

Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 08

Lecture 38 | Ion Exchange: Illustrative Problem

Hello everyone, welcome to this course on adsorption science and technology. Today we are going to talk about this ion exchange as we are continuing in this week. So, in this lecture I am going to talk about some problems related to the equilibrium scenario of this adsorption you know studies on ion exchange process. Now, let us quickly recap on what we discussed so far before moving into the problem. So, as you understand that this ion exchange is nothing but a process of ionic equilibrium which exist between the solution phase and the solid phase which is mostly the resin. And, there is you know this ion exchange chemical reaction which takes place and through the you know this law of mass action for chemical equilibrium.

We can write down what is the equilibrium or the selectivity coefficient for this process. In this way this is very similar to an adsorption process where there is an equilibrium governed scenario. Typically this ion exchange are used for applications related to demineralization and deionization of water and these kind of high quality water where the resistivity is very high is typically used for boiler feed waters for you know chromatographic explanations for catalysis reactions and you know this biopharmaceuticals and all that. So, let us look into the problem a real life problem on how we can you know utilize our concepts for ionic equilibrium and we can try to work out the solution for this problem.

Q: Water containing 120 ppm Ca^{2+} , to be treated with resin (8% crosslinked with DVB) in the Na^+ form to remove 95% of the calcium ions. The resin has an exchange capacity of 2 eq./L. Amount of resin needed to treat 10 m^3 of water?






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So, let us consider that water or aqueous solution containing around. So, this water containing 120 ppm of calcium ions to be treated with a resin is like 8 percent cross linked with divinyl benzene in the. So, this is a strong acid resin in a form to remove or exchange 95 percent of the calcium ions. The resin has an exchange capacity of 2 equivalents per liter. So the question is the amount of resin needed to treat you know 10 meter cube of water.

So, you can note that the resin could be like a solid composite you know a bed, it could be also resin beads which are dispersed in water, it could be either of these forms and particularly for this problem it is, is immaterial whether we are talking about the presence of resin in the bed or whether it is the resin beads that is present in the solution. Now let us first you know find out the values of this equilibrium constant. So this equilibrium this K of calcium over sodium is what important. So, this means we have to find out the selectivity of this calcium over sodium. This is k_{Ca} because that is what matters here.

So, which is 5.2 if you recall these are the values that we listed or talked about in the previous class is 2 and this is around 2.6. Next is for the resin phase for the total concentration of ion exchange sites which is defined as Q and that is mentioned here as 2 eq per litre. Please note that typically these values can also be represented in terms of

mass like equivalent ions in terms of mass of the resin or it can also be considered in terms of the you know volume of the resin given that you know the density of this swollen resin right.

Q: Water containing 120 ppm Ca^{2+} , to be treated with resin (8% crosslinked with DVB) in the Na^+ form to remove 95% of the calcium ions. The resin has an exchange capacity of 2 eq/L. Amount of resin needed to treat 10 m^3 of water?

Equilibrium const.

$$K_{\text{Ca}^{2+}, \text{Na}^+} = K_{\text{Ca}^{2+}} / K_{\text{Na}^+} = 5.2 / 2 = 2.6$$

For the resin phase, the total conc. of ion-exchange sites, $Q = 2 \text{ eq/L}$

Total conc. of ions in solution (Ca^{2+} & Na^+ after exchange) expressed as eq. Ca^{2+} ions.

$$C_T = 0.12 \text{ g/L} = \frac{0.12}{40} \frac{\text{g mol}}{\text{L}} = \frac{0.12}{40} \times 2 = 0.006 \text{ eq/L}$$



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Now important is the total amount of or the total concentration of ions in solution. So, which includes calcium and sodium ions after exchange expressed in terms of expressed as equivalent calcium ions. So, it is mentioned it is 120 ppm of the total amount of the you know calcium ions and this equivalent amount of the ions is actually conserved which are whether it is in the solution phase or whether it is partly in solution phase and partly in the resin phase, but the total equivalent amount of the ions present in the solution at any time before or after equilibrium is conserved. So, if you consider this then this turns out to be 120 ppm is equivalent to 0.12 you know grams per liter.

So, which is 0.12 by 40 divided by the molecular weight. So, this is gram moles per liter and this is equal to, we multiply with 2 this is the valency. So, this turns out to be 0.006 eq per litre of the total amount of the ions expressed in terms of calcium that is present in the solution.

So, this quantity is referred to as capital C right maybe it is better to write that as capital CT. So, that we do not confuse with the nomenclature. So, this is the total amount of the ions present in the solution phase. Now, coming looking forward when the problem it is

said that 95 percent of ions are removed at the end of equilibrium. So, which means calcium ions remaining in water is only 5 percent.

So, this is 5 percent of 0.006 right. So, this is equal to 0.0003 equivalent per liter. Now of course, equivalent fraction of Ca plus in water at equilibrium which is the x this is nothing but our x right which could be like 0.05 percent or sorry 5 percent because 95 percent is removed. So, only the remaining 0.05 or you can consider this to be 0.003 divided by the total amount 0.000 sorry 0.006 right.

It is mentioned 95% of ions are removed @ end of equilibrium.

Ca^{2+} remaining in water = $(0.05) 0.006 = 0.0003 \text{ eq/L}$

Eq. fraction of Ca^{2+} in water @ equilibrium, $x = 0.05 \left(= \frac{0.0003}{0.006} \right)$.

So, if 'y' is eq. fraction of Ca^{2+} in resin phase, then.

n : valence of the ions

$$k = \left(\frac{C_T}{Q} \right)^{n-1} \frac{y}{(1-y)^n} \frac{(1-x)^n}{x}$$

$n=2$ for Ca^{2+}

$$k = \frac{C_T}{Q} \cdot \frac{y (1-x)^2}{(1-y)^2 x}$$

$y \sim 0.8657$

$$\Rightarrow 2.6 = \frac{0.006}{2} \frac{y (1-0.05)^2}{(1-y)^2 (0.05)}$$

$\Rightarrow$ Quadratic equation in terms of y

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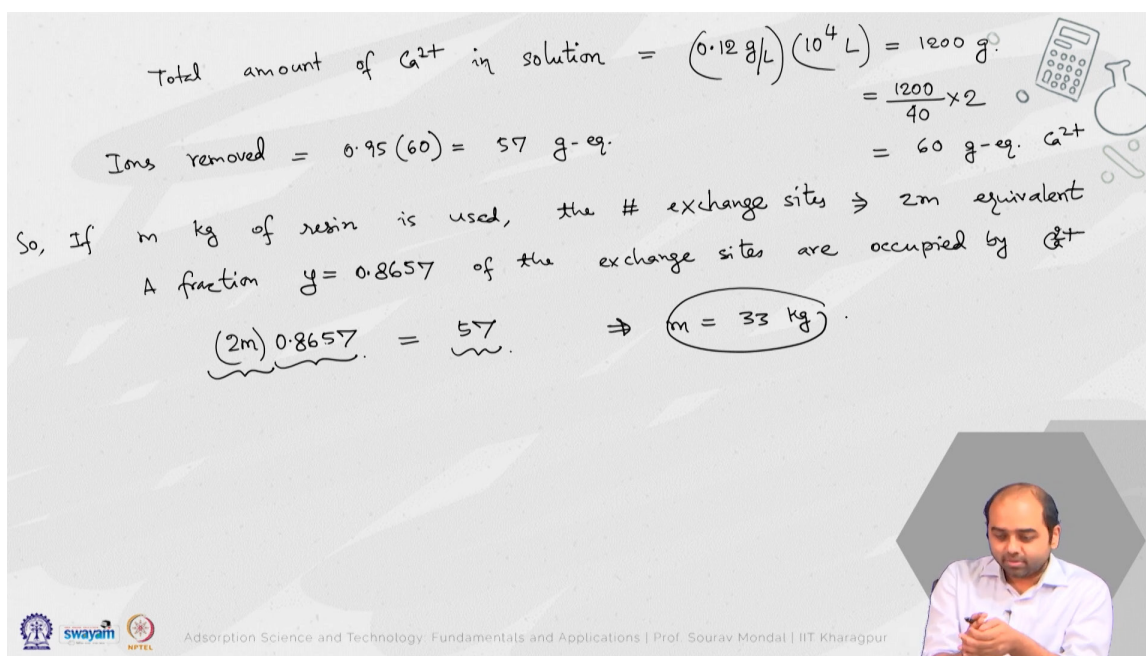
So, if we consider if y is the equivalent fraction of calcium in resin phase right x is in the solution phase and y is in the resin phase then we know this relation right k is equal to C t by q to the power n minus 1 times y by 1 minus of y to the power n and it is 1 minus x square by x sorry not square to the power n. So here n stands for the n stands for the you know this valence. So n stands for the valence in this case valence of the ion and since we are talking about this divalent ions which is calcium is a divalent ion. So n is equal to 2 for calcium. So, k is equal to CT by Q and we have this as 1 minus x square by 1 minus y square x.

Now in this case in the problem the value of k we have already found out. So, let us put the numbers. So, k is 2.6, CT and Q is already something we have worked out.

So, CT is 0.006 equivalent per liter and Q is 2 equivalent per liter, y is unknown, x is 1 minus 0.05 square, this is 1 by y square and 0.05. So, using or using these numbers if you try to solve this, so this is a quadratic equation. So, this is a quadratic equation in terms of y.

So, if you solve this equation you will get 2 roots of this y and one of these roots would be larger than 1 which is of course, not practically possible and other one would be less than 1. So, that value of this y which will be less than 1 is around 0.8657 in fact. So this is the fraction of the ions of y present in the resin phase. Now moving ahead the total amount of ions so the total amount of calcium ions in solution is 0.12 grams per liter and this 10 meter cube. So, this becomes 10 to the power 4 liters and this suggest this is equal to 1200 grams. Now 1200 grams is equivalent to if you work out 1200 by 40 times 2 which is equal to 60 gram equivalent of calcium ions that is present in the solution. Now ions that is removed is 90 percent of it, so it is 0.95 times 60, so that is 57 gram equivalent.

So, if m kg of resin is used, the number of exchange sites is equal to 2 m equivalent. So, a fraction y is equal to 0.8657 of the exchange sites are occupied by calcium ions is not it. So, which means that 2 m times multiplied with this fraction 0.8657 should be equal to the amount that is removed from the solution of the calcium ions.



Handwritten calculations on a whiteboard background:

$$\text{Total amount of Ca}^{2+} \text{ in solution} = (0.12 \text{ g/L}) (10^4 \text{ L}) = 1200 \text{ g}$$

$$= \frac{1200}{40} \times 2 = 60 \text{ g-eq. Ca}^{2+}$$

$$\text{Ions removed} = 0.95 (60) = 57 \text{ g-eq.}$$

So, If m kg of resin is used, the # exchange sites $\geq 2m$ equivalent

A fraction $y = 0.8657$ of the exchange sites are occupied by Ca^{2+}

$$(2m) 0.8657 = 57 \Rightarrow m = 33 \text{ kg}$$

At the bottom right, there is a video inset of a man in a white shirt, likely the professor, looking down at his hands.

So, this is the fraction of calcium ion that is the number of active sites which are occupied by calcium ions and this is the amount of calcium ions which is removed and then that goes into the resin phase. So, this is how we are bringing in this equality that the amount which is removed is goes into the resin phase and for that amount to be removed how much of the resin quantity is needed is something that we are calculating here. So, this gives us an idea that the value of m is 33 kgs. So, 33 kg of this particular resin is needed to treat 10 meter cube of solution containing 120 ppm of the calcium ions right. So, here you can consider I mean the I mean this is here to consider what is I mean if any point of time as you realize you will be needed to calculate the density of this water solution because we are converting the density to the from the concentration and in this case we can consider it to be like 1 kg per liter of the density of water.

Now we will also look into another problem that is again relate to this equilibrium. So, in this problem we so another problem. So, question 2, I would say this an amberlite IR 20 ion exchange resin is used to remove you know cupric ion from a stream. I hope all of you realize that ion exchange is a extremely selective process of you know this equilibrium governed process and ion exchange sites play a role.

So, which contains 9.75 millimolars of you know copper sulfate. This corresponds to around 19.5 milli-equivalent cupric ions per liter. Equilibrium reaction is given to make sure that we understand what is the ion exchange that is happening here. So, the resin is not in the sodium form rather it is in the acid form here is in the aqueous solution, is a strong acid not the salt form of the resin.

So, as this ion exchange take place the equivalent amount of the cations which is the cupric ions in the aqueous solution and in the resin is always conserved right. So, the following data is provided data for cupric ions is obtained. So, this is a relation between the at equilibrium whatever is the solution or whatever is the concentration of the ions in the solution and in the resin phase that equilibrium data is provided very similar to the isotherm data that we have seen before. So, this is like the equilibrium concentration C this is given in terms of milliequivalent copper and this is CE I will write milliequivalent of copper per gram of resin right. This is in the solution per liter of solution, is per gram of resin.

So, for different values of this concentration in the solution the resin concentration or the concentration of this ions in the resin is also mentioned. As you can see with increasing equilibrium concentration the uptake in the resin phase also increases. So, the equilibrium constant in this case which is for copper over H plus is can be considered as 2. This value is something different if you look into the table of the properties, but for this problem let us simplify the scenario. So, now the question is, from the data compute the resin capacity Q in terms of equivalent per liter of bed volume? And the (b) is predict the this equivalent amount of cupric ion exchanged at equilibrium from 10 liters of this solution containing 20 milliequivalents using 50 gram of resin.

Q2: An amberlite IR-20 ion exchange resin is used to remove cupric ion from a waste stream containing 9.75 mM of CuSO_4 ($\sim 19.5 \text{ meq. Cu}^{2+}/\text{L}$).

Eq. reaction $\text{Cu}^{2+}_{(\text{aq})} + 2\text{HR}_{(\text{s})} \rightleftharpoons \text{CuR}_{2(\text{s})} + 2\text{H}^{+}_{(\text{aq})}$

Following data for Cu^{2+} is obtained

C_e (meq Cu^{2+}/L of soln)	0.022	0.786	4.49	10.3
q (meq Cu^{2+}/g resin)	0.66	3.26	4.55	4.65

The equilibrium const. $K_{\text{Cu}^{2+}, \text{H}^{+}} = 2.0$

(a) From the data, compute the resin capacity Q (in eq./L of bed volume)

(b) Predict the meq of Cu^{2+} exchanged at equilibrium from 10 L of 20 meq Cu^{2+}/L , using 50 g of dry resin.

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The first step is to quantify the value of this resin capacity Q. So for this problem let us once again write down the you know the expression of this Q in terms of x and y. So if you recall we already have used this relation for divalent monovalent systems in the last problem. So the ionic equilibrium relation applicable in this divalent monovalent system is this, CT by Q, n is equal to 2 here. So, we write y 1 minus x. So, this is all written in terms of the mass fraction sorry the mole fraction equivalent fraction of cupric ions in the solution and in the resin phase. So, y stands for the mass mole fraction in the resin phase x is so this is like equivalent fraction of cupric ions in solution and y is equivalent fraction of cupric ions in resin phase. So here the total concentration of the cupric ions in the solution is mentioned as 19.5 milli-equivalents which is 0.0195 equivalent per liter. x is written as c which is already written down in terms of equivalent concentration C_e by CT and this y is q by capital Q, where capital Q is unknown. So, this value is 0.0195. C_e and Q values, so C_e and this Q values are given in the table right.

So, if you note down the C_e values, the Q values, so this becomes 0.022. 0.66 is the first value x can be computed so that is 0.00113 y cannot be computed because y depends on the value of q right.

Ionic equilibrium relation applicable in this divalent-monovalent system:

$$K_{Cu^{2+}, H^+} = \frac{C_T}{Q} \frac{y(1-x)^2}{x(1-y)^2}$$

Here $C_T = 0.0195 \text{ eq./L}$

$x = \frac{C_e}{C_T} = \frac{C_e}{0.0195}$ $y = q/Q$

x : eq. fraction Cu^{2+} in solution
 y : eq. fraction of Cu^{2+} in resin phase
 C_e & q values are in the table.

C_e	q	x	y	Q (two roots)
0.022	0.66	0.00113	$0.66/Q$	3.0, <u>-1.67</u> not feasible
0.786	3.26	0.0403	$3.26/Q$	6.105, 0.415
4.49	4.55	0.230	$4.55/Q$	8.58, 0.517
10.3	4.65	0.528	$4.65/Q$	8.77, 0.528

$K = \frac{C_T}{Q} \frac{(q/Q)(1-x)^2}{x(1-q/Q)^2}$

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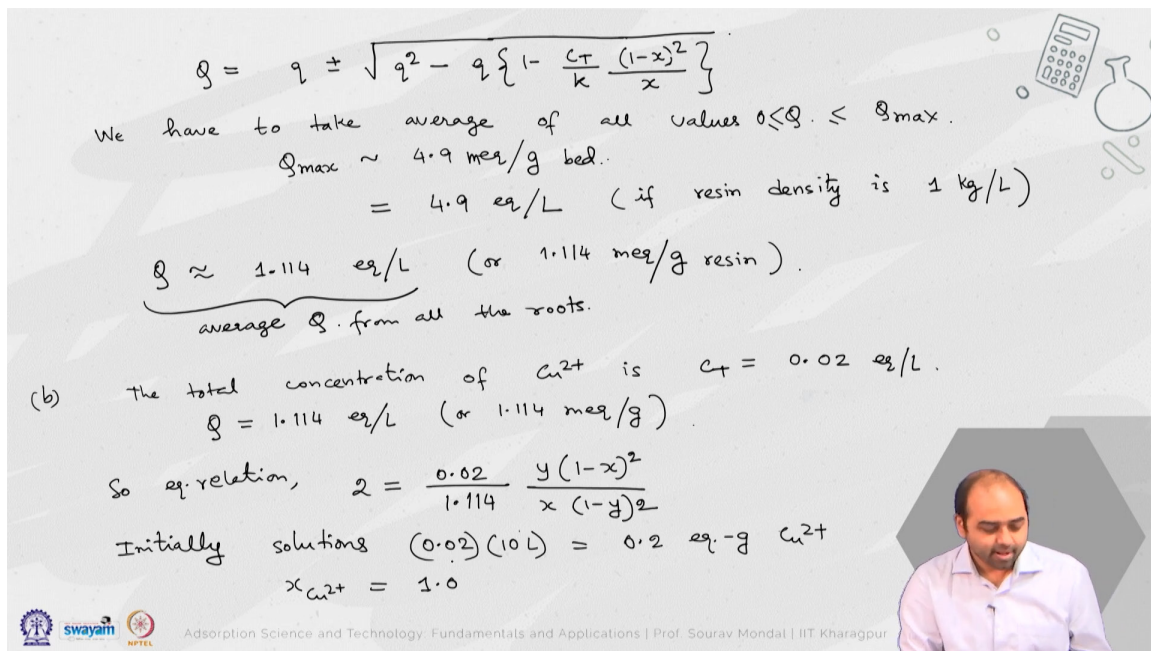
Similarly for different values of C_e and q you can calculate what would be your x from this information.

This would be $3.265/Q$. This is 4.49, 4.55, 0.230, $4.55/Q$ is the last value. So, in all these cases Q is the unknown and now using this relation this equilibrium relation, which you can solve out for the you know values of Q this is going to be a quadratic equation because y is an unknown in this relation and since this is a quadratic in y it will also be a quadratic in terms of Q . So, Q for all the situations both the roots if you calculate these are the solution is a quadratic equation and this is something that you can already solve it out yourself and you will get these values of Q , the two solutions. Clearly we see that there is one solution which is larger than 1 and rest of the solutions are less than 1.

Of course, they are still possible solutions, negative solution is not possible. So, this is not not feasible. So, how do you get the solution of Q in case it is not very clear I can tell you that this relation that you have from here if you substitute. So, then this is going to

look like this where you will have relations in terms of capital Q. So, if you rearrange this equation I mean this equation if you rearranged, you can work out the steps in that case you will get capital Q is equal to like Q plus minus Sridharacharya's formula for quadratic equation.

We are going to get this as, something like this. So, this this solution of this equation is what I have written down here for sorry yes solution of this equation is something that I have written down here for all these values. Clearly one of these roots turned out to be negative and that is something not feasible in this case. So, what we have to do is that we have to take average of all values of Q right for greater than equal to 0 and less than a particular value Q max. Now of course, the value of Q max is not mentioned in this problem if you see that this value of Q max is not something which is mentioned in this problem. So, that can be you can consider a particular Q max value or you know if that is not mentioned then you take the average for all the positive values of Q that you get from this solution.



$$Q = q \pm \sqrt{q^2 - q \left\{ 1 - \frac{C_T}{K} \frac{(1-x)^2}{x} \right\}}$$

We have to take average of all values $0 \leq Q \leq Q_{\max}$.
 $Q_{\max} \sim 4.9 \text{ meq/g bed.}$
 $= 4.9 \text{ eq/L (if resin density is 1 kg/L)}$

$Q \approx 1.114 \text{ eq/L (or 1.114 meq/g resin)}$
average Q from all the roots.

(b) The total concentration of Cu^{2+} is $C_T = 0.02 \text{ eq/L}$.
 $Q = 1.114 \text{ eq/L (or 1.114 meq/g)}$

So eq. relation, $2 = \frac{0.02}{1.114} \frac{y(1-x)^2}{x(1-y)^2}$

Initially solutions $(0.02)(10\text{L}) = 0.2 \text{ eq. of } \text{Cu}^{2+}$
 $x_{\text{Cu}^{2+}} = 1.0$

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But if there is an average let us say we consider generally for such kinds of you know this amber light resins the Q max value is you know known and this is typically around 4.9 equivalent per litre of bed, I mean. So, generally this is sorry I should write it in terms of 4.9 milli equivalent per gram of bed. Now, if this bed density is 1, then this can be written down as equivalent per liter if resin density is 1.1 kg per litre equivalent to the water density almost. So, if you consider your Q max to be this value and then you sort out these values or screen out the values which are larger than this value of 4.9, then you

can get a value of Q like the average value of Q as 1.114 equivalent per litre or this can be also equivalent per gram of resin considering the resin density to be 1. So, please note that this is a average quantity this is what we get a average Q right from all the roots which is positive and below $Q_{\max}$. So, this is the value of Q that one can find out in this case.

Now, coming to the second problem or the second part of this problem, the total concentration of cupric ions is given as C_T is equal to 0.02 equivalent per liter and Q we can consider as 1.114 equivalent per liter or 1.114 milli-equivalent per gram.

So, equilibrium reaction, equilibrium relation is this. So, what we are going to do is we are going to find out what is the value of y in this case for a given x . So, initially the solution contains 0.02 times you know 10 liters. So, that is equal to 0.2 equivalent gram of cupric ions with x as 1 because there is no other you know salt or cations in the solution.

Now let us say that say that ' a ' is the equivalent amounts or the gram equivalent amounts of cupric ion that is exchanged. Then from the mass balance sorry from the this equivalent fractions we can write this x for cupric ion as 0.02 minus the amount that is removed a by 10, I am writing down in terms of concentration divided by 0.02.

And y would be ' a ' that is exchanged goes into the resin phase. So, this is like the mass fraction or the mass equivalent divided by the total capacity of the resin which is 1.114 into 10 to the power minus 3 you know equivalents per gram of the resin. So, this quantity is equivalents of equivalent gram of cupric ions per gram of resin. Now, if you substitute this it into the equilibrium relation.

Say $a \equiv$ eq. of Cu^{2+} exchanged.

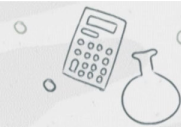
$$x = \frac{0.02 - (a/10)}{0.02} \quad y = \frac{(a/50)}{1.114 \times 10^{-3}} \quad \text{eq. Cu}^{2+}/\text{g resin}$$

Substitute it into the equilibrium relation,

$$2 = \frac{0.0179}{\frac{0.02}{1.114}} \frac{\left[\frac{a/50}{0.0014} \right] \left[1 - \frac{0.02 - (a/10)}{0.02} \right]^2}{\left[\frac{0.02 - (a/10)}{0.02} \right] \left[1 - \frac{(a/50)}{0.0014} \right]^2}$$

$a \sim 0.199$ eq. of Cu^{2+} exchanged.

So, $\frac{a}{(0.02)(10)} \approx 0.995$ (or 99.5% of Cu^{2+} removed):




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We get 2 is equal to 0.0179, 'a' by 50 and 0.0014 is the y, this is the x, 0.02 minus 'a' by 10 by 0.02. So, 0.0179 is something that we got from the value of you know this is nothing but equal to 0.02 by 1.114. So, divided by 0.02 that is x here by 0.02, and this is 1 minus of y square 'a' by 50. So, this in terms of 'a', it becomes a non-linear equation it is no longer a quadratic equation, but it becomes a non-linear equation. And if you work out the roots of this equation you will find that there is only one feasible root and this calculation of this non-linear equation can be done even with a simple programmable calculator turns out to be 0.2 which is equivalent of copper ions that is exchanged.

So, we get 'a' by 0.02 multiplied with 10 that is around sorry it is 0.199 that is very important. So, this turns out to be 0.995 or 99.5 percent of cuprous ions that is exchanged or removed right. So, I hope all of you found or have understood this problem utilizing the you know this concepts that we have developed for this ion exchange or this ion exchange mechanism. In the next lecture we are going to talk about ion exchange cycles in a column operation. Thank you and see you everyone in the next lecture.