Course Name: Industrial Wastewater Treatment

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Week – 05

Lecture 1: Coagulation, Precipitation and Heavy Metal Removal

Welcome back. So, we are in module 5, lecture 1 and we will be talking about the Coagulation, Precipitation and Removal of the Heavy Metals by Using Precipitation and Coagulation flocculation Methods. So, the concepts covered in this lecture will be the fundamentals of the coagulation and flocculation processes, the colloidal particles which are found in wastewater which needs to be removed by coagulation and flocculation process, the factors affecting coagulation and flocculation and the particle solvent interaction that happens when the particles like colloidal particles are present in a solvent, the solvent in this case may be the water. So, because we are talking of the water and wastewater treatment, so how the particles they interact with the solvent that we are going to discuss in this lecture. So, all of you know that the removal of the heavy metals can take place by ion exchange process, the adsorption process that we have studied earlier also. Similarly, we can also use the membrane processes for the removal of the metals, and we can also use the method like precipitation, coagulation, flocculation for the removal of the metals which can be utilized by a number of industries.

So, we are going to cover today about the coagulation and flocculation process first of all. So, the wastewater can be a mixture of variety of solids where basically we can have the suspended solids and the dissolved solids. So, we have already studied about the suspended solids and dissolved solids in the characterization of the wastewater lecture. So, here also we can mainly classify the solids into two parts that is we can have the suspended solids, we can have the dissolved solids where the suspended solids are larger and heavier particles that may settle under the influence of the gravity, and they have a size above 1 micrometer and they can be visible by the naked eyes they include the sand, grit and larger organic particles.

So, dissolved solids are the solids which are generally less than 1 nanometer in size, and they are too small to be seen by the naked eyes they may contain the solids which are created by the organic materials such as sugars, proteins, humic substances. Inorganic substances also like for example, salts, the dissolved metals as well as the dissolved gases. So, they all serve as a dissolved solids in the water. Similarly, we can have colloidal particles which may range from 1 micrometer to 1 nanometer. So, the particles lying between 1 nanometer and 1 micrometer are called the colloidal solids and they are having the size which lies in between the two solution and the suspension.

So, that is why they remain dispersed in the solution and they do not settle quickly and that is why they are known as the colloidal solids and they are termed as the non-settlable solids and that is why we have to use a number of chemicals so that these type of solids can be removed from the water or waste water and they continue to the controllability of

the water and these colloidal solids that is why they are very difficult to be removed by the cavitation process. So, you can see here that when the water sample may contain different type of solids for example, when we evaporate the water sample, we can get the total solids which are there which comprises of the total suspended solids and the total dissolved solids, and these solids can be differentiated by use of the filtration method. So, the whatever remains on the filter paper so that contributes to the total suspended solids, whatever goes into the filtrate so that is contributes to the total dissolved solids. And similarly, these total suspended solids and total dissolved solids may be further classified into volatile suspended solids and fixed suspended solids as well as the volatile dissolved solids and fixed dissolved solids where the volatile means the organic parts and the fixed means the inorganic part. Similarly, the sample of the water may also contain the solids which can settle down within one hour so we use Imov cone so that we can find out the solids which are also known as the settler solids.

So, the main concern here is the solids which are colloidal in nature which cannot settle down on their own which do not settle down by the gravitational technique. So, when we go for the fundamental of chemical coagulation so the colloidal particles that are found in the wastewater, so they have got a negative charge on their surface and this negative charge basically leads to the repulsion of the different particles when they come closer to each other. So, this repelling force because of the electrical charge it dominates over the attractive body force particles they come near to each other so they may be repelled because the electrical charge which is present on the surface that is the negative charge whereas Van der Waal force which may be there if the particles they are coming close to each other so the Van der Waal force is not as high as the repelling force and because of which the particles they do not coalesce and these particles may not settle down and because of which they remain in the suspension and they keep moving in the suspension because of the Brownian motion. The Brownian motion refers to the constant thermal bombardment of the colloidal particle by the relatively smaller water molecules. So, the coagulation is the process in which we destabilize the colloidal particles because we know that when the particles, they are stabilized they are having the negatively charged on the surface so when they come closer to each other also then also they will not settle down, so they are more or less stabilized.

So, the coagulation process means that we want to destabilize this particle so that as soon as they come closer to each other then the Van der Waal forces they can act and the attraction can happen and because now the charge is not there so they will now coalesce and they will settle down that is the particle size will increase and because the increasing particle size these particles can settle down. So, coagulation is a very complex process, and it depends upon the characteristics of the water. So, the characteristics of the water may change with the season, it changes daily also right. So, it is necessary that we fix the dose of a coagulant that is needed so that we can achieve the maximum removal of these colloidal particles. So, the different type of coagulants or flocculants which are present so they may be the natural and synthetic organic polymers, they may be metals such as alum and ferric sulfate, they can be pre-hydrolyzed metal salts such as poly ammonium chloride or poly iron chlorides.

So, the fundamentals of the chemical coagulation so there are certain definitions that we need to understand. For example, the first is the coagulation that is coagulation is the process of the chemical destabilization of the particle and this can happen if we are adding a certain chemical to it so that the charge which is there on the particles so it can be neutralized and then the particles can be chemically destabilized. So, this process is known as coagulation. Similarly, the population refers to the process by which the particle size can increase as a result of the particle collision. So, flocculation means that is we are bringing these particles nearer to each other so that as soon as they are destabilized, they can come closer to each other and then the Van der Waal forces may play an important role and because of which the particles can coagulate, and these particles can settle down.

So, the flocculation means that is we are providing a mixing to the system so that these particles may come closer they can collide and then they can settle down. And similarly, the coagulant are the chemical salts which are added so that we can destabilize the colloidal particles. Flocculants are also the chemical polymers that can be added so that we can increase the floc formation. So, there can be different type of flocculation for example, we can have micro flocculation, we can have macroflocculation. Micro flocculation means that is particle aggregation may take place because of the thermal motion of the fluid molecules, and which is also known as the Brownian motion.

So, because of Brownian motion these particles may come closer to each other and then because as they are destabilized already so they can form floc. So, this process is called microflocculation. Whereas macro flocculation means the providing a mixing in the fluid or providing velocity gradient so that the particles may come closer to each other they come in contact with each other and then they can be flocculated, and they can settle out from the mixture. Macroflocculation can also be brought out by differential settling. For example, if we are having a bigger particle size and we are having smaller particles so bigger particles will settle fast whereas, the smaller particle will settle at a lower velocity.

So, these two particles when they come closer to each other during this settlement so they can coalesce and then they can form a bigger particle and then they can settle down at a higher velocity. So, this is also known as the macro flocculation, and this happens due to the differential settlement of these larger and the smaller particles. So, we can see here that a coagulant is added, and we know that the colloidal particles they are having negatively charged on their surface. So, the coagulant may be added which is positively charged and then this coagulant can neutralize the charges on the surface of the particles and as soon as these particles will come closer to each other they can form floc and similarly we can also add a polymeric flocculant which is nothing but a polymer. So, these polymers can also bind these particles together and then it can help in the formation of a bigger floc and then ultimately these flocs can settle down.

So, there are a number of important factors which influences the coagulation flocculation process. The coagulation flocculation process is used to aggregate the colloidal particles so that they can form bigger particles and then it will be easier for us to remove or separate out these particles from the liquid. So, there are a number of factors which can influence this process. For example, first is the particle size and the numbers of the colloidal particles. For example, the particle size of the colloidal particles it ranges from times of minus 3 micrometers to 1 micrometer.

So, these particle size it influences the properties as well as the behavior of the entire colloidal systems because we know that the smaller particle size, they are more stable, they are having higher charge and that's why they are resistant to coagulation and flocculation process because they are having a larger surface area also as well as the larger charge. So, this makes them more resistant towards the coagulation flocculation process. The larger particles they are likely to aggregate because they are having smaller charge and basically the large particles can also come closer to each other and then basically it will be easier for us to aggregate in comparison to the smaller colloidal particles. Similarly, the number of particles will also affect the coagulation flocculation process because as the number of particles will increase the chances to come closer to each other will be higher and in that case the process of coagulation and flocculation may be efficient, but if the number of particles they are smaller so then in that case the chances of coming closer to each other though they are destabilized then also it will be very very difficult for us to remove these particles by settling because they will not come closer to each other and they will not basically collies and they will not form flocs and that's why they will not settle down. So, they remain suspended in the solution for longer time.

So, that's why the smaller number of particles it adversely affects the coagulation flocculation process. So, particle shape and flexibility also impact the coagulation flocculation process. For example, we can have variety of shapes of the colloidal particles which depends upon their composition, which depends upon the manufacturing process, which depends upon the environmental conditions. So, we can have different type of shapes for example, we can have spherical shape, we can have semi-spherical shape, ellipsoids or rods or random coils. So, number of shapes basically can be there and these shapes of the particles it can have a significant impact on the behavior, the interactions and the applications and it will affect the electrical properties, the particle-to-particle interactions as well as the particle solvent interactions and ultimately it will impact the process of coagulation and flocculation.

So, that's why it is very important for us to analyze that what those of coagulant needs to be added so that we can effectively remove such type of particle. The nature of the colloidal particles is also important in the sense that the composition and nature of colloidal particles depends like the surface chemistry and the structure. So, it can also impact the coagulation flocculation process. So, understanding and controlling these factors will lead to the optimization of the coagulation process for various type of water as well as wastewater treatment as well as the industrial wastewater treatments. The particle charge is also an important factor because we know that the electrostatic charge which is present on the colloidal particles it plays a very significant role because the light particles which are having the similar charge.

So, they will be having a force of repulsion, and this will repel their aggregation, and the particles will not be able to coalesce, and they will not be able to remove from the system. And similarly, it is also very important to note that the charge utilization becomes very very necessary when we want to remove these particles which are having charge on their surface. So, the charge utilization can be achieved by adding a certain type of coagulant which can reduce the repulsion between the light charges which are there on the particles. Similarly, the pH of the solution can also affect the coagulation flocculation process

because the pH affects the charge on the colloidal particles. So, as the pH changes, so the charge on the particles may also change and there may be a certain pH at which the charge may become equal to 0.

So, there may be alternation of the charge depending upon the pH. So, it may be negative for some time and then at a certain pH the charge may become equal to 0 which is also called as point of 0 charge and after which the charge on the particle may be reversed. So, in that case it is very very important to find out that at what pH or at what specific pH ranges the maximum coagulation flocculation can take place, or the maximum neutralization of the particles can take place and then they can coagulate out from the wastewater or the water. Similarly, the ionic strength of the solution also plays a very important role because in the presence of the ions the solution can influence the stability of the colloidal particles. So, and we are having very high ionic strength, so it can shield the repulsive forces which are present, and this basically can promote the aggregation of the particles.

Similarly, the high ionic strength can also compress the double layer which is formed around the charged colloidal particles. So, the compression of the double layer may also lead to the coagulation of the particles and the particles may be removed from the system. For example, you must have seen that as the river meets the sea, so a story is formed, so there you will find that a number of particles they basically settle out because of the very high ionic strength of the sea when it merges with the river water which is having a very low ionic strength. So, in that case the compression of double layer takes place and a delta formation, or the estuary formation takes place because of the settlement of these particles which are charged in nature and because of the high ionic strength, so they settle out from the water. The temperature can also affect because the temperature impacts the kinetic energy of the particles.

So, it will increase the rate of the collisions and the interaction between the particles, and it will facilitate the coagulation process and then basically it will also enhance the coagulation flocculation of the particles. The concentration of the coagulant and flocculant also will decide the efficiency of the coagulation flocculation process because the coagulants are used so that we can utilize the surfaces and then the particles can come closer to each other, the particles have formed larger flocs and then they can settle down. So, it is very important to decide the dose that is how much dose of the coagulant or flocculant is needed, so that the efficient coagulation flocculation process can happen, and the particles can settle down and the stability of the solution can be reduced. For example, if we are adding a coagulant because the coagulant is neutralizing the charges which are there on the surface, suppose the particle is having a negative charge on the surface and we are using a coagulant which is having a positive charge. So, then it will utilize the negative charge on the particles up to a certain dose and after which it will reverse the charge which is there on the particles.

For example, when we are adding the positive charge, and a higher amount of positive charge may again induce the charge reversal on the particles and the particles may get converted to instead of the negative charge they may be converted to the positive charge. So, then again, they will be repelling each other because of the similar charge and that is why the coagulation flocculation process will fail. So, that is why its effectiveness depends

upon the specific characteristics of the colloidal system. So, the shear forces are also very important. For example, agitation or shear forces they can hinder the aggregation process.

So, it is very necessary that when we are going for the agitation or mixing we have to see that at what level of mixing is to be adopted so that the aggregation process may not be prevented by the particles because of the higher agitation or higher shear forces the particles may be again separated out or the flocs that is formed they may again be broken because of which the coagulation flocculation process may be hampered. So, we have to adjust the level of agitation so that we can get the highest efficiency of the coagulation flocculation process. So, the time of contact also is a very very important factor because if we allow the particles to have a sufficient contact time so that they can interact they can aggregate and then they can be removed from the system. So, it is very very important that the retention time to be decided beforehand before you go for the actual removal of these colloidal particles from the water wastewater solutions by conducting certain tests at the laboratory scale so that we can know that what should be the maximum amount of contact time that should be provided so that the efficient aggregation of these particles can take place. Similarly, the presence of other chemicals like the dissolved ions or organic matter so they also can interfere with the process of the coagulation flocculation they can enhance the process also whereas, some substances they can interfere with the process also.

For example, if we are having the higher concentration of the ions so it may increase the process of the coagulation flocculation whereas, some other materials where basically we are having the charge reversal is taking place or some other interactions are taking place so it may also interfere with the process of the coagulation flocculation. Similarly, the particle solvent interaction is also a very important process when we are talking of the coagulation flocculation process. So, here the interaction between the colloidal particles and the solvent it is very crucial, and it influences the stability and behavior of the colloidal system. So, we can have three type of particles which are found in the liquids depending upon the nature of the particle and solvent interaction. For example, we can have the hydrophobic or the water heating, we can have the hydrophilic particles which are water-loving and similarly we can have the association colloids and here the solvent is water so that is why we are using the term of hydrophobic and hydrophilic that is the water heating and water-loving colloids which are present in the water.

So, the first two types are based on the attraction of the particles surface for the water. For example, hydrophobic means it is basically having a lesser attraction, or it is having little attraction for the water whereas, the hydrophilic means it is having a greater attraction for the water molecules. Then the third type of colloids also known as the association colloids which is surface active agents like soap, detergent, dye stuffs and they form an organized aggregate which is also called the micelles, and these particles are also known as the amphiphilic colloids and because they possess two groups that is they possess the polar group also as well as the nonpolar group also. For example, the polar group is hydrophilic in nature and the nonpolar group is hydrophobic in nature. So, as the concentration of these particles that is these amphiphilic colloids it increases.

So, they form a micelle that is when the concentration increases above the critical micelle concentration. So, they may form such type of micelle structure where the head which is hydrophilic in nature. So, it basically is towards the water whereas, the tail which is having

hydrophobic characteristics. So, they aggregate together, and they form a micelle structure in the water. So, nature of these interactions is described in terms of the particle solvent interaction potential and the different type of interactions that are involved in the colloidal system they include first of all is the Van der Waal forces about if you are talking earlier also.

So, these Van der Waal forces they are weak attractive forces, and they may arise from the temporary fluctuation in the electron distribution around the particles. For example, if we are having two atoms here atom 1 and atom 2 when they come closer to each other. So, they may be polarized, and they may have attractive forces in between them and which are very weak attractive forces, and this is known as the Van der Waal forces. So, these forces they may contribute to the attraction between the colloidal particles and the surrounding solvent also and they may basically lead to the aggregation of these particles and these forces may become very prominent as the distance decreases between the two particles. Similarly, we can have electrostatic interactions where we can have the electrical charge on the surface of the particles and because of this electrical charge if the charges are similar.

So, they can be repulsive whereas, the charges are different. So, there can be attractive force between these two particles. So, the particles repel when basically they are brought closer to each other right when they are having the similar charges whereas, they will attract each other when they are having the different charges and this will also determine the stability of the colloidal system because if the particles they are having the different charges then it is easier for us to coalesce the system whereas, if the particles they are having same charges. So, then it is very difficult for us to coagulate and coagulate these particles together. So, the forces between these two particles can be determined by using the electrostatic force equation and this electrostatic force equation says that the charges on the particle that is Q1 and Q2 divided by the square of the distance between these two particles and into the coulombs constant or the electrostatic constant.

So, it is equal to the force between these two particles. So, that is how the electrostatic force can be calculated when there are electrostatic interactions between the particles. Similarly, there can be hydration forces that is the water it may form a structure layer around the colloidal particles, and this may also lead to the hydration forces and these hydration forces also play a very important role in the particle solvent interactions. Similarly, we can have steric stabilization where a layer of the adsorbed molecules such as polymers or suspectants. So, they may create a barrier that may prevent the aggregation of the colloidal particles together.

So, the steric hindrance may also help in maintaining the stability by resisting the attractive forces, but it may also reduce the efficiency of the coagulation population processes. Similarly, solvent structure also plays a very very important role where the structure and properties of solvent it can also impact the colloidal stability. For example, the dielectric constant of the solvent as well as it affects the electrostatic interactions between the particles and the viscosity of the solvent can also influence the rate of the particle motion and collision and it will also hamper the movement of the particles if the viscosity of the solvent is high. Similarly, there can be other specific interactions for example, we can have hydrogen bonding or chemical bonding. So, they can occur between the colloidal particles and certain solvents.

So, they also can be lead to the decline in the efficiency of the coagulation population because these interactions are much much stronger, they are higher than the Van der Waal forces that we have discussed just now, and they can significantly influence the stability and behavior of the colloidal system. So, understanding and controlling these particle solvent interactions, so they are very very necessary so that we can manipulate the stability of the colloidal dispersion. For example, suppose we are working on the drug delivery, or we are going for the nanoparticle synthesis. So, in that case it is very very important for us to choose appropriate solvent so that desired colloidal stability can be achieved, and we can have a stable suspension made out of it. For example, suppose we are manufacturing the nanoparticles and let's say the nanoparticles are made up of iron.

So, in that case if we are not choosing a proper solvent in that case the particles may coalesce, they may condense with each other because of the magnetic forces which are there, and this may result in the increase in the size and the particles may not no longer be the nano size. So, that's why it is very very important to find an appropriate solvent so that we can disperse the particles depending on their applications. Similarly, the knowledge of the colloid and interface science is also very very important so that we can design and optimize the colloidal system for specific applications. So, now development and measurement of surface charge is also important in the coagulation and population process. For example, the surface charge is developed in different ways depending upon the chemical composition of the medium and the nature of the colloids.

For example, the surface charge development can be because of different factors and for example, we can have isomorphous replacement, we can have structural imperfections, we can have preferential adsorptions, we can have ionizations. Surface charges are needed to be overcome if these particles need to be aggregated and settle down. So, we need to find out the factors which are responsible for the surface charge development. For example, isomorphous replacement means that the ions which are present in the lattice structure of the particles for example, when we talk of the clay or the soil particles. So, these ions which are present in the in their lattice structure, so they may be replaced with the ions from the solution.

So, that is called the isomorphous replacement. Whereas the structural imperfections also can lead to the charge development. For example, when we are having broken bonds on the crystal edge or when we are having imperfections on the formation of the crystal. So, it can also lead to the charge development on the particles. For example, when we talk of the clay particles or similar type of particles, so structural imperfections can also lead to the charge development. We can have preferential adsorption also which can lead to the charge development.

For example, the ions from the surrounding solution they can adsorb onto the surface of the colloidal particles, and this may result in the electrical double layer formation where the outer layers of the ions they carried a charge which is opposite to the that of the particle charge. So, it basically creates surface charge on the particles. For example, when we talk of the oil droplets or gas bubbles or any other chemical inert substances which are dispersed in water, so they may have a negative charge which can be developed because of the preferential adsorption of the anions which are present in the solution or in the water.

Similarly, ionization can also lead to the charge development. For example, many colloidal particles they may possess a certain functional group which can ionize in the solution.

For example, we can have hydroxyl ions, hydroxyl groups, we can have amino groups, or we can have carboxyl groups, so they may undergo ionization as they go into the solvent, and this may lead to the development of charge on the particle surfaces. For example, when we talk of proteins or microorganisms, so they may acquire the charge through the ionization of the carboxyl and amino groups. That is how the charge development takes place on the surface of the colloidal particles and that is why it is very important for us to analyze that how the charge development is taking place, what type of charges are there on the particles and what type of coagulant or flocculant we need to add, so that we can destabilize the particles and these particles can ultimately be removed from the system. These are the references that we have used during the preparation of this lecture, and we stop here, and we will talk about the coagulation flocculation process in detail in the coming lecture.

Thank you.