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Indian Institute of Technology - Kharagpur Module No #05 Lecture No #21 ION Exchange Processes

Welcome friends to this NPTEL online certification course of environmental soil chemistry and today we are going to start week 5 or module 5 and in this week, we will be basically discussing about ion exchange process and several aspects of ion exchange phenomena.

So, these are the topics or concepts which we are going to cover in this week, first of all we are going to cover the ion exchange capacity, then we are going to cover what is cation exchange capacity or CEC, then we will be considering, we will be focusing on the methods of cation exchange capacity determination, then characteristics of ion exchange, percent base saturation, we will be also learning about the cation exchange equilibrium constants, then selectivity coefficients and finally we will be seeing the thermodynamics of ion exchange. So, what is ion exchange? Ion exchange is basically, it is a very important process as far as the soil chemical, soil chemistry is concerned. These ion exchange basically governed several aspects of soil, soil fertility and soil biological activity, several things have been are governed by these ion exchange process. So, this ion exchange can be defined as the interchange between an ion in solution and another ion in the boundary layer between the solution and a charged surface.

So, source of surface, source of cation exchange in soils are basically, clay minerals, organic matter and amorphous minerals. If you remember we have already, we have already discussed that how this clay minerals and amorphous minerals and organic minerals governed basically the chemical you know, the soil chemical process due to the charged development. All these ion exchange process are dependent on charge development which cannot be seen in case of sand and silt particles.

However, in case of soil clay, we can see that negative charge you know, in case of soil clay, it can develop negative charge by either permanent charge or through variable charge, variable charge is also known as the pH dependent charge, which depends on the pH of the surrounding solution whereas, in case of permanent charge, it based on the isomorphous substitution of the clay minerals. The amorphous minerals are also important for charge development because these iron oxides, and aluminium oxides and hydroxides are basically developing this pH dependent charge and most of the charge which develops in organic matter are pH dependent charge and organic matter produces couple of fold high H you know, negative charge than that of the clay minerals. So, these sources of cation exchange are basically, these charge which develops in the clay minerals, amorphous minerals and organic matter.

Now, sources of anion exchange in the soil, so obviously this clay mineral develop the negative charge, organic matter developed negative charge, amorphous mineral develop negative charge in the alkaline condition, so in this these are the negative charge which are responsible for cation exchange in soil. Now, the opposite of cation exchange is called the anion exchange, now sources of anion exchange is again clay minerals.

Because for example, in case of kaolinite, it shows high pH dependent, you know it is basically showing whatever charge it develops basically, pH dependent charge and this pH dependent charge can be positive depending on the surrounding solution pH, in case of acidic medium it can develop positive charge and also primarily 1 is to 1 type of clay such as kaolinite, metal oxides and amorphous mineral they can develop positive charge and these positive charge can attract these negatively charged anions in the soils.

So, cation exchange capacity basically develops due to clay minerals, organic matter and amorphous mineral, in case of anion exchange capacity, it basically is a resulted from clay minerals primarily 1 is to 1 type of clay such as kaolinite and metal oxides and amorphous mineral like allophane.

Now, the ion exchange capacity is the maximum adsorption of readily exchangeable ion on soil particle surfaces, now ion exchange capacity can be you know, ion exchange capacity is basically is the summation of both cation exchange capacity as well as anion exchange capacity. Cation exchange capacity is the total capacity of the soil to hold exchangeable cations, however anion exchange capacity which is the sum of the total exchangeable anions that a soil can adsorb.

So, again ion exchange capacity is basically a broader term which encompasses both cation exchange capacity and anion exchange capacity. Cation exchange capacity is the total capacity of the soil to hold exchangeable cations, whereas ion exchange capacity is the sum of the total exchangeable anions that a soil can adsorb. So, the magnitude of cation exchange capacity in soil is usually greater than an ion exchange capacity.

Because permanent charge is always higher than that of variable charge, so soil lacking the ability to retain anions you know that can show lower anion exchange capacity, so you may ask that okay, if the soil has lower anion exchange capacity what is the problem in that; the problem is there are certain minerals which are available to the plant in terms of negative anions so, for example sulphate, phosphate.

So, the sulphate can readily leach away and is no longer available to support the plant growth, if the soil is lacking the ability to retain the anion, so soil needs to have both cation exchange capacity, anion exchange capacity to supply both cations and anionic nutrients to the plants.

So, you know this picture basically shows the 2 different condition, in one condition you can see a high development of negative charge in the clay surface and obviously, the bounded cations are also higher in case of this condition, condition A and in case of condition B, you can see the development of negative charge is very less as a result of that, you know the attachment of positive charge counter hence also very less. So, basically it is clear that in case of condition A, the cation exchange capacity is higher of as compared to the condition B, so CEC of soil A is higher than CEC of soil B.

So, the CEC or cation exchange capacity of a soil is a measure of the quantity of negatively charged site on soil surfaces that can retain positively charged ions are cations okay, such as calcium, generally these cations are calcium, magnesium, potassium and these are basically attracted to the negatively charged clay surface by electrostatic forces, these electrostatic forces are you know, so the electrostatic forces of the major binding force between the cations as well as the negatively charged clay surface.

Now, cations can retain electrostatically of you know, which are retain electrostatically or easily exchangeable with cations in the soil solution, so a soil with a higher cation exchange capacity has a greater capacity to maintain adequate quantities of calcium, magnesium and potassium than a soil with the low CEC obviously, when the soil has the higher capacity to retain more cationic nutrients, it has also greater capacity to maintain adequate quantities of calcium, magnesium than a soil in the with a lower CEC.

So, a soil with a higher CEC may not, this is that is you know, there is a condition, so a soil with a higher CEC

may not necessarily be more fertile because of the soil CEC can also be occupied by acidic cations such as hydrogen and aluminium. Now, you know this hydrogen, aluminium are not very beneficial to the plant, for example aluminium, in the acidic soil when the pH goes beyond below 5, these aluminium concentration increases.

And when the aluminium concentration increases it basically, interferes with the root growth and it kills the plant, so this Al^{3+} although it is a cation, it is not beneficial for the plants, so and also H+ ion increase in H+ ion also increase the acidity of the soil which is not beneficial for the plant growth, so or for soil fertility, so if the soil has higher CEC that may not necessarily be more fertile because there may be presence of these H+ ion, aluminium ion.

However, when combined with other measures of soil fertility, then CEC can be considered as a good indicator of soil quality and productivity, generally if a soil has high CEC, then we can consider that soil has a high soil quality or productivity.

Now, cation exchange sites are found primarily on clay minerals and organic matter surfaces because clay mineral develop this permanent you know, permanent charge due to isomorphous substitution and in case of organic matter also, these you know, these aromatic functional groups, aromatic aliphatic functional groups like carboxylic, like carboxyl function group, then phenolic groups, they basically dissociate to form the negative charge on the organic matter surface.

And as a result they can attract positively charged cations, so soil organic matter will develop a greater CEC at near neutral pH than under acidic condition because of pH dependent CEC and acidic condition positive charge development in case of variable charge surface, so obviously near neutral condition, organic matter will develop greater CEC because there will be more negative charge.

In case of acidic condition, there will be positive charge; there is the possibility of positive charge development. So, addition of organic matter will likely increase soil cation exchange capacity over time and on the other hand, a soil cation exchange capacity can decrease with time as well through natural or fertilizer induced acidification and a organic matter decomposition. So, soil CEC also can decrease with time through you know, natural fertilizer induced acidification, there is some fertilizer which are acidic; acid forming fertilizers.

So, when we apply this fertilizer into the soil, they form acidic reaction and the soil become acidic, so this CEC can decrease in that condition, so soil CEC is normally expressed in one of two numerically equivalent sets of units, either you can express so earlier, people used to express this cation exchange capacity in terms of milliequivalent of charge per 100 grams of dry soil.

Nowadays, we generally use this cmole per kg that is centimoles of charge per kilogram of dry soil to express this cation exchange capacity, so these 2 are the generally used you know, units of cation exchange capacity.

Now, what are the methods of determining the cation exchange capacity, so for soil classification purpose, a soil cation exchange capacity often measures at a standard pH value, so examples are, for example generally, you know we use ammonium acetate method you know, following these Schollenberger and Dreibelbis method of 1930 which is buffered at pH 7 and also barium chloride and triethanolamine method of Mehlich which is buffered at pH 8.2.

So, basically we use 2 different solution, one at pH 7, so it is buffered at pH 7, another method we use the barium chloride and triethanolamine method, so which is buffered at pH 8.2. So, buffer CEC method, why it is important and what is their drawback? So, buffer CEC method, the buffer solution basically we apply to the soil, so if the pH of the buffer is more than the pH of the native soil, then these method measures not only the cation exchange sites active at the pH of the particular soil but also pH dependent exchange site that would become negatively charge, if the soil pH were raised to 7 or 8.2.

So, here you see 2 different; when we add 2 different reagents, one is buffered at pH 7, another is buffered at pH 8.2, so if the native soil has a pH dependent charge and its pH is less than 7 or 8.2, when we add these buffer, they will due to this negative charge surface, due to this variable charge, they will develop negative charge, so the CEC which can be measured by using this method can exaggerate the true CEC of the acid soils.

So, the acid soils generally have the lower pH than 7 and 8.2 and in this acid soil, when we apply these 2 buffer solution, they will basically increase the negatively charged surface due to the pH dependence and as a result, the CEC will be exaggerate, so the buffered method that is ammonium at pH 7 or barium at pH 8.2 measures the potential or maximum cation exchange capacity of the soil.

So, we can see that when we are using the buffered method in the laboratory, it is basically giving us the potential or maximum cation exchange capacity of the soil.

Another method is called the unbuffered method, so unbuffered method can gives us the effective cation exchange capacity, so the unbuffered method can measure only the effective cation exchange capacity in the soil, and this method gives result when the pH of the native soil is lower than that of buffer pH. So, again we can see that there are 2 methods; one is buffered method and unbuffered method.

Buffer method use the pH of 7 in case of ammonium acetate and in case of barium, you know, in case of barium chloride, and triethanolamine mixture, it uses the buffer of basically 8.2 and when we add these buffer into the acidic solution due to the variable charge surface, this variable charge surface can turn into negative charge by increasing the pH while adding this buffer and as a result, they will have more cation exchange capacity and as a result, this buffer method can show exaggerate CEC so, effective CEC you have to use the unbuffered method.

So, let us see 2 widely used methods for determining the cation exchange capacity, the first method is distillation method of or ammonium saturation method where we are using the 1 neutral normal ammonium acetate at pH 7 and

another method is called centrifuge method with sodium saturation method where we are using 1 neutral number 1 normal sodium, ammonium acetate, I am sorry, 1 normal sodium acetate with the pH of 8.2.

So, these 2 methods are widely used methods for determining the cation exchange capacity, however we will be discussing the distillation methods in details later on.

So, what are the basic steps; the idea shows the steps for determining the CEC is basically, the soil is leached with ammonium salt solution, so you can see this is; for example this is a funnel and in this funnel, we are packing the soil which contains basically calcium, magnesium, potassium and H+ and $A1^{3+}$ ions. So, when we are leaching the soil with this ammonium acetate or ammonium salt solution, these ammonium basically replaces all the cations which comes into the leachate, okay.

So, after removing the excess of ammonium salt solution, soil is further again leached with potassium solution. So, in the first step we are basically leaching the soil you know, cations using the ammonium solution, in the second step, we are basically further leach; we are basically leaching the ammonium solution with a ammonium adsorbed soil with the K+ solution, okay and this, with this K+ solution or potassium solution which basically replaces this ammonium.

So, finally what we get; so ammonium washed into the lower container and the concentration in the ammonium will be determined with the CEC of the soil, so these; 2 to 3 step process, first step we are leaching the soil with the ammonium solution and all the ammonium get adsorbed by replacing the all the cations and in the second step, we are basically leaching these ammonium saturated soil with the potassium solution, so that all the ammonium get leached down and this is saturated by potassium.

So, let us see one calculation based on that, so you know based on that, so after leaching let us see that let us assume that after leaching a soil with a 0.4 litre of ammonium solution, let us consider that we have used only 0.4 litre of ammonium acetate solution, all the exchangeable cations shown in the soil samples were displaced off the colloids and washed into the beaker along with the excess of ammonium ions.

Now, the solution in this beaker was analyzed for calcium, magnesium, potassium, aluminium and H with the following results, so we got for calcium 200 ppm of calcium, 60 ppm of magnesium ions, 97 ppm of K+ ions, 5 ppm of H+ ion and 67.5 ppm of Al^{3+} ion, so because only we have use 0.4 litre of solution was collected from the

soil samples and the soil sample weighted only 0.1 kg or 100 grams.

These results can be multiplied with 0.4 and 10 to give the amounts of each ion collected in ppm or mg per kg in soil, so basically we have to multiplied it with 0.4 and 10 to convert into the milligram per kg or ppm. So, as an example we can show the calculation for the calcium, so let us consider this calcium, we have measured the calcium in the leached and which comes around 200 milligram per litre.

So, if we see it is; if you see it as a 200 milligram calcium per litre so, basically we are multiplying it with a 0.4 litre and then we have multiplying it with a 10 grams, so get ultimately milligram per kg, so ultimately we are getting 800 milligram of calcium per kg of soil.

Now, how to convert it to CEC; now for calcium we know the atomic weight is approximately 40 gram per mole, so 1 mole of calcium contains 40 grams, so we could calculate the centimole of exchangeable calcium ions in 1 kg of soil, so we already know that we have 800 milligram of calcium ions per kg of soil. So, if we convert it to centimole by considering 1 mole is equivalent to 40 grams, so basically we are multiplying it 1 gram by 1000 mg, so it can convert to mg. And then 1 mole by 40 grams we know that and then we can convert into centimoles, so ultimately by simplification, we can get this 800 mg of calcium ions per kg of soil can be represented by 2 mole calcium ions per kg of soil, okay.

So, now depending this calculation for each element provides the following results, so we can get 2 centimole of calcium ions per kg of soil, 1 centimole of magnesium ions per kg of soil, 1 centimole of K+ ion per kg of soil, 2 centimole of protons or H+ ion per kg of soil and 1 centimole of Al^{3+} per kg of soil. Now, we now must multiply the centimole per kg of each element by the corresponding valency of the ion.

To convert it to centimole of charge, so when you convert; when you multiply the centimole with the corresponding charge we get centimole of charge, so cmolc which is the ultimate; cmolc per kg, so which is the ultimate unit of cation exchange capacity, so basically using the Ca2, you know let us consider the Ca²⁺ as an example again, so basically we got 800 mg per kg, 800 mg calcium per kg of soil, from that we calculated, it is basically 2 centimole of calcium per kg of soil.

So, then we multiply it with the 2 centimole c from calcium per centimole of calcium, so one centimole of calcium basically contain 2 centimole charge from calcium, so because it is valency of 2, so we get ultimately 4 centimole charge from calcium per kg of soil. So, for calcium ultimately we get 4 centimole charges from calcium per kg of soil.

So, repeating this calculation you know provides the following results, 4 centimole you know, 4 centimole charge of calcium for per kg of soil, 2 centimole charge of magnesium per kg of soil, 1 centimole charge of potassium per kg of soil, 2 centimole charge of H+ per kg of soil and 3 centimole charge of $A1^{3+}$ per kg of soil. Now, assuming the 5 elements measured account for nearly all the exchangeable cations, the sum of their charges that is 4 + 2 + 1 + 2 + 3, it is 12, equals to the total CEC or cation exchange capacity of the soil that is 12 centimole of charge per kg of soil.

So, this is how we can calculate the cation exchange capacity, so summarily we have started with a particular cation, we converted that particular you know, we have calculated, if we just go back a little bit, so we have started with the concentration of the analysed leached and then basically we converted into milligram per kg depending on whatever amount of you know solution we have taken. And what is the weight of the initial weight of the soil, so from there we can convert into milligram per kg, once we convert into milligram per kg, the next step is to convert into the centimole per kg, once we converted to centimole per kg, the next step is to convert into centimole charge per kg of soil, so we can convert this for each and every cations which are present into the solution.

And once you do that, it is basically the summation of all the centimole of charge to calculate the total CEC of the soil, so this one of the approach of calculating based on the laboratory data of CEC.

Another approach, the second method is measuring the amount of ammonium plus, now you know that the I have shown you that when we are using excess of K^+ ion to leach whatever ammonium which was adsorbed into the clay surface, that ammonium can be further leached and these ammonium concentration in the leached can be measured, so assume that the ammonium concentration in the beaker D that is the last beaker to be 540 milligram of ammonium per litre.

So, as in method 1 because only 0.4 litre of solution was collected from the soil sample and the soil sample weighted around 100 grams of 0.1 kg, these results can be calculated as following to give the amount of ammonium

ions collected in mg per kg, so similarly in the previous example we have collected we have calculate it based on individual cation, here we are considering the ammonium cations.

And then using the ammonium cations, we have calculated this that is 2160 milligram of ammonium per kg of soil.

Now, if we convert this 2160 milligram per kg of soil ammonium to the centimole, so basically we will get 12 centimole of ammonium per kg of soil and since ammonia valency; ammonium valency is 1, so obviously the centimole charge will be also the same, so basically the answer is here, 12 centimole charge per kg of soil, so the CEC is basically the 12 centimole charge per kg of soil.

So, this is how we can calculate the CEC, again CEC to basically if we just recap whatever we have covered, so CEC is again the cation exchange capacity, it is basically the capacity of a soil to exchange its adsorbed cation to the surrounding to the cations in the surrounding solution, cation exchange capacity basically is an indicator of the soil fertility, although some time it may be misleading because of the presence of H+ ion and Al^{3+} ion which are not suitable for the plant growth.

And anion exchange capacity is just opposite to the cation exchange capacity, in the soil cation exchange capacity generally develops due to the presence of the permanent charge as well as the organic matter as well as the positive, as well as the negative charge, negative variables charge in the amorphous clay mineral, however the anion exchange capacity generally develops from the 1 is 1 type of mineral like kaolinite as well as amorphous mineral and basically these are the minerals which produces the variable charge and from there we can calculate the anion exchange capacity.

Now, cation exchange capacity can be measured by both buffered method and unbuffered method, in the buffered method we use the you know, ammonium acetate with a buffer, pH of 7 and basically these ammonium acetate is ammonium ions from the solution basically replace all the cations and then we can measure the cation exchange capacity either by measuring the individual cations or by measuring the ammoniums which are further leached by another solution called potassium enriched solution.

So, this is how we can calculate the cation exchange capacity by 2 different methods okay, so the I told you that another, the most widely used method in the laboratory is the distillation method or ammonium saturation method, so what is the principle of this distillation method? So, the principle of this distillation method, in this method the CEC of the soil is measured by leaching with neutral 1 normal ammonium acetate just like we have seen and this results saturation of the exchange complex with the ammonium ions, we know that.

Then, these adsorbed ammonium ions are determined by distillation of the soil, so in this step, we are basically these adsorbed ammonium ions are determined by distillation of the soil with magnesia that is MgO, now the ultimately ammonia gas will evolve during the process which is basically absorbed in known amount of acids which is taken in excess amount and then the unreacted acid is back titrated with the standard alkali.

So, here again we take the soil and then we saturated with the neutral normal ammonium acetate, ammonium replace all the cations and these ammonium can be further in the presence of magnesium oxide, these ammonium produces the ammonia which is basically absorbed in the excess amount of a standard acid and whatever acid is remaining unreacted can be back titrated with the standard alkali, from there we can calculate what is the generation of the ammonia and these from these generated ammonia we can calculate the CEC.

So, the reaction which is involved in this distillation method is basically we start with the ammonium acetate which is disassociated into ammonium and acetate ions, so if the soil has a particular cation, so these ammonium basically replace that cation and produce and saturating the soil with ammonium, now in the next step, this magnesium oxide in the presence of water produces magnesium ions as well as 2 hydroxyl anions.

And these ammonium saturated soil in the presence of these magnesium ions as well as 2 hydroxyl ions can produce these ammonia gas as well as magnesium saturated soil and water, so these ammonium get adsorbed into the; absorbed into the some acid solution and whatever acid is remaining unreacted after this absorption of ammonia can be back titrated with the standard alkali.

So, this is how in the laboratory, using the distillation method, we generally measured the cation exchange capacity of the soil. So, guys I hope that you have learned some basic overview of ion exchange processes and cation exchange capacity, anion exchange capacity, how we measure cation exchange capacity, how to calculate the cation exchange capacity, so let us meet in our next lecture to discuss more on the ion exchange phenomena and how it changes and what are the implications of ion exchange processes in the soil, thank you very much.