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Environmental Soil Chemistry
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Module # 06
Lecture # 30
Kinetics of Soil Processes (Contd.,)

Welcome friends to this last lecture of week 6 or module 6 and in this week we are talking about the chemical kinetics of different soil chemical process. Now in the previous four lectures we have discussed different rate limiting steps, different transport processes and also we have discussed details about the zero order reactions, first order reaction, second order reaction, their integral as well as differential forms and how to plot them and what are the shape of this plot, what are the abrasions.

And also we have discussed about in the soil how we can identify the order of the reaction using either initial rate or integrated form as well as least square analysis. Today, in this final lecture we are going to talk about some other kinetic models and also how different soil chemical processes are dependent on different chemical kinetics law.

So, let us start with the kinetic models of soil chemical processes. Now we know that the first order models have been widely used to describe the kinetics of soil chemical process and the various order equations like zero order then zero order reaction then second order reaction, fractional order reaction and Elovich reaction, power function or fractional power and parabolic diffusion models are used.

Now we have already discussed zero order second order and first order now we are going to discuss about the fractional order, Elovich reactions, power function as well parabolic diffusion models.

So, let us start with the okay, but before going to the Elovich equation just let me show you what are the different forms of this linear kinetic models. So this is very obvious that it is a zero order reaction you know this is the integral form of zero order reaction. This is the first order reaction because we are taking the logarithmic we are having this factor of 2.303. We are converting from natural logarithm to log.

So, in case of second order reaction we know this already this is a linear form of linear integrated form of the second order reaction. Now this is another three equations are Elovich reactions, parabolic diffusion as well as power functions. So, we are going to discuss all of this in the next couple of slides.

Now Elovich reactions is basically the equation was originally developed to describe the kinetics of heterogeneous chemisorptions of gases on solid surfaces. Now, to describe a number of reaction mechanism including bulk and surface diffusion and activation of and deactivation of catalytic surfaces we general use the Elovich equation. Now in soil chemistry, the Elovich equation has been used to describe the kinetics of sorption and desorption of various inorganic materials in the soil.

Now the general form of Elovich reaction is basically qt = 1 / beta natural log of alpha beta + 1 / beta in natural log of t. So, you can see here qt is basically the amount of sorbent per unit mass of solvent just like we have seen in case of Freundlich equation. So basically qt is the amount of sorbent per unit mass of sorbent. Now it is basically at time t and alpha beta are constant during any one experiment.

So this basically the presentation of the Elovich equation and this Elovich equation is widely used to define different types of soil chemical reactions.

Now again we see that it is the Elovich reaction so if we plot the qt versus ln of t so here we can ln of t versus qt we will basically give a linear relationship so if the Elovich equation is applicable with a slope of obviously with a slope of alpha by beta. So here you can see this is the slope and an intercept of this term so 1 / beta ln of alpha beta. So to plot an Elovich equation this plot basically showing a plot of Elovich equation for phosphate sorption on two soils.

Where basically C0 is the initial phosphate sorption and C0 basically is the phosphorus concentration added at time 0 and C is the phosphorus concentration in soil solution at time t. Now the quantity basically C0 – C can be equated to qt which is the amount of sorbed at time t obviously this is the difference is the amount which is basically getting absorbed. So, this is an Elovich equation you can see, this is the concentration we are putting in the y.

In the y axis, in the x axis we are putting the logarithm of natural log of t and we are getting two straight lines. So this is how we represent the Elovich equation remember the C0 – C is basically the another representation of qt.

Now another kinetic model which we use is called parabolic diffusion equation. Now the parabolic diffusion equation is often used to indicate the diffusion control phenomena are basically rate limiting. Now we have already discussed about different type of diffusion in our first lecture of week 6. So it was originally derived based on radial diffusion in a cylinder where the ion concentration throughout the cylinder is uniform.

Remember that it is also assumed that ion diffusion through the upper and lower faces of the cylinder is basically negligible in case of this parabolic diffusion equation.

So following the scientist Crank that in 1976 the parabolic diffusion equation as applicable to soil can be expressed in terms of this equation where qt / q infinity = 4 / pi to the power 1/2 into capital D t to the power 1/2 / r square – Dt / r square whereas this r is average radius of the soil particle qt we have already defined amount of sorbate per unit absorbent and this q infinity is basically the corresponding quantity of sorbate at equilibrium and D is the diffusion coefficient.

So this is basically representation of I mean detailed representation of parabolic diffusion equation however we can simplify this. So let us see the simplified form of this parabolic equation.

So if we simplify this parabolic equation it will basically can be expressed in terms of qt / q infinity = RDt to the power 1/2 + constant. So here RD is the overall diffusion coefficient and if the parabolic diffusion law is valid then if we plot the qt / q infinity versus t 1/2 then it should yield a linear relationship obviously as you can see from there. So if we can use this is an intercept and if this RD is the slope then if we plot this qt / q infinity versus time.

Then we will basically get a linear relationship because it is expressed in terms of the straight line. Now the diffusion equation has successfully described metal reactions on soils and soil constituents, feldspar weathering and pesticide reactions. So not only from the delusion point of feldspar or primary minerals into the secondary minerals, but also from pesticide reaction into the soil it is very important this parabolic diffusion equation. We will see one example in the coming slides.

Now let us talk about the fractional power or power function equation. So this equation can be expressed in terms of this that is q – kt to the power v where q is the amount of sorbate per unit mass of sorbent and k and v are the constant where v is positive and less than 1. Now remember equation 15 this equation is basically empirical and except for the case where v = 0.5 when these equation basically convert into parabolic diffusion equation.

So fractional power or power function equation can convert into the parabolic diffusion coefficient when the constant v takes a value of 0.5. Now the equation is used to describe the kinetics of the different soil chemical processes also.

So we have defined different types of kinetic models which are basically useful for defining different types of soil chemical reactions. Now let us talk about the multiple site models. Now the simple kinetic model such as ordered reaction, power function, Elovich model they are not very much appropriate to describe the reaction in heterogeneous systems like soil because in this system there is a considerable heterogeneity.

And in this system where there is a range of particle size, multiple retention sites so both chemical, kinetics as well as transport phenomena are occurring simultaneously. You will see that huge heterogeneity exist in this type of system. So there is either chemical kinetics or transport phenomena or simultaneously both these are occurring. So the first reaction sometime is often followed by a slower reaction.

Now in such systems in heterogeneous system like soil the non equilibrium models that describe both chemical and physical non equilibrium and that consider multiple components and sites are more appropriate. So for a heterogeneous component like soil we require non equilibrium models instead of equilibrium or the simple kinetic models which describes the chemical and physical non equilibrium which consider multiple component and sites that are more appropriate.

Now physical non equilibrium is ascribed to some rate limiting transport mechanism such as film diffusion we have already seen, film diffusion is nothing, but the diffusion through the particle liquid interface. We have discussed in our first and second lecture or interparticle diffusion, interparticle diffusion we have seen also in our first lecture. While the chemical non equilibrium is due to the rate limiting mechanism at the particle surfaces.

So let us discuss what is the multiple site models or non equilibrium model basically include two site, multiple site, radial diffusion which is another name of pore diffusion. We have also discussed pore diffusion in our first lecture, surface diffusion or multipurpose sorry multiprocess models. Now the term sites can have a number of meanings. First of all the site can represent a specific, molecular scale reaction sites.

Secondly it can indicate the site of different degrees of accessibility either external or internal. You remember that in terms of Kaolinite the sites are external, in case of Smectite the sites are internal and also they also represent a site of different sorbent type like whether it is organic matter or inorganic material surfaces. It also define what type of site it is. Also sites with different sorption mechanics.

So based on these different variations there are multiple site model present are present to define soil chemical processes.

Now if we consider the chemical non equilibrium models I will in describing the chemical non equilibrium with two site model, two types of sorbent sites are assumed. Once I involved an instantaneous equilibrium reaction and the other the time dependent reaction. Again, one site involves an instantaneously equilibrium reaction and the other site shows the time dependent reaction.

So the former is described by an equilibrium isotherm equation while the first order equation is usually employed for the later. So in case of chemical non equilibrium again let me clear it that in case of chemical non equilibrium one site there are multiple sites. So one site involves a instantaneously equilibrium which is basically denoted by which can be described by an equilibrium isotherm equation which you have already discussed in our previous weeks.

And other side the time dependent reactions which can be expressed in terms of first order equation can be employed. So with the two site model there are two adjustable of fitting parameters those two adjustable fitting parameters are basically the fraction of sites at local equilibrium which is denoted by X1 and the rate constant which is basically denoted by k. Remember that a distribution coefficient or partition coefficient which is denoted by either kd or kp is determined independently from the sorption and desorption isotherms.

So in case of chemical non equilibrium I hope you are clear. There are two sites in one site instantaneously equilibrium are prevalent which can be expressed in terms of isotherm equation in other side time dependent first order reaction are prevalent and obviously we need to these fraction of sites for local equilibrium X1 and also the rate constant for defining these two site non equilibrium models chemical equilibrium models.

So physical non equilibrium models focus on diffusion in the immobile phase or interparticle or diffusion processes such as pore and surface diffusion we have discussed this in the first lecture. Now the transport between mobile and immobile region is also accounted for the in physical non equilibrium model in basically three ways. First of all explicitly with Fick's diffusion law to describe the physical mechanism of diffusion transfer.

Secondly, to explicitly by using an empirical first order mass transfer equation to approximate solute transfer and thirdly implicitly by using the effective or lumped dispersion coefficient that includes the sink source coefficients or difference and hydrodynamic dispersion and axial diffusion. So what are these we will discuss?

Now let us see one important thing a number of methodologies can be broadly classified into methods for slower reactions. So methods for slower reaction are basically denoted by a timeframe of greater than seconds which includes batch and flow techniques. So, remember we have talked about some relaxation techniques. So relaxation techniques are basically used for determining the kinetics of any chemical processes. So number of methodologies are there batch method and flow method are basically slower reactions which is taking greater than 15 seconds.

However in case of rapid techniques can be measured in milli and microseconds using the relaxation techniques so we will discuss. Now it should be recognized that none of these methods obviously is a panacea for kinetic model so it cannot be a solution for all. It depends on various conditions we applied different techniques. So let us discuss one by one.

So batch method we are not going to talk about the batch method, we are going to talk about the flow methods in using some diagrams, but let us give you some brief idea about the batch method. Now it is the simplest batch technique an adsorbent is basically placed in a series of vessels such as centrifuge tubes with a particular volume of adsorptive and the tubes are basically then mixed by shaking or stirring in the centrifuges.

At various time the suspension is basically filtered to obtain a clear supernatant for subsequent analysis we know that, so this is a batch method. However, this batch method has two different advantages, two main advantages. First of all too much mixing may cause abrasion of the adsorbent. For example in case of adsorbent when we are using soil too much mixing may cause abrasion of the adsorbent altering the surface area while too little mixing may enhance the mass transfer and transport process.

Often and the second disadvantage is often the reaction is completed before the measurement can be made. So, this is the another major disadvantage of batch method. So to remove this disadvantage we generally go for the flow method.

So what is the flow method? So flow method can range from continuous flow method techniques to stirred flow method techniques. So in case of continuous flow method technique which is similar to liquid phase chromatography and in case of stirred flow method that combine the aspect of both batch method as well as flow method. However, problems with continuous flow methods is that the colloidal particles may not be dispersed.

So if this is an example of continuous flow method you can see this is a diagram it shows the setup of a continuous flow method. Now in the continuous flow method basically this is an experimental setup, you can see here the reservoir with a solution. So this solution is pumped up by a peristaltic pump with a constant rate of loop and then the adsorbent is basically placed and also supported within the thin disk on membrane filter.

So basically the solution is basically run through this membrane filter which contains the adsorbent or the soil at a particular rate through this peristaltic pump from the bottom and the background solution basically pump from the reservoir within this and then it is basically the aliquots are collected by this fractional collector. So here the soil is basically dispersed or soil is basically rested on this supported on this thin disk supported on this membrane filter.

And the solution the background solution is basically pumped up by this peristaltic pump at a constant weight and this aliquot is basically collected by this fractional collector. So this is called the flow method now problem with the continuous flow method is that the colloidal particles may not be dispersed. So here the colloidal particles are basically rested on this thin disk.

So there is no chance of dispersion of this colloidal particles where we are moving or where we are pushing the solution through this peristaltic pump. So, this is one of the major disadvantage.

Now the stirred flow method now has several advantages over the constant flow techniques and other kinetic methods. So basically if you see the reaction rates are independent you know these are the 7 advantages. Reaction rates are independent of the physical properties of the porous media then same apparatus can be used for adsorption and desorption experiment, desorbed species are removed, continuous measurement allow for monitoring reaction progress, experimental factors such as flow rate and adsorbent mass can be easily altered.

A variety of solids can be used with this technique and the adsorbent is dispersed and dilution errors can be measured. So these are some advantages of using the stirred flow method.

Now in the stirred flow method we are using again the background solution through this peristaltic pump. However we are basically we are basically putting the solution into the stir reactor containing the solid phase and are collected as aliquots in this fractional collection. So the separation of the solid, liquid phases is accomplished by the membrane filter which may be adjusted at the outlet of the stirred reactor.

So, here the adsorbent is more dispersed so that is why the more reaction time it can mimic the actual reaction which is actually going in the soil system.

The third method is relaxation technique which is very first technique. So the chemical relaxation methods must be used to very rapid relaxations. These methods are basically divided into pressure jump method, electrical field pulse method, temperature jump method and concentration jump method and concentration jump method. Now remember all these chemical relaxation methods are based on the theory that the equilibrium of a system can be rapidly perturbed by some external factors.

Such as pressure, temperature, electrical field strength. So when there is a perturbation or when there is a sudden change we can measure using some sophisticated electrical technique so that is called relaxation technique.

Now what is the effect of temperature on reaction rate? Now temperature has a marked influence on the reaction rate. Arrhenius noted that this is basically the following the relationship between k and T. You can see here k is reaction rate whereas Af is the frequency factor Ea is the energy of activation you know that. Converting this equation to a linear form will get this linear form.

And from this linear form if we plot the natural logarithm of k versus 1 / T we would get a linear relationship with the slope which is equal to – Ea / R and intercept equal to log of Af or natural logarithm of Af. So this is basically the effect of temperature on reaction rate.

So energy activation values from various reaction you can see there are different energy of activation typical ranges of energy of activation for different reaction. In the physical absorption 8 to 25, aqueous diffusion it is less than 21. In case of pore diffusion it is 20 to 40. So for different process energy of activation are different. So low energy of activation values usually indicate diffusion controlled transport and physical adsorption processes whereas higher energy of activation would indicate chemical reaction or surface controlled processes.

So let us see the kinetic this is the last point there is a kinetics of important soil chemical processes. So we will start with a heavy metals and oxyanions. So this two scientist Zhang and Sparks studied the kinetics of selenate adsorption on goethite using the pressure jump relaxation method which is a important relaxation method and found that the adsorption occurred mainly under the acidic conditions.

And the dominant species were this selenate. So a single reaction was observed in the mechanism proposed was this XOH + H + proton then selenate and then you can see the selenate is basically adsorbed on to the surface. So how it happens?

So basically where XOH is basically one mol of reactive surface hydroxyl bound to an ion in goethite. Now if we basically convert these equation into a linearized form it can assume these linearized equation. So where terms in the brackets which we can see are the concentration of species at the equilibrium stage. So basically these adsorption of selenate on to this surface hydroxyl group to an Fe ion can be expressed in terms of this linear equation.

Now since the reactions was conducted reaction was conducted at the solid liquid interface the electrostatic effect must be considered to calculate the intrinsic rate of constant which is basically noted by k1 and k – 1.

Now using the modified triple layer model to obtain the electrostatic potential we can see a first order reaction. So the whole reaction of these absorption of selenate into this surface hydroxyl group of iron atom can be expressed in terms of this first order reaction and we can clot this you can get this type of straight line. So this is an example of chemical kinetic which is happening while adsorption of different metals as well as oxy anions.

Not let us see an example practical example here, here you can see there are three graphs and this first graph it basically shows the kinetics of nickel sorption on pyrophyllite which is an important clay mineral then Kaolinite and also gibbsite and montmorillonite from a 3 mill molar nickel solution with an ionic strength of 0.1 molar of sodium nitrate and the ph of 7.5 and this graph B basically shows the kinetics of lead sorption on a soil from 12.25 millimolar lead solution with an ionic strength of 0.05 molar and a pH of 5.5.

And the c is basically the graph is basically showing the kinetics of arsenite form which is AsV sorption of ferrihydrite pH 8.9, 8 and 9. So this is showing how different metal ions and oxyanion solved on to the clay surfaces and following different where we plot them what type of linear form it will assume. So this is an practical example of kinetics of metal and oxyanions sorption on mineral or soil.

Now if we consider the kinetics of metal hydroxide surface precipitation solution. So metal hydroxide is also precipitates and can form a phyllosilicates form of phyllosilicate metal oxide and soils. So in over the soil and phyllosilicates the metal oxides can precipitates. So it has generally been thought that the kinetics of formation of surface precipitates was slow. Now here you can see this is basically this graph basically showing mixed Ni-Al hydroxide precipitates formed on pyrophyllite with 15 minute and then they grow in intensity.

As you can see the intensity is increasing as the time is increasing. So this is basically perfect example of metal hydroxide precipitation how it can form on the phyllosilicates and its intensity changes overtime. So this is basically showing nickel sorption on pyrophyllite for reaction time up to 24 hours starting from 15 minutes. It basically demonstrating the appearance and growth of the second shell which is peak at 2.8 angstrom continuation due to the surface precipitation and growth of the mixed Ni-Al hydroxide phase.

So this is another example of how this chemical kinetic occurs in case of metal hydroxide surface precipitation or dissolution.

When we talk about the organic contaminants the slow diffusion of the organic contaminants in soil organic matter by considering we can consider the diffusion is slow because of it is soil organic matter has the combination of rubbery and glassy polymers. Now the rubbery polymers as you can see here there is light shaded portion are characterized by expanded, flexible and highly solvated structure with pores of sub nanometers with pores of sub nanometers with pores of sub nanometer dimension.

And sorption in this rubbery phase results in linear, non competitive and reversible behavior. However, there is another polymer another phase is there which is called the glassy phase it shows the pores that are also sub nanometer in size and sorption in this phase is characterized by nonlinearity and it is basically competitive. So you can see based on these two different polymers or two different phases or two different phases glassy phases as well as rubbery phases. The linearity varies.

The linearity of adsorption varies and as a result also as a whole the organic contaminants shows that there is a slow diffusion of organic chemicals in soil organic matter.

So ion exchange kinetics also depended on adsorbent of the ion you know the reaction rates are much more rapid on kaolinite we have already discussed because of the external site then the exchange sites are reactions rates are more rapid in case of kaolinite as compared to vermiculite and type of ion has a pronounced effect on the rate of exchange. As you can see the rate of reaction is quite high in case of kaolinite as compared to the vermiculite.

Now exchange of ions like potassium, ammonium and Caesium is often slower than that of chemical and magnesium and that shows that type of ion has a pronounced effect on the rate of exchange.

So kinetic of mineral dissolution it basically consists of different rate limiting steps and so dissolution of minerals involve several steps like mass transfer of dissolved reactants from bulk solution to the mineral surface, adsorption of solutes, interlattice transfer of reacting species, surface chemical reactions, removal of reactants from the surface and mass transfer of products into the bulk solution.

So basically dissolution of minerals involve this 6 different steps. Now this first step and sixth step is basically mass transfer, however, the other steps are occurring in the reactive species on the surface of the reacting species.

So let us see what is the implication? So kinetics of mineral dissolution under field condition. Mineral dissolution is slow and mass transfer of reactants of products in the aqueous phase is not rate limiting. So basically we know that step 1 and step 6 are mass transfer they are not rate limiting and mineral dissolution is slow under the field condition. So that is the rate limiting steps. What are the rate limiting steps?

So the remaining steps are rate limiting steps so the rate limiting steps are either transport of reactants and products in the solid phase that is step 3 or surface of chemical reactants which is step 4 and removal of the reactants from the surface which is step 5. So this 3 steps maybe the rate limiting steps as opposed to the step 1 and step 6. There are two types of mechanism. One is transport controlled dissolution process another is surface controlled dissolution process.

Now in case of transport controlled dissolution process those controlled by mass transfer or diffusion can be described by a parabolic rate of law. We know this is a form of parabolic rate of law where r is the reaction rate, c is the concentration in solution, t is the time and k is the reaction rate of the constant we already know that. So this is basically transport controlled dissolution reaction which is denoted by this parabolic rate of law.

As we integrate that we will get this form which is basically C = C0 2k t to the power 1/2 where C0 is the initial concentration in solution. So if the surface reaction are slow compared to the transport reaction dissolution is surface controlled. So surface reaction is slow compared to the transport reaction the dissolution is surface controlled and dissolution reaction for example this type of reactions occur in case of silicates and oxides. The second type of reaction is surface controlled reaction.

The concentration of solutes next to the surface are equal to the bulk solution concentration and the dissolution kinetics are zero order is steady state conditions are operational on the surface.

So since it is following the dissolution rate r is basically r = k into A r is proportional to the mineral surface area A. Thus, for a surface controlled reaction the relationship between time C and the relation between time and C should be linear. So this is how the dissolution rate in case of surface controlled reaction can be expressed in a linear form.

So here you can see the graph of transport versus surface controlled dissolution is the schematic representation in solution C as we can see as the function of distance from the surface in case of transport controlled the concentration continuously decrease with the increase of distance. However, in case of surface controlled the concentration is constant with the change of distance.

And on the lower part of the figure you can see that change in concentration is given as a function of time. So you can see in case of time and in case of concentration it is following the parabolic curve and it is following the straight line. This is showing the transport controlled as well as surface controlled phenomena in case of dissolution of a mineral. So I hope it is now clear to you.

If you see that increasing the distance there is a concentration decrease from the surface and obviously with the increase of time with the pass of time the concentration increase. However, in case of surface controlled the concentration in the bulk of the solution is basically constant, however, the rate is also increasing linearly.

This is also showing the linear dissolution kinetics observed in dissolution of this alumina representative of process which rate are controlled by the surface reaction and not by the transport reaction. As you can see in this process if we plot concentration versus time you will get a linear like plot. So similarly you can see these reactions are basically controlled by surface reaction and not by transport reaction.

So, guys I hope that you have learned quite a few new things which useful things in this week and you have learned in details about different order of reactions and their implications how they are affecting different soil chemical process. We do not have time to discuss all the important soil chemical processes. Remember these chemical kinetics are important also for ligand exchange we do not have time to discuss in details.

But if you are interested to if you are interested to see more details of the application of chemical kinetics in soil chemical process you can consult this books. One is environmental soil chemistry by Donald Sparks, principle of soil chemistry by Kim H Tan and then Petrucci general chemistry. You can follow these books this book detailing this book have more details of this reactions.

And you will be having more knowledge while you go through this chapters from this books. So, I hope that you have learned something new. Let us wrap up this week and let us go to our next week of lecture where we will discuss some new aspects of environmental soil chemistry. Thank you.