

Course Name: Industrial Wastewater Treatment

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Lecture 2: Coagulation, Precipitation and Heavy Metal Removal

So, welcome back. We are in module 5, lecture 2 and we are discussing on coagulation, precipitation and heavy metal removal. So, the concepts covered in this lecture will be on the electrical double layer formation during the coagulation and coagulation process on the colloidal particles. We will talk about the particle destabilization with potential determining ions, they are also known as the counter ions and the electrolytes. Similarly, we will talk about the particle destabilization using polyelectrolytes. We will also talk about the action of hydrolyzed metal ions on the coagulation and flocculation process and lastly, we will discuss about the mechanism of the coagulation.

So, the perikinetic and orthokinetic flocculation refers to micro flocculation and macro flocculation respectively. So, micro flocculation as you have already discussed that it is brought about by the random thermal movement of the fluid molecules or the Brownian motion. So, the flocculation happens because of the Brownian motions and thermal movement of the fluid molecules, and they bring about the micro flocculation and this process is also known as the perikinetic flocculation. Whereas the macro flocculation which is brought about by the velocity gradients which can be induced due to the mixing or the differential settling processes where the bigger particles they are settling at a faster rate whereas, the smaller particles they are settling at a smaller rate.

So, when they come closer to each other, so in that case the macro flocculation may happen, and this process is also known as the orthokinetic flocculation. So, when we talk about the colloidal particles which are present in water or wastewater, these particles may have a certain charge, the inherent charge on the particle. So, these particles for example, the colloidal particles present in the water or wastewater they are generally negatively charged. So, the counter ions may get attached because of the electrostatic force of attraction. So, they may get attached to the surface of these colloidal particles.

These particles basically they form a layer around the colloidal particles and this layer which is tightly attached to the negatively charged colloidal particles, so this is called the stern layer and these layers which are formed, so they are very very strong in the sense that it cannot be overcome by the thermal agitation simply. So, that's why this layer basically they remain attached to the particles and as the particles move, so these layers also move along with it. So, we can see here that for example, if we are having a negatively charged particle, so the positive charge ions they form a very tight layer to it which is called the stern layer and as we go further away, so the concentration of these counter ions or the positive ions in this case, so this may start decreasing and it is possible that at a certain point which is called the slipping plane, so this layer may be moving along with the particle that is the negatively charged particle and this layer that is the diffuse layer as well as the stern layer, so this combines and this forms the electrical double layer. So, this electrical

double layer is the layer, which is formed around the particle, which is in form of the clouds, so whenever the particle they will move, so this layer will also move along with it. So, we can see here that the potential or we can say the charge on the surface of the negatively charged particles that is the colloids, so this is called the surface potential whereas the charge or the potential on the stern layer is called the stern potential and as we go further away in the diffuse layer the charge decreases and it reduces to nearly zero and the charge which is there or the potential which is formed at the slipping plane, so this is known as the zeta potential.

So, we can see that the potential drops from ϕ_0 to ϕ_s when it is basically moving from surface to the stern layer and then the potential may drop further to nearly equal to zero as we move further away in the diffuse layer. So, we can see here that the electrical current when it is passed in us water or the wastewater which contains these colloidal particles, so the particles may move to the electrodes to which they are attracted. For example, if the particles are negatively charged, so they may be attracted towards the anode, so when they are moving, so this cloud of the ions, so they also start moving with it and this cloud of the ions which is formed, so this is known as the electrical double layer and similarly the potential at the surface of the clouds is measured by a zeta potential. So, zeta potential is used for measurement of the charge which is there on the surface of the electrical double layer and zeta potential may vary depending upon the composition of the water or the wastewater. So, we can see here in this diagram that if we are having the positively charged particles, so a negatively charged counter ions, so they get attached to the surface of the colloidal particles and as we go away, so the concentration of these counter ions may decrease, and it may basically decrease to a certain level till the ionic balance is maintained.

So, this layer is known as the diffuse layer whereas, the plane at which this diffuse layer may be sheared off, it is also known as the shear plane and this layer moves along with the particles wherever the particle moves and this part of the diffuse layer it basically forms the part of the double layer. So, we can see here that the surface is having a charge of ψ_0 which is also known as the surface charge, or it is also called as the Nernst potential. Similarly, the charge decreases as we go further away from the surface and the potential at the surface of the stern layer is called the stern potential whereas, the charge at the surface of the shear plane, so this is called the zeta potential. Here, we may be having particle to particle interactions when the particles they come closer to each other. So, there may be certain forces that may be acting on these particles.

For example, if we see that as the separation distance decreases, so we can see that the coulombic or electrostatic repulsive potential it increases slowly and similarly the van der Waal forces of attraction, so they also increase slowly. So, if the coulombic or electrostatic repulsive potentials, so they are higher in comparison to the van der Waal force of attraction, so in that case it is possible that whatever the energy curve we get here this is called net energy curve. So, this net energy curve may be having repulsive maximum which needs to be overcome if we want to aggregate the particles or if we want that the van der Waal force of attraction they dominate over the coulombic or electrostatic repulsive potentials. So, then we have to overcome this barrier, which is called the energy barrier, so that the particles where they come closer to each other they can aggregate with each other,

they can form flocs, and they can settle down easily. So, this means that if we want that the particles to be removed by the micro flocculation or very kinetic flocculation, so the repulsive forces which are there because of the similar charge on the particles, so this needs to be reduced and we can see here that this can be brought about by addition of certain chemicals which we will just now discuss and when we are adding these chemicals it is possible that these repulsive potential may be reduced and the particles when they come closer to each other they can aggregate, they can coagulate and they can form flocs.

So, we can see from this diagram that as we go further away, so the repulsive forces decrease, and the net energy curve is showing no energy barrier. So, this means that the particles may form floc at a larger separation distance. So, in that case the force that holding these two particles, so it may be so weak that the flocs which may be formed, so they may be ruptured easily that is why the floc basically may not be formed if the particles are further away from each other. So, we can see here that there are two conditions which are shown in this curve that is we are having the repulsion curve 1 and repulsion curve 2 in which the repulsion curve 1 is having a higher repulsive force whereas in case 2 the repulsive forces are lesser in comparison to the condition 1. So, we can see that the Van der Waal force of attraction is represented by this curve which is constant.

So, here in condition 1 we can see that there is a certain energy barrier which is formed which needs to be overcome so that when the particles they can come closer to each other, so they can get coagulated, they can get aggregated and removed from the system whereas in condition 2 we can see that there is no energy barrier to be overcome and whenever the particles which are having lesser repulsive forces or potential, so they will be easily coagulating as they are coming closer to each other. So, when we are talking of the particle destabilization that is if we want to reduce the repulsive forces which is there because of the similar charges on the particles, so it can be brought about by addition of a potential determining ions or, so they are also known as the counter ions. So, these ions may reduce the surface charge on the colloidal particles, and this can reduce the repulsive forces that can happen when the particles are coming closer to each other. Similarly, addition of electrolytes can also destabilize the colloidal particles where they are responsible for the reduction in the thickness of the diffuse electrical layer and thereby they can reduce the zeta potential of the particles and that may lead to the coagulation and aggregation of the particles and this may lead to the destabilization of the particles as well as it may lead to the reduction in the turbidity of the water or the wastewater. So, when we are adding different type of counter ions and electrolyte in the solution so it can happen by addition of the strong acids or bases so that it can reduce the charge of the metal oxides or the hydroxides.

So, it is possible that this charge may be reduced to nearly zero and this may lead to the coagulation of the particles. For example, we can see here that this curve is having a higher repulsive forces and as we are adding counter ions on the particles the charge on the surface may decrease and the repulsive forces may also start decreasing and similarly it is possible that as the dose is increased so this charge may also reduce to a certain value so that it may go to nearly equal to zero. So, addition of these counter ions may lead to the charge neutralization and as soon as the charge neutralization takes place the Van der Waal forces

of attraction may dominate, and they can start aggregating the particles together and this will lead to the formation of the flocs easily and these flocs can settle down as they grow in the size during the process. Similarly, if we go on adding further counter ions or electrolytes in the solution so it may lead to the reversal of the charges and the charge now may become instead of negative charge it may become positive charge and then it may again lead to the stabilization of the particles and it may again lead to the generation of turbidity in the solution. So, the magnitude of the effect of these counter ions it depends upon the concentration.

So, as we are increasing the concentration so we can see that how the things are changing that is how the surface of the colloidal particles, so it is changing, and it is leading to the aggregation of the particles. So, the Schulz Hardy rule has been used to assess that what is the effectiveness of the potential determining or the counter ions so they can be used. For example, the Hardy-Schulze rule states that the greater the valency of the flocculating ions which is added the greater is its power to cause precipitation. So, this means that if we are having the aluminum ions in comparison to the barium and sodium ions so they will be having the highest potential in comparison to the barium and sodium ions because they are having a higher valency. So, this means that as the valency of the ion increases the coagulating powers also increases and if we talk about the concentration of such type of ions so in that case the monovalent ions may be required in a very high concentration in comparison to the divalent and trivalent ions.

This rule states that the ratio of the concentration of these ions so this may vary as 1 is to 1 by 2 raised to power 6 where 2 is the valency of the divalent ions is to 1 by 3 raised to power 6 where 3 is also the valency of the trivalent ions. So, this means that if we require a concentration of 100 for the monovalent ions so the same effect can happen with the concentration of 1.6 for the divalent ions whereas 1.3 for the trivalent ions. So, as the dosage of the counter ions is increasing so the particle surface charge also basically varies.

So, we can see that as we are increasing the concentration of the counter ions so slowly and slowly the charge on the surface of the particle it reduces it goes nearly equal to 0 and then the charge reversal takes place and the charge which is there on the counter ions so this start dominating the surface of the colloidal particles. So, if the particles were negatively charged and we are adding a counter ion of positively charged so slowly and slowly the charge neutralization takes place and after a certain value it when it attains a neutral surface so after that further addition of the coagulant or further addition of the counter ions will lead to the formation of positive charge on the surface of the particles. So, these two lines so they are representing the thermal kinetic energy of the particles, and we can see here that as the surface charge is greater than the thermal kinetic energy of the particles so then basically having the particles are stabilized. So, this means that if we are adding a certain counter ions onto the colloidal particles so slowly and slowly as the charge will decrease and as the charge basically goes below the thermal kinetic energy of the particles so then the coagulation process or the aggregation of the particles takes place and we can see here that the turbidity of the water or the waste water starts decreasing and as soon as the surface charge it reaches to nearly equal to 0 so in that case the turbidity will be minimum and as we are increasing the dose again so slowly and slowly the surface charge increases because of which the repulsion forces, repulsive forces may again

increase and because of which the turbidity is again increasing and it may reach to the similar values that we have attained earlier values or the initial values as the charge basically goes beyond the thermal kinetic energy of the particles. So, this means that when the surface charge is greater than the thermal kinetic energy of the particles, the particles will not populate, and we can see that the original turbidity is observed again.

So, use of the counter ions in water and wastewater may not be feasible because of very high concentration requirement of the counter ions so that they can compress the electrical double layer so that the perikinetic flocculation may happen. So, particle destabilization and aggregation can also take place with the help of the polyelectrolytes and these polyelectrolytes may be divided into two categories that is they can be natural, or they can be synthetic in nature. So, the natural polyelectrolytes they include the polymers which are derived from the biological origin like the starch products or the cellulose derivatives and alginates. So, similarly the synthetic polyelectrolytes they consist of simple monomers that are polymerized, and they can form a high molecular weight substances and these two types of polyelectrolytes they are used for the aggregation of the colloidal particles in water or wastewater. So, depending upon what charge these polyelectrolytes they are carrying for example, the charge can be negative, the charge can be positive, or the charge can be neutral.

So, these polyelectrolytes can be classified as anionic or cationic or non-ionic respectively. So, if they are having negative charge so it is called anionic polyacrylate, it is having a positive charge it is called cationic and if it is having no charge then it is called non-ionic polyacrylate. So, the action of the polyelectrolytes may be three-fourths. For example, we can have the charge neutralization taking place because of the addition of the polyelectrolytes. So, polyelectrolytes may act as a coagulant, and it can neutralize the charge which is present on the surface of the colloidal particles.

For example, if we are having the cationic polymer electrolytes so they will basically neutralize the surface charge which is present on the negatively charged colloidal particles. So, this means that the polyelectrolyte can lead to the reduction in the charge on the surface of the colloidal particles. So, it must be adsorbed onto the surface of the particles so that this charge neutralization or the reduction in the charge can happen. So, if we are giving a proper mixing so then it is possible that sufficient adsorption may take place on the surface of the colloidal particles and charge neutralization can take place in that case. But if we are having no proper mixing or if we are having inadequate mixing then this polymer will not adsorb onto the surface of the colloidal particles, and it can hold back on itself, and this can lead to the reduction in the efficiency of the polyelectrolytes for reducing the charge on the colloidal particles.

So, one of the ways by which the polyelectrolytes act so this is called the charge neutralization. So, we can see here that the particles are present in the water or wastewater. So, these particles when the polymer are added so these polymers can basically adsorb onto the surface of the colloidal particles, and which can be brought about by using the rapid mixing. So, initially we have to go for rapid mixing so that the polyelectrolytes which you have added so they can get adsorbed onto the surface of these colloidal particles and later on the floc formation can take place either by perikinetic flocculation or by orthokinetic flocculation and we can see that inter-particle bridging takes place and the large flocs are

formed and these flocs can ultimately settle down in the water or waste water. So, this polymer bridge formation can be another mechanism by which the polyelectrolyte act.

So, here the polyelectrolytes are having a long chain compound so these long chain compounds can lead to the inter-particle bridging where the polyelectrolytes can get adsorbed to a number of particles and it can lead to the inter-particle bridging. So, if we are having the polymers which are anionic or non-ionic in nature so they may act in a way that they cannot neutralize the surface charge of the colloidal particles. So, in that case they go for the adsorption of the particles on the surface of the colloidal particles. So, they go for the polymer bridge formation where basically they can get attached to the adsorption sites on the surface of the particles which are found in waste water and they can form a bridge between two or more particles and the number of particles can get adsorbed along the length of the polymers and these bridges they can again intertwine with the other bridges which are formed and which can lead to the flocculation process which can lead to the larger floc formation and ultimately this floc may grow in this way and then it can be lead to the sedimentation of these flocs and that is how the turbidity can be removed from the system. So, in addition to the charge utilization and polymer bridge formation we can also have the charge utilization as well as the polymer bridge formation that is the combined action can take place for the removal of the colloidal particles present in water or wastewater.

So, here we use cationic poly electrolytes which is having an extremely high molecular weight so that they can lead to the charge utilization of the negatively charged particles also as well as it can also lead to the polymer bridge formation which can lead to the removal of the colloidal particles from the water or wastewater. So, particle destabilization can also happen by using the hydrolyzed metal ions. So, here the addition of alum or ferric sulfate which are hydrolyzed metal ions so this can be used for the removal of the colloidal particles present in water or wastewater, but this process is a more complex process in contrast to the process that we have just now discussed for the counter ions and for the poly electrolytes. So, here instead of the ions of ferric or aluminum, so hydrolysis of the metal ions is responsible for the particle destabilization process. So, Fafir in 1902 and 1907, so they have proposed that the hydrolysis of trivalent metal salts such as chromium, aluminum or iron so it can be represented by this equation where Me represents the metal ions and it can be dissociated in this way and this dissociation depends upon the anions which are associated with the metals and it will also depend upon the physical and chemical characteristics of the solution in which they are placed.

So, on addition of the sufficient base, it is possible that dissociation may also lead to the formation of negative ions like this. So, the complex compounds which are formed, so they are called the coordination compounds, and the central metal ion is attached to a number of surrounding molecules or ions which are by coordinate covalent bonds and these surrounding molecules or ions, they are called lesions and the atoms which are directly attached to the metal ions, they are also known as the lesion donor atoms. So, in the water or wastewater, typically these lesions are carbonates, they can be chlorides, they can be hydroxides, they can be ammonia or even water. So, there can be number of coordination compounds which can be amphoteric in nature. So, amphoteric means that they can exist in strong base as well as in strong acid.

For example, if we talk about the aluminum hydroxide, so this $Al(OH)_3$ both hydrides can be present in Al^{3+} plus form in acidic conditions as well as it can be present in aluminate form in the basic conditions. So, here however the equation 2 may not be as simple as it is described here. So, there can be a number of complex processes that can be happening in the formation of this aluminate ions. For example, Stumm has proposed a model where in the presence of base, a number of mononuclear species as well as poly nuclear species, they may be formed, and it may result in the formation of mononuclear species of aluminate ions. But all these species which are formed in the intermediate, so they can be responsible for the coagulation and flocculation process.

So, the process which is involved in the formation of these mononuclear species like aluminate ions, so this is much more complex in contrast to the simple equations that we have written earlier. So, action of hydrolyzed metals can also lead to the destabilization and removal of the colloidal particles, and it can happen because of various processes. For example, it can be adsorption and charge neutralization that is taking place, it can be adsorption and inter-particle bridging and it can be enmeshment in the free flock. For example, here the adsorption of the mononuclear and poly nuclear metal species which are formed during the process of the hydrolysis, so they may be responsible for the adsorption and charge neutralization. For example, if we are having the colloidal particles and the mononuclear or poly nuclear metal hydrolysis species, so they are positive in nature, so they can lead to the adsorption and charge neutralization of such colloidal species.

Similarly, the adsorption and inter-particle bridging can also lead to the reduction in the turbidity of the water or wastewater solutions. So, here hydrolysis species they can form particle polymer bridges, and which can lead to the reduction in the turbidity of the water or wastewater solution. Similarly, the metal hydroxides, so they can also get precipitated out and during this precipitation the flocculation may happen, and this flocculation is known as the free flocculation. So, this happens when we are adding a higher amount of metal ions into it which leads to the metal hydroxide precipitates as basically the adsorption and charge neutralization process has been satisfied and we go on adding the further metal ion species to it, so it will lead to the precipitations, and this may lead to the free flocculation. So, if the sufficient amount of these metal salts are present, so it may lead to the metal hydroxide flocculations and this metal hydroxide flocculation which may be because of the micro flocculation process, so it will form a large flock particles and they may settle down readily and during the settling down of these precipitates they may sweep the water which contains the colloidal particles and these colloidal particles may get enmeshed into the flock and ultimately these colloidal particles will be removed and that is why this process is known as the sweep flocculation.

It is sweeping the particles along with it and the particles are getting enmeshed in the precipitate and they are being removed from the system in such a way. So, if we talk about the alum dose versus the turbidity, so we can divide the entire process into four zones. For example, the zone 1 as we can see here, so this is the part where the sufficient equivalent has not been added and the particles are not destabilized, the particles are in the stable form and slowly and slowly the adsorption charge neutralization it happens and then the particles basically gets destabilized and we see that the turbidity basically values they go down because of the adsorption charge neutralization which basically reduces the surface

charge on the colloidal particles and it can lead to the aggregation of the particles which leads to the reduction in the turbidity. So, when we go on further adding the alum dose for example here, so what the charge reversal may take place because the positively charged ions or the hydrolysis species, so they may start accumulating on the surface of the colloidal particles and the colloidal particles may now become the positively charged. So, this means that the charge reversal process is taking place and slowly and slowly we see that the turbidity again comes back into the solution.

So, the zone 3 means that the particles have now again become stable, and the turbidity is again regained. Whereas, if we keep on adding the alum dose, so aluminum hydroxide flocs basically may form and these flocs may then settle down, the precipitates may settle down and these precipitates will enmesh a number of particles which are causing the turbidity and these colloidal particles they get enmeshed in the precipitates and then again, the turbidity will go down which is represented by the zone 4. So, the renewal of the turbidity will also depend upon the dose of the coagulant as well as on the concentration of the colloidal particles which are present in the water or the base water. For example, we can see here that we are having four scenarios that concentration of the colloidal particles is highest in S4 whereas the concentration of the colloidal particles is lowest in S1. So, we can see here that the higher concentration of the particles is present in S4 whereas the particles concentration reduces in S3 and further in S2 and we are having the least concentration in S1.

So, as the particle concentration is highest in this figure in S4, so we can see that as we are adding the coagulant dose, so the zone 1 basically that is the particles are getting destabilized and slowly and slowly as the charge utilization happens and because the particles are very high, large in numbers, so they can easily flocculate, they can easily interact, they can easily come closer to each other and we find that the zone 2 where adsorption and charge utilization may lead to the reduction in the turbidity of the such water or base water. Whereas as the concentration of the colloidal particles may reduce, it may be seen that as the coagulant dose is increasing, the turbidity reduces but because the particles are lesser in concentration in comparison to S4, so the charge reversal may take place and these particles may again be destabilized and as we go adding the dose further, so we find that the sweep flocculation may result in the removal of the turbidity from the solution. So, if the concentration of the colloidal particles reduces further, then we find that though the adsorption and charge utilization is taking place which leads to the reduction in the turbidity but because the particles are very less in numbers, so as soon as the charge reversal happens, these particles may again separate out and we find that the zone 2 is reduced a bit in comparison to the S3 colloidal concentration and then we as we go on adding the alum dose, so these particles basically may get removed from the system by the sweep flocculation process. So, if the particles concentration declines to a very very low values, so in that case, we find that there are only two zones that is zone 1 and zone 4 because if the adsorption and charge utilization process is also happening, then also the particles may not come closer to each other because of their lower concentration and they cannot be removed even though the adsorption and charge utilization has happened. So, in that case, we have to add a very high amount of coagulant dose, so that the sweep flocculation may happen, and this sweep flocculation will lead to the enmeshment of the

particles which are present in the water or wastewater and then it can be ultimately removed from the system.

So, we can see here that when the concentration of the particles is very very high, so in that case, we can have the formation of zone 1 and zone 2 only which can lead to the removal of the colloidal particles, whereas in the intermediate concentration, we will find that all four zones will be present during the removal of the turbidity, whereas in the last case, when the concentration of the colloidal particles is very very low, so in that case, only zone 1 and zone 4 will be dominant. So, we stop here, and we will continue our discussion on the next turn. So, these are the references that I used in this lecture.

Thank you.