batch reactor and this batch reactor basically can come in contact with the resins and this can be continuously stirred and when the equilibrium conditions happen after that the water can be removed and we get the soft water out of it. That is an example of a continuous process and the batch process. So, let us also talk about the ion exchange materials for example, we can have the naturally occurring materials which can act as an ion exchange material and similarly we can also have a synthetic ion exchange material. Naturally occurring materials are mostly minerals which are also known as zeolites. So, they are highly micro-porous crystalline Aluminosilicate materials.

The zeolite is having general formula of aluminate and silicate which is there and here the M which is used here is mainly the H^+ ions or the sodium ions. You can see here that the microporous structure of the zeolites it helps in treatment of the water and exchange of the ions through this microporous structure. So, it can be used for water softening, it can be used for ammonium ion removal etc. Similarly, we can also have the synthetic ion exchange materials which are called resins, or they are also called phenolic polymers, and they are manufactured by using styrene and divinylbenzene. So, they co-polymerize so that we can get a tough structure which is insoluble structure and that is known as resin.

So, styrene here serves as the basic matrix of the resin and the divinylbenzene is used to crosslink the polymers so that we can produce an insoluble tough resin which is mostly required because we want that the resin will be in contact with a solvent or with here, we are talking of water. So, it remains in contact with water continuously. So, it should be tough, or it should not be soluble inside the water so that it can sustain the reactions that are taking place during the ion exchange. You can see here; this is an expanded view of the polystyrene bead. You can see here that we are having certain ions which are fixed to the polystyrene bead.

So, they are negatively charged SO_3^- ions, which are basically fixed in nature, and we are having the mobile positively charged exchangeable cations. For example, here in this case, it is Na+. So, these ions can move and these ions can be exchanged by the cations present in the water or the wastewater and similarly you can see here that the long chain compound that is the polystyrene chain is there which acts as a base and similarly we can have the crosslinking which is done by the divinylbenzene which acts as a crosslinking and the shaded portion that you see here is representing the water of the hydration. Because as soon as these polystyrene beads they will come in contact with water they will swell, and it will increase in volume depending upon the osmotic pressure that is developed inside the polystyrene bead and this swelling behavior can be influenced by the chemical composition of the polystyrene bead.

It will also be influenced by the polymer structure and degree of crosslinking plays a very-very important role here in the swelling of the polystyrene bead and resins have which have higher degree of crosslinking they tend to exhibit lower swelling tendencies as compared to the those which are having the lower crosslink. So, this may increase the toughness, this may increase the non- solubility, this may increase the lesser degradation of the resins in case when we are having high degree of crosslinking, but crosslinking can also have a certain disadvantage that is if we have very high degree of crosslinking it may also restrict ions movement through it, and this may also reduce efficiency. So, we can have different type of resins which can be there that is these are the synthetic resins which are made, and we can have different type of resins which are present. For example, we can have a strong acid-cation exchange resins and these strong acid-cation exchange resins, so they behave in a similar manner as that of the strong acid and they are highly ionized, and they are ionized at a different pH range. So, we can use such type of resins for a long range of pH, and they are in the form of for example, they can be in the acidic forms for example, they can be R−SO3H sulfonic group is there and similarly we can have in the salt form that is R−SO3Na also.

So, these two forms can be there for a strong acid cation exchange resins and as the name says so they are mainly used for the exchanging the cations which are present in the water or wastewater. Similarly, we can also have a weak acid-cation exchange resins where the weak acid functional group that is carboxylic acid group is present and they are weakly distributed. So, this means that they can work in a very short range of pH or generally in the acidic pH they will not work as they will not ionize. Similarly, we can have strong base anion exchange resins where the anions basically can be exchanged by the functional groups for example, here we can have the OH^- as the functional group which are present and they as a strong base resins they are also highly ionized and they can be used for a long pH range and they can be represented by the general formula that is R−NH3OH. Similarly, we can have the weak base anion exchange resins where the weak functional group for example, NH3Cl will be used and these are having a low degree of ionization and again at alkaline pH it may not work and that is why basically because it depends upon the degree of ionization where the ionization will not be possible and that is why the use of such type of resins can be limited by the pH condition, and in the last we can also have a heavy metal selective chelating resins which also behave like weak acid cation exchange resins and they also have a very high degree of selectivity for the heavy metal cations that is why they are called selective chelating resins. For example, we can have EDTA ethylene di-amine tetra acetic acid you must be well versed as you must have used it in during the experiment of total hardness and the resin structure is in the form of R-EDTA-Na. You can see here that the two structures one is on the left-hand side is the cation exchange resin it is a strong cation exchange resin similarly we can have strongly basic anion exchange resins. So, here you can see that our SO3H group is there where H^+ basically, is replaced by the cations which are present in the water or the wastewater. Similarly, you can see here that the strong anion exchange resin so this is basically the OH^-group is present which is mobile, and it can easily go into the solution or the water and the anions which are present in the water they can be exchanged by this OH^-.

The typical reactions that happen in the ion exchange for example.

❑**For natural zeolite (Z) :**

$$ZNa_2 + \begin{bmatrix} Ca^{2+} \\ Mg^{2+} \\ Fe^{2+} \end{bmatrix} \leftrightarrow Z \begin{bmatrix} Ca^{2+} \\ Mg^{2+} \\ Fe^{2+} \end{bmatrix} + 2Na^+$$

❑**For synthetic resins (R):**

(a) Strong acid cation exchange

$$RSO_3H + Na^+ \leftrightarrow RSO_3N_a + H^+$$

$$2RSO_3N_a + Ca^{2+} \leftrightarrow (RSO_3)_2C_a + 2Na^+$$

(b) Weak acid cation exchange

$$RCOOH + Na^+ \leftrightarrow RCOON_a + H^+$$

$$2RCOON_a + Ca^{2+} \leftrightarrow (RCOO)_2C_a + 2Na^+$$

(c) Strong base anion exchange

$$RR^1_3NOH + Cl^- \leftrightarrow RR^1_3NCl + OH^-$$

(d) Weak base anion exchange

$$RNH_3OH + Cl^- \leftrightarrow RNH_3Cl + OH^-$$

$$2RNH_3Cl + SO_4^{2-} \leftrightarrow (RNH_3)_2SO_4 + 2Cl^-$$

So, the typical thing is that these reactions are reversible and they basically they can happen in both the ways and this type of reaction basically generally happens when equilibrium conditions are maintained.

So, we come to the properties of ion exchange resins. So, the first and the foremost important property of the ion exchange resin is the exchange capacity. So, the capacity of ion exchange can be expressed in the quantity of the ions that can be taken up by a specific volume of it. Either it can be volume of the resin also it can be the weight of the resin also which can be either dry weight or it can be wet weight.

So, exchange capacity is always expressed in equivalents per liter or equivalents per kg or grams also. So, it depends upon that is how many equivalents of the ions are replaced by the ions which are present on the resins per unit volume or per unit weight of the anion exchange or cation exchange resins. So, this is how the exchange capacity is defined, and this exchange capacity will be very beneficial when we calculate that how much amount of cations or anions have been replaced and similarly it can also tell us about what should be the amount of resins that needs to be placed if you want to do in particular amount of cations or anions in the solution. Similarly, a very important property is the particle size which affects the hydraulics as well as the kinetics of the ion exchange. For example, if we are having a column and in which we are packing the resins as the size will lower down the hydraulics of the ion exchange column will be impacted as the lower the size the lower is the movement of the water through this ion exchange column and if the ion exchange column becomes highly packed then it becomes very difficult for the water to move through it and that basically becomes a constraint.

Similarly, the kinetics of the ion exchange is dependent upon the size and as the size reduces the kinetics increases. So, as the rate of exchange is inversely proportional to the $1/_{D^2}$ that is the diameter of the resin particles that's why as the size decreases kinetics of the ion exchange increases whereas the hydraulics of the ion exchange is adversely impacted. And the last property is the stability which again is very important factor for example, when we are putting this ion exchange in contact with water or waste water so the stability plays a very important role because ion exchange may shrink or it may swell depending upon the osmotic pressure that is developed inside the resins and it may also basically cause degradation of the resin if we are not having very high degree of the cross link. Similarly, these properties also become important when we are storing ion exchange resins, and this property also becomes of utmost importance. The ion exchange capacity of the resins: we can divide it into two parts that is the total exchange capacity and the operating exchange capacity. We will talk about the operating exchange capacity later on.

First of all, let us talk about the total exchange capacity. It is defined as the total ions exchanged per unit mass or volume of the resin. So, this means that whatever the number of ions which we want to remove from the water or the solution so the equivalents of ions or basically the number of ions that are exchanged per unit mass or per unit volume of the resin, so this is known as the total exchange capacity till the resins that we are using that is basically if we are using cation exchange resin or the anion exchange resin, so they become exhausted that is the initial concentration which is being put into the contact with the ion exchange resin, so this becomes equal to the effluent concentration. So, this means that our ion exchange has totally exhausted and then we can define that whatever the number of ions that have been exchanged till then, so this represents the total exchange capacity of the ion exchange resin. So, it can be again expressed in meq.per liter or equivalents per liter or milliequivalents per grams or meq. per kg or equivalents per kg whatever.

So, these units can be used for defining for representing the total exchange capacity of the ion exchange. For example, we can see here the synthetic resins they are having a capacity of around 2 to 10 equivalents per kg whereas zeolites they may be having a low capacity that is from 0.05 to 0.1 equivalents per kg. Now, how to measure the total exchange capacity of the ion exchange resin. So, it involves placing the resins in a known chemical state.

For example, when we are having a cation exchange resin so it will be first washed either with a strong acid or with a strong brine solution so that whatever the sites which are there on the ion exchange resin, so they are totally exchanged by H^+ions or they are totally exchanged by sodium ion. After doing this thing then we basically take a water or wastewater which contains a known concentration of the exchangeable ion. For example, let us say we are having a solution which contains lot of calcium ions. So, we should know that what is the initial concentration of the calcium ions which is there, and this is introduced into the resin column and the calcium ions they basically replace the sodium ions or the H^+ ions which are present on the resin. Basically, when the resins become exhausted that is all the sites are exchanged by calcium ions. So, this means that the in the concentration of calcium which is being put onto the column is equal to the effluent concentration.

So, at that point of time we stop the operation, and we measure that how many total equivalents of calcium ions were exchanged by the unit weight or unit volume of the resins. So, this tells us about the total exchange capacity of the resins. Now, exchangeable capacity can also be defined in terms of gram calcium carbonate per cubic meter of resin that is one equivalents per cubic meter is equal to the 50 grams of calcium carbonate per cubic meter that is we know that equivalent weight of the calcium carbonate is 50 grams. So, this the one equivalents per cubic meter may also be represented as 50 grams of calcium carbonate per cubic meter. In contrast to the total capacity operating capacity is measured by the useful performance obtained with the ion exchange material that is which depends upon the prescribed set of conditions.

For example, suppose we want to remove from water or wastewater a certain amount of cations or anions or we are having a certain limit, a prescribed limit, that is it should not exceed in the water or wastewater the effluent the concentration of certain cations or anions should not exceed in the wastewater beyond the permissible limit. So, that defines the operating capacity now. So, this means that though the resin may not have reached its total capacity, but because the concentration of the targeted cations or anions have exceeded a certain limit. So, we have to stop the operation and that defines the operating capacity of that resin for that particular type of ion. So, it will depend upon a number of factors for example, it will depend upon the total capacity of the resins, it will depend upon the level of the regeneration that is being done to the resins, it will also depend upon the composition of the solution that is to be treated how many type of ions basically it contains or what is the ionic strength of that water or waste water basically being treated.

Similarly, the flow rates through the column will also define the operating capacity that is higher the flow rates the operating capacity reduces. Similarly, the temperature basically affects the kinetics of the reaction. So, also define the operating capacity. Particle size and distribution we have already discussed, right. So, that also defines the operating capacity and similarly the selectivity of a certain type of cations or anions that we want to remove also defines the operating capacity.

In general, if we represent the operating capacity by 'x' so this may be equal to the number of equivalents of ions of interest which are applied to the column divided by the resin volume minus the number of equivalents of ions of interest passing through the column divided by the resin volume. So, this gives us the operating capacity up to the point at which we stop our operation, we will discuss this in the coming examples. So, this curve you can see here that it basically represents a very good example for the total exchange capacity and the operating capacity of the resin. For example, you can see here that on the y-axis we are having the residual hardness expressed in ppm we can also express it in terms of equivalents per liter also and on the x-axis, we are having the volume which is passing per unit volume of the resin it can be volume per unit weight of the resin also. So, you can see that as the total hardness here is A to B so it represents the total hardness which is present in the feed water.

So, the total hardness that is basically subjected to the resins, so we can see here that as we feed the water which contains a total hardness of A to B. So, this hardness slowly and slowly reduces as then the hardness causing cations, so they are exchanged by the sites which are present on the resin and slowly and slowly it reduces it goes down below a point which sets our quality limits. So, you can see here that suppose we have put a certain quality limit that the product water should not contain a certain amount of hardness. So, this sets up the quality limits and this sets up the point, this point F which defines that now our hardness is going below the hardness that we require in the effluent. So, it may go down further as because the sites are present there and they are exchanging continuously cations of interest.

So, then slowly and slowly the sites get exhausted, and site started getting saturated and then the concentration in the effluent it starts increasing and you can see here that at point C it crosses our quality limits. So, if we continue our operation then we will see that continuously our concentration of the cations of interest they will rise and they will reach to a point D where we are having a concentration same as the feed concentration. So, this means that our C point here is called the break point where we have exceeded our quality limits, and the point G represents the exhaustion point where the quality where the total capacity is now exhausted. Whatever the resins are present, so, they have exhausted at this point and that is why it is called the exhaustion point and the yellow area which represents above the red line it represents the total capacity. For example, this area here that I am basically creating or the yellow area, so it represents the total capacity of the ion exchange resin and similarly if we see the operating capacity so in that case the area which is lying above the CDEF region that is basically wherever we are having the concentration of the hardness lower than what is required what is prescribed by the quality limits.

So, this area will give you the operating capacity of the resin, right. I think the difference between the operating capacity versus the total capacity must be clear to all of you and the total exchange capacity will remain same because it represents the all the exchangeable sites which are present on the resin whereas the operating capacity of the resin will be very specific to the test conditions, it will depend upon the conditions which are laid down for the quality limits. So, let us take an example.

Question 1: 1000 L of water was softened by Ion-exchange method. For regeneration, 150 L of 0.1 N each HCl and NaOH was needed by respective exhausted resins. Calculate the hardness of water sample.

Solution:
In Ion-exchange method, Cation exchanged by Cation exchanger and Anion exchanged by Anion exchanger.

Since, **Amount of acid or alkali used to regenerate the resin = Hardness of water sample.**
Hence, 1000 L of water ~ 150 L of 0.1 N HCl ~ 150 L of 0.1 N NaOH (eq. of $CaCO_3$)

$$= 150 \times 0.1 \text{ L of 1 N } CaCO_3 = \mathbf{15 \text{ L of 1N } CaCO_3}$$

$$\text{Now, } \mathbf{1 \text{ L of 1 N CaCO3} = 50 \text{ g of } CaCO_3}$$

$$\text{So, 15 L of 1 N } CaCO_3 = 15 \times 50 = \mathbf{750 \text{ g CaCO3 eq.}}$$

$$\mathbf{\text{Now, 1000 L of water} = 750 \text{ g CaCO3 eq.}}$$

$$\text{Therefore, } \mathbf{1L \text{ water} = \frac{750}{1000} = 0.75 \text{ g of CaCO3 eq.}}$$

$$= 0.75 * 1000 \text{mg of } CaCO_3 \text{ eq./L}$$

$$\text{So, } \mathbf{\text{Hardness of water} = 750 \text{ mg/L or ppm}}$$

So, we stop here, and we will talk about the ion exchange chemistry in our coming lecture.

Thank you.,