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Environmental Soil Chemistry
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Lecture # 26
Kinetics of Soil Chemical Processes

Welcome friends to this week 6 or module 6 of lectures of NPTEL online certification course of environmental soil chemistry and the topic of this module or this week is basically kinetic soft soil chemical process. Now kinetics of soil chemical process are very very important if you want to understand different reactions which are going inside the soil.

So soil is a heterogeneous mixture as you know it is basically composed of different of different inorganic chemicals as we well as organic compounds and in multitude of different types of reactions and basically chemical reactions are going on inside the soil system. So to understand the dynamics of those chemical reactions they are rate you need to understand the kinetics of soil chemical process.

Soil chemical processes will determine the rate of reaction which will basically govern different soil process like hydrolysis, like dissolution, like crystallization like ion exchange. So it is imperative that you should learn and understand the kinetics of soil chemical process if you want to efficiently use your knowledge of environmental soil chemistry. So in this week we will be basically talking about these concepts.

So first of all we will be talking about rate limiting steps and time scales of soil and then chemical reaction and rate laws then we will be talking about the determination of reaction order and rate. Then we will be talking about constants and kinetic models then we will be talking about kinetic methodologies and multiple site models we will be talking about the effect of temperature on reaction rates and finally we will be talking about kinetics of important soil chemical process.

So these all important aspects will be discussed in this module. so today we will be basically in this first lecture we will be focusing on rate limiting steps and time scales of soil and if time permits then we will also talk about chemical reaction and rate laws briefly.

So let us start with the question that why it is important to study the soil chemical prokinetics. Now soil chemical processes are very much time dependent different process takes different amount of time to occur. Now to understand the kinetics of interaction of soils with different metals , Oxyanions, radio nuclides. Pesticides industrial chemicals and plant nutrients and to predict their fate with time in knowledge of the kinetics of these reactions is very very important.

There are several heavy metals or trace metals which are present in the soils, Oxyanions are also present in the soil radionuclides are also present in the soil, pesticide which is an important organic fraction which is added by differently anthropogenic activities industrial chemicals and plant nutrients. So, these are having a dynamic and complex interaction with different soil solid and soil solution.

So to understand their interaction and to know what is their fate with time so that means where the metal will go from one point of time to another point of time so and where they will depose it so these fates identify this fate of these different elements or different chemicals their knowledge of this kinetics of these reactions are very very important.

Now the first we will be talking about rate limiting steps and time scales of soil chemical reactions. See number of transport and chemical reactions of you know can affect the rate of soil chemical reactions. So the slowest of this transport process will limit the rate of a particular reaction. So the actual chemical reaction which we denote by CR in short at the surface in case of for example in case of adsorption you know adsorption is this surface phenomena.

So the actual chemical reaction at the surface for example in case of adsorption is usually very rapid and not rate limiting and basically these transport process included different you know 6 different processes. So the first process is transport in the solution phase which is basically it rapid and in the laboratory can be eliminated by rapid mixing. So you can see here this is 1 denotes this first process this is transport in the solution phase okay.

So soil chemical reaction involves the transport in the solution phase which is basically very rapid and in the laboratory when we basically mix the soil with some chemical liquid chemical with rapid mixing then it will resemble that transport in that solution phase as you can see here. So the second process is known as the transport across a liquid flame at the particle liquid interface which is also known as film diffusion.

And this is basically denoted here so the first one that is transport in the solution phase is denoted by 1 whereas the transport across the liquid film in the particle liquid interface is denoted by this 2. So this is the basically particle and liquid interface and through this particle liquid interface the transport process is going on. So these two are the important processes.

Apart from that the third process is transport in liquid filled macropores. So you know in the soil there are two types of force one is macropores and another is micro pores. So macropores are those posts which are having diameter of greater than 2 nanometre and those pores which are having diameter of less than 2 nanometre known as micropores. So transport in so the macropore are sometimes you know liquid filled or waterfilled.

So, when the transport occurs in the liquid filled macropores of all of which are nonactivated diffusion process and occur in mobile regions. So transport in the liquid filled macropores basically represent non-activated diffusion processes and occur in mobile region. So nonactivated means you do not need to produce any expense internal energy to facilitate that diffusion. So this is called non-activitated diffusion process and basically it occurs in the mobile region.

So you can see this is basically denoted by 3 so when the liquid in the first process is basically generated in the liquid phase. In the second process it is basically occurring in the liquid interface and the third process that is transferred in the liquid filled macropores it is basically going inside the liquid-filed macropores. The fourth one is known as the diffusion of a sorbate along a pore wall surface that is called surface diffusion and this is basically denoted by 4.

So if we consider this as a pore macropore so the diffusion of a sorbate along pore wall surface is called surface diffusion. So you can see this is basically diffusing along the pore wall of the surface so it is an example of surface diffusion. The fifth one is diffusion of sorbate or occluded in the micropores which are less than 2 nanometre that is called pore diffusion.

So if this is considered as a macro pores if this is a macropore this is an example of micropore. So soil content both micropores and micropores. Macropores are having a diameter of greater than 2 nanometre whereas micropores are having a diameter of less than 2 nanometre and this diffusion is another transporting process where in the diffusion in the micropores is another important transporting process in the soil and basically the diffusion occurs for sorbate which is occluded in micropores.

So basically occluded means it is basically attached to the micropores and the sixth one the final one is basically diffusion process in the bulk of the solid all of which are activated diffusion process. Now you see here this is basically the solid phase now if the diffusion occurs inside the solid it is basically called the diffusion inside so it is basically an activated diffusion process you need to put some energy to make it happen.

So this is an activated diffusion process and the bulk of the solid which basically so this is another important transportation process in the soil. So pore and surface diffusion so we can see here there is macro-pore diffusion another is macro pore surface diffusion another is micropore surface diffusion and finally we are getting the bulk solid diffusion so pore and surface diffusion can be referred to as inter particle diffusion because it is occurring in between the particles.

Whereas the diffusion in the solid is known as intra particle diffusion. So because the diffusion whatever is going on is basically inside the particles. So these are the 6 different transport process which are occurring inside the soil system.

So this is again a bigger picture of this thing this is basically transport in the soil solution. Now we can facilitate this by mixing in the laboratory by facilitated by rapid mixing in the laboratory. The second is basically transport across the liquid filled at the solid liquid interface this third one is the transport of a liquid filled macro pore, fourth one is basically the diffusion of a sorbate at the surface of the solid, fifth one is diffusion of the sorbate occluded in the micropore and the 6th one is the diffusion of the bulk of the solid. So, these 6 different processes are basically governing all types of movement inside the soil.

Now so the soil chemical reactions they can occur over a wide timescale as I have told you at the beginning of this lecture the soli chemical reaction occur over a wide timescale ranging from microseconds and milliseconds for ionization ion exchange and some sorption reactions to years for mineral solution and mineral crystallization reaction.

Now this is basically very clear from this graph that if you put the timescale in the x axis and you can see that ionization ion exchange and to some extent sorption is very rapid process okay however the range of sorption varies widely. Now in case of also gas water relationship it is basically takes hours to days a multi-variant hydrolysis also takes from minutes to basically sometime in years also.

However this mineral solution as we will as mineral crystallization is a very very slow steps and they basically take years for completing these mineral solution and mineral crystallization reactions. So these reactions can occur simultaneously and consecutively to keep. So these are differ you know this is a variation in timeframe for different chemical reaction which are occurring in the soil system.

So the type of soil component can have drastically can drastically affect the reaction rate for example sorption reactions are often more rapid on clay minerals such as kaolinite and smectite type then data vermiculitic and micaceous minerals why because this is because due to the availability of sites for sorption.

Now you might be wondering that where there is sorption you know site for kaolinite. Now in case of kaolinite although they do not have any internal site for adoption kaolinite has readily available planar external sites. So as a result of that they can adsorb different types of you know different types of compounds or ions.

Now smectite also has you know it has a huge internal site because it is highly expanding in nature. So, these sorption reactions basically are very rapid in these kaolinite and smectite type of clay minerals and then can take seconds and milliseconds to execute this rapid sorption process.

Now in case of vermiculite and Mica they have multiple sites for retention of metals and organics including planar age and collapsed interlayer sites. Have sorption and desorption reaction on this side scan be slow, tortuous and mass transfer controlled. So they are basically in case of vermiculite and in case of Mica their inter layer process is almost collapsed because of the presence of various small cation that is potassium as a result of that their sorption and dissorption reactions on these types of soils can be slow, tortuous and mass transfer controlled.

Now apparent equilibrium may not be reach even after several days or weeks so you can see what is you know how these timeframe is differing from Kaolinite to smectite to vermiculite and mica. Now sorption can involve two or three different reaction rates one is high rates of external site second intermediate rates on edge sites and low rates on the interlayer sites. So depending on what type of site it is either it is external site or internal site or edge the rate basically varies.

Now in case of kaolinite these all the surface are almost external. So, obviously they show high rate of you know reaction okay so or high rate of transport.

Now let us discuss another important another important message that is the chemical kinetics and also we will be discussing about the kinetics also general kinetics also. Now chemical kinetics can be defined as the investigation of chemical reaction rates and the molecular processes by which reaction occurred where transport is not limiting. Again it is very important that is basically the investigation of chemical reaction rates and the molecular process by which reaction occur where transport is not limiting.

So given transport is not limiting it is basically the rate of reaction which is occurring inside the soil whereas kinetics is the study of time dependent process okay. Now it is difficult to study the chemical kinetics in case of homogeneous solutions when one studies heterogeneous systems such as soil components and particularly soils which is you know the difficulties are very much increased you know given that the chemical kinetics study in the homogeneous system or homogeneous solution is difficult it will be much difficult in case of heterogeneous system like soil.

So it is extremely difficult to eliminate the transport process in the soil because there are a mixture of several inorganic and organic adsorbates. So it is also very difficult to eliminate the transport process. So these are some of the country consideration when you talk about the chemical kinetics.

Now the rate laws there are two important reasons for investigating the rates of soil chemical process what are those two reason? The reasons are first of all to determine how the rapidly reaction at his equilibrium and to infer the information on the reaction mechanisms.

So not only to determine the rate of reaction but also the information on reaction mechanism we need to investigate their rates of soil chemical process. So one of the most important aspects of chemical kinetics is the establishment of a rate law okay. So we will be discussing now the rate law.

So what are the rate laws? So by definition a rate law is a differential equation okay. So if we consider this reaction where these two are the reactants and these two are the products. So the rate of the reaction is basically proportional to some power of the concentration of the reactants A and B. So these are the reactants A and B so the rate of reaction will be proportional to some power of the concentration of both A and B.

Or other species like C and D in the system now here you can see we are using small a small b small y and small z. These are basically stoichiometric coefficients we have defined stoichiometric previously. Now the power to which the concentration is raised me equal to 0 in case when the rate is independent of that concentration even for reactant A or B. So sometime when the rate is independent of the concentration of the reactants then the power of the concentration maybe equal to 0.

So let us see the laws so you can see here the rates are expressed as a decrease in reactant concentration or an increase in product concentration per unit time we will be seeing this example very frequently. So again the rate in case of rate laws the rates are expressed as a decrease in reactant concentration so it is negatively signed and an increase in product concentration per unit time.

So for the previous equation which you have just saw the rate of reactant A above which has a concentration at any time t is basically can be expressed like this and in negative sign says that is decrease in reactant concentration. So while the rate with which the product y is generating having a concentration of these Y bracket at time t is basically dY/dt because this is an increase showing the in the positive sign showing the increasing process and this negative sign is showing the decrease in the reactant concentration.

So the rate expression for this equation 1 is basically can be expressed in terms of dY/dt = -dA/dt which can be represented by this where k is a rate constant alpha and beta are the order of the reaction with respect to reactant A and with reactant B. Now these alphas is known as the partial order for A and beta is known as the partial order with respect to reactant B.

Now these orders are experimented remember that these orders are experimentally determined and not necessarily integral numbers okay. So from the equation 1 where A and B is reacting to produce the Y and Z then using the rate laws we can define the rate of change of the reactant concentration and rate of change of increase in product concentration by using this equation where k is basically rate constant A and B concentration having the power of alpha and beta where alpha and beta are the corresponding partial order.

Now one thing is important to remember that the sum of all the partial order that is alpha-beta etc is the overall order n and maybe expressed as n = alpha + beta. So, the overall order n can be calculated by summing up all the partial order of the reactants. So once the value of alpha beta etc determined experimentally then the rate law is also defined automatically. Now reaction order provides that information only information about the manner in which the rate depends on concentration.

Now order does not mean the same as molecularity which concerns the number of reactant particles entering into that elementary reaction now what is elementary reaction? Now elementary reaction is one in which no reaction intermediates have been detected or need to be postulated to describe the chemical reaction on a molecular scale. So we just assume that two chemical reactant react together to form a product so that is an elementary reaction.

Now an elementary reaction is assumed to occur in a single step and to pass through a single transition state. Now here in this reaction of two reactants A and B and forming the final product of Y and Z we are basically considering these you know as an elementary reaction and here alpha beta are the partial order which basically sum up to produce the overall order of n.

Now rate laws have three major purposes what are those three major purposes? First of all they assist one in predicting the reaction rate. Secondly the mechanisms can be proposed using the rate laws or chemical mechanisms can be the reaction mechanisms can be proposed using the rate laws and thirdly reaction orders can be ascertained using the rate law. So, these are the three major aspects or utilities of rate laws.

First of all assist one in predicting the reaction rate second is make to predict the mechanism and thirdly reaction orders can be ascertained. Now there are four types of rate laws that can be determined for soil chemical processes one is mechanistic rate law one is apparent rate law, third one is transport with apparent and the fourth one is transport with mechanistic. So we will now see what are the difference between these four different rate laws okay.

Now the first one is the mechanistic rate laws, mechanistic rate laws assume that only chemical kinetics are operational and transport phenomenon not occurring. So there is no transport only the chemical reaction are operating or chemical kinetics are there so that is why it is called mechanistic rate laws.

Now it is difficult to determine the mechanistic rate laws for most of the soil chemical system due to the heterogeneity of the system caused by different particle size, porosities and types of retention sites. So if you do not consider the transport phenomena and only considered the chemical kinetics it is difficult to express the rate law because of these three confounding factors one is particle size variable particle size in case of soil.

Porosities macropores or micropores so variation in the porosity also and the third one is also types of retention sites so this is called a mechanistic rate laws.

The second one is apparent rate law in the apparent rate law it basically includes both chemical kinetics and transport controlled process. So, it basically it considered both chemical kinetics and transport control process. So the mechanistic rate law did not consider transport control process. However apparent rate law considered the transport-controlled process along with the chemical kinetics.

Apparent rate laws and rate coefficients indicate that diffusion other and other microscopic transport process affect the reaction rate. So obviously according to the apparent rate law these reaction rate is dependent on the diffusion transport process as well as other microscopic transport process. Because if this diffusion of the chemicals are not occurring then the chemical reaction will not happen and also soil structure steering mixing and flow rate would affect the kinetics in case of apparent rate laws okay. So this is the second type of rate laws.

The third rate law is called transport with apparent rate laws. So it is basically the transport with apparent rate laws basically focused on or emphasize on transport phenomena and it basically assumes a first or zero order reaction okay. Now transport with mechanistic rate laws this is the fourth and final one it basically described simultaneously the transport control and chemical kinetics phenomena.

So it basically define both simultaneously both transport control and chemical kinetics. So from the physics point of view they basically define these transport control process and simultaneously from the chemical kinetics also a chemistry point of view also they express the chemical kinetics. So these four are these four different types of a rate laws which we generally apply.

Now before discussing the next phase in details about the rate laws we need to understand the difference between first order and second order reactions. So first order reaction rate depends on the concentration of one of the reactants. So, the rate of reaction here basically depends on concentration of one of the reactants. However a second order reaction rate is proportional to the square of the concentration of a reactant or the product of the concentration of two reactants.

So, basically in case of first-order reaction we are this rate depends on the concentration of one of the reactants here products are not considered. However in case of second-order reaction the rate is proportional to the square of the concentration of a reactants. So, in case of a reactant if there is a concentration of the reactant if you take a square the reaction rate will be proportional to that concentration square or the product of the concentration of the two reactants.

So, if there are two reactants A and B then the product of the concentration of the two reactants will be considered while defining the second order reaction. So friends let us wrap up this lecture here and in the next lecture we will be talking more about the different rate laws and how we can calculate that and I hope that you got the basic overview of the kinetic process and why it is important to learn different chemical kinetic process in the soil and let us wrap up the lecture here and in the next lecture we will be talking about you know different rate laws and also their implication and how to calculate different rate laws using different methods.