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Environmental Soil Chemistry
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Module #06
Lecture #27
Kinetics of Soil Chemical Processes (Contd.,)

Welcome friends to this second lecture of week 6 or module 6. In this week, we were talking about kinetics of soil chemical processes.

So basically in this week, we are supposed to cover these topics. So in the first lecture, we have covered these rate-limiting steps and time scales of soil chemical process and then we have also discussed about the chemical reactions and the rate laws. Now today, we are going to focus on the determination of different reaction orders and rate in this lecture. So before going to that, I just want to give a quick recap of whatever we have discussed in the last class, so that, it will be helpful for you to relate whatever we are going to talk about in this lecture.

So let us go ahead and see in our first lecture, we have discussed why study the soil chemical kinetics. Now soil chemical kinetics is very important because soil chemical processes are very time dependent and different metals, oxyanions, radionuclides, pesticides, industrial chemicals and plant nutrients and their reaction is governed by this different chemical kinetics, so that is why it is very important that we should learn about the chemical kinetics.

And we also need to predict these fates of these different metals, oxyanions, radionuclides, pesticides in the environment. So for that also, we need to understand what is the soil chemical kinetics.

And then we have talked about these 6 different rate limiting steps of transport process. The first process, as you know, it is a transport in the solution phase as you can see and which is basically very rapid, because in the laboratory we can facilitate this by rapid mixing. The second step was transport across this particle-liquid interface.

And the third phase we have talked about the transport within these liquid filled macropores, you know, the macropores which are having the diameter of greater than 2 nanometer. So the fourth one, which we have talked about is basically the diffusion of sorbate along the pore wall surfaces, which is called the surface diffusion, as you can see here. The 5th one, we talked about the diffusion of sorbate occluded in micropores, which is denoted in this 5.

And the sixth one, we have talked about the diffusion of the bulk of the solid. So this is the sixth one. Apart from this, so this diffusion from the bulk of the soil it is basically activated diffusion process; however, the movement through the macropores and the transport to these diffusion of the sorbate at the surface of the soil, it is non-active diffusion, examples of non-active diffusions.

There are different rate-limiting steps as you can see here. The different types of soil chemical process are dependent on time. So for example, ionization, ion exchanges you can see here at very short period. They are present for a very short period or these reactions occur in very short period of time varying from microseconds to minutes and just opposite to mineral crystallization, which can take years to millennium to occur. Now these reactions can also occur simultaneously and consecutively also.

Now we know that variation on the different types of soil, clay colors also shows different types of reaction rate. For example, kaolinite and smectites can produce higher reaction rate than that of vermiculitic and micaceous soil. The reason is, in case of kaolinite, the external surface area is more; however, in case of smectite, for example montmorillonite at the internal surface area is high, so these surface areas are available for reactions. So as a result, the sorption mechanisms occur very rapid in these surfaces and basically take seconds to milliseconds to occur.

In contrast in case of vermiculite and mica, you can see that they have multiple sides for retention of metals and organics including the planar, edge and collapsed interlayer sites, because due to the presence of these potassium in the interlayer site, their interlayer space collapse and as a result sorption and desorption mechanisms on this site can be very slow and very tortuous. So these reactions, sorption can involve either 3 reactions; one is high rates of reaction in the external site, intermediate in the edge and lower rate in the interlayer sites.

So we also talked about chemical kinetics, definition of the chemical kinetics. Now it is the investigation of the chemical reactions rates in the molecular process by which their reaction occur where transport is not limiting, whereas in contrast kinetics is basically the study of time dependent process. Now it is difficult for determining the chemical kinetics for homogeneous system and the things become more complicated when you talk about soil, which is highly heterogeneous system.

Now that is why it is extremely difficult to eliminate the transport process in soil, because that is a mixture of heterogeneous. It is heterogeneous mixture of inorganic and organic process and adsorbates.

So we also talked about the rate laws and implication of the rate laws. Now remember that rate laws helps us to determine how rapidly the reaction attains the equilibrium and secondly it helps us to infer the information on the reaction mechanisms.

Different types of rate laws, I have shown you these elementary equations, elementary reactions and here a, b, y and z are stoichiometric coefficients and then, we have defined different types of constants based on that.

So based on these rate laws, we have seen that the rate of reactant A above, which has a concentration, which is given by these bracket at any time t can be denoted by this rate. However, while the rate with regard product y having a concentration of this bracketed y at the time t can be defined by this dY by dt and the rate expression here can be defined as dY by dt equal to minus dA by dt.

Now dA, as you know we are putting a minus sign because as the time progresses, there is a continuous decrease in A concentration, so which can be expressed in terms of this constant multiplied by A alpha and B to the power alpha, whereas in this case k is a rate constant, alpha is a partial order for reactant A, whereas beta is the partial order for reactant B and these orders are experimentally determined and not necessarily they are integral numbers.

We will see this in details in today’s lecture. Now remember these, the sum of these partial orders are always equal to the overall order of n. Once the values of alpha, beta are determined experimentally that rate law is defined and reaction order provides the information about the manner in which the rate depends on the concentration. We will see that in today’s lectures. So order does not mean the same as the molecularity, remember, which concerns the number of reactant particles entering into the elementary reactions.

Then we have talked about different types of rate laws. We have talked about these 4 different types of rate laws, one is the mechanistic rate laws, then apparent rate laws, transport with apparent and then transport with mechanistic.

In case of mechanistic rate laws, it assumes not only the chemical kinetics or operational and transport phenomena and where the transport phenomena is not happening. So it basically nullifies the transport phenomena. So it is difficult to determine the mechanistic rate law in most soil, chemical system due to the heterogeneity of the system caused by different particle size, porosity, and type of retention sites.

The second type of law is apparent rate law where you know it considers both kinetics and transport control process.

The third one, which we have talked about; is transport with apparent rate laws, which emphasizes transport phenomena and assumes first or zero order reaction. What is first order reaction, what is zero order reaction, we will learn today and the fourth one is transport with mechanistic rate laws,that is which can be discussed simultaneously transport control and chemical kinetics phenomena. It basically encompasses both chemistry and physics, best explanation of the total chemical system.

so, today, we are going to start with this definition as well as the concept of these different order reactions. So first we know, we have to learn what is the first order reaction and second order reaction. Now in the first order reaction, the reaction rate depends on the concentration of one of the reactants; however in case of second order reaction, the rate is proportional to the square of the concentration of a reactant or the product or the product of the concentration of the 2 reactants.

In the first order reaction, the rate of reaction basically depends on the concentration of one of the reactants. So we can consider only one of the reactant; however in case of second order reaction, the rate is proportional to the square of the concentration of a particular reactant or the product of the concentration of the two reactants. So we can view it from either aspect, either from a point of view of the square of the concentration of a particular reactant or it is a product of concentration of the two reactants. We will see that in details, while we are going to discuss different differential form as well as integral form of these equations.

So what is the first order and second order reaction? Now, remember we can express these first order reactions, second order reaction. So before going to that the actual soil related first order and second order reactions, I want to discuss the concept of first order and second order reaction as well as we will be talking about zeroth order reaction and then we will be saying how these type order reactions, so in a first order, second order and zero order reactions are actually been implemented in soil chemical process.

So let us first clear our concept of different orders of reaction. So if you see the differential rate laws are generally used to describe what is occurring in a molecular level during a reaction, whereas integrated rate laws are used to determine the reaction, order and the value of the rate constant from experimental measurement. Now remember, any type of reaction order, for example first order reactions or second order reaction or zero order reaction can be expressed from both differential point of view as well as an integrated form.

Now in case of differential form, it basically describes what is actually going on in the molecular level during a reaction, whereas in case of integral form, which we will see right now are used to determine the reaction order and the value of the rate constant. So the differential equation describing the first order kinetics can be given as such. For example, here rate is equal to –dA by dt, as you know that is the negative sign is given because the rate is decreasing.

Here it can be expressed in terms of k multiplied by concentration of A or kA. So basically, here the partial order here for A is 1. So the reaction partial order is 1, so the rate is the reaction time here. This rate is basically the reaction time and it can be expressed as unit of molar per time and k is basically the reaction rate coefficient, which is denoted in the unit of time inverse. So it could be either second inverse or minute inverse. We will see that in a while.

So however, the units of k vary for non-first order reaction. We will see that while we discuss the zero order as well as second order reactions. So this is basically differential equation describing the first order reaction, where the rate of decay of A is basically proportional to its concentration and here the constant is known as reaction rate coefficient.

So these differential equations are separable, which simplifies the solution as demonstrated below. As you can see here, first we can write the differential form of the rate laws, you can see here rate in terms of minus dA by dt, which is basically k multiplied by concentration of A.

Now if you rearrange these, we will get these dA by A, we will get –kdt. So this rearranged, after rearrangement, we can get this form.

Now we know, according to the rule of integration, integration rule, if we can integrate both sides of the equation, so now we are getting dA by A = -kdt. So if you integrate from A0 to A and in this from t0 to t for any specific time duration, we will have this type of expression. So basically, we will get 1 by concentration of A into dA = -t0 to t integrate kdt. So this form, we will get by integrating on both sides of the differential equation.

So now we know that from the integration rules, we know that if we do integration of 1 by x, that becomes log of x, natural logarithm of x. So upon integration, we will get, so basically if you remember the previous equation, which we just saw in our last slide, so this is basically this integral equation. So if you consider this integration equation and convert it to the logarithmic form we will get this equation, where log of A concentration A minus log of concentration A0 that means at time zero, that means at the initial point from where the reaction starts.

We will get A that will be equal to minus kt, because we are integrating from time 0 to time t. Now if you rearrange these equations to solve for these concentration of A, then we will obtain one form of the rate law like this. So log of A = log of A0 – kt. Now you see this can be further rearranged to log of A equal to –kt + log of concentration A at time t0. So this is basically a rearrangement of this form, which is further a rearrangement of this form.

So if we can consider this equation, this equation can be arranged in the form of y = mx + b. Now, you know this y = mx + b is nothing but the equation of a straight line. So here, you can see it is basically taking the form of y = mx + b. So basically, we are getting y = mx + b where mx = -kt and whereas b = log of A. So from here, we can see one thing that here the slope m is basically, if you consider these m as slope, then mx is basically –kt as we have seen and the y intersect b is basically log of A0. So summarily, these equations can be represented in the form of a straight line.

Now once we can describe this equation in the form of a straight line, now recall from the logarithmic laws that if we logarithm of At by A0 = -kt. So basically, we know here is logarithm of At. It was our equation –kt + ln of A0. So if we simplify that, we will get this logarithmic form. Here, A is concentration at time t and A0 is the concentration at time 0 and k is the first order rate constant.

So this equation, which I present here in the logarithmic form is basically if we go back, this is basically the simplified form or rearrangement of this equation, which is basically arranged in the form of a straight line.

So once you get this logarithmic form, now if we plot the time versus logarithm of At, then here the intercept we will get A0 and here you can see we will get this straight decay line. So these are basically called decay profiles for first order reactions. Now here, you can see there are two different constant, in one reaction you are getting smaller k, another reaction you are getting larger K. In case of small k, when the rate constant is small, then the rate of decay is relatively less.

However, when there is a large K, the rate of decay is quite high. So there is a steep slope in case of large K. So this is basically the decay profile. So basically if you plot the time versus logarithmic of concentration at any particular time, then you will get a negative slope as well as a straight line. So this is the most important feature of a first order kinetic. So in any type of reaction, if we just plot the reaction time versus the concentration at a particular time and graphically, you want to see, and if you get a straight line with a negative slope, then you can be confident that it is basically following a first order reaction.

So because the logarithm of numbers do not have any unit, the product of – kt also lacks unit, since it is logarithmic. We have already seen this kt is nothing but the log of At by A0 = - kt, we already know. Now for logarithmic of any number basically do not have any unit. So this kt also do not have any unit. So if this kt is unitless that means, the unit of k should be always time inverse, because if the unit of k is time inverse, then this time unit and this time inverse unit basically nullify each other to get a unitless number.

So, example of time inverse is basically inverse of second or inverse of minute. Thus, the equation of a straight line is applicable here, you can see here: this is what we have discussed in previous two slides. So the straight line and negative slope is the major identifier of the first order reaction.

So to test if it is a first order reaction, you have to basically plot the natural logarithm of a reactant concentration versus time and see whether the graph is linear. If the graph is linear and has a negative slope, then the reaction must be a first order reaction. Now to create another form of this first order rate law, if you take exponential in this previous equation, so we know that in the previous equation, it is basically log of A = log of A0 – kt.

So if you take an exponential in both sides of the equation, then we can get it more simplified form, so this is concentration of A = concentration of A0 multiply e to the power –kt. So this is basically the second form of the rate law where it is following a first order reaction. So here, it is given here. So this is concentration of A equal to can be expressed in terms of this A0 e to the power –kt.

So now the integrated forms of the rate law can be used to find the population of the reactant at any time after start of the reaction. Now plotting the logarithmic A concentration with respect to time for a first order reaction always gives a straight line with the slope of the line equal to –k, we know that. Sometimes in some literature, you will see that –k by 2.303. Why it is k by 2.303, we will see that later, but remember that still the value of k by 2.303 is a constant.

So it does not matter. We can use –k as a constant. So this general relationship in which the quantity changes, that means concentration of a particular reactant changes at a rate that depends on its instantaneous value is said to follow an exponential. So basically this decay, as we can see in the previous decay profile, it is basically following an exponenetial decay. So, exponential relationship are widespread in science and in many other fields.

Remember consumption of a chemical reactant or the decay of a radioactive isotope, all of these follow exponential decay and its inverse the law of exponential growth describes the manner, in which the money in a continuous compounding bank account grows with time or the population of any colony reproducing organisms like bacteria, so bacteria follows an exponential growth. So the reason that the exponential function that is y = ex is so efficiently describes such changes is that, if you differentiate the e to the power x in terms of dy by dx, we will get the output as ex.

So ex is basically its own derivative. So derivative of ex equals to ex. So that makes the rate change of y identical to its value at any point. So that is why these exponential decay shows the best representation of first order differential equation.

Now if you consider why it is called exponential decay, basically if you put the time versus concentration, you will see there it is following an exponential decay. Now, that is basically log normal. So whenever you convert it to logarithmic form, you will get a straight line. So the following curve represents the concentration of a reactant versus time for a first order reaction. So this is basically the identification mark of a first order reaction.

It will show you, if you basically plot the time versus concentration, you will see an exponential function and if you take a logarithm of that concentration, you will see straight line and the straight line has a negative slope. So this is the graphical representation of first order reaction.

So if you graph, just for an example here, it is a good example is given. If you plot logarithm of a concentration of a reactant with respect to the time for a first order reaction, it basically gives a straight line. So basically here, you can see, if the time varies from 0, 1, 2, 3, 4, 5 and you can see first order. In case of first order reaction, the concentration changes from 40 unit to 35 to 30, 25, 20 and 15. So if you plot that, you will get basically straight line.

So basically, it again says that how empirically this first order reaction can be identified by just plotting them or the logarithm of concentration versus time. So guys, I hope that you have learnt something new at least for first order reaction, you have learnt today and in the next lecture, we will be talking about the second order reaction, zero order reaction and how to calculate the half life of the first order reaction and what are the other kinetics model applicable in soil science. So let us wrap up this lecture. In the lecture, we will be talking more about these second order reactions as well as the other types of kinetics models. Thank you very much.