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Lecture – 47 Retention of Pollutants on and within the Soil Solid Phase (Contd.,)

Welcome friends to this second lecture of Week 10. In this week, we are talking about the retention of pollutants on and within the Soil Solid phases. In our previous lecture, we have talked about the major forces which are responsible for; you know retention of organic pollutants in the soil solid phases; you know basically the pollutants on the soil solid phases and then we have discussed what are the mechanisms for attracting the pathogenic microorganisms onto the soil solid phase and also we have started discussing about the negative adsorption.

So in the negative adsorption, we have discussed that it is basically the repulsion between the; like between the ions from the similar charge surface and this repulsion, this coulombic repulsion is known as the negative adsorption. And also we have discussed the relationship of, given by the scientist Sposito where we can mathematically quantify the excess of moles of ions per unit area of suspended solid.

So in today's lecture we are going to extend the discussion on negative adsorption and we will also see what are the other factors which are responsible for retention of nonionic pollutants onto the soil solid surface.

(Refer Slide Time: 02:00)



So let us go ahead and see we have already seen this relationship given by this Sposito in our last class and we are going to; so what is; we are going to discuss some more about the negative adsorption. Now negative absorption we know that in an; if an anion approaches a charged surface, it is subjected to attraction by positively charged sites of the surface, or repulsion by the negatively charged ones, obviously.

Most of the times the negative charge in the clay surface develop due to isomorphous substitution or sometime due to the ph of the surrounding medium. Now when the negative charge develops on the surface of these clay particles if an anion approaches to that negatively charged clay particle there will; it will it will face a coulombic repulsion force or negative absorption and if the charge; if the surface is positively charged, then obviously it will; these negatively charged anions will be electrostatically attracted.

Now since clay minerals in soil are normally negatively charged, anions tends to be repelled from the mineral surface. Example, for again example we have seen that if a dilute neutral solution of potassium chloride is added to a dry clay, then the equilibrium chloride concentration in the bulk solution will be greater than that of chloride concentration in the solution originally added to the clay. So basically the clay is negatively charged. So when we add this potassium chloride which is dissociated to potassium ion and chloride ion the concentration of the chloride will be higher in the bulk solution than that of the; you know which is originally added to the clay due to this negative adsorption.

(Refer Slide Time: 03:56)



Now this process occurring when an anion is added to a dry colloid with no adsorption capacity for the anion at the prevailing ph is called negative adsorption. So now I hope you are clear about the negative adsorption. Now it is related to the unequal ion distribution in the diffuse double layer charged colloids, obviously. There is an unequal distribution in the diffuse double layer charged colloids so obviously that is why there is a repulsion.

Anion negative; you know, adsorption is basically affected by certain factors these factors is the anion charge then concentration then pH then presence of other anions and the nature and charge of the surface. So these are the major, you know, important things which impact the anion negative adsorption.

(Refer Slide Time: 04:55)



Now negative adsorption in the soil can; you know, is basically decreases as the soil pH decreases. So when the soil pH decreases, negative adsorption decreases and when the anions can be absorbed by positively charged soil or soil colloids. So obviously, negative adsorption will be decreased when the pH decreases. Why? Because when the pH decreases obviously there will be formation of positively charged; positively pH dependent charge.

As a result of that, there will be attraction between these anions as well as the positively charged surface resulting in reducing the negative adsorption. Similarly, when anions can be absorbed by positively charged soils or soil colloids so these are two conditions in which we can see reduction of negative adsorption. The greater the negative charge on this/of the surface, the greater is the anion negative adsorption.

Obviously, the greater the negative charge of the surface so that is why we have seen we have discussed that the charge of the anion is, you know charge of the anion is important. So greater is the negative charge of the surface, greater is the anion negative adsorption. Acidic toxic organic compounds in their anionic form are expected to be repelled by negatively charged clay colloids obviously. Acidic toxic anionic compounds in the; in their anionic form are expected to be repelled by the negatively charged clay surface. Now amorphous clays also have some pH-dependent positive charge at low pH values.

Under such condition, most acidic organics are in the molecular form in the soil so that the significant adsorption by formation of anionic bond is improbable. So again during this; you know under such conditions most acidic organics are in the molecular form in the soil so that significant adsorption by the formation of anionic bond is improbable because you know we have seen that, you know acidic toxic organic compounds in their anionic forms are being repelled by negatively charged clay surfaces, okay.

(Refer Slide Time: 07:27)



So the adsorption of; so we have discussed the absorption of ionic pollutants, now we are going to discuss the adsorption of nonionic pollutants. Now remember that the absorption of nonionic pollutants on the soil solid phase surface is subjected to a series of mechanisms. What are those mechanisms? The mechanisms are Protonation, Water bridging, Cation bridging, Ligand exchange, Hydrogen bonding and Van der Waals interaction. So we are going to discuss them in the coming slide.

(Refer Slide Time: 08:11)



So if we consider the nonionic pollutants. What are the important nonionic pollutants? In this class of pollutants, hundreds of compounds belonging are basically chemically different group like as you can see here these Chlorinated hydrocarbons then Organophosphates then Carbamates, Ureas, Anilines and Anilides, amides etcetera. So these are the examples of nonionic pollutants. Now the great differences between the properties of these groups and among compounds within a group are reflected in the variability or the adsorption mechanism and soil organic colloids plays a dominant role in this process.

So obviously all these compounds are basically nonionic pollutants and also among these compounds are also, the properties vary so widely that their adsorption mechanism onto the soil organic colloids plays; you know, adsorption, you know their adsorption mechanisms as well as the presence of soil organic colloids plays an important role in the process of their adsorption or retention.

(Refer Slide Time: 09:39)



So, these two scientists known Hassett and Banwart in 1989, they consider that the sorption of nonpolar organics by soil is due to the enthalpy-related and entropy-related adsorption forces. So there are two types of; you know forces, one is enthalpy-related another is entropy-related adsorptive forces. Now they consider these two scientists they consider that sorption occurs when the free energy of the sorption reaction is negative.

So this free energy that is denoted by this delta G which is basically the difference between this delta H - T into delta S, so this is; when this delta G is negative then we can, you know; and only the; you know when this delta G is negative then only the sorption occurs, okay. So the free energy of the sorption reaction can be negative because of either enthalpy term or the entropy term or the contribution from the both, okay.

So this negative, you know, sign of this free energy can stem from either the enthalpy term or the entropy term or the combination of both, okay. Now the enthalpy term is primarily a function of the difference in the bonding between the adsorbing surface and the sorbate or in other words solute and that between the solvent and the solute. So the entropy term, on the other hand, is related to the increase and decrease in the ordering of the system upon sorption, okay.

So these are the two terms which basically plays the major role for controlling the adsorption of nonionic pollutants and remember that the sorption occurs only when the free energy of the

sorption reaction is negative which is denoted by delta G and this negative free energy can be, you know the contributory; the contributory processes for this negative free energy can be either enthalpy-related processes or entropy-related processes or the contribution from both the processes.

(Refer Slide Time: 12:23)



So for a chemical reaction at equilibrium, the free energy which is denoted again by delta G can be calculated from the equilibrium constant K. We have already discussed equilibrium constant in our previous lecture. So a thermodynamic equilibrium constant if you remember, so the enthalpy change which is denoted by this delta H, so this delta H is basically the enthalpy change can be calculated from the variation of K with temperature and delta S can be calculated as the difference.

So basically this delta S is equal to delta H which is enthalpy change minus change in the free energy by the; divided by the temperature. So this delta S can be calculated by using this formula, okay.

(Refer Slide Time: 13:14)



So let us see the enthalpy-related adsorption forces. Hydrogen bonding can be considered as one of the major enthalpy-related adsorption force. So let us see what is hydrogen bonding? Hydrogen bonding which refers to the electrostatic interaction between a hydrogen atom covalently bound to one electronegative atom that is oxygen and to other electronegative atom or group of atom in a molecule.

So here you can see this is the hydrogen bonding which is occurring between this hydrogen atom as well as this electronegative oxygen atom. Now this hydrogen atom may thus be regarded as a bridge between electronegative atoms. So obviously, you can see this is an oxygen electronegative atom, this oxygen is another electronegative atom. So this hydrogen is acting as a bridge between these two electronegative atoms. Generally, this bonding is conceived as an, you know, of as an induced dipole phenomena.

Obviously, positive and negative, you know dipole so obviously there is an induced dipole phenomena, the H bond is considered, the hydrogen bond is considered generally as the asymmetrical distribution of the first electron of the H atom induced by the various electronegative atoms. So due to the presence of this electronegative atom oxygen there is an induced asymmetrical distribution of the first electron of the hydrogen atom and as a result there is an electrostatic attraction.

So this is called hydrogen bonding. We have discussed the hydrogen bonding while discussing the clay mineral structure if you remember. If you remember the interlayer; the interlayer bonding between the Kaolinite structure has a, you know, has a hydrogen bonding. As a result, they are having the collapsed structure and they are nutrient poor, low internal surface area. So this hydrogen bonding plays an important role for a different clay structure also.

(Refer Slide Time: 15:30)



Now another important process is the Ligand exchange process. Ligand exchange process involves the replacement of one or more ligand by the adsorbing species. Now we have discussed ligand in this; in details. So I am not going to in discuss it further but remember that in some instances, the ligand exchange process can be regarded as the condensation reaction which is; for example, you know reaction between a carbon; carboxyl group and hydroxy aluminum surface under some condition.

This ligand exchange reaction are very likely to be involved when the humic substances interact with the clay mineral. So this is how the; some; sometime these organic pollutants get adsorbed onto the clay surface this ligand exchange process.

(Refer Slide Time: 16:22)



Another important process which is, you know, which is controlled by enthalpy-related adsorptive forces is the protonation process. Now what is protonation mechanism? The mechanism of protonation includes a coulomb electrostatic force resulting from charged surface. Now the development of surface acidity by solid surface of the soil offers the possibility that solutes having proton selective organic functional groups can be adsorbed through a protonation reaction.

Now we know by the definition of acid that the acid is a proton donor, okay. So the development of a surface acidity when there is a surface acidity by the solid surface of the soil so solid surface when there is a surface acidity so that in exchange you know it can donate a proton to that solid which having a proton selective organic functional groups, so as a result of that there is an adsorption and this is the perfect example of protonation reaction.

Another bonding is known as the Pi bond and you can see the figure here of pi bond here. So Pi bond are covalent chemical bonds where two lobes of an orbital on one atom overlaps with the two lobes of an orbital on another atom and this overlap occurs laterally as you can see here two lobes of one atom is overlapping with two lobes of another atom and this overlapping is basically occurring laterally.

So this is an example of Pi bond and this mechanism can be used to explain the bonding of, you know alkenes, alkylenes, and then aromatic compounds to soil organic matter. So this is another important enthalpy-related adsorptive forces.

(Refer Slide Time: 18:22)



The next one is London-van der Waals forces. We have discussed some van der Waals force you know while discussing the diffuse double layer but remember that this London-van der Waals force is a relatively weak electric force that attract neutral molecules to one another in gases in liquefied and solidified gases and in almost all organic liquids and solids. So basically there is a; you know, here you can see there are neutral molecules.

And these neutral molecules are neutral; you know molecules when they, you know instantaneous when there is an instantaneous dipole on A induced a dipole on B then, there is an attraction, so that is called the London-Van der Waals forces. So in this A, when there is an instantaneously dipole on A, you can see positive and there is negative so positive charge negative charge; so there is a dipole.

So instantaneous dipole when results in a dipole in B also then; so here is a negative positive and due to this dipole instantaneous dipole there is an opposite sign developed in the vicinity of the B so you can see here there is another induced dipole also. So this is an example, this is the reason for this Van der Waals force. So these force are generally multiple that is dipole-dipole or dipole-

induced dipole so you can see here dipole-induced dipole interaction produced by correlation between fluctuating induced multiple moments in two in; you know, nearly unchanged polar molecules.

So here you can see two unchanged polar molecules, okay. For example; unchanged polar molecules and there is an instantaneous dipole and as a result of that there is a induced dipole in the second molecule so obviously there is an attraction. So this is called the London-van der Waals force, okay. So this is another important enthalpy-related force.

(Refer Slide Time: 20:25)



So despite the fact that this time-average induced multiple in each of the molecule is zero, the correlation between the two induced moments does not average zero, so as a result of this induced dipole, an attractive interaction between the two is produced at very small molecular distance. Now remember that this is very important so this Van der Waals force basically occurs at very small molecular distance due to this induced dipole between the two polar molecules. So this is one of the important example of enthalpy-related adsorptive force which plays a very important role in the adsorption or retention of pollutants onto the soil solid surface.

(Refer Slide Time: 21:14)



Now the next important enthalpy-related adsorptive force is chemisorptions. There are two types of adsorption one is called chemisorption another is physisorption. However, let us only focus on chemisorption here. Now chemisorption is the short form of chemical adsorption. This is an adsorption in which the forces involved are valence forces of the same kind of those operating in the formation of chemical compounds.

Now it has got some specific features, this chemisorption has some specific features as we can see. One is the phenomenon is characterized by chemical specificity it is very, very chemically specific. Second the elementary step in chemisorption often involves activation energy. Third one is chemisorption may not be reversible. As far as the specificity is concerned this picture shows it more clearly in case of; there is a two example here, you know one is physisorption and chemisorption.

In case of physisorption, we cannot see any specific binding site, however, in case of chemisorption for the substrate surface we can see there is a specific binding site in which the solutes are getting attached. So this is the example of chemisorption. And this is an example of specificity of chemisorption.

(Refer Slide Time: 22:38)



Okay. So we have discussed all the enthalpy-related forces. Let us also discuss the entropyrelated adsorptive forces. Now the entropy-related adsorptive force is also known as hydrophobic sorption. So it is the partitioning of nonpolar organic out of the polar aqueous phase onto hydrophobic surface in the soil where they are retained through dispersion forces. Again it is the partitioning of nonpolar organics out of the polar aqueous phases onto the hydrophobic surfaces in the soil. So where the hydrophobic surfaces in the soil occurs? May be in the organic matter.

So in the organic matter, this hydrophobic surface they can partition out, they can separate out this nonpolar organic compounds from their polar aqueous phase and help their retention into the soil. So this is known as hydrophobic sorption. Now this figure basically shows the diagram or this diagram basically shows the forces which are contributing to the, forces which are contributing to the sorption of hydrophobic organics.

So here you can see, you know; for example, this is an organic pollute this is a; this is a nonpolar organic pollutant and it is their polar aqueous phase, okay. So these small black dots are basically water solvating polar groups, okay and also these are highly structured water, okay. Now you can see here if the soil organic matter the nonpolar moiety is attached and the polar aqueous phase is facing forces favoring solvation.

So obviously, here the polar aqueous phase or polar phase is facing the; you know, forces favoring the solvation because here the solvent is normal bulk water. So this is normal bulk water, so obviously this polar phase will feel the affinity towards this normal bulk water which is a polar, you know the; you know, water is polar so obviously there will be, there will be an attraction of this polar phase for solvation in this aqueous phase.

However, this non polar moiety will feel a force opposing the solvation obviously because this is hydrophobic in nature and you can see here, the hydrophobic sorption is occurring in the onto the soil organic matter which is by default hydrophobic in nature. So this soil organic matter has the capacity to separate out this nonpolar moiety from its mixture of the polar aqueous phase and this is known as hydrophobic sorption.

Now also you can see the similar things in some soil minerals where this nonpolar moiety will be adsorbed and obviously the polar phase will try to go out and then try to be favor the solvation process in the polar aqueous phase. The major feature of hydrophobic sorption is the weak interaction between the solid and the solvent. Obviously, here the solvent is the water normal bulk water so the solute is nonpolar moiety or organic pollutant so obviously there is a very weak interaction between them.

So, so the primary force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the solute from the solution. So we can see when the solute from the solution is changed the large; there is a large entropy change and this is the primary; you know primary force in the hydrophobic sorption, okay. The entropy change is largely due to the destruction of the cavity occupied by the solute in the solvent and the destruction of the structured water shell surrounding the solvated organic.

So basically when the cavities in the soil in the; you know cavities in the solvent which are occupied by the solute get destructed by this; by this separating force, then obviously there is an entropy change. In a hydrophobic sorption being an entropy-driven process provides the major contribution to sorption of hydrophobic pollutants in the soil surface. So obviously, this entropyrelated force entropy related adsorptive force is a major force for adsorption of organic pollutants onto the soil surface, okay.

I hope that you have learned something new in this lecture. Let us wrap up this lecture here and in the third lecture we will be discussing, you know adsorption from; you know from the complex mixture or multiple mixture and other important aspects of the interaction between or the retention of the pollutants onto the soil solid surface and if you find any difficulty, please let me know. I will be more than happy to answer your queries and I hope that we will gather more comprehensive knowledge; you will get a more comprehensive knowledge once we complete this week of lectures. Thank you very much. Let us meet in our next lecture.