Advanced Chemical Thermodynamics & Kinetics

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Lecture - 44
Photochemistry: De-gradation of a dye

Hello everyone in today's experiments we are going to show the Photo De-gradation of dye called Rhodamine B. So this dye is used as a staining fluorescent dye. In the photo degradation of Rhodamine B we will do the photo degradation under solar radiance using TiO 2 as a catalyst, and the degradation in monitored using UV Vis spectrometer. Now, this experiments provides a natural and cost effective way to degrade pollutant organic molecules into carbon dioxide, water, and simple inorganic acids.

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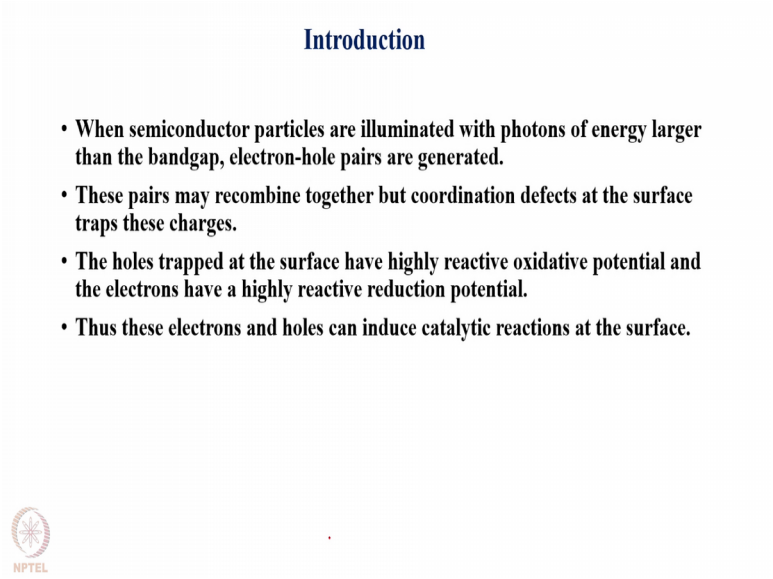

So, in this experiment we are using a semi conductor particles of TiO 2 as our catalyst. So, we need to know how do semi conductors particles degrade a dye an organic molecule. So, when semi conductor particles are illuminated with photons of energy larger than their band gap electron, hole pairs are generated.

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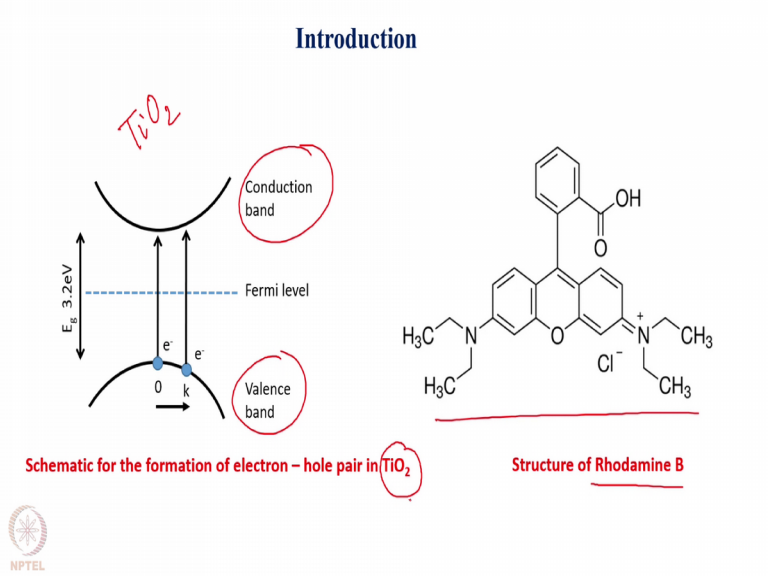

So, we as we know that semi conductors have a valence band and the conduction band; so, when photons of energy higher than this band gap are signed on the semi conductor particles. So, electrons are transferred from valence band to the conductor conduction band, and electron hole pairs are generated where electrons are present in the conduction band and the hole is created in the valence band.

So, now these pairs may combine together in the bulk of the system, but there are coordination defects at the surface which have these charges. Now the hole strapped at the charges have highly reactive oxidation potential means they can take electrons from any material, or any substances.

And electrons at the surface have very high reduction potential means they can reduce any species. Now since these electron and holes because of their high oxidative or reductive potential can induce catalytic reactions at the surfaces. So, the catalyst which we are using here is the TiO 2 which has a band gap of about 3.2 electron volt. Now, we are using a dye whose structure we have mentioned here. So, this dye is Rhodamine B which we will degraded using this TiO 2 semi conductor catalyst.

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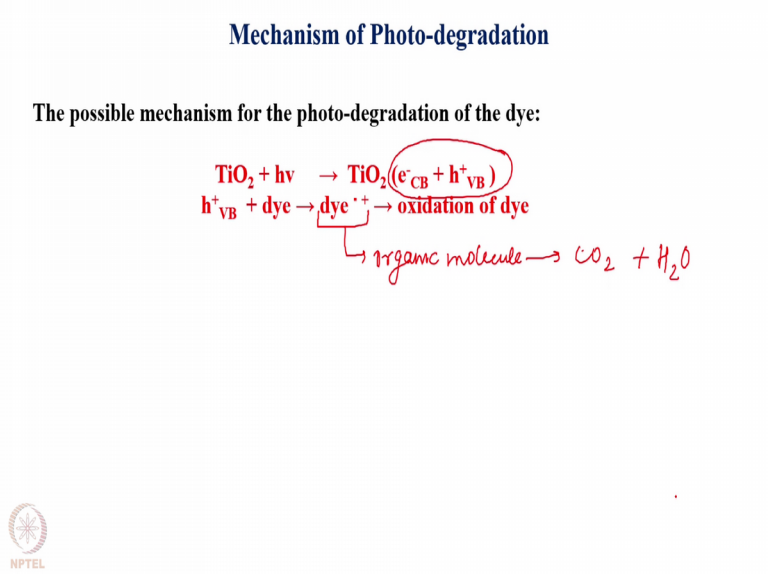

Now, the possible mechanism for photo degradation of dye could be the T i O 2, when is illuminated in sunlight is the energy higher than it is bandgap electron and holes are generated in T i O 2. Now this hole can oxidize the dye, and we know that the final oxidation product of any organic molecule are either CO 2, or water apart from some inorganic species like HCl.

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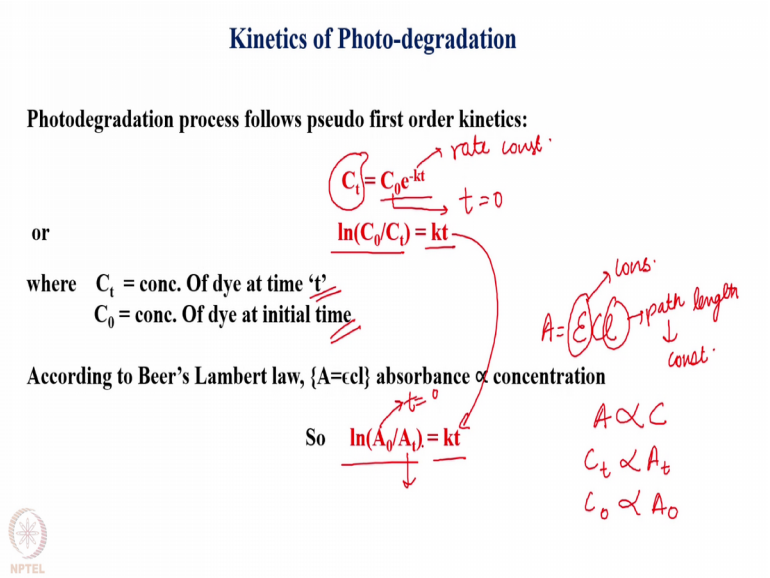

So, we know that this dye follows the first order kinetics, and we know that for first order kinetics the concentration at any time t is given as C naught e to the power minus k

t. Where C naught is the concentration of the molecule at time t is equal to 0, where when the reaction has not yet started and k is the rate constant of the reaction.

Now, we can write this equation as l n C naught by C t is equal to k t, where C t is the concentration of dye at time t, C naught is the concentration of dye at initial time. Now also we know that we have our Beer Lambert's law as A is equal to epsilon c l. So, where epsilon is constant form a dye at a particular wavelength, and l is the path length of our cuvette, in which is also constant.

So, what we are left with A is directly proportional to the concentration of the dye. So, we can replace this C naught by C t or C t can be written as directly proportional to A t; and C naught can be written as directly proportional A naught. So, we can now replace this equation as l n A naught by A t is equal to k t.

So, now using UU Vis spectroscopy we can obtain our A naught that is absorption as time t is equal to 0 and A t that is absorption is at various times. So, we will proceed in this experiment by measuring all these absorbance values.

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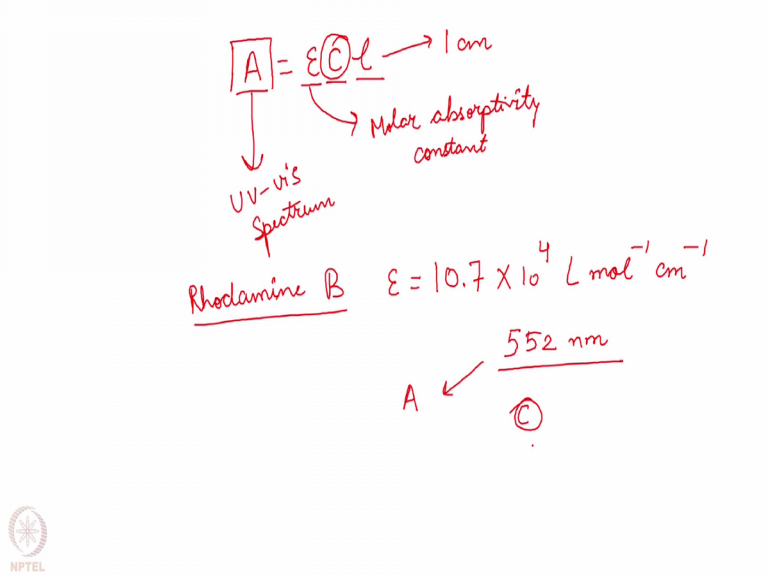

Now, that you know about the Beer Lamberts law which is given by A equal to epsilon C l, where A is the absorption, E is the molar absorptivity constant, C is the concentration of the solution, and l is the path length of the cuvett that we are using. So, if we know the value of absorbance that we can measure using the UV Vis spectrum, or the absorptions

spectrum and if we know the value of epsilon which is the molar absorptivity constant, and we are using a cuvette which has a fixed path length.

Here we are using a cuvette which has a path length of 1 centimeter we can easily back calculate the concentration of the solution. If we know the value of epsilon for a sample which is Rhodamine B here, we can easily calculate the concentration of the solution; if we measure the UVV's spectrum and know the value of absorbance.

So, the value for Rhodamine B as given in literature is 10.7 into 10 to the power 4 deter molen was centimeter inverse. This value is at 552 nano meters, and if we measure the absorbance at this wavelength we can easily calculate the concentration of the solution. For performing this experiment first of all we will be preparing a Rhodamine B solution with a concentration of 10 to the power minus 5 molars.

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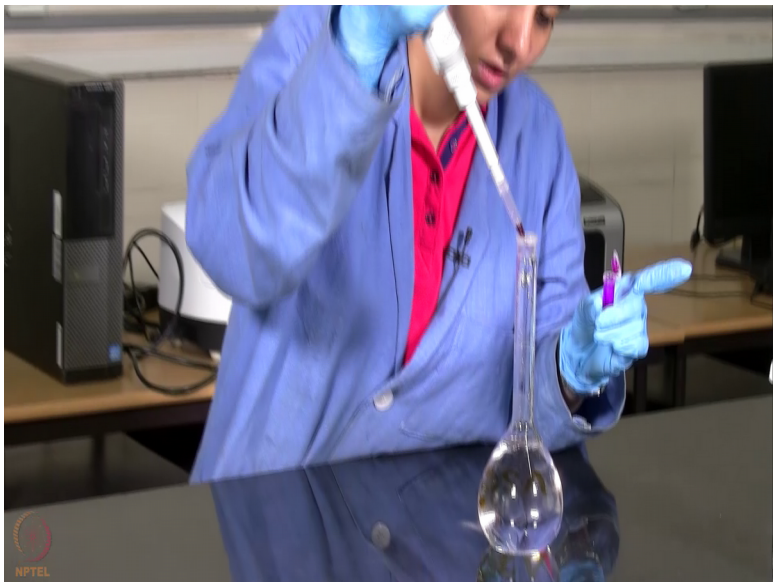

This is a very concentrated solution of Rhodamine B, we will be using this to prepare dilute solution. And we will be adding some amount from this to a 250 ml volumetric flask which already has a some water, distilled water in it. Then we will be shaking the solution a bit and make up the volume to 250 ml.

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This is a UV visible spectrophotometer which is used to record the absorbance values for a sample ranging from 200 nano meters to 1100 nano meters, extending from U V to near I R ranges. And in order to carry out the experiment first of all will do a base line correction using water as a solvent. The purpose of doing a base line correction is that if there is a any absorbance of the solvent in which the sample has been dissolved that could be subtracted cut.

For doing the experiment we will be using a quartz cuvette which does not have any absorbance in the ultra violet region. So, first of all we will be adding water which will be used to do a base line correction to this cuvette. This cuvette has a path length of 1 centimeter, and now I am going to add water to it.

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This is the UVV spectrophotometer which will be using for this experiment it has a light source and the light is entering from here. And there are 8 different sample chambers and 8 samples can be recorded at a time. Now I will be doing a baseline correction for that I am keeping this cuvette containing water in the first sample chamber. And now I will be closing the lid and recording the UV Vis absorption spectrum for this for water.

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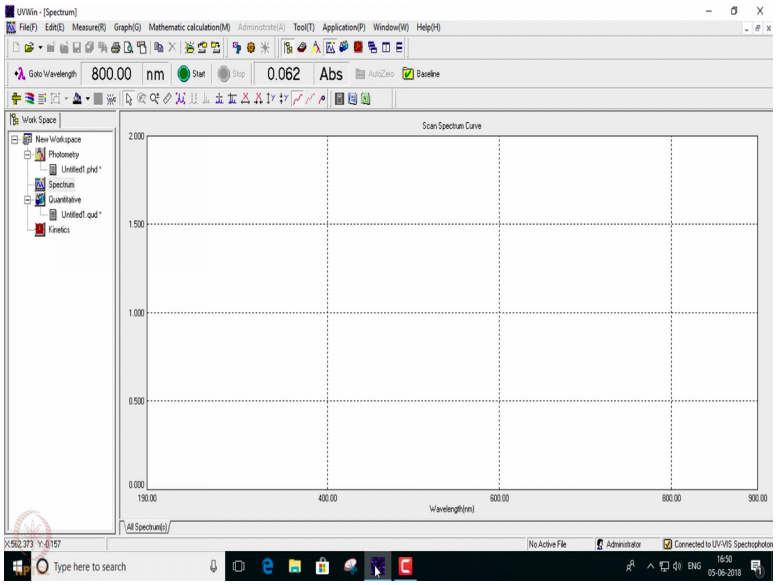

This is the software that is interfaced with the UV visible spectrophotometer that we are using. And the parameters can be set this is the wavelength in nanometers, and this is the

absorbance value. Since Rhodamine B is the sample that we are using here it absorbs in the visible region, which is from 400 to 700 nanometers.

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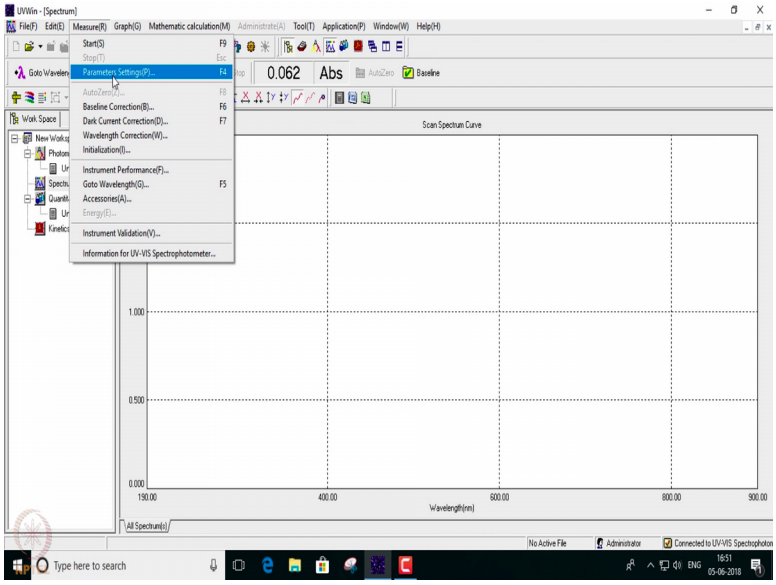

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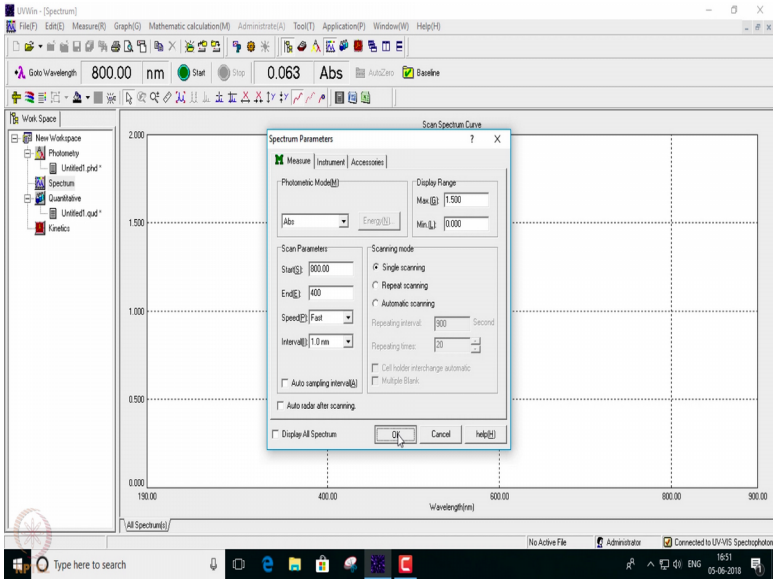

So, we will be setting the parameters first which can be set from here measure and parameter settings.

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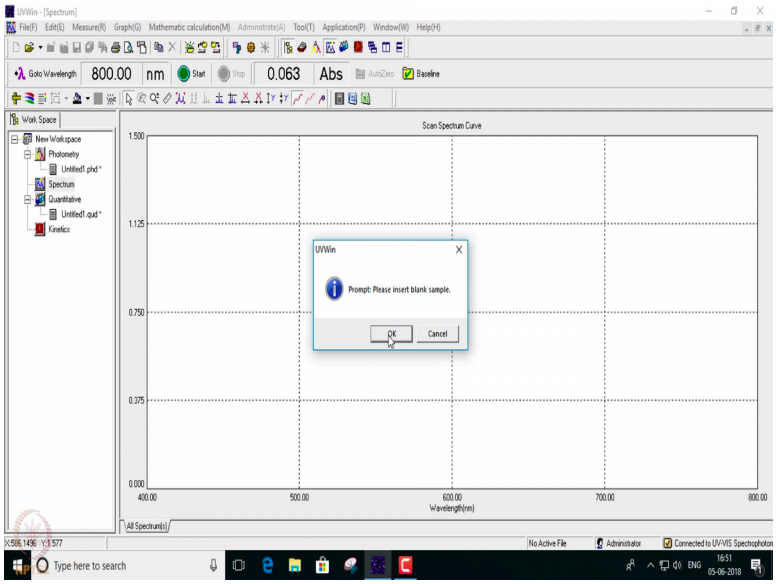

Now that the parameters are set we will be doing baseline correction. And we have in already inserted the blank sample. Now that the baseline correction is done we will be proceeding with a sample which is Rhodamine B solution of concentration 10 to the power minus 5 molar.

Now that the baseline correction is done, we will be removing the cuvette that we had already kept here and we will be inserting a cuvette containing the sample whose absorption spectrum we have to record. Now we will be keeping the sample that we had prepared, and recording the absorption spectrum for this sample of Rhodamine B.

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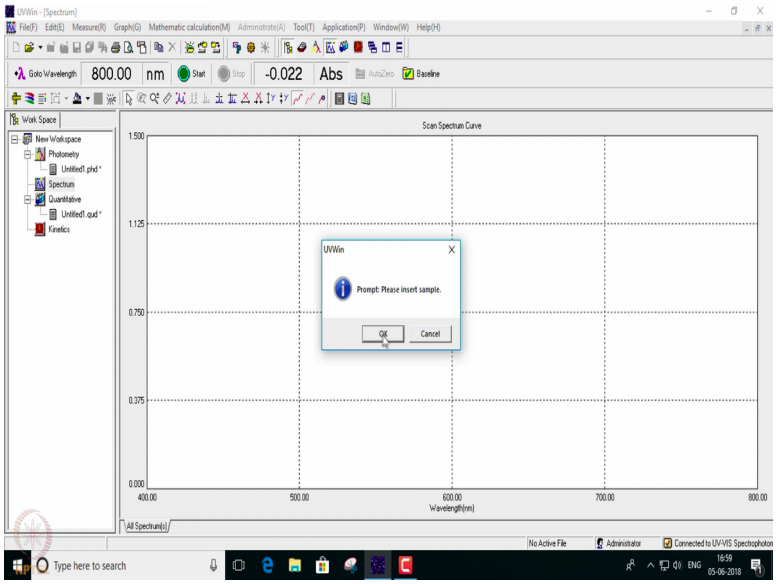

After inserting the Rhodamine B sample into the UV Vis spectrophotometer, we will be starting the measurement. We have already inserted the sample.

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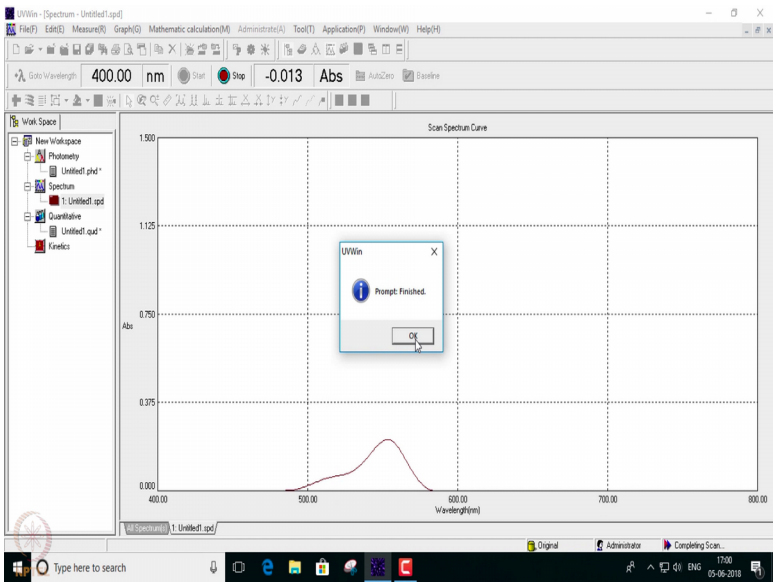

Now, that the measurement is complete.

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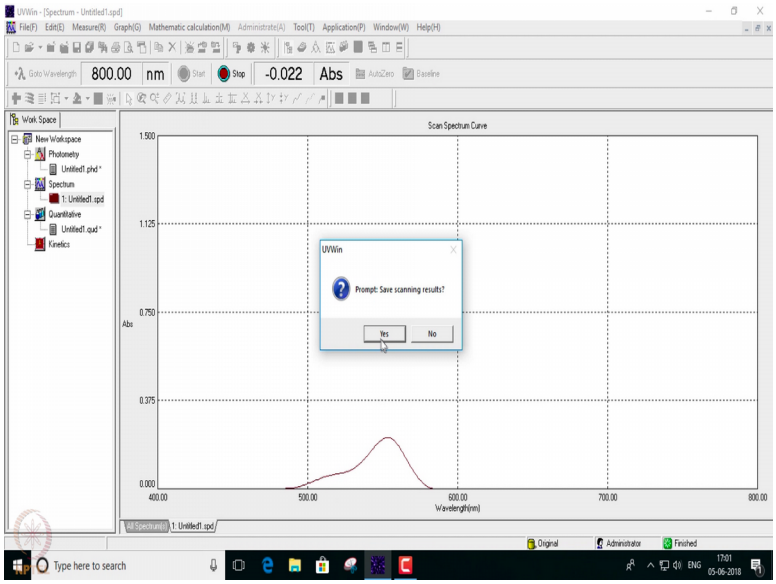

We will save the scanning results.

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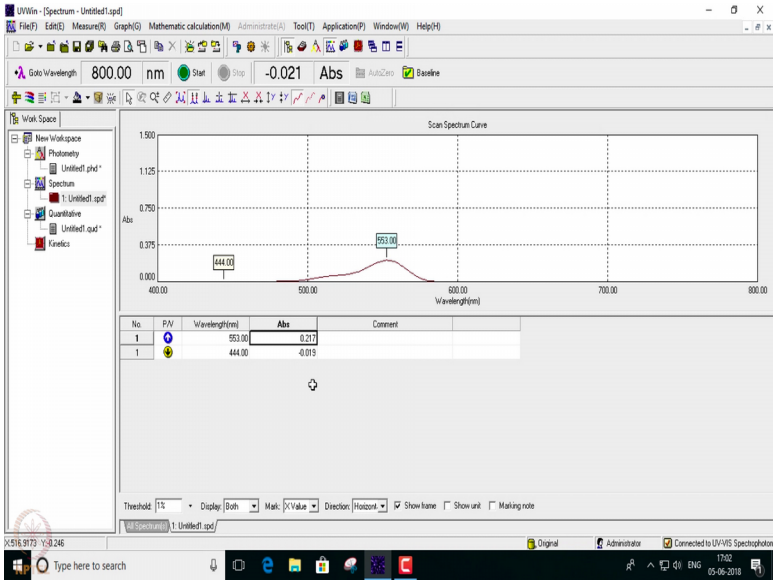

And if we select this option called peak bake we will be able to know will lambda value the wavelength value where the absorption is maximum. So the value turns out to be 553 nanometer for Rhodamine B this value of absorbance which is 0.217 does not correspond to a solution of concentration 10 to the power minus 5 molar. Therefore, we need to concentrate the Rhodamine B solution that we had prepared. So, that the value is around 1.2, and it corresponds to a 10 to the power 5 minus 5 molar solutions.

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Now, we will be adding some solutions from this concentrated solution that we already had to the 250 ml volumetric flask, so that this solution gets concentrated. And then we will be making up the volume to 250 ml. This is the new solution that we just prepared and now we will be recording the absorption spectrum for this. Now we will be recording the absorption spectrum for the new solution that we just prepared.

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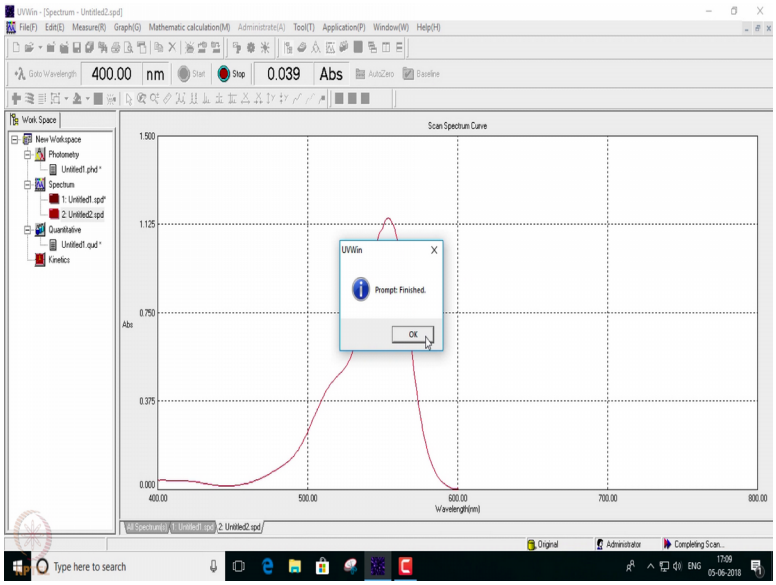

Now, that the measurement is complete. Now we will save the scanning results.

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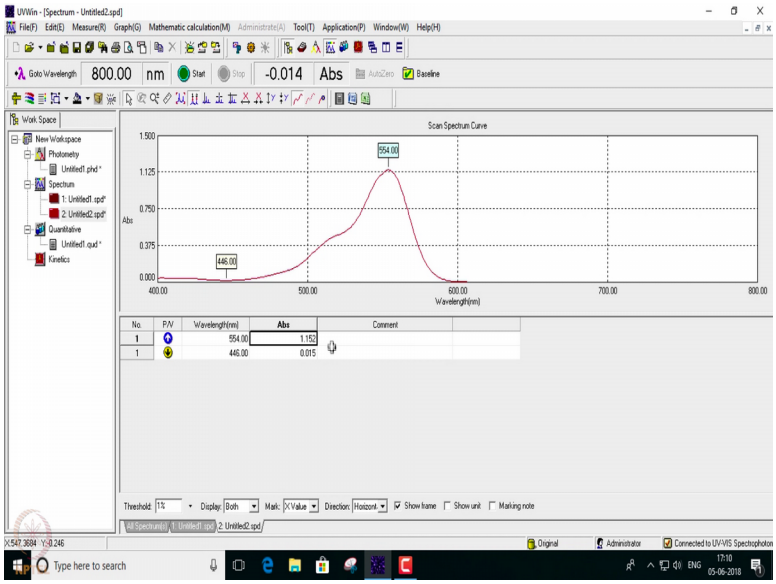

And again if we do a peak big the value of absorbance now comes out to be 1.152. And therefore, the new solutions solution being prepared is of the order of 10 to the power minus 5 molars.

So, now that we have 10 to the power minus 5 molar Rhodamine B solution is ready. We are going to at 30 milligram of titanium oxide to it which we have already wave using a waving machine. So, this will add to it. So, now, that we have added 30 milligram of TiO 2 to it. We have to measure the absorbance of this solution immediately this absorbance will correspond to the absorbance of the solution at time t is equal to 0. So, this now we have over Rhodamine B with added TiO 2 we will measure the absorbance of solution, and take it as the absorbance at time t is equal to 0.

So, I will take some portion from this, and we will add to this cuvette. Now we will measure the absorbance of this solution. We will now start measuring the absorbance of this solution. If mean while our scanning is running will split this solution into two portions; this does not need to be exactly divided into 2 equal halves just roughly 2 equal halves. So, once part will keep under direct sunlight and other solution which we will keep in dark. This portion we will be keeping under dark conditions and this portion we will keep under direct sunlight.

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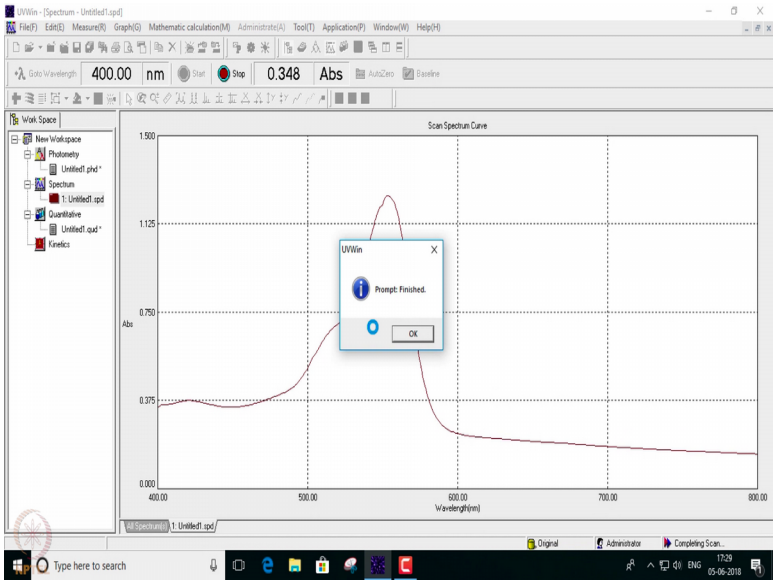

So, now our scanning is complete and we get a UV Vis spectrum as like this. So, this spectrum corresponds to the absorption of the solution at time t is equal to 0. Now the parts which we splitted into two parts for dark and sun light we will measure the absorbance of these two solutions at some regular intervals and measure those absorbance. Those absorbances which correspond to the absorbance at certain time say t is equal to t and we will measure the absorbance of this solution at certain time intervals. And we will withdraw the sample from this solution after certain time intervals.

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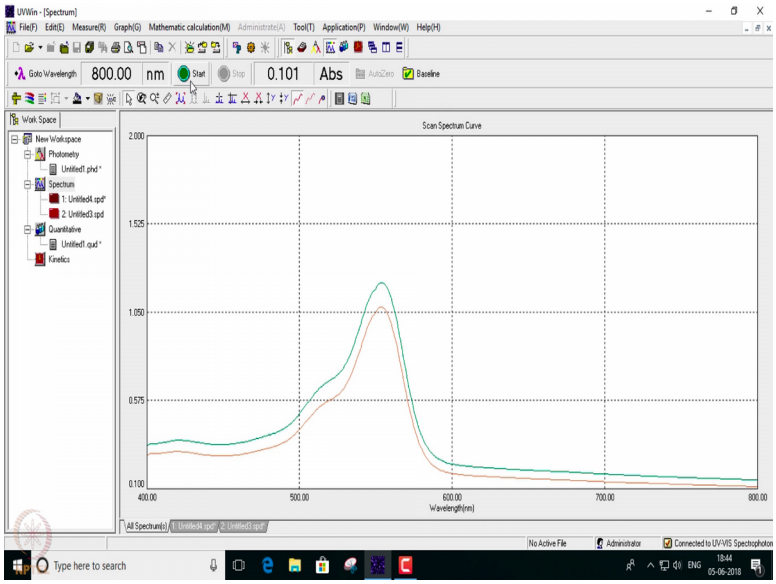

So, this green curve here shows the absorption of our dye at time t is equal to 10 minutes, while this orange color is spectrum shows here the absorption of the dye at t is equal to 30 minutes. So, we can see that over time the absorption of the dye has decayed which is mainly because, of the photo degradation of the dye with TiO 2.

So, now we are going to record the spectrum of the dye at time t is equal to 45 minutes, this time t is equal to 45 minutes is the time which under which we have kept the dye in the solar irradiance. So, we have been kept we have been keeping the sample in solar irradiance for the last 45 minutes.

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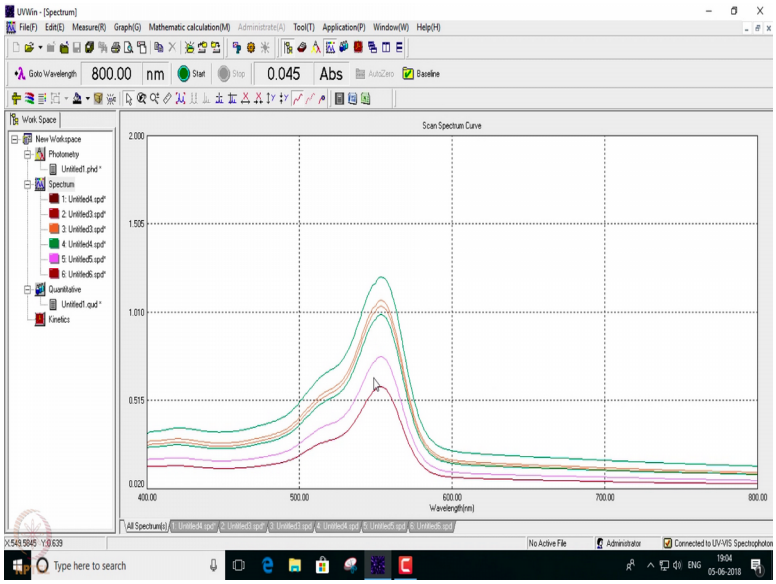

So, we are we have drawn some sample from it and we are now measuring it is absorbance. So, this third spectra which we can see here is the absorption of the dye recorded at t is equal to 45 minutes. So, we can see that the absorption of dye has further decayed after 45 minutes. So, from we here we can see that after 100 minutes the absorption has decayed a lot over time. So, similarly we will so this for the dark dye kept under dark conditions.

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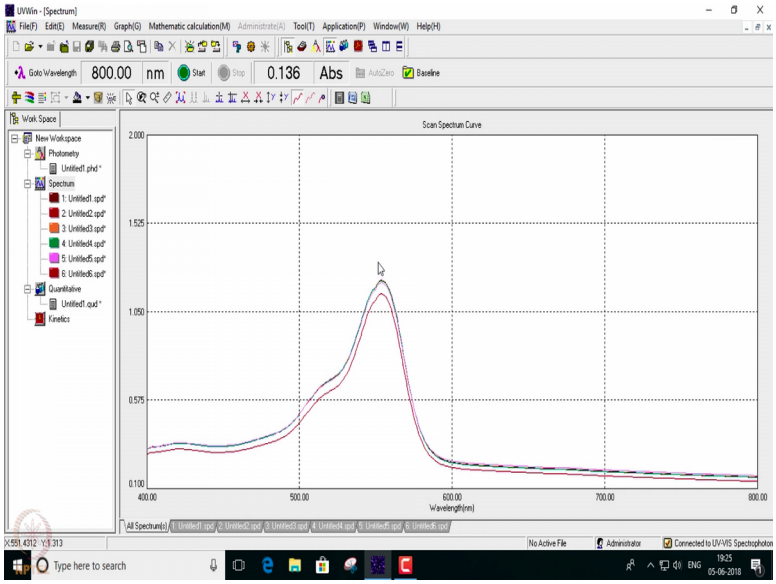

So, from this window we can see that the absorbance of the solution kept in dark has decayed very less over 100 minutes which can be which can be compared with the solution kept in sunlight, where the absorbance of the solution has decade a lot over 100 minutes. So, from this we can see that the dye has really been degraded when captained sunlight and when TiO 2 is added to it as a catalyst.

After recording the absorption spectra for the samples which are withdrawn at different time intervals a both in dark conditions as well as under solar irradiance are then used and a plot of l n A naught by A t versus time is drawn, where the A t values correspond to the absorption at lambda max value for different samples and A naught is the absorbance value for the sample which was taken at t 0.

So, this plot of l n A naught by A t versus time is then used to calculate the slope and then gives the rate constant of the reaction that we have done. If the solar flux is not very high, then UV irradiation of the sample can be used to carry out similar kind of experiment which is photo degradation of the dye.

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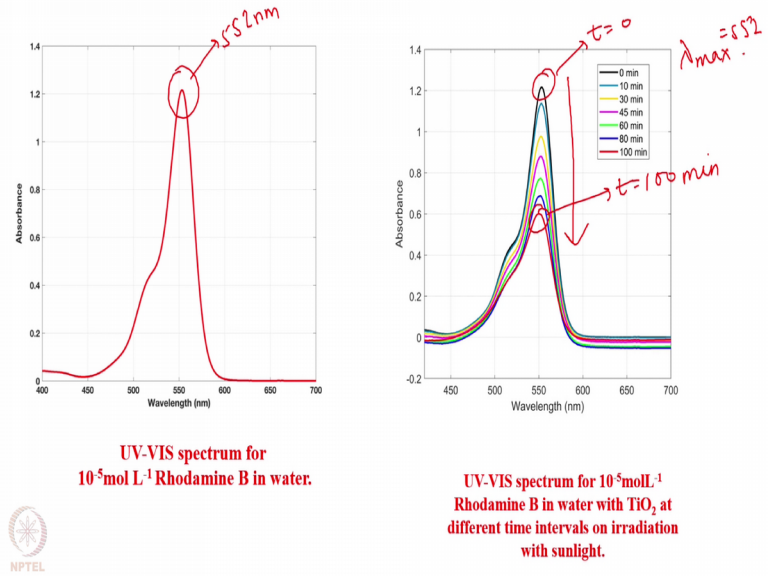

UV-VIS spectrum for 10^{-5}mol L^{-1} Rhodamine B in water.

UV-VIS spectrum for 10^{-5}molL^{-1} Rhodamine B in water with TiO_2 at different time intervals on irradiation with sunlight.

So, this is the UV visible or absorption spectrum for 10 to the power minus 5 moles per liter Rhodamine B solution in water. So, we can see there it has a absorption maxima at 552 nanometers. Now after taking the spectrum at different times and processing the data using some plotting software, we get our results as such in which we can see that there is a continuous decay of the absorption values with time.

So, we can see that absorption is maximum at time t is equal to 0, and is minimum at time t is equal to 100 minute. So, from this we can see that the dye has degraded with time under solar irradiance.

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Time	Absorbance	A_0/A_t	$\ln(A_0/A_t)$
$0(A_0)$	1.216	1	0
$10(A_1)$	1.137	1.0695	0.0672
$30(A_2)$	0.976	1.2446	0.2188
$45(A_3)$	0.879	1.3818	0.3234
$60(A_4)$	0.773	1.5731	0.4530
$80(A_5)$	0.687	1.7674	0.5695
$100(A_6)$	0.601	2.0233	0.7047

Absorption values for
10^{-5} mol L^{-1} Rhodamine B in water with TiO_2
at 552 nm wavelength.

So, we then tabulated these absorption values at absorption maxima that is lambda max is equal to 552 nanometer. At time t is equal to 0 we got the absorbance as 1.216 and time t is equal to 100 we got the absorbance at 0.601. So, we can see that the absorbance has been halved under 100 minutes within if the degradation of dye. Now, what we need to plot is that time versus ln of A naught by A t whose slope will give the rate constant for this reaction.

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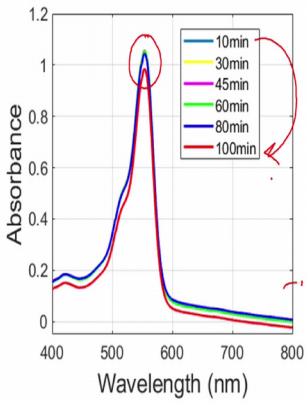

UV-VIS spectrum for $1.14*10^{-5}$molL^{-1} Rhodamine B in water with TiO_2 (kept in dark) at different time intervals.

Also we can see that this is the plot of the dye kept under dark. And we can see that even after 100 minutes the dye has not been degraded much and there is very less change in the absorption of the dye, even when it is kept for 100 minutes under dark. So, we can see that the solar irradiance has really a great effect in degradation of the dye.

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Time	Absorbance	A_0/A_t	$\ln(A_0/A_t)$
$0(A_0)$	1.216	1	0
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Absorption values for 10^{-5} mol L^{-1} Rhodamine B in water with TiO_2 at 552 nm wavelength.

After we have obtained the value of absorbance at different time intervals, we will be calculating the value of A naught by A t. And then calculating the value of ln A naught by A t and then plotting these values versus time.

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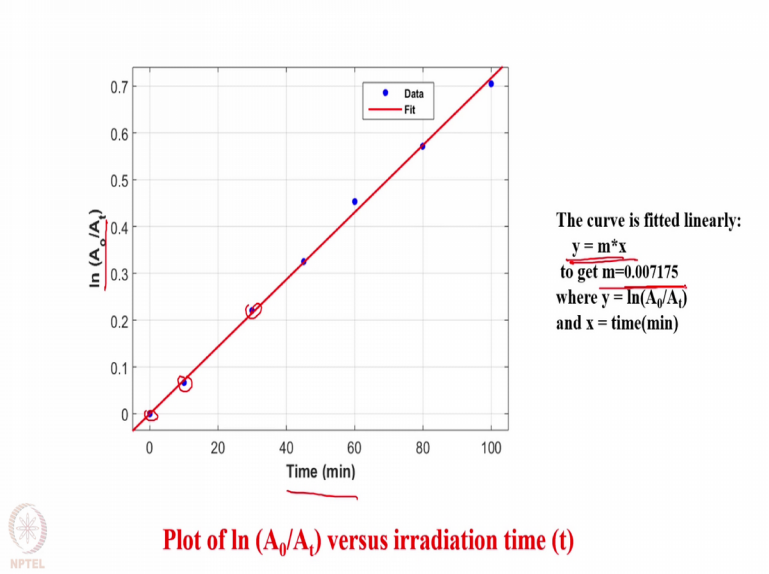

This is the plot that we obtain after plotting these two and then these data points are fitted into an equation which is given by y equal to mx. And the slope which is calculated after fitting the data gives the value of the rate constant. So, the slope value that we obtain here is 0.007175.

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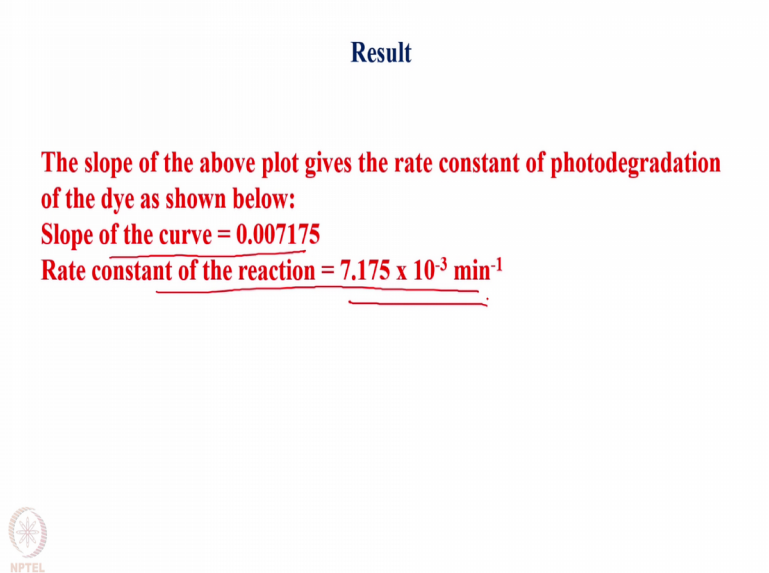

The slope of the curve is 0.007175. So, the value of rate constant for this reaction which is photo degradation of the dye is given by is given as 7.175 into 10 to the power minus 3 minute inverse.

So, from the experiment we can see that the Rhodamine B has degraded a lot over time when kept in sunlight. So, we can see from this experiment that this can provide a cost effective and natural way to degrade it, degrade organic pollutant dyes which are persistent in nature. Also we can see that the dye solution which was kept under dark condition did not go photo degradation a lot as compared to the one kept under solar irradiance.