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Lecture - 34 Physico-Chemical Treatment

Hello everyone, welcome back to the latest lecture session. In the last session, we started discussing about how to remove the suspended solids that are in water. And we are primarily concerned with those suspended solids which take too long to settle down. And then we looked at why these that are brief looked at why it is that these particles do not come together why is this system so stable? And let me just look at that and we will go through.

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So, we were looking at it in the context of water treatment. And after course screen, I am looking at suspended solids. Yes. And, particles have an electrical charge, yes, typically, it is negative, we looked at the relevant reason, isomorphic substitution, natural organic matter being adsorbed onto the relevant particle. And moreover, depending on the pH of solution will typically be negatively charged.

So, the particle will also have negative charge yes. And now these negatively charged, , colloids. They will not come together. Why is it? You have this net negative charge here, net negative charge here, so, these 2 particles will not come towards each other or cannot rather because when they come towards each other, we see that that is going to be ultra static repulsion.

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In that context, we came across one aspect that is relevant. Electrical double layer and this stands from the fact that the particles have a negative charge. And we already looked at this, let me go to the figure. So, 2 layers, one is the adsorb layer, which is also called the stern layer, and it is of relatively less thickness that is one aspect and after this fixed layer or the stern layer, you have a diffuse layer, which forms beyond this fixed layer.

And in this diffuse layer 2, diffuse layer will have a net negative charge that is one aspect and more importantly, you can see that its thickness if I can say so, is relatively much higher compared to the thickness of the first layer. So, this is the electrical double layer.

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Let us look at that in the picture. Please note that the reference in this slide is slightly different than what we looked at earlier, but the picture is more or less the same. Why I chose? This is here we have some sense of the particle or the distance from the surface here. So, here we have the negatively charged particle, you can see the negative charge u and because of that the positively charged counter ions in the solution the cations are going to be what we say, pull towards this particular particle.

And that we are calling that as the fixed layer. Or some people even call that the handholds layer, but typically fixed layer or stern layer. But please note that the thickness is pretty less. And then you have shear, zone if I may say so. And then you have this diffuse layer. Yes. And this has a net negative charge. And that is why, the counter ions which are the cations will be pulled towards this particular zone.

Yes, you will also have some, negative charge but in general, because of the net negative charge, the cations will be pulled or the counter ions which are the cations will be pulled towards it. So, and this is what we have. And we see that for this particular layer, , from the shear plane, we see that it is called what we say, the potential is called zeta potential.

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And how can you measure this? Fine. We will not go into this in detail talk, but you are going to apply a potential and then look at the potential in the shear plane and then this context or from this, we will be able to get this zeta potential, this zeta potential, which is mentioned out here. And why is the zeta potential important? Because typically it is , around 80 millivolts and for this particular case, let me try to draw it here.

So, what happens when 2 particles try to come near each other? Or what are the relevant aspects? We know that this is the case and this x axis is the distance. This is the distance and my negatively charged particle is here. this is zero distance. And as the other particle which is also negatively charged, tries to come towards this edge is going to experience a

electrostatic force what we say, force of repulsion and repulsion, we are going to plot it in this location repulsion .

As you see, as it comes closer, it does increase, but maybe I should not have drawn it so, close to this particular, distance out here. We will look at the figure later. We have a better figure but for understanding we look at it now. So, maybe this is what it looks like. And this is due to the ultra static force of repulsion. What else will come into the picture?

As you come much nearer though much, much closer, you are going to have van der Waals forces of attraction. It is like this . As you can see, with distance it increases a lot. So, this is attraction van der Waals forces of attraction. And here we have repulsion due to the electrostatic forces , same charge, negative charge. And this is what the particle will encounter as the particle moves towards this negatively charged particle and the particle moving towards the negatively charged particle.

So, what does the net look like? What does the net look like? The net will look something like this. So, initially this as it comes in then a maximum of repulsion and then attraction. So, as you can see, as the particle moves towards the or one particle moves towards another negatively charged particle, what does it experience? It experiences a peak of repulsion .

Net of these 2 repulsion and attraction, this is what we see this peak. But after that, , we see that attraction r net is attraction, so it pulls the particles together. But how do I see to it that? The particles can come close enough so that the r net is attraction. Why is that important? If not, when the particles come closer together, you have this peak out here. So, the particles cannot over come this force of ultra static or r net repulsion that is.

So, how do we go about getting that done? In general, I maybe I might have mentioned this in my previous session too. We look at or we talk about charge neutralisation that is a general term. So, let us look at what are the aspects involved here. So, here different ways to go about it, but one aspect is, we look at this particular aspect distance from particle surface A, I mean in Armstrong units, and another way to measure the distance.

So, here if I decrease this double layer or the double layer thickness such that this by that increasing the ionic strength typically by increasing the ionic strength of the water, then I can

see to it that , the particles can come close enough without being overwhelmed by that peak of repulsion, they will come close enough and then the van der Waals forces of attraction will take over and the particles will come together.

Now, these 2 smaller particles which I find difficult to settle, will now form a bigger particle form flocs or colloids, 2 colloids come together, many more come together flocs and heavier bigger particle I will be able to settle them down. So, here we are talking about increasing the ionic strength such that this electrical double layer the thickness decreases. So, that is the issue.

So, for example, after adding , the relevant ions maybe the r net, I am talking about r net might be something like this. Why is that? Because the electrostatic forces of repulsion compared to the previous one if I can get this, maybe they are relatively lesser because of the higher ion extract but the van der Waals forces will still be the same.

So, now as you see in the second case, where we have the, let me draw this. So, this is the attraction, this is the repulsion after adding the, what we say, the relevant coagulant such that the ionic strength increases high ionic strength, high ionic strength and low or usual ionic strength . So, here I decrease the, , electrical double layer thickness, everything and seeing to it that r net profile changes from this to this. So, that is what we have seen.

Let us move on and zeta potential, yes. And one aspect to look at is that the zeta potential effects 80 millivolts. It is difficult for the particles. Typically, it is around that but if it is less than 20 millivolts that is when you can have or you will have correlation or will that is when you will be able to destabilise a stable solution such that the particles can come together that is something to keep in mind. And how do we measure zeta potential that is already discussed in the last class.

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Particle stability

- Particles in natural waters remain stable when there is a balance between the electrostatic force of the charged particles and attractive forces known as van der Waals forces
- The particles have a net negative charge, the principal mechanism controlling stability is electrostatic repulsion

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So let us move on. So, this is what we have. So, this is my particle and this particle is coming towards this side. So, initially, I have this repulsion force and where is my attraction here and this is my attraction. As it comes in the r net is going to be something like this repulsion is net. And now the particle cannot cross this barrier. So, it will not come together, but after adding a coagulant such that the ionic strength (10:43) is high and the electrical double layer is relatively less.

Now, what is the profile here? The profile for the repulsion curve or electrostatic repulsion is this and now r net is here. So, as the particle comes towards the other particle, you see that it does not undergo any net repulsion or there is no net repulsion here. And as it comes nearer, there is more and more attraction and then , much more attraction so, the particles come together and stay together. So, that is the aspect that we are trying to promote.

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So, we already looked at this removal process. Overall, what am I trying to do in correlation, no need to mock up definitions, there will be different people with different versions of their definitions. Here in correlation, we are talking about the working definition, we are going to add chemicals or coagulants to the relevant particles, so that I neutralise the charge or decrease the thickness of the electrical double layer by increasing the ionic strength, so that the particle or the system is now unstable and can initially colloids.

And flocculation the process of aggregation of the destabilise particles as a now these particles are not stable, they are relatively unstable. And they can come together and form flocs and that is what we have or we call as flocculation. Here, we are destabilising the particles. Here, we are seeing to it that we are talking about the particles coming together and forming flocs.



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And another thing is if it has a high charge density, as we were talking about a particle here that is negatively charged and thus, it pulls these ions together. So, for the double layer thickness to decrease, I can add , anions or cations pardon me, such that the ionic strength will be high and electrical double layer will decrease, but if I have add mono-valent Na⁺ or NaCl which is Na⁺ and Cl⁻.

I will have to add a lot of it to be able to achieve that ionic strength, ionic strength is typically $0.5 \times Z^2$. Z is the charge on that particular what we say particle or such , Na⁺. There is some other variable here too, but as you can see, at least one relevant aspect is equal to is going to be depend upon the charge. So, , you are going to have the stoichiometry, not stoichiometry concentration of the relevant compound to which I am not writing here.

But in general, we certainly have this charge and to the power of 2. So, , , if you think of it 2, the more charge that I can provide with maybe, if I should not say lesser mass, the more charge I can concentrated charge I can provide thus, the surgical doubler thickness will be lesser at lesser dosage. So, that is one thing to keep in mind, we will come back to this later.

And it is insoluble typically in the neutral pH range, but , not of great aspect or great relevance, especially if we are talking about the different mechanisms of coagulation, . (Refer Slide Time: 14:15)



So, let us move on what are the types of coagulants. So, we will look at typically addition of , coagulants, such that , you are going to have charge neutralisation or form, what we say,

bridges between different particles. So, here we have 2 major aspects, one is charge neutralisation The other one is bridges. These are with respect to the soluble ones and then if you have the insoluble ones .

We know that if we add a compound to be at high enough concentration and look at the relevant pH and the ligand concentration, the compound will not stay dissolved, it will want to precipitate out. It will precipitate out. So, when it precipitates out, it will also see to it that it adsorbs other what we say, particles of interest. And this type of removal is called sweep coagulation.

So, 3 major aspects will come at, we will look at that. So, charge neutralisation I am going to add those that have higher charge Al^{3+} or Fe^{3+} , but the reason for adding Al^{3+} in Fe^{3+} is not only due to the high charge. Why is that? We will look at that later, but as you can see, in general Al, Al aluminium, a lot of compounds with aluminium, and then with respect to iron, Fe fabric is Fe^{3+} ,.

Yes, , you can see that we are adding the relevant counter ion but for ultra neutrality, you will also have to have the anion. So, that is something to keep in mind.





We will not just have inorganic coagulants. We will also have some organic cationic coagulates. So, we see them here, but in general, they are not added as the primary coagulants. In general, primary coagulants, you will typically add to neutralise discharge and

these, organic coagulants you will add such that they act as bridges. What are these bridges? We will look at that soon.

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So, correlation mechanism, this is what we just discussed earlier. So, what do we want? I want to see to it that the electrical double layer thickness is decreased or compressed. So, that is what we have and then van der Waals forces of attraction will take over and the particles will come through. So, what is important here? As I mentioned ionic strength and the charge of the counter ion are important. Well, this charge of counter ion, we just talked about it.

So, greater the charge density of the counter ion, down the electrical double layer thickness will be relatively lesser. So, two aspects, ionic strength and the charge of the counter ions, . And what is it that we are trying to achieve? We want to decrease this double layer but to what extent. So, looks like this model says that we the van der Waal forces or relevant from about 1 nano-meter.

If the double layer can be reduced to less than this, then we are going to have what is this, suspension or flocculating suspension. So, that is something to keep in mind just try to understand this distance.

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So, we have effects of solution concentration on double layer. So, here is the potential. Here, we are looking at the effect of concentration of the counter ion or effect of the increase in the ionic strength on the double layer. So, here we have 60 milligram per litre. And you see the profile, the potential . this is with respect to the distance, we are talking about the repulsion in general here.

As we go to towards the particle, it is increasing. Yes and if I increase the ionic strength by adding 600 milligrams of NaCl, well, I see that this is the profile. And if I increase it 10-fold or one order of magnitude, further increasing the ionic strength and this is the, , repulsion that the particle will experience as the particle moves towards or the particle of interest. So, that is something to keep in mind.

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And let us look at the effect of charge on the double layer. So, if I am seeing to it that I am adding particle, NaCl and for Z^{3+} , it is FeCl₃, meaning I am adding Fe³⁺, so you see with Z at 1 plus same concentration, this is the profile. But with increasing charge, you see that it is something like this. Visually, you might not able to capture the information, but we have a table and we will look at that.

But in general, the charge will be such that $1/1 : 1/2^6 : 1/3^6$. So, this is how charge will be affected. you can calculate the ratios, I think it will be 1 : 1.6 : 1.14 or something, you can check that but this is how charge will affect it the concentration required will be in the range of, this is not 1, 100, . So, 100 is to 1.6 is 0.14.

But, this is with respect to the charge raise to the power of 6. So, that is the effect of a charge. So, you can look at the relatively less concentration of the compound required if you have higher charge that is. So, that is something to keep in mind.

(Refer Slide Time: 19:50) 22 Molarity z+ : z-I, mol/L ĸ, cm⁻¹ 1:1 A (100.0) 1.04×10^{6} 0.001 2.08×10^{6} + 2:2 0.004 3:3 0.009 3.12×10^6 1:1 0.01 0.01 3.29×10^{6} 2:2 0.04 6.57×10^{6}



This is the table that I was trying to look at. So, the molarity the concentration is one milli molarity, one molar and ionic strength is here. Yes. And here is the charge. Yes. So, I am adding it at 0.001; charges, one. So, ionic strength is also 0.001. And this universe will give me an idea about the thickness of the electrical double layer. So, this is one measure of the thickness, fine. Where did we see this picture earlier?

Let me just point that out earlier. So, we see this here, . It is just giving us an idea about distance from the particle surface, . Let us move on and here with the same concentration, but

with charge of 2. Now, what is the ionic strength coming out to be? You see that I mentioned that it is Z square. So, that is why you see 2 to the power of 2 = 4. So, that is why you see 0.004.

And then, 1 by k or the distance, the electrical double layer will decrease. And if it is 3, , Z square 9. So, you see that it is 0.009. Even though the concentration is the same, ionic strength is relatively high. And then this particular electrical double layer thickness is relatively low. So, if I increase the concentration from 0.1 milli molar to 0.1 molar, 1000 times, 100 times higher, , so, what do we have here?

So, , same aspect 1 is to 1; ionic strength is 0.1. , it is much lesser. Why? The concentration is higher compared to what we have here to concentration here or the ionic strength is much higher compared to what we have here. And for that concentration, if I increase the charge, and now, I am going to have higher ionic strength and thus, much , lesser or much thicker electrical double layer.

So, you can now see the effect of the concentration and also effect of charge on the electrical double layer thickness. So, that is something to keep in mind.





So, concentration required for flocculation. Typical concentration seems to be 25 to 15 milli moles per litre. So, , if it is di-valent or tri-valent, it is going to be relatively less that was illustrated when we looked at this particular table presented by or given (()) (22:23). This is a

good book if you are looking at water treatment, any aspect that is one thing I wanted to mention.

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So, adsorption and charge neutralisation, let us look at the factors at play when we are trying to bring about coagulation. When we say hydrolyzed metals salts what is it we are seeing, AI^{3+} is what I am adding and I am adding it to water. So, it is going to hydrolyze; the metal salt is going to hydrolyzed.

$$Al^{3+} + H_20 = Al (OH)^{2+}$$

So, pre-hydrolyzed metal salts and cationic polymers have a positive charge.

So, it can be $Al(OH)^{2+}$, $Al(OH)_{2^+}$, typically Al^{3+} but OH^- has a negatively charge. So, these typically have a positive charge, . These are the various complexes that we are talking about. This destabilise the particles through charge utilisation. So, this is something that can happen. Why? Here, we have a positive charge we are importing positive charge.

So, the issue here to note is that Al^{3+} when you add it to water, will not stay only as Al^{3+} At electron deficient, it is a metal. If you have a ligand, and what is the ligand here, in this context that is always available that OH^{-} , . Electron rich and electron poor. Metals is electron poor like and electron rich, so, they will try to form a complex . So, you need a metal and a ligand.

The ligand here most common ligand in water is OH minus. WHY? H_2O will be in equilibrium with H^+ and OH^- . So, Al^{3+} in solution will not stay only as Al^{3+} . It will form

complexes and as you can see, it depends on concentration of OH⁻, for example. There will be an equilibrium but between these, this complex and Al³⁺ and OH⁻, I am writing it in the simple form.

So, if I either change the pH or the change the concentration of Al^{3+} , the concentration of the complex will change. And also even the type of complex it will be this one or one with no charge or one with even a positive charge, it will depend upon the pH. So, these are the different complexes that aluminium can form with OH⁻. , you do not need to go into detail but what I am trying to say is when I add a metal, it will not stay as the free metal Al 3 plus or Fe³⁺. It will form complexes with the ligands present there.

So, when we talk about charge neutralisation, you see that even though I am adding something Al^{3+} charge, in effect, it can have two plus also charge or it can even have a negative charge depending on the kind of complexes that it is for. And also, if I add high enough aluminium concentration or ferric iron concentration or enough ferric iron, what will happen?

It can even precipitate out of the solution, this is something that we looked at co-precipitation or sweep coagulation. So, we will come back to that. So, it is not as if it is only charged neutralisation that is something I wanted to mention.

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So, here what is happening? This is , what is being mentioned here. So, we have a source of aluminium and you have Al dissociation into Al^{3+} and SO_4^{2-} and these ions tend to bind

either directly to the particle surfaces meaning adsorbed or to NOM on those surfaces. Please note that Al^{3+} well or can bind to the particles of interest or as I mentioned, it can form a complex with OH⁻ or it can also form a complex with the natural organic matter, which typically has a negative charge.

So, these are the relevant aspects or if the particle itself has NOM adsorbed onto it. Al^{3+} can also go there and , neutralise the charge of this particular natural organic matter. we know that the particle itself is getting charged, how is it? One of the way is that NOM is adsorbed onto the particle and that the relevant charge of NOM is imparted to the particle.

So, if we add Al^{3+} and this Al^{3+} neutralises the charge on the NOM by forming a complex with NOM, , the charge of the particle is also going to be utilised, .



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if we have a good figure. So, this is what we see. So, typically, we see COOH, but this H was released that is what you see here. And that is why it has a negative charge. This is the typical structure of NOM typical, and also OH. And that H seems to have been given out, so, that is why we have OH or O⁻ here, . The charge is negative and thus, Fe^{3+} or Al^{3+} that I add, can go out here.

And , you can have complex between NOM and the metal and thus, neutralisation of the charge. So, that is one aspect of coagulant combining with NOM.

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So, what is this about adsorption charge utilisation? We spoke about it. So, when surface potential are high, this is what we already looked at earlier. So, we cannot really see to it that they come close together. So, repulsion is stronger as the particles come together, but by adding this coagulation such that I neutralise the charge, now the particles can come together and they can form these or start forming these flocs by colliding and sticking together. And in that context, I wanted to mention adsorption.

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Let me see if we have that here. Let us look at this. So, colloidal particles in general, and after adding the coagulant, I destabilise the particle and now they are relatively unstable and can come close together and form flocs. So, you can see the increase in the particle or size for all increase, colloidal particles too small to settle out and floc particles relatively bigger and they can settle, but there are other aspects.

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Adsorption and Interparticle Bridging

 Adsorption and inter particle bridging - coagulant is large molecule, adsorbs on two colloids



So, here we have adsorption and inter particle bridging. Until now, I or we looked at charge neutralisation or how charge on the particle and I am neutralising the charge. As I mentioned, though we have other aspects, one is inter particle bridging and adsorption. So, adsorption and inter particle bridging, when does that happen? Coagulant is a large molecule and it adsorbs on to colloids, I think I have a picture.

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So, here you see that. So, here, wet correct mixing and excessive mixing, we will come back to that. So, here is my polymer, cationic and anionic or non-ionic depending on the situation. And so, what happens is, this is a destabilise particle earlier stable now, after charging utilisation or just adsorption, you have this case and now, you have it, adsorbing onto two different particles and this does forms a bridge.

So, you have the bridge being formed. So, inter particle bridges form, sometimes when you have excess dosing, , you are going to have, , all the sites being taken up on one particle due to what we say, a lot of the coagulant or the polymer being added that is not good, but depending on the type of , polymer being added, you can also have enmeshment.

But, this is something that you typically want to avoid, ,. Because you added too much. And if I do not mix it well enough, what is going to happen after some time?, this is the initial case, my polymer has come and adsorbed onto one of the particles or a few of or one of the particles. And because of poor mixing, it is not able to form a bridge with another floc. So, not floc under colloid.

So, what is going to happen after sometime? It is going to be adsorbed onto the same , colloid. And we have particle re-stabilization. So, leading to poor floc formation, though, that is something to keep in mind. And what else do we have here? So, here I have excessive mixing. This is one issue. So, after I initially destabilise the particles, what do they want to do, I want to see to it that the particles come together and form flocs, though we will discuss this later.

I wanted to mention it here, because the figure has all the relevant aspects clearly illustrated here. So, what do we see here? Here, the flocs are formed. But after the flocs are formed, if I still mix it at , great or such that the turbulence is very high. And for a prolonged period, what is going to happen? The flocs are going to break up. So, that is why we have it here excessive mixing and correct mixing.

So, the amount of energy that you are going to impart to the relevant solution is also important. We will look at that later. So, here we looked at some aspects, at least in this figure, what is it inter particle bridging due to the addition of catatonic or non ionic or anionic polymers. Yes. And also we looked at issues when we add a lot of what is this, the polymer or when we add relatively what we say, or we see to it that the turbulence is too high or we do not mix it properly, what happens? The flocs will not form later.

So, with that, I will end today's session, but one aspect to notice that in today's session, what is it that we looked at, we looked at compressing the electrical double layer by increasing the

ionic strength and what is a better way to increase the ionic strength by adding what we say, a particles that have a higher charge on that. So, we saw the effect on the electrical double layer at the same concentration for particle having charge 1 and particle having charge.

So, in the context of destabilising, we know that charge neutralisation is one aspect. Yes. And now, we saw that or see that inter particle bridging is another aspect. So, inter particle bridging and adsorption, I will put it in the same way. And the other aspect, we are going to discuss later is some of these metals that I add, do not stain solution the aluminium it does not stay as Al^{3+} .

It also forms complexes, but even the complexes are soluble, but aluminium does not stay only as this dissolved metal or as the complexes. What will we do? If the conditions are , it will start precipitating out. So, you will have a solid being formed and it will precipitate out and the solid can enmesh or see to it that other particles are entrapped. So, you are going to have what is called co-precipitation or sweep coordination, but that we will discuss it in the next session. And thank you for your patience.