Transcriber's Name: Prabhavathi

Environmental Soil Chemistry

Prof. Somsubhra Chakraborty

Agricultural and Food Engineering Department

Indian Institute of Technology-Kharagpur

Lecture-19

Soil Solution-Soil phase Equilibria and Sorption in Soils (Contd.)

Welcome friends to this fourth lecture of week 4 of this course of environmental soil chemistry. And were discussing about in the last lectures we have discussing about the adsorption isotherms. Today we are going to discuss about specific adsorption isotherms as well as partitioning coefficients and also we will be talking about the diffuse double layer. Now, what is partitioning coefficient, if you see in the slide a partitioning mechanism is basically suggested from linear adsorption isotherms.

Now, in the previous lecture we have seen the C type linear adsorption isotherms. So, this shows the partitioning mechanism. And this partitioning mechanism, you know, this linear adsorption isotherms are reversible showing the reversible adsorption and desorption in a small temperature effect on adsorption and the absence of competition when other adsorptives are added.

That means adsorption of one of the adsorptive is not affected by the inclusion of a second adsorptive. So, you can see here this is a, linear reaction this is a linear type of adsorption, linear trend between the adsorptive as well as the amount adsorbed. So, basically here you can see there is absence of competition when other adsorptions or adsorptives are added, so this is a special type of situation. Now a partitioning coefficient which is denoted by this K p is given by this formula where q is basically as you know it is an amount adsorbed, K p is the partitioning coefficient and C is the equilibrium concentration of the adsorptives.

So, basically it is the concentration of that particular species of ion in the soil solution and this K p is the partitioning coefficient and q is the amount of adsorbed ions in the soil adsorbent. So, this is the relationship between the partitioning coefficient and the amount adsorbed.

So, if we move ahead and see that the partitioning coefficient provides a measure of the ratio of amount of a material adsorbed to the amount in solution. Obviously since it is a ratio since since, you know, since this q since q is basically K p multiplied by C, so we can see that K p equal to q by C. So, that shows the ratio of the amount of a material adsorb to the amount in solution.

So, a convenient relationship between the K p and the fraction of organic carbon that is denoted by f oc in the soil is the organic carbon-water partitioning coefficient which is denoted by K oc which can be expressed by this term. So, basically K oc equal to K p by f oc or the fraction of organic carbon in the soil. So, this is another important fractionation or, you know, partition coefficient which is basically used for different purposes.

Now equilibrium based adsorption model, let us discuss different equilibrium based adsorption models. Now, there are 3 basically 2 widely used equilibrium adsorption models are there one is Freundlich equation, there is Langmuir equation and third one we will be discussing that is double layer models including the diffuse double layer, Stern and surface complexation models ok.

So, let us first talk about the Freundlich equation, now this Freundlich equation was first used in gas phase adsorption and solid adsorbent adsorption. So, here q is K d multiplied by C to the power 1 over n. So, here K d is basically the distribution coefficient, K d is the distribution coefficient and n is the correction factor. A linear form of this equation, if you take a log, we will see this linear form of this equation.

And if this correction factor n equal to 1, that means if 1 by n equal to 1 then equation becomes q equal to K p into C where K p is the partitioning coefficient you know. So, basically if we plot these, we will see if we plot the log q in the y axis and log C that means logarithmic of equilibrium concentration in the x axis, we will see these adsorption isotherms. So this is called Freundlich adsorption isotherms.

And basically here you can see this Freundlich adsorption isotherm is used for showing the zinc adsorption as this as well as desorption. So this is called the adsorption and here you can see these are the desorptions and this part 1 is basically refers to the linear portion. As you can see this is the linear portion of the isotherm, while part 2 refers to the nonlinear portion of the isotherm.

So, these are basically example of how Freundlich equation can be used to describe the adsorption and desorption process. Now, what is the disadvantage of this Freundlich equation, disadvantage of this Freundlich equation is it does not predict an adsorption maxima.

So, to remove this, you know, drawback Langmuir equation is basically used. Now this Langmuir equation is developed by, you know, Irving Langmuir in 1918 to describe the adsorption of gas molecules on a planar surface. And it was first applied to soil by Frye by Fried and Shapiro in 1956 and Olsen and Watanabe in 1957 to describe the phosphate sorption in soils.

So, Let us see what are the assumption of the Langmuir equation, so Langmuir equation assumptions are 4. Basically the first one is adsorption occurs on planar surface, so we basically assume the planar surface of the adsorbent. And that have a fixed number of sites that are identical and the size can hold only one molecule thus only mono mono layer coverage is permitted.

While discussing the basic forms of adsorption isotherms we discuss L type of isotherm it is Langmuir isotherm and I showed I told you that it is basically for the monolayer adsorption. So, this is one of the basic assumption, it is a monolayer assumption, so thus only monolayer coverage is permitted which represents the maximum absorption. Second one is adsorption is reversible, third one is there is no lateral movement of molecules on the surface.

And the fourth one is the adsorption the adsorption energy is the same for all sides and independent of surface charge. That means the surface is homogeneous and there is no interaction between adsorbent molecules that is the adsorbent behaves ideally. So, most of the assumptions are not valid for heterogeneous surface bound in soils because as you know the soil surface is highly heterogeneous.

So, as a result although the Langmuir adsorption equation is generally assume for different adsorption practices. In case in as a result, you know, in practical the Langmuir equation should only be used with purely qualitative and descriptive purposes because of these limitations.

Now let us see what is the equation of Langmuir equation. So, the Langmuir adsorption equation can be expressed by this where q equal to k into C into b over 1 plus kC, where k is the constant related to the binding strength, q already you know, b is the maximum amount of adsorptive that can be adsorbed. That is in the monolayer remember it is for monolayer and rearranging all these thing you can and C, you know, it is the concentration in the equilibrium solution ok.

So, and q you know the amount adsorbed, so rearranging to a linear form these equation 1 becomes C by q equal to 1 by k b + C by b. So, basically if we, so slope is here you can see 1 by the slope is 1 by b and the intercept is 1 by kb, so slope is 1 by b and the intercept is 1 by kb. So, so here if we put the equilibrium concentration in the x axis and C by q in the y axis that is amount of adsorbed. So, we can see this type of isotherm, so this is an example of Langmuir adsorption isotherms.

So, Langmuir equation also can be valid for two site or two surface. So, in case of two site or two surface, the Langmuir equation is used to describe sorption data for an adsorbent which two sites of different affinities. Now, this diff this equation can be expressed as, you know, q equal to b1 k1 C over 1 + k1 C + b2 k2 C + over 1 + k2 C. So, at the subscript referred to site 1 and 2, so subscript 1 refers to site 1, subscript 2 refers to site 2, so adsorption on high and low energy site.

So, if you assume that site 1 is a high energy site, and site 2 is the low energy site then we can represent this equation in this form. Now, this above equation is used to describe the sorption of soils of different physiochemical and mineralogical properties. But does not prove that multiple sites with different binding coefficient exists.

So, once we have covered this Freundlich equation as well as Langmuir equation then let us talk about the diffuse double layer which is very important. Now, you know that clay particles have a negative charge because of different processes like either isomorphous substitution or permanent charge or due to the pH dependent charge or variable charge. So, due to the presence of this negative charge they adsorb cations which are positively charged.

So, under dry condition these cations are basically tightly bound to clay surface by electrostatic attractions. However these electrostatic force depends on charge, position of the charge and valence of the exchangeable cations obviously. Now, however one thing when it is when it is dry soil, then they are tightly bound because there is no water molecule. However when their weight, the cation adsorbed try to diffuse away from the surface due to their high concentration near surface, due to the Brownian movement.

So, you can see here in this picture, this is dry condition where these cations are tightly bound into the negative colloid, negative charge colloid soil colloid. However, when there is a fully hydrated due to the higher concentration near the negative charge colloid there will be repulsion as a as a as a result there will be some Brownian movement and these positive charge cations will train to diffuse away to the surrounding solution. So, these are these are two different conditions which you can see depending on either the soil is dry or fully hydrated.

So, when these ions try to diffuse into the, you know, bulk solution we will see some particular trends. So, the concentration of the cations basically decreases with distance from the surface where that of anion increases from with the distance from the surface obviously. At the adjacent vicinity of the surface obviously due to the presence of negative charge in the clay colloid there will be concentration of the positively charged cations.

So, due to the diffusion of the cations obviously as we go further from the clay surface we will see in the bulk solution zone, there will be continuous decrease of concentration of the cations. And obviously we will see continuous increase in the concentration of the anions because anions are lowest at the immediate vicinity of the clay colloids because of negative charge, so there will be repulsion.

Obviously as there is increasing distance obviously we will see the concentration of anions will be increased. So, after some distance there will be a bulk solution as you can see this is a bulk solution phase. So, there will be bulk solution with the concentration of cations and anions are equal and unaffected by clay surface. So, at at a particular distance where the cations and anions you can see the cation concentration is decreasing, anion concentration is increasing.

In the bulk solution phase, you know, they will be basically equal and unaffected by clay surface, so this is basically showing the diffuse layer diffuse double layers. So, basically you can see here two layers, one layer is positively charged cations which are basically adjacent to the immediate vicinity of the negatively charged colloid and further away from the clay surface there is another diffuse layer, so you can see it is called the diffuse double layer.

So, the diffuse double layer thus consist of two different layers one is the permanent negative charge of the clay and second is the cations diffused into the soil solution that balance the negative charge of the clay, so that is why it is called the diffuse double layer. The innermost layers are strongly, so, you know, the the innermost layer is strongly held by the clay is known as the Stern layer we will be discussing in details. And the water in the Stern layer is known as adsorbed water and is more viscous than free water. A layer basically extending from the Stern layer away from clay surface is called the diffuse layer we will see that.

Now this is a complete picture of the diffuse double layer, you can see one thing here. If this is a negatively charged colloid, you can see it is a black color just adjacent to the negatively charged colloid. You can see there will be very high concentration of the positive charge cations and this is called the Stern layer. So, basically Stern layer is the layer of cations which are tightly adsorbed by the colloid which are located in immediate vicinity of the colloid.

Now as we go further from the colloid surface we will see the concentration of the cations are going down and the concentration of anions are increasing. So, diffuse layer is basically the layer of cations beyond Stern layer diffuse due to the combined electrostatic force and diffusive force. So, the layer which is beyond this Stern layer is known as the diffuse layer and it is basically occurs due to the combined electrostatic force and diffusive force.

And finally, further away from the diffuse layer you will see the ions in equilibrium with the soil solution. So, here these are the positively charged cations and negatively charged co-ions and we can see this is the diffuse double layer. So again this is the highly negative colloid and this is the adjacent Stern layer which is a positively charged counter ions and beyond this positively charged counter ion layer there is a diffused layer, so this is how we call it diffuse double layer.

Now, let us see the different models given by different scientists to describe this diffuse double layer, let us first see the Helmholtz double layer model. Now in case of Helmholtz double layer it assume that the negative charge and the colloid is considered to be evenly distributed over the surface with the charge density of sigma. Now the total counter charge in the second layer is concentrated in a plane parallel to the surface at distance x.

So, here you can see all the negative charge are equally distributed in the surface with a charge density of charge density of sigma and the total counter charge in the second layer is concentrated at a distance x at a distance x at a parallelly at a distance x. So, the total, you know, if the medium has a dielectric constant of D then the electro kinetic potential zeta is the same as the total potential size, so basically it can be represented by this equation.

Now, the electrochemical potential is maximum at the colloid surface obviously it is the maximum at the colloid surface or the clay surface and drops linearly as you can see it drops linearly at the location with increasing distance from the surface within the double layer. So, again in this Helmholtz double layer we assume that the negative charge is evenly distributed in the colloid surface with the charge density of sigma.

And the total counter charge in the second layer is concentrated in a plane parallel to the, you know, to the colloid surface at a distance x. And if the, you know, and the and the electrochemical potential is highest at the clay at the clay surface which linearly drops and ultimately which linearly drops with increasing distance from the from the clay surface. So, this is the exam this is the Helmholtz double layer model.

Now the second model is known as the Gouy-Chapman double layer model, now the in the Gouy-Chapman double layer model the negative charge is again considered distributed evenly over the colloid surface. However the counter ions are dispersed into the liquid layer as the gas molecule in the earth atmosphere. And this theory is therefore known as the diffuse double layer theory of Gouy and Chapman.

So, what is the difference between the Helmholtz double layer and Gouy double layer in case of gouy double in case of Helmholtz double layer they are they assume that the, the positive counter ions that is positive ions are basically arranged in a plane parallel to the clay surface at a distance x. However Gouy-Chapman is saying that, no, these, you know, counter ions positive counter ions are basically diffused into the bulk solution and as with an increasing distance. So that is why it is somewhat different than that of Helmholtz double layer.

Now what are the assumption of Gouy-Chapman model, there are, you know, 5 to 7 different assumption in the Gouy-Chapman model we will see one by one. First of all, the distance between the charges on the colloid and the counter ions in the liquid exceeds molecular dimensions. Second, the counter ions since they are mobile do not exist as a dense homoionic layer next to the colloid surface.

But as a diffuse cloud with this cloud containing both ions of the same sign of at the surface. So, they are saying that the counter ions since they are mobile they cannot be, you know, concentrating at a dense harmone homoionic layer next to the colloid surface. However rather they are diffusing away from the clay surface. As the colloidal is negatively charge, the colloid is surface is negatively charge. Fourth assumption was, the ions in the solution have no size that is they become they behave as point charge.

The fifth assumption was the solvent adjacent to the charges charge surface is continuous and has properties like the bulk solution. Again the solvent adjacent to the charge surface is continuous and has the properties like the bulk solution. Sixth one was the is the electrical potential is a maximum at the charge surface and drops to 0 in the bulk solution just like in case of Helmholtz double layer.

And the seventh one is the change in ion concentration from the charge surface to the bulk solution is nonlinear, this is one of the major difference with the Helmholtz model. Now in case of Helmholtz model the charge in the, you know, the change in ion concentration was from the charge surface to the bulk solution was kind of linear basically the change of ion concentration, there was no, the ion concentration was basically the ions or the counter ions positive ions were basically arranged in a plane parallel to the clay surface.

However in this case, they are basically diffusing away nonlinearly and finally only electrostatic interaction with the surface are assumed here. So, this is basically Gouy-Chapman layer and you can clearly see that the positive charge cations are basically concentrated at the adjacent vicinity of the negatively charged colloid. And then it they are slowly diffuse away with the increasing distance from the particle surface. So, surface is negatively charge, the counter ions are most concentrated near the surface and decrease exponentially, it is very important.

Their exponential decay we can say exponential decay in concentration of the positive charge with distance from the surface, excess of positive ions near the surface should equal to the negative charge of the fixed layer. Then there is a deficit of anions close to the surface, obviously since the close, since the surface itself negative charge there will be repulsion, so there will be deficit of anions close to the surface.

So, the important relationship and parameter that can be derived from the Gouy-Chapman theory basically includes the relationship between potential and distance from the surface. So, we can guess basically we can get this relationship and this relationship tanh is equal to Ze psi by 4 kT equal to tanh Ze psi 0 4 kT e to the power-kx, where Z is basically valence of the counter ions, tanh is the hyperbolic tangent and e is basically electronic charge which is basically measured in coulombs.

And the psi is electrical potential in volt and psi 0 is potential at the surface. Here psi 0 basically denotes that the the the distance from the surface is 0, K is Boltzmann constant we know K and small k is basically the reciprocal of the double layer thickness in inverse of meter and T is absolute temperature, x is distance from the surface in meter. So by using these, we can establish the relationship between the potential and the distance from the surface.

Now there is another relationship between the number of ions that is n i that is denoted by n i and the distance from the charge surface. You can see, it is basically n i equal to n i 0 and 1-tanh – Ze psi 0 by 4 kT e to the power -kx over 1 + tanh –Ze q Ze Ze psi 0 -4 KT e to the power kx. Now we know all these terms here n i is basically the concentration of ith ions that at a point where the potential is psi and n i 0 is the concentration of ions in the bulk solution. So, this is how we can calculate the relationship between the number ions and the distance from the charge surface.

Another important relationship is there, that is the thickness of the diffuse double layer is the reciprocal of k. So, we know K is basically, so is the reciprocal of k that is 1 by k. So, k can be calculated by using this formula that is 1000 dm cube, m to the power -3, e square NA Z i square M i summation by e KT. Where this NA basically stands for the Avogadro number, Z i stands for the valency of the ion, M i stands for the molar concentration of ion.

And this E stands for the dielectric constant and E can be calculated by this formula E r multiplied by E 0 where E 0 is 8.85 into 10 to the power -12 coulomb square per joule per meter. Whereas this E r is the dielectric constant of the medium, for water this dielectric constant is basically 78.54 at 298 Kelvin. So, we can put all these values to calculate the thickness of the diffuse double layer.

Now, the Gouy-Chapman theory predicts that the double layer thickness that is 1 by k is inversely proportional to the square root of the sum of the, you know, square root of the sum of the product ion concentration and the square of the valency of the electrolyte in the external solution and directly proportional to the square root of the dielectric constant. So, in other words as we can see the concentration of ions of opposite charges to that particle, you know, basically increases.

So, the concentration of ions of opposite charges to that the particles increases from 0.01 to 1 to 100 milli mole per dm cube. So, you can see in case of thickness of the double layer basically decreases thickness of the double layer basically decreases for both monovalent ions as well as the cat divalent ions. And so the double layer thickness is inversely proportional to the square root of the sum of the product of the ionic concentration and square of the valency of the electrolytes.

So, for both the monovalent and divalent ion, as you can see we are increasingly, you know, concentration of the opposite charge in the particle. So, if the monovalent cations and divalent cations concentration increases in the solution. Obviously, the thickness of the double doub diffuse double layer will decrease in both monovalent ions and cat divalent ions. In other words, as we are increasing the concentration of particular cation whether it is monovalent or divalent, the thickness of the difference double layer will decrease.

And actually the thickness of the electrical double layer cannot be measured but it is defined mathematically as the distance of a point from the surface when d psi by dx equal to basically 0. So, what we have learned here, we have learned that as the concentration of a particular ion increases in the solution the diffuse double layer thickness get decreased and this decreasing of this diffuse double layer is can be can be evident in case of both monovalent as well as divalent ions.

So, let us see 1 numerical problem, so in this numerical problem the problem is plot the relationship between electrical potential and distance from the surface x. So, electrical potential psi and the distance from the surface x for the following values of x. So, the following values of x is zero, then 5 into 10 to the power -9, 1 into 10 to the power -9 8 and 2 into 10 to the power -8 meter.

So for these three distance one, two, three, four distances we have to calculate this electrical potential according to the Gouy-Chapman theory. Now given is this psi 0 that means potential at 0 distance is basically this one M i we know. And then e also value is given, eta value is given and then Avogadro number or any constant is Avogadro constant is given and also k is given and R also given, T is also given. So, let us see how we can calculate this.

So, since we have already got all this information to calculate the to to calculate the potential at several distances, first we have to calculate the thickness of the diffuse double layer or K. So, here you can see for using the K we have to use this formula, so all these values are given. So, substituting all these values we can get a value of K that is 1.04 into 10 to the power 8 per meter.

So, basically therefore 1 by k on the double layer thickness would equal to 9.62 into 10 to the power -9 meter, so we can get this double layer thickness value ok. So, to solve this for function to solve this for psi as a function of x. So, basically we put all these values here and to simplify x equal to 0 here and E value of k is given here we can see, so, the thickness is given here.

So, from there, we can calculate this equation simplify if you simplify this equation it will turn tanh equal to tanh 9.76 into 10 to the power -1 multiplied by 1, so tanh equal to 0.75. So, if you take the inverse of tanh then obviously we will get this value that is Ze psi by 4 KT equal to 0.97 and substituting this value into that equation. So, you know this equation is already been given, this is the equation.

So if we value if we substitute the value in this equation we will get the value of it is substitute in these values. So, from there we can get the value of psi ok, so psi equal to 9.96 into 10 to the power -2 joule per coulomb. So, again the idea of calculating this problem is to first to we have to calculate the thickness by getting all the information, all the information are given you have to calculate the thickness.

Once you calculate the once you calculate the thickness you have to input all these information into this Gouy-Chapman equation. And you have to calculate the value of this right hand side part of the equation. Once you calculate this right hand side part of the equation you take a tan inverse and after that you calculate the value of the psi. And this will be basically calculated for a value of 0.

Similarly for any distance you can calculate this value of psi. So, the psi values for the other x values are we have been calculated here ok, we have calculated in the similar way. Once we calculate these values in the similar way, the next step is to plot them. Basically in the x axis we are plotting the x, you know, the distance in 10 to the power -8 meter and the y axis basically we are putting the surface potential.

So, we are getting this type of, you know, we can see that there is an exponential decay of the potential and this basically, you know justify the Gouy-Chapman diffuse double layer theory. So, guys I hope that you have learned something new in this lecture. And in the in the last lecture of this week we will be discussing about the, you know, Stern layer then zeta potential and then speciation of the metals and other important things.

And so let us wrap up our lecture here and if you have any questions just email me. For any clarification, I will be more than happy to answer your queries. And in the last lecture of this week we will be discussing in details about the Stern layer, zeta potential and other electro kinetic potential, thank you very much.