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Lecture – 48 Retention of Pollutants on and within the Soil Solid Phase (Contd.,)

Welcome friends to this third lecture of module 10 or Week 10 of this NPTEL Online Certification course of Environmental Soil Chemistry and in this module our topic is the retention of pollutants on and within the soil solid phase.

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So in our previous two lectures, we have covered these aspects; these topics. First of all, we have covered the; what is adsorption and then adsorbed; we have also covered the adsorption of ionic pollutants. We have also covered adsorption of nonionic pollutants. Today, we are going to talk about the adsorption of complex mixtures as well as the kinetics of adsorption then we will be talking about factors affecting adsorption, if time permits.

So, the next couple of lectures basically will deal with the adsorption of complex mixture then kinetics of adsorption and then factors affecting adsorption and then we will be talking about non-adsorptive retention and then we will see some examples of organic and inorganic pollutant adsorption on soil solids. So, just to give a quick recap of what we have covered very briefly.

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So we started with the introduction of the; in the introduction, we talked about what are the major forces which are responsible for pollutant retention in the soils and then, we talked about the physicochemical processes, adsorption on the surface, then chemical reaction on with the solid phase and mechanical trapping of the pollutants in the solid soils, solid phase pores.

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We talked about the concepts about the; the concepts of surface adsorption of pollutants and how this excess concentration of pollutants occurred in the soil-solid interface compared with that the bulk solution on the gaseous phase, we know, regardless of the nature of the interface region of the interaction between the adsorbate and the solid surface which basically causes the excess. **(Refer Slide Time: 02:47)**



Then we talked about the surface adsorption.

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We covered the adsorption of ionic pollutants. In defining the ionic pollutants, adsorption of ionic pollutants we discussed the diffuse double layer, which we have already covered previously. Then, based on that we also discussed the negative adsorption and also adsorption of pathogen in the soil; negative, you know adsorption of pathogens soil was discussed in terms of reaction between the bacterial cell wall and, you know, and different charge negatively and positively charged ion exchange resins.

And I had showed you two examples where these ion exchange resins are reacting with the surface of the bacterial cell so that; you know the pathogen cell getting attached to the soil surface.

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Then we discussed in details about the negative adsorption remember, when a charged solid surface faces an ion of light charge in an aqueous suspension, the ion is repelled from the surface by columbic force and this phenomenon is known as negative adsorption and then we have discussed why the distribution of anions based on these negative adsorption. Remember, the concentration of anion in a negative charge clay surface is very low nearer to the clay surface however their concentration generally increases as the distance from the clay surface increases further.

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Then we discussed, you know this negative adsorption based on the; this equation given by Sposito and where these Ti(w) basically shows the excess of, you know excess in the moles of the ions per unit area of suspended solid. So we related that with the mass of total water and then molality of, you know molality of the ions and also; S that is the specific surface area of the suspended solids.

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Then we also talked about the; what are the factors which affects the anion, you know negative adsorption. For example, the anion charge, concentration, pH, the presence of other anions etcetera, the nature and charge of the surface and so, we discuss in details about the negative absorption.

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And then we talked about the adsorption of the nonionic pollutants and different mechanisms like Protonation, Water bridging, Cation bridging, Ligand exchange, Hydrogen bonding and Van der Waals interactions.

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We talked about you know, some examples of the nonionic pollutants.

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And then we discussed their attachment or discussed their adsorption based on the thermodynamic principle where both enthalpy and entropy based, you know, processes are of you know; are equally active.

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Then, we discussed, you know the enthalpy-related different adsorption process you know, while discussing the enthalpy-related adsorption processes, we talked about the hydrogen bonding and we also talked about the ligand exchange processes and protonation mechanisms.

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In the protonation mechanisms we talked about the Pi bond. We also talked about the Pi bond. Remember the Pi bonds are covalent chemical bonds with two lobes of an orbital on one atom overlaps with two lobes of an orbital on another atom and these overlaps occurs laterally. So this Pi bond we have discussed and then we discussed the London Van der Waals forces and why these Van der Waals; and how these Van der Waals forces generally occur due to the dipoledipole or dipole-induced dipole, how it occurs and what is the range of these, you know, remember these Van der Waals attraction is, you know, active with a very narrow range.

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So, we have discussed all the properties of the Van der Waals force.

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And then we talked about the chemisorption and using this picture we have expressed; we have discussed why chemisorptions is very, very specific in nature. And then we saw the difference between the physisorption and chemisorptions as you know, with respect to the specificity. **(Refer Slide Time: 07:34)**



Then we talked about the entropy-related adsorptive forces specifically hydrophobic adsorption and while talking about the hydrophobic adsorption we talked about the nonpolar moiety, how this nonpolar moiety adsorbed to the soil organic matter and what are the different forces which are acting for these attachment of nonpolar moiety in the soil organic matter or soil mineral surfaces and you know, what are the interactions between these solute and the solvent we have discussed in details.

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So, today we are going to start with the adsorption of complex mixture. Remember a system characterized by the presence of multiple solution and multiple solvents. So these are the two prerequisite for a complex mixture remember there has to be either multiple solutes and multiple solvents so then we call it complete complex mixture. Now, remember that since soil pollution under a waste disposal site generally occurs as a complex mixture.

Because there is a; you know, these areas are generally containing both inorganic and organic pollutants. So, obviously the adsorption occurs in the complex mixture. So, in general the adsorption mainly involves organic pollutants and the sorption might occur from the complex solvents containing partially miscible or completely, you know miscible organic solvents. So these type of adsorption generally occur. Now, you might ask me okay how to represent these adsorption, you know of a complex mixture.

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To represent mathematically this adsorption from a complex mixture adsorption of complex mixture, we generally follow an equation given by Rao et al in 1985. They proposed a theoretical approach based on the predominance of solvophobic or hydrophobic attractions or interactions for predicting sorption of hydrophobic organic chemicals from mixed solvent. Suppose they are in mixed solvents and we want to adsorb some hydrophobic organic chemicals within the soil surface then we have to; then this reaction generally follows these.

You know theoretic equations where these ln of Km that is logarithm of Km is basically Kw minus alpha i, Sigma i, and F i where the Sigma i basically denotes the delta, gamma i HSA by KT. Now here let us define all these terms here, this K is basically the sorption coefficient and the unit of this sorption coefficient is moles of solvent per kg of solvent and with the, you know here we have used to superscript one is m and other is w.

So m basically stands for the sorption from the; sorption from the mixed solvents whereas w basically stands for sorption from the water. So obviously, as we have seen previously in case of mixed solvents where there are many co-solvent with water then, the solubility depends on the solubility of the water plus or minus with another term. So similarly, we are finding here in case of complex mixture, here the solubility term is related to the solubility of the water and with this term.

So, in this term this Sigma i is basically is a dimensionless term unique to each solvent-sorbate combination so it is a very specific and this delta gamma 1 is a differential interface; interfacial free energy which is, at the solvent sorbate interface. HAS, this term, this HSA basically is the sorbate hydro-carbonaceous surface area and also K is the Boltzmann constant in Joule Per Kelvin and T is the thermodynamic temperature in Kelvin. And f I, here this f i is basically the volume fraction of the i-th cosolvent and alpha i is the empirical constant.

So this is how we define these each of the term and remember for sorption of an organic molecules or organic chemical from a complex mixture to the soil surface generally follows this mathematical equation.

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So, so the adsorption is the process leading to a net accumulation of a compound at the interface of two contiguous phases and we know that the adsorbent, you know basically when we talk about the soil adsorption here, the adsorbent is the soil solid phase and the sorbate can be in a gaseous or a liquid phase as a solid. Now when the; when the measured adsorption data are plotted against the concentration value of the adsorbent at equilibrium a graph is obtained, which we call adsorption isotherm.

Now guys, we have already discussed these four adsorption isotherms in our previous lectures. So S type, L type, H type and C type we have already discussed. And also we have discussed the mathematical description of the isotherms or models of the isotherms for example, Freundlich isotherms and then Langmuir isotherms.

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So I am not going to discuss them in details, just for a quick recap just remember that, that S type isotherm where, you know this is an S type of isotherm where slope initially increases with the adsorptive concentration but eventually, you know, eventually decreases and becomes zero as vacant adsorbent sites are filled. At low concentration generally, the surface has a low affinity for the adsorptive which increases at the higher concentration as you can see.

At higher concentration, the surface, you know, adsorption generally increases. However, at the lower concentration the surface has a low affinity for the adsorptive. So, we can see this; this is an S type isotherm, we have already discussed this. I am just giving a quick recap.

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Now L shaped or Langmuir isotherm we have discussed, it is basically decreasing the slope as concentration increases since vacant adsorption sites decreases as the adsorbent become covered. As we can see that it is basically decreasing as the concentration is increasing. Now explained by the high affinity of the adsorbent for the adsorptive at low concentrations which then decreases the concentration increases. So basically, that follows the Langmuir isotherm.

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Then third one is the H type or high-affinity isotherm. High-affinity isotherm or H-type isotherm basically shows the strong adsorbate as you know, adsorptive interactions such as inner-sphere complexes. We have already discussed what is inner-sphere complex and outer-sphere complex. And you can see here there is a, you know, it is very, very steep. The relationship is very, very

steep so it shows basically the high affinity isotherm. So here there is a strong interaction or strong affinity of the adsorptive for the adsorbate molecule.

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Now the last one was the C type isotherm. It is basically shows the partitioning mechanism, here adsorptive ions are partitioned between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and adsorbate and you can see here, this is the shape of this C type isotherm; adsorption isotherm.

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Now, if we talk about the kinetics; if we talk about the kinetics of the adsorption in the case of soil cation exchange, charge-compensation cations are held in soil solid phases, so basically in 3

fashion, one is within; one is within crystals in interlayer positions, for example, mica and smectites we have already seen that. This is a structure of the Muscovite, which is a potassium containing mica. And you can see that in the interlayer space are occupied by these potassium ions.

So that shows that the adsorption of these soil cations are occurring in the interlayer positions. Similarly, in case of smectite if you remember the smectite structure, it has got a huge interlayer space, and in this huge interlayer space there are several different types of you know, species can adsorbed. So cations also can adsorbed in that huge interlayer space of smectite. Now, second one is structural holes of feldspars.

Now, you know that feldspars are the most abundant primary minerals and their structure which I will show you in the next slide contains some holes and you know, in these holes these you know, these cations can reside and third one is basically on the surface and in the cleavages and faults of the crystal on external surface of the clays and clay minerals and organic matter. Now as you can see from this picture, this is a clay particle and obviously these cations are present in the external surfaces of the clays and results are present in the surfaces of the clay particle.

Now cations held on external surfaces are remember, they are immediately accessible for; to the soil solution as compared to those cations which are adsorbed to the internal surfaces cations, which are adsorbed to the external surfaces are more you know, accessible to the soil solution and once removed from this phase. So, if we remove from these external surface area where they are adsorbed, they move to a region of smaller concentration.

Obviously, there is a; you know, they tend to diffuse away from the surface of the clay particle to maintain in equilibrium. And finally, the movement is controlled by the diffusion and the diffusion coefficient through the soil, which we will discuss in our coming slides. So, what do you have we have learned from this slide? We have learned from this slide that the cation exchange processes; in case of cation exchange process charge compensation cations are held in the soil solid phases in 3 fashion one is within the interlayer space.

For example, in case of mica, in case of smectite and second in the structural holes, for example, incase of feldspars and thirdly, on the surface in the cleavages of the crystals and on the external surface area of the clay and clay minerals from where, and also organic matter from where these cations basically goes to the soil solution through the process of desorption and these movement from the external surface is controlled by different types of diffusion and diffusion coefficients. **(Refer Slide Time: 19:19)**



So this is basically the feldspar structure and you can see there are some holes where these cations can reside. So this is also a site for you know, cation; cation, you know; it is a site for cationic species.

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Now, if we see the kinetics of adsorption, obviously, we have; we need to know what is the diffusion coefficient, what is the mathematical expression of the diffusion coefficient, we had just seen that the diffusion; diffusion coefficient plays important role for the desorption and movement of the cations from the external surface of the clay particles and clay minerals to the bulk solution.

Now this diffusion coefficient can be; which is denoted by these D can be calculated using the equation of these Nye and Tinker these two scientists, so you can see that is D = De then theta f dC solution by dC sol. Now, we can see that this De is basically the diffusion coefficient, you know, in water, okay and theta is the water content of the soil, F is the impedance factor related to the soil tortuosity, okay.

Tortuosity means the solid pores, the soil solid; know soil pores are interrelated to each other making a tortuous path or zigzag path or inconsistent path so that is called soil tortuosity and C is the cation concentration of the soil in the solution that is mass/volume ratio. Now, here in the last term that is dC solution to dC sol. So, basically shows the buffering capacity of the system and it is specific constant for the soil.

Obviously, when the concentration of, you know when the concentration of a particular ion in the solution get depleted then the adsorbed ions from the soil clay surface or other secondary mineral surface basically goes to the solution to maintain the equilibrium and that is a representation of the buffering capacity. Now, two cation exchange properties are generally involved.

First of all, the number of exchange sites occupied by the cation investigated and secondly the selectivity of the cation relative to the concentration of the exchanging cation, okay. So these two are important properties, which are involved in the cation exchange; in the cation exchange process.

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So, if we see; discuss the kinetics of adsorption. Now, this Weber diagram given by the scientist Weber in 1984, gives us the rate-determining steps in a heterogeneous soil system. By nature, soil is heterogeneous in nature. So you can see here this is the picture which basically shows these are the clay particles so these are the clay particles and you know, surrounding this clay particle there is a thin film of water and then you can see the bulk solutions, okay.

So, when the ions basically move from bulk solution to through the film to this particle site and the actual chemical reaction exchange to occur for actual chemical reaction to occur the ion must be transported to the active fixed side of the particles. So these are the active fixed; you know active fixed sites of the particles. So, for the actual chemical reactions basically exchange to occur, the ion must be moving from this bulk phase through the film to the active particle surface.

Now, remember that the film of water adhering to the surrounding the particles and the hydrated interlayer space in the particle are both zones of low concentration which are constantly being depleted by ion adsorption to the sites. So here if these are the active sites for ion adsorption obviously, these ions are coming from these inter-particle you know, hydrated; you know interlayer space of the particles or from this thin, you know from this thin film of water adhering to the particle.

So the; both these areas are having the low concentration because the concentration of the cation are basically excess in the surface. So basically when the cations from this liquid phase goes to this specific sites obviously, these two phases are showing low concentration of the cations. So, what that means?

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So basically that says, the decrease in the concentration of ions in these interfacial zone is then compensated by ion diffusion from the bulk solution. So when due to the adsorption of cation in this specific adsorption sites of the clay particle occurs and as a result of that, the inter particle you know, inter particle liquid layer and also the film adhering to the particles are losing the cation so they became somewhat less in concentration for that cation.

So this decrease in concentration of the ions in this interfacial zones is then compensated by the diffusion from the bulk solution. So here this is the bulk solution. Now thus if; this ion basically will diffuse away to maintain the concentration of the film as well as the inter-particle or you know inter-particle liquid phase, so thus in most soil and soil-constituent system, either this particle diffusion, so this is basically particle diffusion process or film diffusion, so diffusion through the film maybe the rate limiting factor.

So we are; we are seeing that the; you know the diffusion through these, you know diffusion through this between the particle as well diffusion through the film are basically the rate limiting steps in the kinetics of cation or ion exchange.

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Now the characteristics, if you see the characteristic period of ion exchange in soil, it generally varies from, you know the time varies from few seconds to days. And basically this is due to two things one is the properties of inorganic and organic constituents of the soil solid phase and the properties of the pollutants; pollutants ions change and; basically properties of the pollutants ion charge and radius.

So the slowly exchangeable cations are situated on exchange sites in interlayer space of the soil mineral that is mica or in cages and channels of soil organic matter and an exchange out into solution by diffusive flux. So, basically that says again, the slowly exchangeable cations are situated on the exchange site in the interlayer space; we have already discussed that as compared to the external surface area those cations those are adsorbed into the external; internal surface or interlayer spaces just like in case of illite, in case of mica, in case of smectite these are you know, slowly exchangeable in nature.

So the slowly exchangeable cations are situated on the exchange site in the interlayer space of the soil minerals like mica or in cages in or channels of the soil organic matter and exchange out into solution by diffusive flux. So we have already discussed that. Two properties again you have to remember one is the properties of inorganic and organic constituents of the soil solid phase and the properties of the pollutants, you know ion charge and also their radius.

So guys, I hope that you have learned something new. We have discussed some important, you know kinetics of adsorption and also how these you know, ion exchange occurs in the; in the particles heterogeneous soil particles, and we also have mathematically defined the diffusion coefficients in this lecture. So I hope that you have gathered some new knowledge. And let us wrap up our lecture here and in the next lecture, we will be talking about the; you know other aspects or; of kinetics of adsorption and also we will see some examples of pollutant adsorption onto the soil solid phases. Thank you very much. Let us meet in our next lecture.