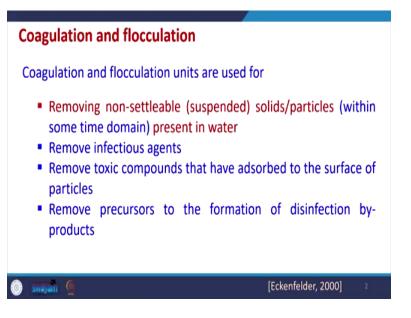
Physico-Chemical Processes for Wastewater Treatment Professor V. C. Srivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture - 18 Coagulation and Flocculation - I

Good day everyone and welcome to this lecture again on treatment of wastewater and water and in the previous lectures we studied regarding the characterization of water and wastewater and thereafter we started the treatment of how the treatment of water and wastewater is done for various uses.

Now, within those there are a number of operations which can be performed. So, we studied in detail like flow equalisation in detail, thereafter, we studied aeration in detail up till previous lecture. Now, in the aeration we try to remove the various gases which are dissolved in the water and as well as during that process some amount of organic degradation may also happen.

Thereafter, removal of gases there is always our desirability is to remove all the suspended and some amount of dissolved materials which are there in the water and which can be removed very easily. So, one of the easiest method is the coagulation method. So, coagulation and flocculation they are combined together they are taken as a unit and this whole process is done so, as to remove most of the settleable, non-settleable solid which cannot settle by itself within certain time domain.

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So, coagulation and flocculation is the unit operation that we are going to study in detail now, with respect to water or wastewater treatment. So, this coagulation is a very generic term and we come across this term many times during various household activities also like coagulation, blood coagulation, whenever we are shaving and there is a cut.

So, we use alum commonly known as phitkari in our language. So, that is used and through that we actually coagulate the blood on the chin or the skin and then further the blood is not coming out of their skin. So, that is blood coagulation. Similarly, there can be other types of coagulation also here in this particular lecture we are studying regarding the chemical coagulation we are adding some chemicals and which are causing something so, that the unsettleable solids which are there or suspended solids dust particles which are there present in the water or wastewater they can settle down. So, this is the coagulation but here we add some chemicals from outside and then we perform this operation.

So, that we can remove all the most of the suspended solids which cannot settle by themselves within certain time domain. So, that is there besides chemical coagulation, many wastewater, in particular industrial wastewaters can be treated by thermal coagulation methods also. So, thermal coagulation methods in this we heat the water up to a certain temperature and during that process, the suspended materials actually they form bigger flocs and they settle down.

So, many of the suspended materials which otherwise do not settle down, they get settled down at higher temperature. So, thermal coagulation is also possible, but we will be discussing more about chemical coagulation. Now, using adding some coagulants or chemicals from outside. So that we can settle down all the suspended solids or particle very quickly.

So, this is the desirability. Now, during this settling because these suspended particles may contain some infectious agents et cetera, some toxic compounds, which may have got a job onto the surface of particles. So, all these materials also settle down. So, they are also getting removed.

Also they can many times that disinfectant by products will study disinfection later on so there is a formation of disinfection by products. So, all those colloidal materials or smaller molecules may also get removed by a various mechanism which happens during the process of coagulation. So, we are going to study in detail all these aspects. (Refer Slide Time: 05:27)

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Coagulation During coagulation, chemicals/coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on non-settleable solids (such as clay and color-producing organic substances). Once the charge is neutralized, the small suspended particles are capable of sticking together. Rapid-mixing is done to properly disperse coagulant and promote collisions among coagulants and suspended particles to achieve good coagulation. Over-mixing does not affect coagulation, but insufficient mixing will leave this step incomplete.

So, starting with like coagulation, during coagulation, what we do is that we add some chemicals and coagulants from outside and these chemicals have generally we select these chemicals in such a manner that they have charged opposite to those of suspended solids. And because of the addition of these charges, the non-settleable solid, the suspended solids they are generally they are negative charge.

[Eckenfelder, 2000]

So, that negative charge is neutralised by these chemicals which are added and because of that, they can come together once the charges are neutralised the suspended particles are able to stick together we certainly use some, provide some force initially some energy to them so that they start moving and sticking to each other.

And for this during the coagulation what we do is that as soon as we add any chemical or coagulant depending upon the, their solubility product et cetera they may get ionised into respective ionic forms and those ionic forms for mixing ionising first they should ionise and then they should also mix with all the material inside the water all the particles inside the water.

So, for doing this, we use coagulants rapid mixing, so that everything gets mixed and the charge neutralisation is very quick. Over mixing may not affect the coagulation, but over dosing certainly affects the coagulation processes so that we will discuss in later on. Insufficient mixing will leave the step incomplete. So, charge neutralisation or other mechanisms, which may work during the coagulation process may not work properly and they may not act well. So, overall the

process may get hampered because of this. So, we have to see that the mixing is very well during the coagulation process or initial mixing of coagulants inside the water.

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Flocculation A gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. Microfloc particles collide, causing them to bond to produce larger, visible flocs. Floc size continues to build with additional collisions and interaction with added coagulant. Once floc has reached it optimum size and strength, water is ready for sedimentation.

Now flocculation is after very quick mixing within a 1 minute or so. We have a gentle mixing stage and at this stage is called as flocculation and inside within this stage, the particle size of the micro flocs which get formed that increases and they the size becomes greater and this micro flocs become colloids and those colloids actually they bond to produce larger and visible flocs.

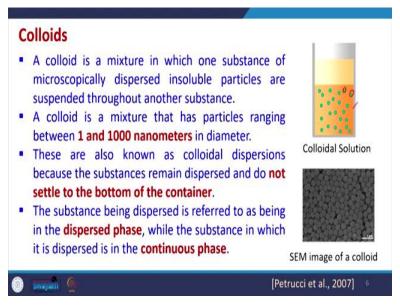
So, floc size continues to build up with additional collisions and interaction. But in this case, the mixing is not very quick here very gentle mixing is done. So, that the flocs, bigger size flocs which have formed they may not break again and form smaller size floc. So, the gentle mixing is very important.

And once the floc has reached its optimum size and strength, so it will settle down because of the increase in the size. So, this is called flocculation. So, before starting the coagulation and flocculation learning about different types of coagulants, flocculants and how to perform some design calculations or basic calculations.

We will first study regarding the basics of coagulation or colloids in general. So, that is very important we should have understanding of colloids which are there why they are not settling down and what are the properties that are important to understand the nature of the colloids

before actually adding the chemical coagulant from outside. So, this is very very important aspect and that we are going to study in detail.

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So, colloid in general is a mixture in which one substance is dispersed and an insoluble particles are suspended throughout another substance. So, here we can see the these particles small sized particles are suspended and they are not settling down. And this is because their size is also very small.

So, colloid is a mixture that has a particle size ranging from 1 to 1000 nanometres in diameter. So, they have very small size and in they will take lot of time to settle down and if we want to target removal of these without adding any coagulants et cetera. So, the size of the overall unit will become very large until unless we use some chemical coagulants from outside to settle these colloidal particles.

So, this because of this we add some chemical coagulants from outside. Now, there are different types of dispersed and continuous phase. So, basic definition is that the substance which is dispersed is referred to as dispersed phase. So, like for our case pollutants will be the dispersed phase and the substance in which it is dispersed it is the continuous phase.

So, generally we will be having the aqueous phase as the continuous phase. So, for wastewater treatment the pollutants and other suspended particles are dispersed phase and the continuous

phase is the water and we need to settle these dispersed phase at the bottom of the system. So, this is what is that desirability.

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Classification of Colloids	
 Sol is a colloidal suspension with solid particles in a liq Emulsion is between two liquids. Foam is formed when many gas particles are trapped in liquid or solid. Aerosol contains small particles of liquid or solid dispension a gas. 	in a
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Now, the colloids can be classified into various categories like sol, emulsion, foam, aerosol et cetera and these collides are not only used in wastewater treatment, they have a lot of uses in petrochemicals, petroleum refining many other places pharmaceutical et cetera. So, they are classified into 4 broad categories to sol is like a colloidal suspension with a solid particles in a liquid. Emulsion is like a collide between two liquids, then foam is formed when many gas particles are trapped in a liquid or is solid. So, we get foam gets formed and aerosols they contain small particles of liquid or solid disperse in a gas. So, that will be called as aerosol. So, there are different types of colloids which are possible.

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Dispersion Medium	Dispersed Phase	Type of Colloid	Example
Solid	Solid	Solid sol	Ruby glass
Solid	Liquid	Solid emulsion/gel	Pearl, cheese
Solid	Gas	Solid foam	Lava, pumice
Liquid	Solid	Sol	Paints, cell fluids
Liquid	Liquid	Emulsion	Milk, oil in water
Liquid	Gas	Foam	Soap suds, whipped cream
Gas	Solid	Aerosol	Smoke
Gas	Liquid	Aerosol	Fog, mist

Some examples of collides with different dispersion medium and dispersed phase are given here and their name is also given like if solid is dispersed in solid as a dispersed phase also then, it is called a solid sol and the ruby glass will be classes like example. So, there are many possibilities. Similarly, solid disperse in a liquid so we have solid emulsion solid liquid dispersed in a gas so, we have solid foam. So, there are examples which are given also similarly liquid dispersed in a solid it is a sol. So, like paints cells, cell fluid et cetera.

Then liquid in a liquid, so, it is called emulsion. So, milk or oil water. So, this is there. Similarly, liquid in a gas again foam and gas in solid is aerosol a gas in a liquid is again aerosol, but we are more interested in solid in liquid. So, that means we have suspended particles which are dispersed in a liquid phase. So, this is what will be generally discussing more.

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Colloidal particles
 Colloidal particles are in the size range between dissolved
substances and suspended particles.
 Colloidal particles can be removed from the liquid by physical
means:
 High-force centrifugation
 Through filters ✓
 Colloidal particles are too small to be removed by
sedimentation or by sand filtration processes.
The object of coagulation (and subsequently flocculation) is to
turn the small particles into larger particles called flocs, either
as precipitates or suspended particles.
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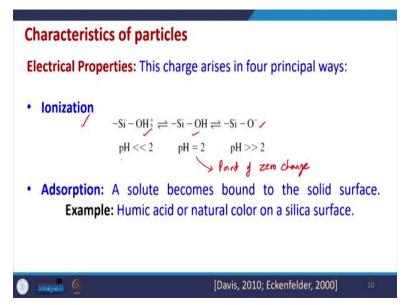
Now, colloidal particles they have various size ranges and because of small size range, generally they cannot get settled down and they are dissolved and suspended. So, we want to remove these suspended particles during the wastewater treatment or water treatment. Now, they can be removed by physical means also.

So, one of the means is high force centrifugation. So, we can remove some sections of colloidal particles using filters also we can use, but remember in the wastewater treatment because we are at the primary treatment stage so amount of suspended particles which are there are very very large and also the amount of water generated is also very large.

So, centrifugation if we use we will be using very high energy and that will not be good. So, centrifugation is ruled out for a very high amount of water containing high amount of suspended materials. Similarly, if we use filter or any of the filtration mechanism, so, filter will get clogged easily because we have large amount of suspended particles which are there. So, these processes these physical measures may not be that much helpful.

So, what we do is that we start adding chemical from outside. So, colloidal particles are too small to be removed by sedimentation or by sand filtration processes alone and sedimentation many of these the sedimentation unit will be very very large in size if we start using the try to settle down the colloidal particles within a sedimentation unit. So, the objective of the coagulation and flocculation which is just followed after coagulation is to turn the smaller particles into larger particles which are called as flocs either as precipitate or suspended particles and then they can be removed. So, this is what is desirable.

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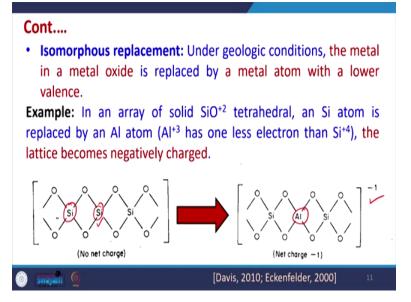


Now, there are certain characteristics of particles that we must study and one of the first characteristic is the electrical properties which are there inside any colloids or colloidal particles which are not getting settled down. So, they always they may contain charge and which may arise because of four principal ways one of them is ionisation.

So, depending upon the pH, the same silica particle is we can see the negative form, positive form and neutral form. So, this we are going to discuss at what pH range. So, this is in general referred to as point of zero charge. So, this is called as point of zero charge. The pH at which any colloids or any particle has zero charge it in either negatively charged it is positive, neither positively charged.

So, this is we are going to study in detail how this is determined, but before that we must study other properties also. So, depending upon the pH, the particles may get ionised into different forms. So, this is one thing. So, ionisation is one of the basic thing. Second, these particles may acquire charge because of getting bounded with some solid surfaces also. So, they may have some electrical properties. So, like a solute becomes bound to the solid surface the example is Humic acid or natural colour on a silica surface. So, because of that adaption may happen and they may impart some charge may arise on the particle itself.

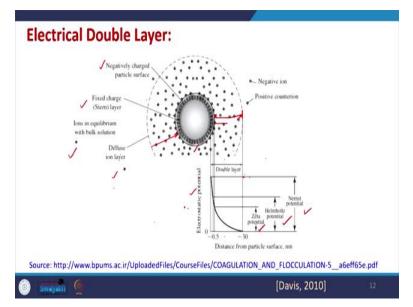
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Now, then we have isomorphous replacement. So, in this condition like example is given for metal oxide. So, any metal oxide within a metal oxide its metal may get replaced by another metal atom and which may have a different vacancy. So, if it has it is having a lower vacancy, then it is going to impart in negative charge on the overall metal oxide.

So, example is given here in an array of solid silica tetrahedral this is an Si atom actually is replaced here we can see Si atom is being replaced by Al aluminium atom. Now, because of this, the lattice becomes negatively charged. So, that, we are told that these suspended particles they are not able to settle down because generally they have negative charge while they are present in the water, and since they have negative charge, different colloidal particles cannot come together because they will electrically repel each other electrostatically and thus, they cannot come together and form bigger flocks.

So, we want to neutralise these charges which are there if we can neutralize these charge and if we can impart certain amount of force and that force should be good enough to overcome the Van der Waals force. So, if they can come together as a Van der Waals force of attraction may come into picture and they may form bigger flocks. So, this is one of the these are the mechanisms by which these any other collides may acquire charges on them. (Refer Slide Time: 19:43)



Then there is a concept of electrical double layer. So, this we are, little bit we will discuss this. So, any collateral particle when present in a aqueous solution or otherwise. Generally it will have some charge. So, it may be having a negative charge so negative charged particle surface is there. Since negative charge particle surfaces there, it will be bounded by positive ions. So, that is called a stern layer and it is bounded by positive ions all throughout.

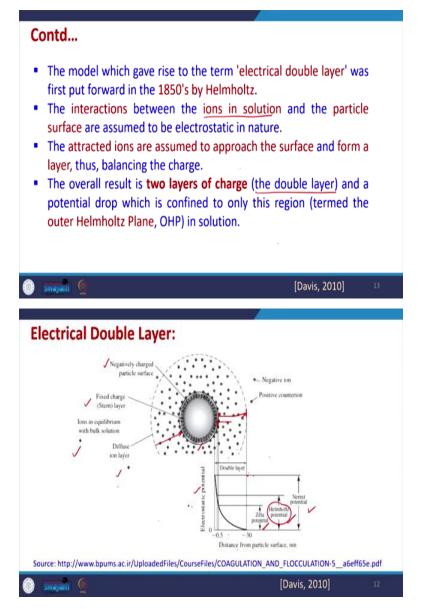
So, that the overall charge is negative. Now, stern layer will be there and from external layer since, there are ions present in the bulk of solutions, so, because of the negatively charged ions, negative nature of the collides, these ions positively charged will diffuse to the they will try to diffuse to the surface of the collide.

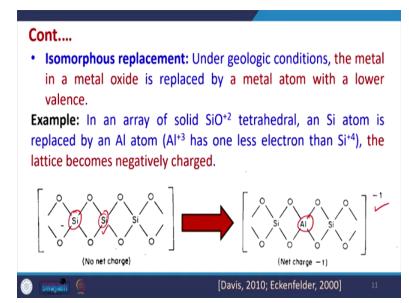
And because of that, they will be having a layer will be created where both negative and positive charge will be there and that layer is called the like double layer. So, it generally will move along with the collide itself. Now, there are different types of potentials, which are listed or which for which the theories have been given and these potentials are called Nernst potential, Helmholtz potential and Zeta potential and also the distance from the particle surface up to the electric double layer is given.

So, we can see up to 30 nanometre, up to 30 nanometre also there is a possibility of electric double layer. So, collide will move along with this layer. So, this is there. Now, we will try to have an idea regarding Nernst potential, Helmholtz potential and Zeta potential out of this the

Zeta potential is most important and in the in the coagulation we always try to see that the thickness of electric double layer it gets reduced, we want to reduce this electric double layer. So, the compression of double layer is one of the important mechanisms we use for performing the coagulation. So, this happens during the coagulation.

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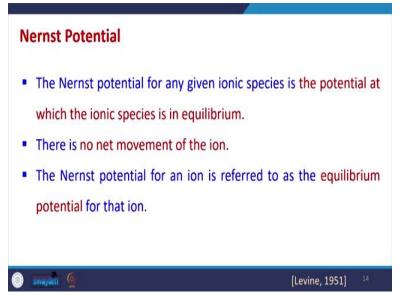




So, we will go ahead with the model for the electric double layer was given by Helmholtz. Different types of theories have been given out thereafter by different scientists, we are not going to study those in detail if you want to study that it will take, you can refer to many books and articles for studying different theories related to electrical double layer. But some basic idea only will be discussed.

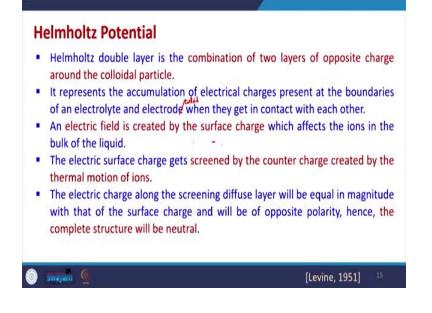
So, the interaction between the ions in the solution there will be ions always some ions present in the solution and the particle surface is assumed to be electrostatic in nature and this happens because the particle has a charge and the ions present in the solution may also have a opposite charge. So, electrostatic opposite or same charge. So, depending upon that, electrostatic interaction may happen. Now, the positively charged ions suppose the surface, collide surfaces negatively charged. So, they are the positively charged ions which are attracted will always approach towards the surface and form a layer and this, through this they will balance the charge which is there.

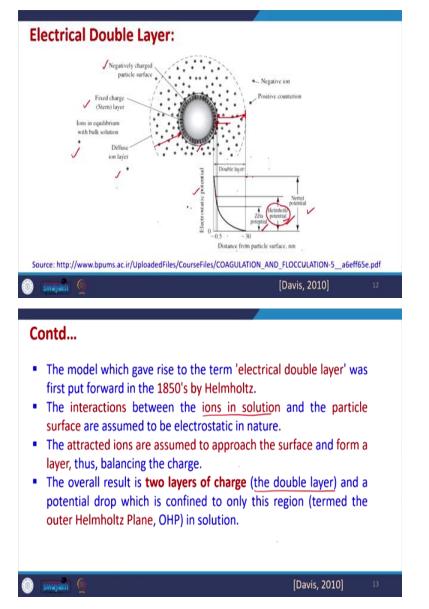
So, the overall result because of this moment of the opposite charge towards the surface is that we have two layers of charge the double layers and the potential drop which happens because of this, that electrical double layer and that potential is called as Helmholtz that potential is counted from the outer Helmholtz plane in the solution. So, we have outer Helmholtz plane. So, this is the plane which is bounded and from this measure this potential which is called as Helmholtz potential. So, this is there, we will discuss this little bit more. (Refer Slide Time: 24:19)



Now, one of the first potential which is discussed here is Nernst potential. So Nernst potential is very common, it is the potential at which ionic species in the solution are in equilibrium. So, and because of since they are in equilibrium that means, there is no net movement of the ion and this particular potential is called equilibrium potential the Nernst potential.

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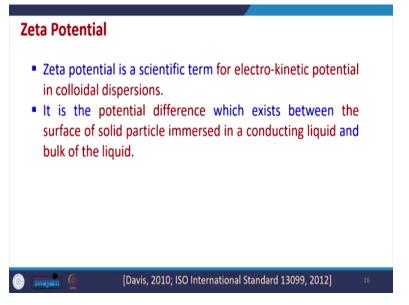


Then we have Helmholtz potential. Helmholtz double layer is the combination of two layers of opposite charges around the colloidal particles. And they represent actually the accumulation of electric charge at the boundary of electrolyte and the collide when they are getting in contact so, they are always in contact.

So, this is at the boundary and an electric field is created by the surface charge which affects the ions in the bulk of the liquids and that this electric field and corresponding potential is with respect to it is called as Helmholtz potential, the and this electric surface charge further gets screened by the counter charge created by the motion of the ions.

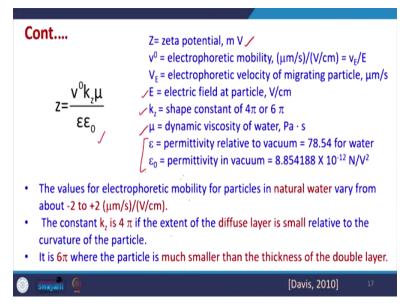
So, that motion maybe thermal motion or diffuse any of the different motions are possible. So, that is there and this electric charge along with the screening diffused layer there generally there will always be equal in magnitude, so, that the complete structure in neutral. So, we measure the Helmholtz potential from this point where the bounded positive charge is over and up to the distance where up to the bulk of the solution. So, this this potential is called Helmholtz potential. So, this is there and we want to measure this actually the measurement of Helmholtz potential is a little difficult.

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So, as compared to that, we generally measure the Zeta potential. So, it is a scientific term for electro kinetic potential in the colloidal dispersions. So, we always measure Zeta potential and Zeta potential gives lot of idea regarding the stability of the colloidal particles within the dispersed medium et cetera. So, potential, it is a potential difference which exists between the surface of the solid particles immersed in a conductive liquid and the bulk of the liquid and Zeta potential gives lots of idea regarding the stability of the solution as well.

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Zeta potential could be calculated as follows:

$$z = \frac{v^0 k_z \mu}{\epsilon \epsilon_0}$$

Z= zeta potential, m V

 v^0 = electrophoretic mobility, (μ m/s)/(V/cm) = v_E/E

 V_E = electrophoretic velocity of migrating particle, μ m/s

E = electric field at particle, V/cm

 k_z = shape constant of 4π or 6π

 μ = dynamic viscosity of water, Pa · s

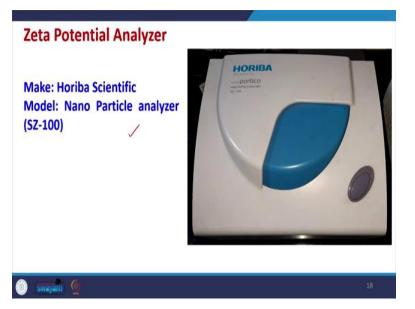
 ε = permittivity relative to vacuum = 78.54 for water

 ε_0 = permittivity in vacuum = 8.854188 X 10⁻¹² N/V²

So, Zeta potential in general can be measured using this equation and it is measured in millivolts. And we have what we do is that we can use different types of instruments for measurement of Zeta potential et cetera and this overall term can be equation can be used for finding out Zeta potential there are certain variables in this.

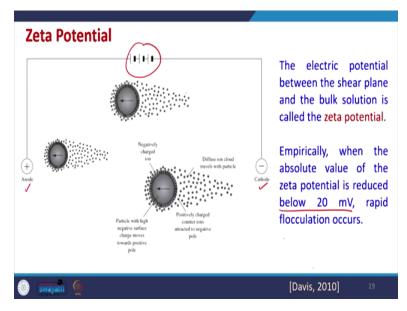
So, what is the electric field applied across which the movement of the particles we are trying to check also what is the viscosity of water and these things are constant and then a safe factor whether the most of the particles are spherical or otherwise. So, that is also taken, so, the we measured the electrophoretic mobility of the particles in natural water by implying some electric field and that movement is measured and through that, we try to measure the Zeta potential. So, different equipment's can also be used for measurement of Zeta potential.

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One of the instrument is like this one. So, this is the example for Horiba scientific and we have a Nano particle analyser it can measure the Zeta potential up to a certain range.

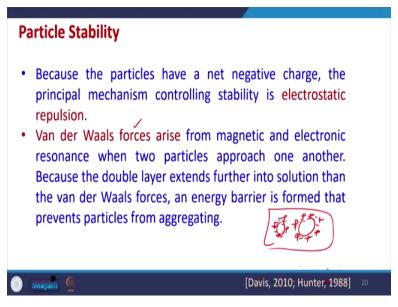
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Now, what we have is that, we have two electrodes one cathode, one anode, and across that some electric field is applied, and we try to see that what is the movement of the colloidal particle. So, this we measure. So, empirically the absolute value of Zeta potential is for the flocculation, coagulation we try to see that the Zeta potential is reduced to 20 millivolt.

So, if this is within this range, the stability is reduced and we can use other types of chemicals and other things to destabilise the particle and thus we can remove them. So, and before that, we can measure the Zeta potential using Zeta potential analyser, there are many other techniques as well.

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So, partial stability always related to Zeta potential and the particle stability is there because they always have a negative charge. So, we want to see that what is the amount of the negative charge. So, that can be measured. So, principal mechanism controlling the stability is electrostatic repulsion.

So, all the colloidal particles so, like suppose this is the colloidal particle and they have negative charge and there is a second colloidal particle which is having a negative to charge. So, they cannot come together because they are repelling each other. And, if, however, if we can use some additional coagulants and which have positive charge and they can neutralise these particles, there is a possibility that they can come together and form a bigger floc and which may settle down. So, this is there.

Also Van der Waals forces arise from magnetic and electronic resonance when two particles approach one another. So, we want this Van der Waals force of attraction to be dominant or the repulsion. So, if the this can be done, we can always form bigger flocs and we can the particles stability particle can be destabilized, and they will form bigger flocs and they can settle down. So, this is what is the target.

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	bid depending on zeta potential	
Zeta potential (mV)	Stability behavior	
0 to ±5	Rapid coagulation or flocculation	
±10 to ±30	Incipient instability	
±30 to ±40 🗸	Moderate stability	
±40 to ±60	Good stability 🦯	Ř
>61	Excellent stability	

Now, with respect to Zeta potential, we have lots of ideas we can get like if Zeta potential is in the range of 0 to plus minus 5. So, we can use the rapid coagulation and flocculation techniques from plus minus 10 to plus minus 30 instability is there. Then it can also be managed from plus minus 30 to plus minus 40 it is moderate stability. Then very good stability if plus minus 40 to plus minus 60 and greater than 60 it is excellent stability. So, it will be very difficult to break those collides. So, this is there.

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These are the various references that we have used in this slide. And we will be using them in other future coagulation related lectures also. So, thank you very much and we will continue with the basics of this colloidal particles in the next lecture. And we will further try to understand that what are the different other important properties that must be known.

And one of them is like point of zero charge, which is very, very important the pH at which the colloidal particles may have naturally zero charge. So, this is possible also the colli, the coagulant that we add when they have the zero charge. So, all these aspects are very important in coagulation and flocculation and later on, in absorption also they have some important. So, this is it will end today's lecture, and we will continue in the next lecture. Thank you.