Environmental Geotechnics
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Lecture - 25
Geomaterial Characterization -5 (Specific Surface Area- I)

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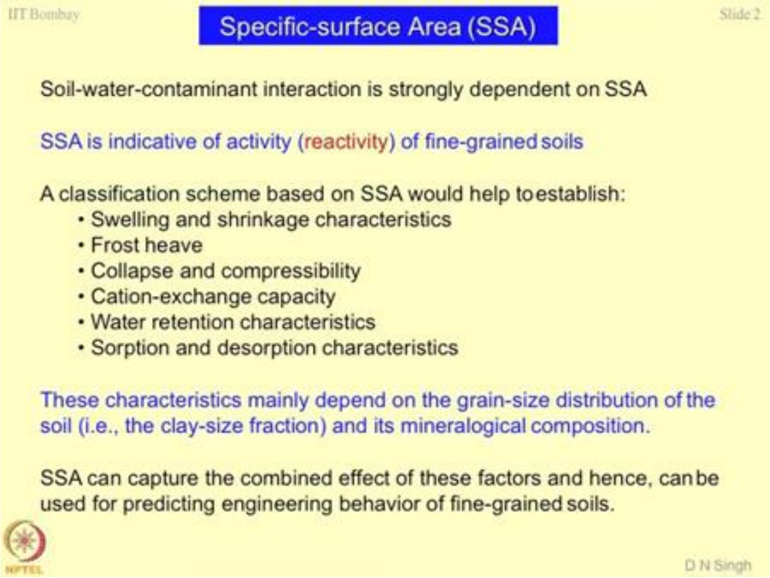
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Slide 2

Specific-surface Area (SSA)

Soil-water-contaminant interaction is strongly dependent on SSA

SSA is indicative of activity (reactivity) of fine-grained soils

A classification scheme based on SSA would help to establish:
- Swelling and shrinkage characteristics
- Frost heave
- Collapse and compressibility
- Cation-exchange capacity
- Water retention characteristics
- Sorption and desorption characteristics

These characteristics mainly depend on the grain-size distribution of the soil (i.e., the clay-size fraction) and its mineralogical composition.

SSA can capture the combined effect of these factors and hence, can be used for predicting engineering behavior of fine-grained soils.

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So, let us begin with the specific-surface area which is also represented as SSA. If you want to study the soil-water-contamination interaction, this is the parameter which can be used as a good tool. So, this is a parameter which acts like a black box. And it so happens that any interactions, which starts has to be first of all a physical interaction like I am interacting with you physically.

So, this is how soil-water and contaminants are going to interact. And the most crucial parameter or the most defining parameter would be a specific-surface area which is a physico-chemico-mineralogical property of the soil if you remember, because for each mineral and for a given shape or size for a given properties, the specific-surface area is going to be a fixed value almost.

Now, over the years what we have being doing is that we are trying to understand how to determine SSA precisely, because many people had not given much focus or much thought over this. So, I will try to cover different methodologies which are adopted for determining a specific-surface area of the geomaterials or the soil mass. Most interestingly you will find that SSA will be an indicative parameter for defining the activity of the fine-grained soils.

Now, here in bracket I have written reactivity. So, my question to you is, are they same or they are different activity and reactivity? Suppose, if they say that activity and reactivity are similar or they are same, do you have any argument in favour of this, how do you define activity of the soil? Water holding capacity is a different mechanism altogether, how do you define activity of fine-grained soils that is right? So, plasticity index divided by percentage fines or the clay content.

As I said previously that that this definition of SSA is not sorry, this definition of activity is not complete, because here we do not talk in terms of the total mechanism which is responsible for soil-water interaction or soil-water contaminant interaction. So, that is why very conservatively I am using the word activity which I mean to connote to reactivity that means reactivity is a larger term or the bigger term than the activity.

So, if you say that how soil is going to react to the environment or to a contaminant or to water, this is where SSA becomes a very important parameter. So, we are interested in finding out SSA to the precise limits, but then what is the philosophy of doing this. The philosophy is so that we can define reactivity of the material.

A good example comes in mind if you take let us say cement and you spray a bit of moisture on this, what happens, it hardens immediately. For that matter any pozzolanic material if you bring it in contact with water, it hardens. Now, this is a sort of a reactivity; and you must be appreciating this point that this reactivity can be captured if you can determine the heat of hydration of cement clear and that is why we say we assume cement to be a standard material.

Now, the question comes in mind if manmade materials are standard where the natural materials fit in on this scale, and that is where actually we tried to derive a scale you can say in terms of reactivity to understand the soil-water contaminant interaction. Is this ok? And this is where we find that SSA becomes a very important parameter and its determination becomes essential that too precisely. So, this thought pleads to the concept that rather than talking about your conventional classification schemes. USCS, ISSIS, Indian Classification Scheme, AASHTO and so on, which we have already discussed are not very befitting to classify the soils because of their limitations.

So, this is where people are thinking of classifying the soils based on specific surface area. Now, this will be a onetime parameter detection or determination which should give you all the properties of the soils. Now, these are the mechanisms or properties of the soils which can be linked with a specific-surface area. The first one is if you want to identify swelling and shrinkage characteristics of the soils or first step would be to differentiate between the soils which are non-swelling and swelling, just by seeing what SSA values they exhibit.

So, this is a very important and very interesting concept on which lot of researchers are working these days. They are talking about relationship of SSA with swelling and shrinkage characteristics of fine-grained materials. The second issue is frost heave; I hope you will appreciate the point that swelling and shrinkage characteristics are the interaction of soil with water or even the contaminants in the liquid phase, but when you talk about frost heave what type of interaction it is, is a interaction with the environment under sub zero temperatures alright.

So, if you want to study how frost heave is going to affect the stability of the structures, SSA seems to be a good parameter. Similarly, collapse and compressibility; when you want to differentiate between the soils which are collapsible and compressible. Again specific surface area seems to be a good parameter over here. This is the response of the material when there is the interaction going on between water, soil and contaminant and the external loading which is a form of mechanical loading. You got this point?

So, when you say collapse and compressibility the difference between swelling shrinkage, frost heave is and collapse and compressibility would be that these are the fundamental properties of the soil. However, collapse and compressibility would be the response of the system to the external loading. So, this is where the boundary conditions or the environmental conditions are coming to the picture.

Then comes cation exchange capacity, most of the time cation exchange capacity and SSA that is specific-surface area, they are supposed to be related to each other. And the idea is if you determine one you can find out the another one. So, it is a vice versa. If you know SSA, you should be able to know CEC Cation Exchange Capacity or if you know CEC, you should be able to get SSA. Why it is so? This parameter CEC happens to the best possible parameter to define soil, water, environment contaminant interaction, because this is the capacity of the soil to exchange the ions, cations particularly; is it not? So, this talks about the reactivity and that is why I use the word reactivity rather than activity. Because activity is blind of this interaction, you are simply talking about their plasticity index divided by the percentage clay content which does not include the effect of environment on the type of the loading which is going to come on the system.

Now, another philosophy is cation exchange capacity happens to be primarily a physico-chemical phenomenon, that means, the physical properties and the chemical properties in combination with mineralogical properties are going to be responsible for exchange of cations which a soil will exhibit. But determination of CEC is a tedious task, because you have to go through a complete process, and as on date somehow there is controversy which method to adopt. There are different codes available and if you follow the codes and the codal procedures, you end up getting different results.

The reason is the cation exchange capacity will depend too much on the atmosphere conditions particularly the pH of the soil, the temperature of the soil, the pressure which is being applied and the fluctuation in these values. So, intelligently people what they have done is they have utilized a specific-surface area to determine cation exchange capacity. So, this is one of the applications of determining CEC if you know SSA.

Water is retention characteristics; now this is where the unsaturated soil concepts come in to the picture. You are talking about water retention characteristics. You think of a situation where some load is applied and the moisture is migrating out of the soil mass. Now, this could be a situation because of mechanical loading as happens in case of consolidation. However, if you air dry the sample under thermal flux, again the tendency of the moisture is to migrate from the soil mass. Now, the question is what is the limit beyond which the sample will not release moisture from itself; clear. So, this is where the residual moisture concept comes into the picture.

So, when you talk about water retention characteristics of the soil, though this happens to be a physical phenomenon the way people have studied till now, they talk about soil water characteristic curve. And depending upon the packing of the grains that is a compaction curve they can tell you how much water is going to be retained for a given suction pressure, but truly speaking we have to go one step further and water retention characteristics will not be only physical property determinant, they should be dependent upon chemistry and mineralogy of the material and that is where the concept of osmotic suction comes into the play. These things we will be talking slightly later when we would be discussing how to determine suction of the soil mass.

Then comes sorption and desorption characteristics, which I will be talking about quite in details. The mechanism of how sorption takes place on the system. Yesterday, I showed you a slide where cations are getting pugged on the grains of the soil alright, that means the surface happens to be so high or so active material that the tendency of the cations is to get pugged as if they are getting pugged in a parking lot. So, more the surface area, the more sorption is going to take place.

Now, you think of a situation where the bond between the grains of the soil and cations is very strong. And even after washing with water, these cations will not leave the surface; that means, in that case we can say that desorption capacities are very very low. Now, these type of studies become very important in various environmental engineering issues where you are talking about environmental cleanup strategies. A contaminated soil is going to be cleaned up by some method. So, this is where sorption-desorption characteristic become very important.

For the time being, I will just say that we can use some parameters or some coefficients to define sorption and desorption characteristics, normally the term which is used is k d distribution coefficient. And if you can correlate k d with specific-surface area, this would be an achievement; clear? So, coming back to the issue, I have shown you here that a specific-surface area happens to be so important parameter that unless you estimate it or determine this, it will be very difficult for you to quantify the interaction between soil, water and contaminant, is this clear?

Student: (Refer Time: 13:57).

Now, it is so happens that all this characteristics will depend upon the grain size distribution of the soil that is the amount of clay size fraction which is present and its mineralogy ok. So, SSA should be a strong function of mineralogical composition and that is the reason quartz will show you less specific-surface area as compared to montmorillonite illite kaolinite and so on, though their sizes may remain same. So, please if you understand one issue there is a very big you know what you call it as a myth, I should use the word or a contradiction, particle size does not indicate everything unless you talk about the mineralogy. I can crush sand to achieve any size of the particle, but this is where the mineralogy comes into the picture and makes it more active and reactive all right.

So, this is where actually you have to understand that how SSA also gets influence because of the mineralogical composition. I believe that SSA can capture the combined effect of all these factors, and hence can be used for predicting engineering behavior of fine-grained soils. Our group is working very actively in these areas, I will show you some of the results which we have achieved till now, and how these results can be utilized in determining the fundamental properties of the fine-grained materials.

Any doubts? Is the philosophy clear, that why surface area is being studied in details? So, in short SSA and cation exchange capacities of the soils are the key elements or the key parameters for defining the entire soil water interaction scenario. Then the question is the philosophy is clear that why we should measure SSA?

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Determination of SSA of fine-grained soils

A. gas or vapor adsorption techniques
BET nitrogen adsorption
    water-vapor adsorption

B. absorption of the polar liquids and dyes on the soil surface
Ethylene glycol (EG) method
    Ethylene Glycol Monoethyle Ether (EGME) method
    p-Nitrophenol method
    Methylene blue (MB) dye method

C. application of the state-of-the-art instruments
Mercury intrusion porosimetry (MIP) Internal reflectance spectroscopy
    X-ray diffraction
    Gas pycnometer

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Now, the question is how to determine this, what type of test should be done? So, there are several techniques which are available in literature the most popular one is gas or vapor adsorption techniques. And within these techniques, there will be several methods or the methodologies. This is the first group of methodologies, where you expose the material or the geomaterial to a gas or vapor. And let these two get adsorbed on to the material and then see how reactive the system is. A good example is sauna bath. When you go and stand in a sauna bath chamber, what happens? Your skin reacts with the vapors of steam and then cleanses the skin, clear. So, there is again sweating exchange of salts from the body, they get diluted.

The second category of the methodology is absorption of the polar liquids and dyes on the soil surface. There are different type of dyes which are normally used, dyes are nothing but the colour coatings or the colored materials with some chemical reactivity. And the third class of the methodologies belongs to application of the state-of-the-art instruments. So, depending upon your pocket and the time and the precision which you are looking for, you can fit in any one of these methodologies.

But the basic question is which bothers everybody, suppose for the same material if I adopt all the three techniques or the classes or the problems where would I land up, it should not create more confusion. But it so happens that we follow all the three methodologies, the results may be very haywires. Let us not go into that right now. Let us try to understand what are the methods which are used for determining the specific-surface areas of fine-grained soils.

Under the first category where you use a gas or a vapor and this gas or the vapor is getting adsorbed on the material surface. So, this is where we talk about BET nitrogen adsorption. I will be discussing this in details and the water vapor absorption. Sometimes I use the word absorption, sometimes I use the word adsorption. As long as we are working with water, there is no difference between the two, but the moment water gets replaced by a contaminant, the connotation differs.

So, absorption is a simple physical phenomenon, you have water spilled over somewhere, take a foam or a cloth, just put it on this it soaks everything clear, this is the first step. But if this liquid happens to be highly reactive, what is going to happen? Even after getting soaked into the system it will start reaction with the matrix of the material. So, this is where the adsorption term comes into the picture.

Now, what is the difference between the two terms? When you find out the moisture content of any geomaterial or for that matter when you determine let us say porosity of rocks or concrete, how did perform this test. You soak the core of the sample in the water body or in the water container for 24 hour, 48 hours. So, initial weight you take and the final weight you take, difference between the two divided by the weight of the solids will give you the moisture content or the porosity. What type of process is this? This is the absorption process, adsorption process? It is a simple absorption process.

But suppose if I dissolve some salts in the water in which you are dipping the core, now what is going to happen? This absorption process going on, but at the same time once the water goes into the pores of the system, there will be a redistribution of the contaminants in the matrix of the material, and that is where the adsorption process starts, clear. So, simple moisture content determination happens to be in absorption process in case of the materials which are nonreactive, sands.

But if I replace this material with clays, and if I replace them liquid by adding some contaminants into it, it becomes a combination of the two. So, up to a certain time, there will be absorption process going on, but later on the adsorption process will take over from the absorption process. So, put together absorption and adsorption we call this mechanism as sorption clear. So, that is why we tend to study sorption characteristics rather than absorption and adsorption, because sorption happens to be a larger set of properties as compared to absorption and adsorption. Is this part clear?

The second group of methodology is absorption of the polar liquids and dyes on the surface of the soil. So, this is where we use first ethylene glycol it is a dye. This is known as EG method. Ethylene glycol monoethylene ether, which is known as EGME method; then sometime people use p-Nitrophenol, another type of a dye sometimes they use methylene blue MB dye method. It depends upon which school of practice you are coming from, so that school of people normally follow one method, because they have mastered that technique.

The methodology instrument which are normally used for fine-grained soil SSA determination are mercury intrusion porosimetry. I discussed a bit about this is in the previous lecture. Internal reflectance spectroscopy you can literally see how many cations are getting parked on to the surface of the soil mass. X-ray diffraction simple, XRD should also give you an idea of what type of alteration has gone over the material properties, and of course, the gas pycnometer. Out of these techniques I will talk about a few of them giving you an idea about how these different methods are used for determining the SSA of the soil mass. You should appreciate the point that these techniques are quite intricate in nature and they require very sophisticated environment to work in plus lot of care and meticulous temperament.

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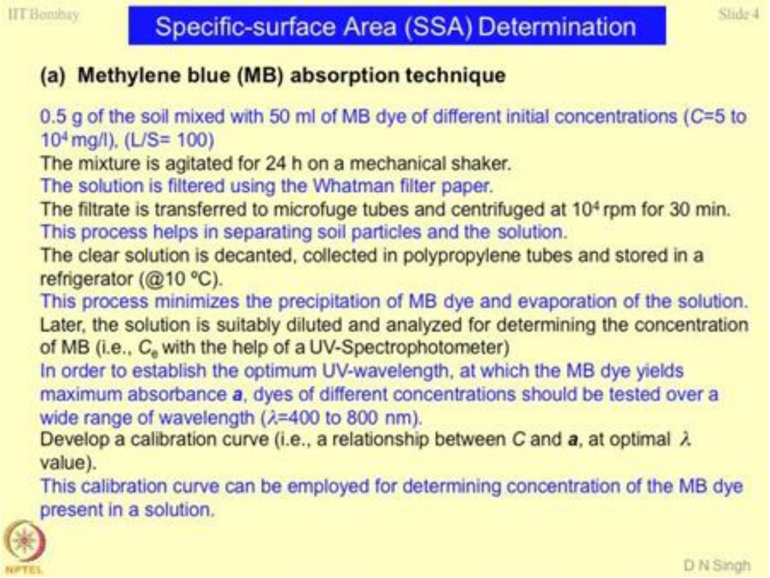

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Slide 4

Specific-surface Area (SSA) Determination

(a) Methylene blue (MB) absorption technique

0.5 g of the soil mixed with 50 ml of MB dye of different initial concentrations (C=5 to 10^4 mg/l), (L/S= 100)
The mixture is agitated for 24 h on a mechanical shaker.
The solution is filtered using the Whatman filter paper.
The filtrate is transferred to microfuge tubes and centrifuged at 10^4 rpm for 30 min.
This process helps in separating soil particles and the solution.
The clear solution is decanted, collected in polypropylene tubes and stored in a refrigerator (@10 °C).
This process minimizes the precipitation of MB dye and evaporation of the solution.
Later, the solution is suitably diluted and analyzed for determining the concentration of MB (i.e., C_e with the help of a UV-Spectrophotometer)
In order to establish the optimum UV-wavelength, at which the MB dye yields maximum absorbance **a**, dyes of different concentrations should be tested over a wide range of wavelength (λ=400 to 800 nm).
Develop a calibration curve (i.e., a relationship between *C* and **a**, at optimal λ value).
This calibration curve can be employed for determining concentration of the MB dye present in a solution.

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So, let us start with the first methodology, where methylene blue is used as a absorbing material. Now, the moment you say that it is a absorption technique something clicks to your mind that whatever you are going to get that is SSA would this be total or external surface or internal surface, correct. So, when we talk about the specific surface area, a specific-surface area will also have two components that is the specific surface area total and the specific-surface area which is going to be external alright. What it indicates is that entire surface need not be available for a contaminant to interact at a given time.

Now, this is where a very interesting philosophy comes to the mind is there is a sort of a competitive you know behavior of the ions to interact with a particular soil. Now, this is what is known as a competitive sorption. So, given a chance, if you have calcium and sodium ions in contaminants which ion is going to get adhere to the clays sodium or calcium, why?

Student: Calcium (Refer Time: 25:12).

That is right, your answer is correct. So, calcium competes over sodium because of its higher valency clear. So, this is where there is a competition between the ions, and they wish to get parked easily on to the surface. Even if sodium gets parked you know in the long run it will again leach out because of the less valency.

So, here the methodology is like this. You take approximately 0.5g of the soil and mix it with some 50 mL of the methylene blue dye of different initial concentrations. So, normally the concentrations are varied from 5 to 10^4 mg/L. And L by S, which is known as liquid to solid ratios that means, you take 50 mL of the liquid in the water and 0.5g of the soil mass. So, this becomes 100. So, you can vary L by S also. I can do different tests at different liquid to solid ratio.

What is the meaning of this? If I put L by S equal to 1, this is the slurry where the consistency is very high. All the surfaces may not get exposed to the environment. It is a near dry situation, but as I move on the L by S scale and as I make it more and more, each particle is free to react with the contaminant or with the solution which have lot of contaminants in it.

So, you can vary L by S depending upon your requirement, and for each L by S you will be getting different results. Now, this mixture is agitated for 24 hours in a mechanical shaker. And why do we do shake? So that each particle gets coated with the MB dye; the solution is filtered using the Whatman filter paper. Whenever you get a chance to come to the lab you can see what type of filter papers are available nowadays in the market, I think there are hundreds of pore sizes of filter paper which are available. So, depending upon your requirement and what is that you want to filter, you can use a given Whatman filter paper.

Now, this filtrate is transferred to a microfuge tube. Microfuge tubes are the tubes which are normally used in small centrifuges biological centrifuges. You must have gone to a blood bank. So, there you must have seen a centrifuge. So, what the centrifuge does? It separates out the platelets form the blood. So, the same way you can separate out the denser material and the liquid solution from this. So, you have to centrifuge at 10^4 rpm for 30 minutes. So, this process helps in separating soil particles and the solution. We are interested in solution only. So, the clear solution is decanted collected in a polypropylene tube, and then it is stored in the refrigerator at some temperature. This process minimizes the precipitation of MB dye and evaporation of the solution.

Now, for this solution, you have to determine what is the amount of methylene blue which is present clear; so, the initial minus this amount will nothing be the amount which is getting absorbed onto the clay particles. So, later the solution is suitably diluted and analyze for determine the concentration of methylene blue, using a UV spectrophotometer, ultraviolet spectrophotometer. So, in order to establish, the optimum ultraviolet wavelength at which the methylene blue dye is maximum absorbance dyes of different concentrations are to be tested over a wide range of wavelength. I will show you the typical graphs later on. These are the methodologies, and then you develop a calibration curve between concentration and absorbance alright.

So, next time when you are going to find out for a given solution, you just measure the absorbance that will give you the concentration of the MB in the solution alright. So, this is a simple methodology. So, this calibration curve can be employed for determining concentration of methylene blue present in a solution. So, the method is quite simple.

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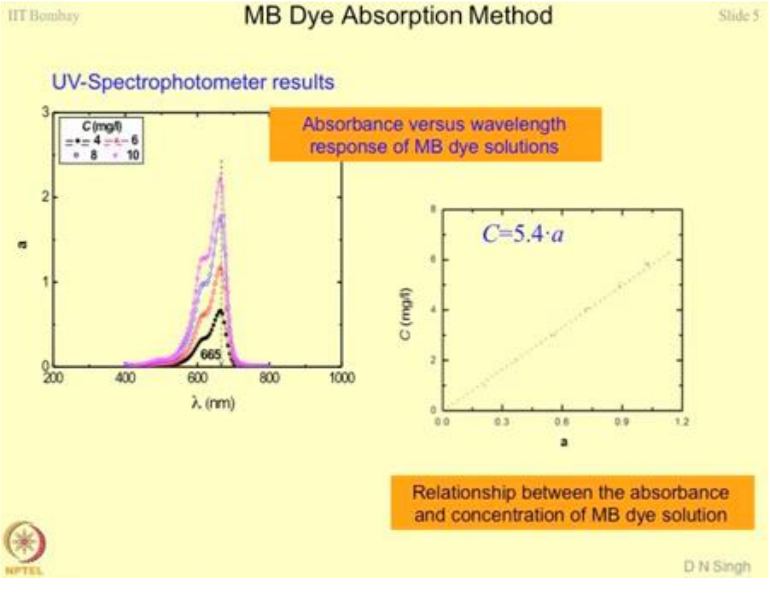

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MB Dye Absorption Method

Slide 5

UV-Spectrophotometer results

Absorbance versus wavelength response of MB dye solutions

Relationship between the absorbance and concentration of MB dye solution

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And once you follow this method, these are the results which you will get. On y-axis you will see the absorbance of the UV spectrophotometer. You might have used ultra violet spectrophotometer in undergraduate I am sure for doing water quality analysis. How did you find out turbidity of the water and the color of the water? Anyway, this is where you can use UV spectrophotometer quite easily. So, if water is very turbid, again you can work out using this concept absorbance of the light for a given wavelength of the ultra violet wave.

So, for different concentrations of the solution, you keep on changing the concentrations and vary the wavelength, and see what is the absorbance value which you are getting. So, this is a typical absorbance versus wavelength response for MB dye solutions. So, what we are doing here is we are basically training the set up for absorbance for a given wavelength. So, wavelength can be controlled on depending upon the instrument and the waves which you are selecting.

Then what happens is I can develop a relationship between the concentration of the dyes and their absorbance values. If you remember we work with five, six concentrations of the dye. So, for each dye concentration, you will be getting a point and you will be getting an absorbance value. So, you draw a relationship between concentration and absorbance, this will give you a linear relationship of this order meaning thereby if I know the absorbance of any solution containing MB, I can find out its concentration that is it a simple detection method. So, this is a relationship between the absorbance and concentration of MB dye solution.

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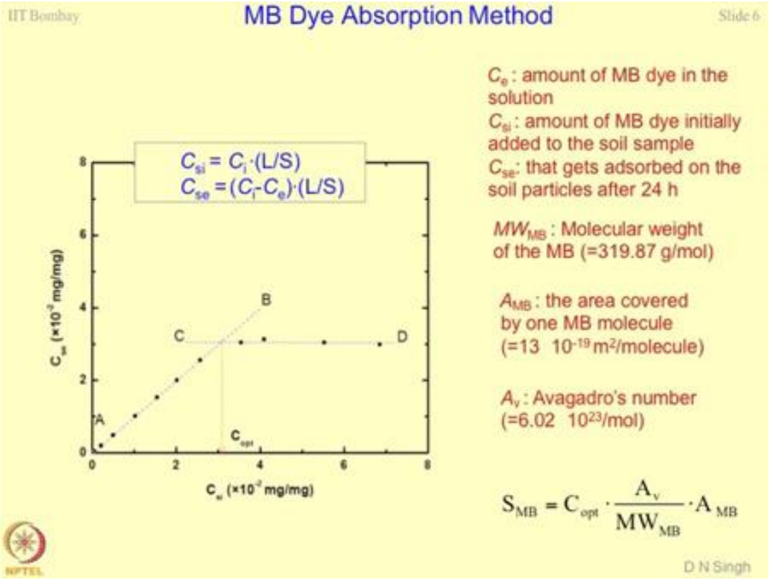
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MB Dye Absorption Method

Slide 6

$C_{si} = C_i \cdot (L/S)$
$C_{se} = (C_i - C_e) \cdot (L/S)$

C_e : amount of MB dye in the solution
C_{si} : amount of MB dye initially added to the soil sample
C_{se}: that gets adsorbed on the soil particles after 24 h

MW_{MB} : Molecular weight of the MB (=319.87 g/mol)

A_{MB} : the area covered by one MB molecule (=13 10^{-19} m^2/molecule)

A_v : Avagadro's number (=6.02 10^{23}/mol)

$$S_{MB} = C_{opt} \cdot \frac{A_v}{MW_{MB}} \cdot A_{MB}$$

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So, ultimately what we get is we have to determine C_{se}, where C_{se} is the amount of MB, which is getting absorb on to the clay particles. So, initial concentration is nothing but initial concentration of the dye multiplied by liquid solid ratio. And the amount which is getting absorbed onto the particle will be the initial minus final concentration into L by S. So, this way when you plot C_{se} vs C_{si}, there will be a break in the curve and the point of break will be giving you the C_{opt}.

So, if you know the C_{opt},

If you know the Avagadro's number $=6.02 \times 10^{23}$/mol divided by MW_{MB} molecular weight of the methylene blue multiplied by A_{MB}. So, A_{MB} happens to be the area which is covered by the MB for forming a mono layer.

$S_{MB} = C_{opt} \times A_v \times A_{MB}/(MW_{MB})$

So, the first layer the coating which gets on the surface this much area the MB will exhibit. Now, these are the standard values. So, these are the standards which are normally used for this method. So, then you can get S_{MB}. So, S_{MB} corresponds to surface area which were getting from methylene blue method.

Again, I will ask you the question, this is going to the total surface or external surface area? It is basically external surface area. That is, right because the absorption is going to be only on the surface. Chemically it will not be active. Is this part clear? All these techniques require very sophisticated instrumentation. So, unless you have a ultra violet spectrophotometer, you cannot really do this studies that is right.

So, in that case, you should repeat the test several times to make it a representative value; otherwise your L by S will become quite high. So, you take one gram and then dissolve it into appropriate L by S. So, it is just like training the solution for a given L by S depending upon the amount of soil which you are using; otherwise create several batches from the soil and then repeat the test.