Environmental Soil Chemistry
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Lecture 46
Retention of Pollutants on and within Soil Solid Phases

Welcome friends to this week 10 of lectures for this NPTEL online certification course of environmental soil chemistry and in this week or in this module 10, we are going to talk about the retention of pollutants on and within the soil solid phase. So this is a very important chapter. In the previous chapter or previous module, we have talked about the interaction of pollutants with the soil solution.

Now in this week, we will be talking about the interaction or retention of these pollutants within or on the soil solid phases. So basically, while talking about these interaction or retention of these pollutants in the soil solid phases, we are going to talk about more comprehensively on the adsorption.

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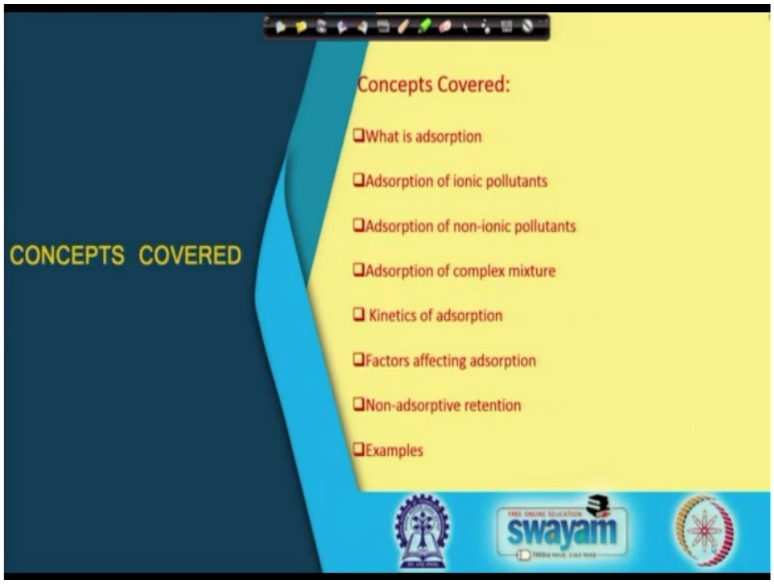

CONCEPTS COVERED

Concepts Covered:

- ☐ What is adsorption
- ☐ Adsorption of ionic pollutants
- ☐ Adsorption of non-ionic pollutants
- ☐ Adsorption of complex mixture
- ☐ Kinetics of adsorption
- ☐ Factors affecting adsorption
- ☐ Non-adsorptive retention
- ☐ Examples

So, these are the concepts, which we are going to cover in this week or module 10. First of all, we will be talking about adsorption and then we will be also talking about the adsorption of ionic pollutants and then, we will be talking about adsorption of non-ionic pollutants and we will be also discussing adsorption of complex mixture, kinetics of adsorption, then factors affecting adsorption, then we will be talking about non-adsorptive retention and we will also see some examples. So these are in summary the major concepts, which we are going to cover in this week 10 or module 10. So let us start.

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Introduction

- Pollutants retained on and within the soil solid phase have reached the soil directly as solute, water-immiscible liquid, suspended particles, or in the gaseous phase.
- Pollutant retention is controlled –

1. By the physicochemical and physical properties of the soil solid phase
2. By the properties of the pollutants themselves, and
3. By environmental factors such as temperature and soil moisture content

So one thing is clear, in this week that, in this module that, while we are talking about the interaction or retention of pollutants on or within the soil solid phases, these are mainly manifestation of different types of sorption process, specifically adsorption. So we will be discussing the adsorption process in more details. Remember that, we have already discussed some aspects of adsorption in our previous weeks or previous modules.

For example, adsorption isotherms, adsorption types, mathematical formulas of adsorption models, we have discussed in details. Diffuse double layers, we have discussed in details. So whatever we have covered previously I am not going to talk in details in this lecture, however, I am going to cover some other aspects, which we have not covered yet, while discussing the adsorption processes.

Now so pollutants retain on and within the soil solid phase have reached the soil directly as solute, water immiscible liquid, suspended particles or in the gaseous phase. We know that. So they can reach in the soil as solute or water immiscible liquid or suspended particles or in the gaseous phase. Now this pollution retention on the solid phase is basically governed by mainly 3 important processes. One is physiochemical and physical properties of the soil solid phase.

Second, by the properties of the pollutants themselves and third, by environmental factors such as temperature and soil moisture content, so these 3 are the major, you know, controlling factors for pollutant retention on soil solid phase ok.

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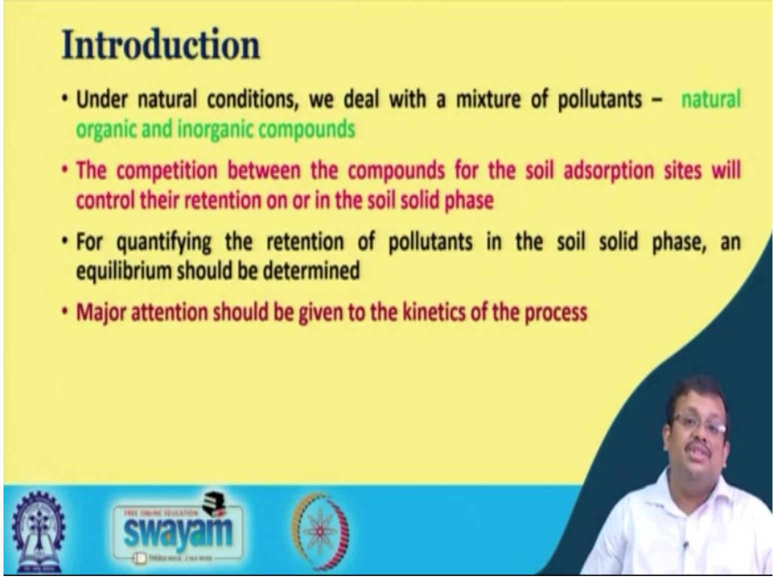

Introduction

- Under natural conditions, we deal with a mixture of pollutants – natural organic and inorganic compounds
- The competition between the compounds for the soil adsorption sites will control their retention on or in the soil solid phase
- For quantifying the retention of pollutants in the soil solid phase, an equilibrium should be determined
- Major attention should be given to the kinetics of the process

So under natural condition, we generally deal with a mixture of pollutants, natural organic and inorganic compounds. It is not simple, only natural organic compounds or inorganic compounds, it is basically mixture. It is a complex mixture of pollutants. If you see, if you go to any landfill site, if you go to any waste disposal site, you will see there is a mixture of natural organic as well as inorganic compounds. So it is always a complex mixture.

Now the competition between the compounds for the soil adsorption sites will control their retention on or in the soil solid phase. Now for quantifying the retention of pollutants in the soil solid phase, an equilibrium should be determined. It is very clear. So obviously, there is some competition between the compounds for the soil adsorption site, we have already seen during our lecture of adsorption, soil sorption process that there is always some competition between the cations to attach to the negatively charged clay surface.

Similarly, there is also a competition between the compounds for the soil adsorption sites and this basically controls their retention in the soil solid phase. Now for quantifying the retention of the pollutants in the soil solid phase, an equilibrium should be determined. We have also discussed equilibrium thing in our sorption lecture. Now remember that major attention for these should be given to the kinetics of the process. So this kinetics, adsorption kinetics we are going to discuss in this week or in this module.

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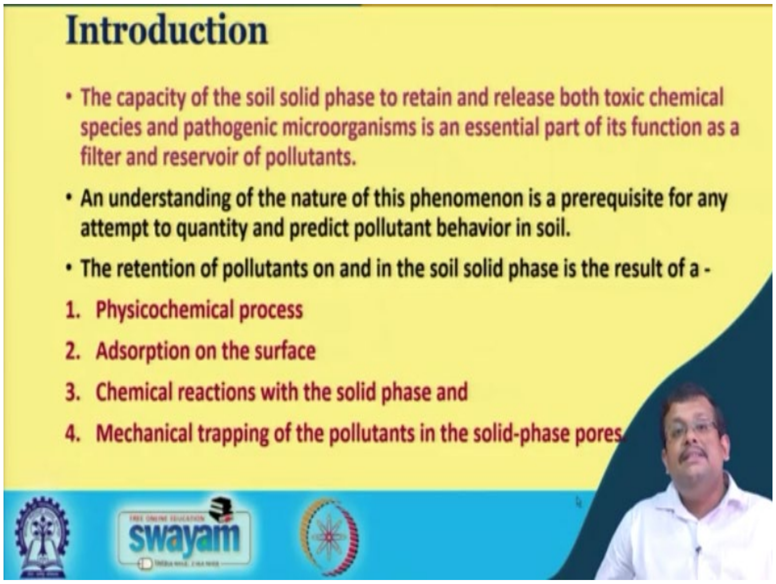

Introduction

- The capacity of the soil solid phase to retain and release both toxic chemical species and pathogenic microorganisms is an essential part of its function as a filter and reservoir of pollutants.
- An understanding of the nature of this phenomenon is a prerequisite for any attempt to quantity and predict pollutant behavior in soil.
- The retention of pollutants on and in the soil solid phase is the result of a -

1. Physicochemical process
2. Adsorption on the surface
3. Chemical reactions with the solid phase and
4. Mechanical trapping of the pollutants in the solid-phase pores

Now, the capacity of the soil solid phase to retain and release both toxic chemical species and pathogenic microorganisms, so when we are talking about the retention, we are not talking about retention of only toxic chemical species, we are also talking about pathogenic microorganisms, because they are also source of hazard. So the retention and release of both toxic chemical species and pathogenic microorganisms is an essential part of its function as a filter and reservoir of pollutants.

So the capacity of the soil solid phase to retain and release of this toxic chemical species and pathogenic microorganism is basically governed by their filtering nature. Now an understanding of the nature of this phenomenon is a pre-requisite. Being an environmental soil scientist, you need to understand the nature of this filter and reservoir attribute of this, you know, of this soil media for any attempt to quantify and predict pollutant behavior in the soil.

Now the retention of pollutants on and in the soil solid phase is basically the result of four major processes. What are these processes? One is physiochemical process, adsorption on the surface, chemical reaction with the solid phase and mechanical trapping of the pollutants in the solid pores. One is physiochemical process. Second is adsorption on the surface, which we are going to discuss in details and also chemical reaction with the solid phase and finally mechanical trapping of the pollutants in the solid phase pores.

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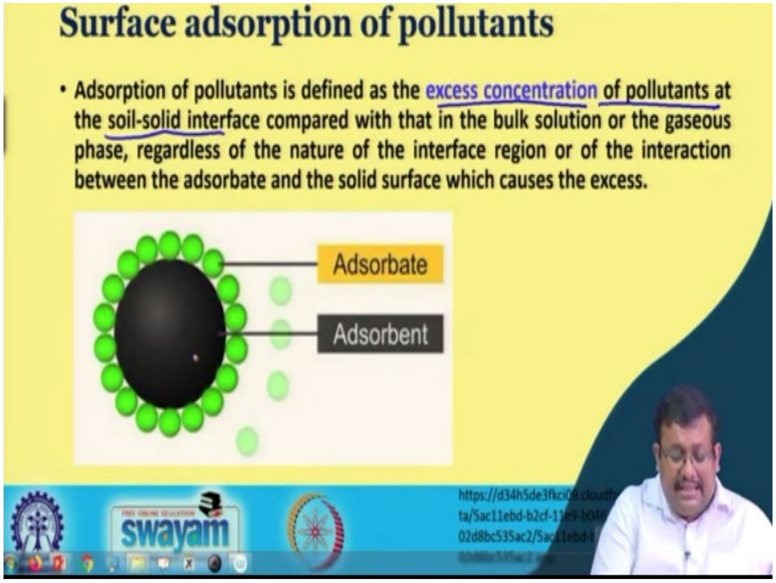

Surface adsorption of pollutants

- Adsorption of pollutants is defined as the excess concentration of pollutants at the soil-solid interface compared with that in the bulk solution or the gaseous phase, regardless of the nature of the interface region or of the interaction between the adsorbate and the solid surface which causes the excess.

So, if you consider the surface adsorption of pollutants, the adsorption of pollutants is basically defined as the excess concentration of pollutants at the soil-solid interface. So if we consider this black ball as an adsorbent on soil solid particle and these greens are basically the pollutants, which are basically adsorbed. So, you know, adsorption of pollutants is basically defined as the excess concentration. So you can see, here also some pollutants are present.

However, the concentration is higher at this soil-solid interface. So basically, this is an excess concentration, we can see at the adjacent to the soil solid as compared to the bulk solution. So if we consider, this is the bulk solution and this is the soil-solid interface. We can see the higher concentration here as compared to the bulk solution. Regardless of the nature of the interface region or of the interaction between the adsorbent and the solid surface which causes the excess.

So this is an example, perfect example of surface adsorption of pollutants. So basically, the concentrations of pollutants are increased. There is an increased concentration of the pollutants in the soil solid interface as compared to the bulk solution.

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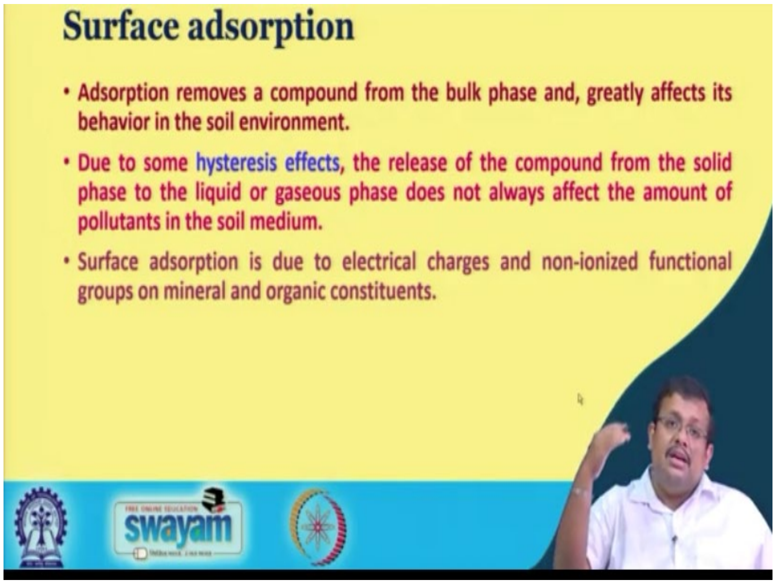

Surface adsorption

- Adsorption removes a compound from the bulk phase and, greatly affects its behavior in the soil environment.
- Due to some hysteresis effects, the release of the compound from the solid phase to the liquid or gaseous phase does not always affect the amount of pollutants in the soil medium.
- Surface adsorption is due to electrical charges and non-ionized functional groups on mineral and organic constituents.

Now remember that adsorption removes a compound from the bulk phase and greatly affects its behavior in the soil environment obviously. When there is an adsorption, there is an increased concentration along the or around the soil-solid interface and there is a less concentration in the bulk phase. So obviously that greatly affects its behavior in the soil environment. Now, due to some hysteresis effect, we will see hysteresis effect later on, the release of the compound from the solid phase to the liquid or gaseous phase does not always affect the amount of pollutant in the solid medium.

So this is an important point. So hysteresis effect is one important process, which impact the release of compounds from the soil solid to the liquid or gaseous phase and remember that the surface adsorption is due to the electrical charges and non-ionized functional groups on mineral and organic constituents.

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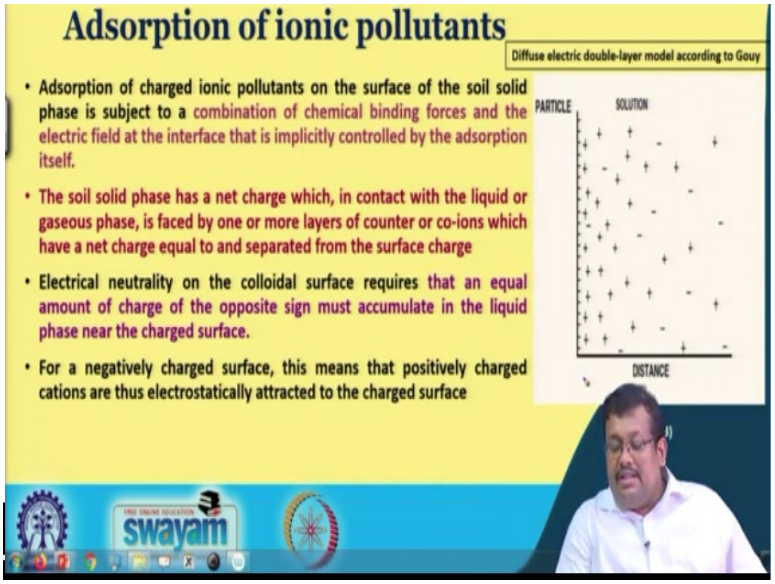

Adsorption of ionic pollutants

- Adsorption of charged ionic pollutants on the surface of the soil solid phase is subject to a combination of chemical binding forces and the electric field at the interface that is implicitly controlled by the adsorption itself.
- The soil solid phase has a net charge which, in contact with the liquid or gaseous phase, is faced by one or more layers of counter or co-ions which have a net charge equal to and separated from the surface charge
- Electrical neutrality on the colloidal surface requires that an equal amount of charge of the opposite sign must accumulate in the liquid phase near the charged surface.
- For a negatively charged surface, this means that positively charged cations are thus electrostatically attracted to the charged surface

Diffuse electric double-layer model according to Gouy

Now if we see the adsorption of ionic pollutants, we have already discussed, remember diffuse double layer in details in our previous lectures. Now in the diffuse double layer, we have seen that the negatively charged clay particles. This is a Gouy diffuse double layer model. So we can see if this is a negatively charged clay colloid and adjacent to this negatively charged surface, there is a concentration of positive cations, and as we go further from the surface of the particle, we will see that the concentration of the cations are going down.

So there is a concentration gradient from the surface of the particle. So we see that this is an example of diffuse double layer and this was given by Gouy. We have already seen it. We have discussed in details in our previous chapters. Now remember that adsorption of charged ionic pollutants on the surface of the soil solid phase is subject to a combination of chemical binding forces and the electric field at the interface, that is implicitly controlled by the adsorption itself.

We can see here there is an electric field generated, so basically there is an electrostatic attraction between these positively charged cations and negatively charged clay surface. Now the soil solid phase has a net charge, which in contact with the liquid or gaseous phase is faced by one or more layers of counter ions or co-ions which have a net charge equal to and separated from the surface charge. So you can see here, these are positively charged cations and these are negatively charged clay surface.

So there is an attraction between these two counter ions. So, electrical neutrality on the colloidal surface requires that an equal amount of charge of the opposite sign must accumulate in the liquid phase near the charge surface. We have seen here. So this is the reason of development of this diffuse double layer. Now for a negatively charged surface, this means that positively charged cations are thus electrostatically attracted to the charged surface. Just we have seen in this picture. So, this is a negatively charged surface and this positively charged cations are electrostatically attracted to the positively charged surface.

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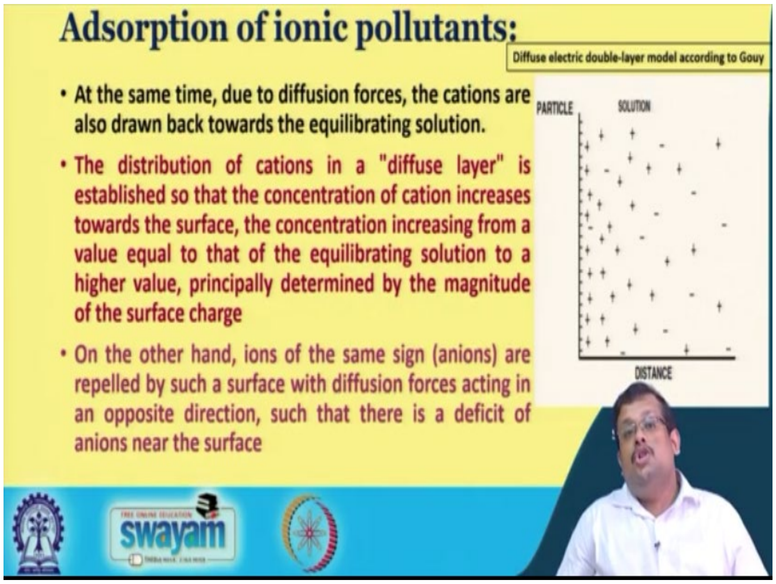

Adsorption of ionic pollutants:

- At the same time, due to diffusion forces, the cations are also drawn back towards the equilibrating solution.
- The distribution of cations in a "diffuse layer" is established so that the concentration of cation increases towards the surface, the concentration increasing from a value equal to that of the equilibrating solution to a higher value, principally determined by the magnitude of the surface charge
- On the other hand, ions of the same sign (anions) are repelled by such a surface with diffusion forces acting in an opposite direction, such that there is a deficit of anions near the surface

Now at the same time, due to the diffusion forces, the cations are also drawn back towards the equilibrium solution. So there is some diffusion forces are also there. So there is a movement of ions from the high concentration to low concentration due to the diffusion gradient. So the distribution of the cations in a diffused layer; so that is why it is producing a diffused layer. You can see here, there is a high concentration layer and there is a diffuse layer.

So this is why it is called the diffuse double layer. So the distribution of the cations in a diffuse layer is established, so that the concentration of the cations increases towards the surface obviously and the concentration increasing from a value equal to that of the equilibrium solution to a higher value principally determined by the magnitude of the surface charge. On the other hand, ions of the same sign that is anions are repelled by the surface.

Obviously, this is a negative charged clay surface. So any anion, which has got the same sign that is negative charge, they will be repel to each other. So obviously, the concentration of the anions will be minimum at the adjacent to the negatively charged clay colloid and as we go further away from the negatively charged clay colloid, we will see the concentration of these negatively charged anions increases, such that there is a deficit of anion near the surface obviously.

You can see here, there is a deficit of anions near the surface, however, as we go further from the surface of the clay colloid, you will see the concentration of the anions are increasing. So, this is how these electrostatical attraction or repulsion produces diffuse double layer in a soil clay surface.

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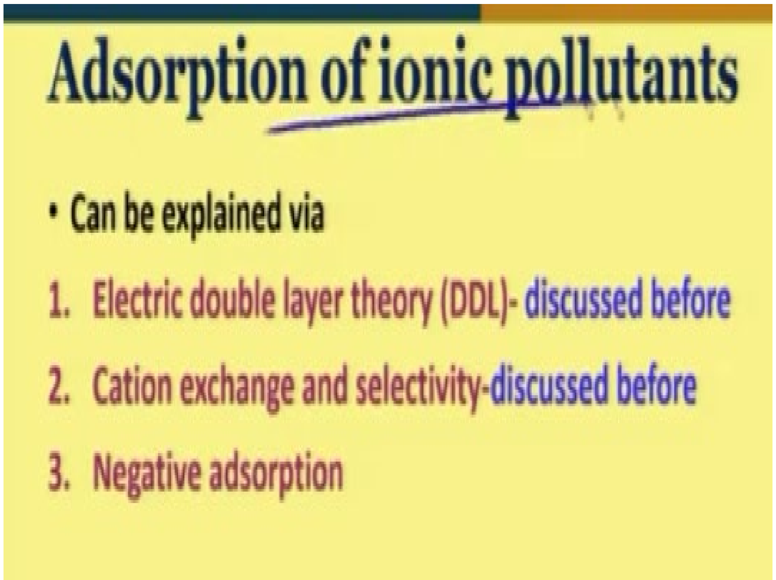

Adsorption of ionic pollutants

- Can be explained via

1. Electric double layer theory (DDL)- discussed before
2. Cation exchange and selectivity-discussed before
3. Negative adsorption

Now this adsorption of pollutants, we can explain these adsorption of ionic pollutants. So we are going to talk about the adsorption of ionic pollutants. So this adsorption of ionic pollutants can be explained by 3 important things. First of all, electrical double layer theory, that is diffuse double layer, we have already discussed it before. So I am not going to discuss it further. Second is the cation exchange and selectivity.

We have also discussed the cation exchange and selectivity in our previous module. So we are not going to discuss this in details. The third important thing is the negative adsorption. So we are going to discuss this third thing that is third important point that is negative adsorption. So let us see what is negative adsorption.

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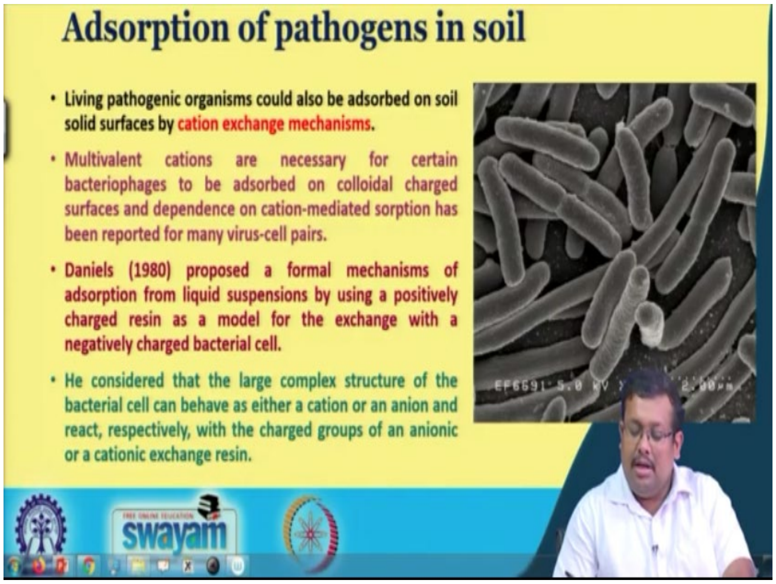

Adsorption of pathogens in soil

- Living pathogenic organisms could also be adsorbed on soil solid surfaces by cation exchange mechanisms.
- Multivalent cations are necessary for certain bacteriophages to be adsorbed on colloidal charged surfaces and dependence on cation-mediated sorption has been reported for many virus-cell pairs.
- Daniels (1980) proposed a formal mechanisms of adsorption from liquid suspensions by using a positively charged resin as a model for the exchange with a negatively charged bacterial cell.
- He considered that the large complex structure of the bacterial cell can behave as either a cation or an anion and react, respectively, with the charged groups of an anionic or a cationic exchange resin.

Before going to the negative adsorption, let us discuss also the adsorption of pathogens in the soil. Now interestingly, living pathogenic organism could also be adsorbed on soil solid surface by cation exchange mechanism. As you can see here, this is one of the pathogenic bacteria. So pathogenic microorganisms can also be adsorbed on to the soil surface by cation exchange mechanism.

Now remember that multivalent cations are necessary for certain bacteriophages, which are viruses, so to be adsorbed on colloidal charged surfaces and dependence on cation mediated sorption has been reported for many virus cell pair. So let us see the mechanism. Now the scientist Daniels proposed a formal mechanism of adsorption from liquid suspension by using a positively charged resin.

So he used a positively charged resin as a model for the exchange with a negatively changed bacterial cell. So for depicting the exchange of the negatively charged bacterial cell using a positively charged resin, he basically established the mechanism for adsorption of pathogens in the soil. Now he considered that a large complex structure of the bacterial cell can behave as either a cation or an anion and react respectively with the charge group of an anionic or cationic exchange resin. The resin can be either cationic or anionic, so depending on the cationic and anionic nature of the bacterial cell, it can attach to the oppositely charged exchange resin. So let us see how.

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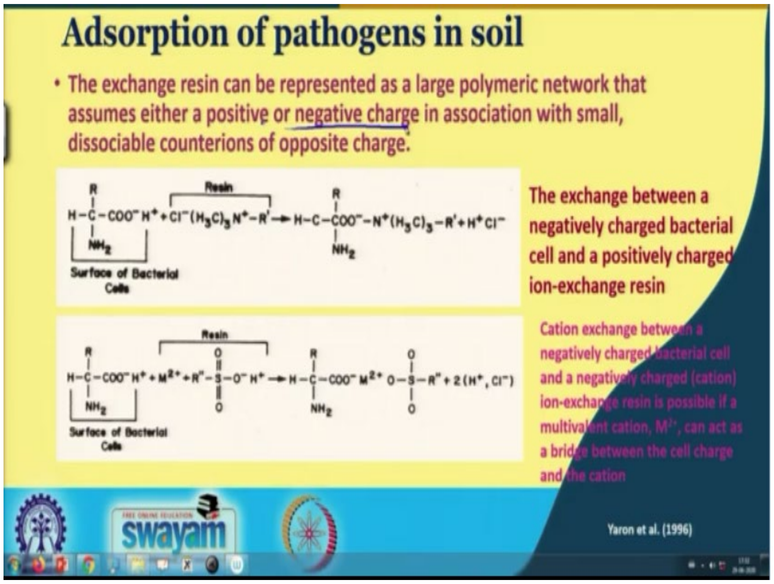

Adsorption of pathogens in soil

- The exchange resin can be represented as a large polymeric network that assumes either a positive or negative charge in association with small, dissociable counterions of opposite charge.

$$\text{H-}\overset{\text{R}}{\underset{\text{NH}_2}{\text{C}}}\text{-COO}^-\text{H}^+ + \text{Cl}^-(\text{H}_3\text{C})_3\text{N}^+\text{-R}' \rightarrow \text{H-}\overset{\text{R}}{\underset{\text{NH}_2}{\text{C}}}\text{-COO}^-\text{-N}^+(\text{H}_3\text{C})_3\text{-R}' + \text{H}^+\text{Cl}^-$$

The exchange between a negatively charged bacterial cell and a positively charged ion-exchange resin

$$\text{H-}\overset{\text{R}}{\underset{\text{NH}_2}{\text{C}}}\text{-COO}^-\text{H}^+ + \text{M}^{2+} + \text{R}''\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{-O}^-\text{H}^+ \rightarrow \text{H-}\overset{\text{R}}{\underset{\text{NH}_2}{\text{C}}}\text{-COO}^-\text{M}^{2+}\text{O-}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{-R}'' + 2(\text{H}^+, \text{Cl}^-)$$

Cation exchange between a negatively charged bacterial cell and a negatively charged (cation) ion-exchange resin is possible if a multivalent cation, M^{2+}, can act as a bridge between the cell charge and the cation

Yaron et al. (1996)

Now, the exchange resin can be represented as a large polymeric network that assumes either a positive or negative charge in association with small dissociable counter ions of opposite charge. Now you can see here this is one scenario, which basically shows the exchange between a negatively charged bacterial cell and a positively charged ion exchange resin. So this is an ion exchange resin and this is basically negatively charged surface of bacterial cells.

So we can see the H+ and Cl- from these, H+ from the bacterial cell and Cl- from these resins are basically reacting and then basically they are creating this HCl and these bacterial cells are getting attached to these resin groups. So basically this negatively charged bacterial cell is getting attached to the positively charged ion exchange resin. So this is one of the mechanism for attaching the negatively charged bacterial cells, ok.

Here, it is showing another mechanism, which is a cation exchange between a negatively charged bacterial cell. So this is a negatively charged bacterial cell and a negatively charged ion exchange resin. So basically, we can see here, resin is possible if a multivalent cation. So here this is a multivalent cation M^{2+} can act as a bridge, so bridge between the cell charge and the cation.

So we can see here these M2+ is acting as a bridge between these, so this H+ is basically dissociating from there and producing this H+ Cl- and this M2 is basically acting as a bridge between this negatively charged bacterial surface and this negatively charged resin surface. So this is one of the examples of exchange between negatively charged bacterial cell and a positively charged ion exchange resin.

This is an example of a negatively charged bacterial cell and a negatively charged ion exchange resin through a multivalent cation. So this is how this adsorption of pathogens in the soil generally occurs.

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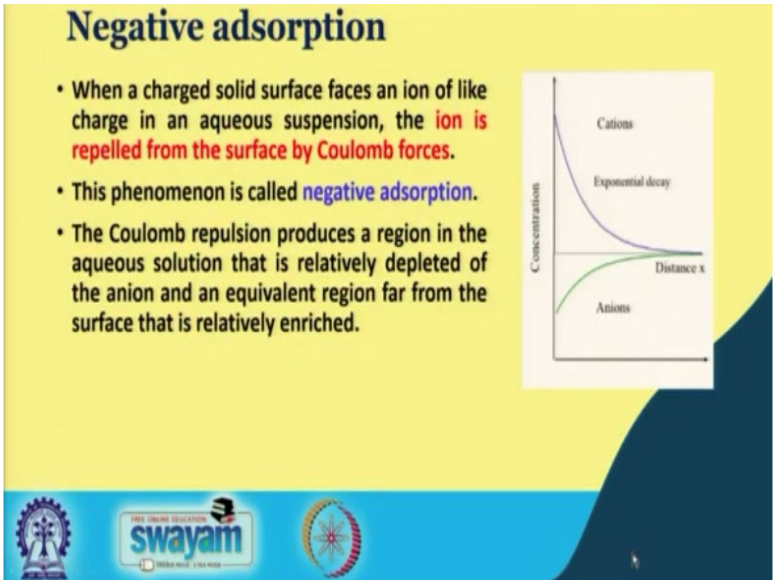

Negative adsorption

- When a charged solid surface faces an ion of like charge in an aqueous suspension, the ion is repelled from the surface by Coulomb forces.
- This phenomenon is called negative adsorption.
- The Coulomb repulsion produces a region in the aqueous solution that is relatively depleted of the anion and an equivalent region far from the surface that is relatively enriched.

Now let us discuss the negative adsorption. Now negative adsorption is when a charged solid surface faces an ion of like charge in an aqueous suspension, the ion is repelled from the surface by Coulomb force. Again, when a charged solid surface faces an ion of like charge in an aqueous suspension, the ion is repelled from the surface by Coulomb force and this phenomena is known as negative adsorption.

Now this Coulombic repulsion produces a region of the aqueous solution that is relatively depleted of the anions and an equivalent region far from the surface that is relatively enriched. So this thing we have also discussed during our diffuse double layer discussion. Obviously in case of negatively charged clay colloid, obviously if you assume that the surface of clay is negatively charged, so obviously there will be electrostatic attraction between the positively charged cations.

So we can see the concentration of the positively charged cations will be highest at the interface between the particle as well as the liquid; however, the concentration of the cations will gradually go down as the distance from the particle surface is increasing. So, this is quite natural. Similarly, due to the negative adsorption, the anions which are having the similar negative charge, when we consider the negatively charged clay surface, obviously there will be a repulsion.

As a result of repulsion, the concentration of anions will be minimum at the surface of the clay colloids. However, their concentration will increase as the distance from the clay surface is increased and this phenomena is known as negative adsorption. Again, the negative adsorption is the Coulombic repulsion, which an ion basically encounters when they reach in vicinity of a similar charged clay surface or similar charged surface. So this is called the negative adsorption.

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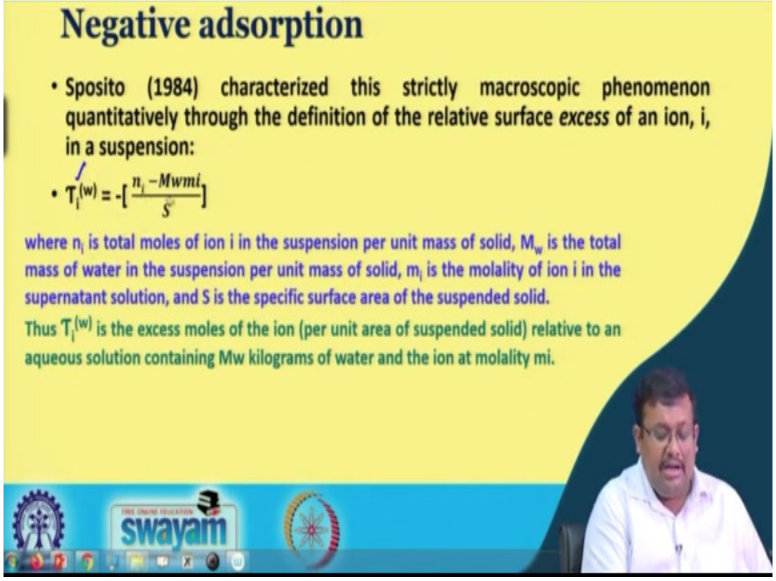

Negative adsorption

- Sposito (1984) characterized this strictly macroscopic phenomenon quantitatively through the definition of the relative surface *excess* of an ion, i, in a suspension:
- $T_i^{(w)} = -[\frac{n_i - Mwmi}{S}]$

where n_i is total moles of ion i in the suspension per unit mass of solid, M_w is the total mass of water in the suspension per unit mass of solid, m_i is the molality of ion i in the supernatant solution, and S is the specific surface area of the suspended solid.

Thus $T_i^{(w)}$ is the excess moles of the ion (per unit area of suspended solid) relative to an aqueous solution containing Mw kilograms of water and the ion at molality mi.

Now how to express this negative charge in mathematically. Now the scientist Sposito in 1984 characterized this strictly macroscopic phenomenon quantitatively through the definition of the relative surface excess of an ion i in a suspension. So he gave this formula, that is, this expression is equal to this expression, where this is basically the excess mole of ions per unit area of suspended solid relative to an aqueous solution containing Mw kilograms of water and the ion at molality mi.

So this is ion at molality mi, Mw is basically the kilograms of water, and this is basically the excess moles of the ions per unit area of suspended solid. Now where ni is basically the total moles of ion i in the suspension per unit mass of solid. Mw we have already defined, this is total mass of water in the suspension per unit mass of solid and mi is the molality of the ion i in the supernatant solution and S is basically the specific surface area of the suspended solid.

So basically again, if we summarize according to Sposito, the excess moles of ions per unit area of suspended solid can be, which is the driving force of the repulsion Coulombic repulsion between the negatively charged clay colloid as well as the anions can be represented by this expression, where this is the excess moles of ions, ni is basically the total moles of ion and Mw is the weight of water and mi is the molality of ion and S is the specific surface area of the suspended solid.

So this is how we can quantitatively measure the negative adsorption. So I hope that you have learnt something new in this lecture. We have discussed some important features of adsorption. We have discussed how these pathogenic microorganisms get attached to the soil solid surface and what are these mechanisms? There are two mechanisms we have discussed. We have also discussed the negative adsorption and also we have expressed the mathematical formula for calculating the negative adsorption. So I hope you have learnt something new. Let us meet on in our next lecture to discuss more about the retention of the pollutants in the soil solid phases. Thank you very much.