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Nitrogen Doped Titanium Dioxide in the Photocatalytic Degradation of Methylene Blue

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NITROGEN DOPED TITANIUM DIOXIDE IN THE PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

AN HONORS THESIS

PRESENTED TO

THE DEPARTMENT OF CIVIL ENGINEERING

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OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELORS OF SCIENCES, WITH UNIVERSITY HIGH HONORS

AND HONORS IN CIVIL ENGINEERING

BY

ASHRAYA UPADHYAYA

MAY 2018

This thesis is dedicated to my parents, Seema and Ashutosh, my brother, Aavash, and my grandparents for their endless support and encouragement.

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Abstract

Titanium dioxide(TiO_2) is a stable, effective and well-known photocatalyst for degradation of pollutants. However, its practical applications are limited due to the need for energy higher than 3.2 eV, or a wavelength lower than 390 nm (high frequency waves, ultraviolet and above) hindering its ability to effectively work in the visible light region (about 400 nm to 700 nm). Nitrogen-doped TiO2 (N-TiO2) has garnered some attention as a photocatalyst as it appears to work even in the visible light region. This could allow the utilization of a larger part of the solar spectrum. This thesis presents the results of photocatalytic degradation of methylene blue (MB) carried out under simulated visible light by using TiO_2 and N-TiO_2(doped in the lab) to evaluate and compare their efficiencies under similar conditions.

Key Words: Titanium dioxide(TiO_2), Nitrogen-doped TiO_2(N-TiO_2), Methylene Blue(MB), Visible Light, Photocatalysis.

1.0 Introduction

1.1 Background:

Photocatalysis is a process in which a catalyst facilitates and speeds up a process in which sunlight (solar energy) is used to either oxidize and/or reduce a given compound into other compounds or elements without being used up itself. The photocatalyst appears in the rate expression describing a thermal reaction, but it doesn't appear in the stoichiometric expression.

In 1972, Fujischima and Honda,[1] synthesized hydrogen via water photocatalysis in the presence of a Titanium Dioxide(TiO_2) electrode. The scientific community has been fascinated ever since by this approach of breaking down compounds by using sunlight and therefore has increasingly studied and researched this phenomenon. In the aforementioned process, TiO_2 is analogous to the chlorophyll pigments involved in photosynthesis. Both substances are semi-conductors. Through this process, humans successfully translated a naturally occurring event into practical, beneficial use, opening up new methods to treat wastewater and clean polluted air [2,3,4].

To date, much research has been done to efficiently use photocatalytic systems. Important applications have been developed in the field of water and wastewater treatment. Because photocatalytic reactions successfully oxidizes and reduces unwanted substances determined by each particular system, experimentation have produced some promising results that show applicability in large scale environments. An example of this versatility is the use of photocatalysts to oxidize harmful organic substances in wastewater into harmless carbon dioxide and water, and reduced dissolved inorganic substances [3,4].

As far as photocatalysts go, P-25 anatase TiO_2 is the most widely known and effective one currently in use. It is, however, one of many effective semi-conductors that work as photocatalysts. TiO_2 is highly used due to its high reactivity, chemical stability and lower costs [1].

However, TiO_2 has limitations. For instance, TiO_2 has a large band gap energy. Also, it clumps up if used in high concentrations [5]. These drawbacks are significant when considering the science behind the working mechanism of TiO_2.

TiO_2 works by absorbing photons from an energy source and uses them to excite an electron from one energy level to the other. In doing so, high energy electrons and hole pairs (left behind by the excited electron) are generated. The high energy electrons reduce dissolved metals while the hole oxidizes substances, making TiO_2 effective in the treatment of organic and inorganic pollutants. The main limitation of this process lies in the need for energy higher than 3.2 eV, or a wavelength lower than 390 nm (high frequency waves UV and above) to effectively excite and eject the electron. So, this photocatalyst is efficient only when UV light is used. This is expensive because the sunlight that the Earth receives has a very small percentage of UV.

Another drawback is the clumping of TiO_2 powder when used in high concentration in the slurry type systems. When TiO_2 powder is used in a wastewater treatment plant, most of it would be lost in the process if not properly recovered. And the process of recovery is expensive and energy intensive.

To address the issue of limited bandwidth of the TiO_2, it has been found through prior research that doping the lattice structure of of TiO_2 with nitrogen [6] has increased photocatalytic reactivity toward organic molecules under visible light. The previously known range of wavelengths 390 nm and lower for P-25 anatase TiO_2 was now increased to up to 600 nm if the structure was doped with nitrogen [7]. This phenomenon and technique are explored in this research in order to compare the efficiency of nitrogen doped Titanium Dioxide (N-TiO_2) and non-doped TiO_2 at a bench scale.

A process known as hydrothermal amination is used to accomplish the catalyst doping. Here, TiO_2 is mixed with a triethanolamine solution, sonicated and then heated in an oven to ensure that doping occurs.

To address the issue of TiO_2 powder clumping, an alternative is to integrate the nitrogen-doped TiO_2 into a Polyacrylonitrile (PAN) membrane [8]. This will effectively remove the need to recover the powder downstream after treatment. Since the photocatalyst should in theory be trapped in a membrane, it will ensure that the membrane can be recycled several times. Also, as the membrane will be very thin (high surface area to volume ratio), it should work efficiently much like how leaves work in photosynthesis[9].

2.0. The Thesis

This thesis presents the theory and the background information related to photocatalytic experiments performed by using anatase TiO_2 and N-TiO_2, its doped counterpart. The N-TiO_2 was synthesized in University of New Orleans (UNO) labs and used in photocatalytic experiments, since literature review provided evidence that this was a promising use of the catalyst [7,10,11] .

The results of such experiments are presented herein. This thesis also discusses and attempts to explain these results. It also proposes potential usage of technology discussed above and what needs to be done in the future to gain more insight into it.

3.0. The Project

To bring some of the theory discussed to life, a series of experiments were conducted. While the specifics of each step will be explained in detail later, this section provides an overview of the experimental procedure.

Firstly, following the method presented in [7] by Feng Peng et al. ,nitrogen doped titanium dioxide was synthesized in the lab. This was done using a hydrothermal method and required a convection oven. This was one of the most challenging steps, as it took a succession of failed batches to finally manufacture a batch of doped TiO_2 that matched the description given in the aforementioned paper.

Secondly, a batch reactor (Figure 1) was setup underneath a solar light simulator lamp from Solux with 120V and 50 Watt power, that emitted light primarily in the wavelengths of 400 nm to 800nm and up to 0.85% below 400 nm. This most realistically mimicked the visible light that the Earth’s surface receives which makes up upwards of 45% of the energy comprised in the solar radiation. The reactor itself was placed inside a water bath filled with cool water to avoid excessive temperature change. The reactor was also kept at a distance of 15 cm away from the top of the light source.

Thirdly, a dispersion of sonicated methylene blue (MB) and the catalyst (doped or undoped TiO_2) was added to the reactor and stirred with magnets for the duration of the experiment. MB solution was picked as model contaminant due to it being a common organic pollutant from many industrial plants. Studies have shown it to have negative impact on humans, animals and plants [12] .

A typical photocatalytic experiment consisted of stirring the mixture in the dark for an hour to allow adsorption equilibrium of the MB molecules onto the catalyst and then turn on the lamp and irradiate the target dispersion for two hours. Samples were taken every 30 minutes and analyzed in a spectrophotometer for absorbance at different wavelengths. The sample would be replaced in the reactor as soon as the measurements were made. A thermometer monitored the temperature at each reading and the velocity of the magnetic stirrer was kept constant throughout the entire duration. The procedure was developed after [10] by Jia Wang et al., with some modifications.

The purpose of this experiment was to evaluate whether the doped catalyst is more efficient at degrading MB then TiO_2 under similar conditions.

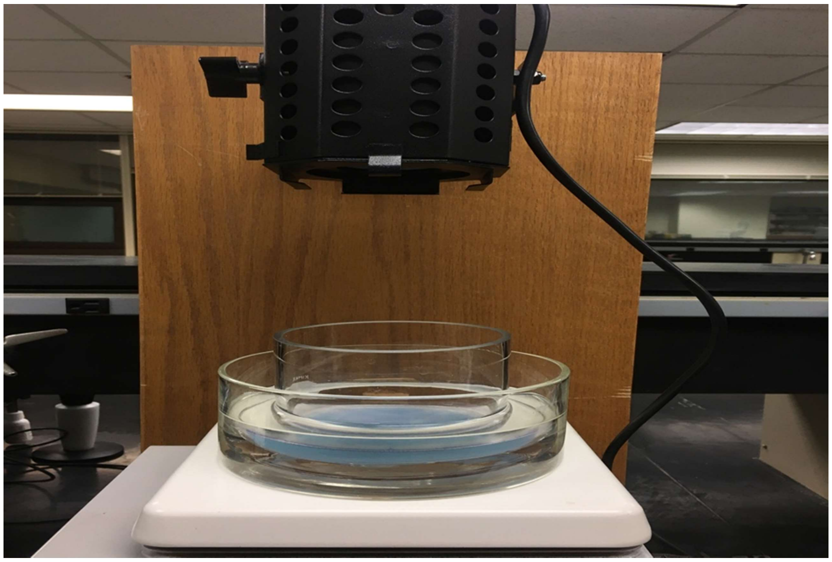

Figure 1: Batch reactor

4.0. Theory

4.1 Methylene Blue

MB was selected as the model contaminant for this experiment. With a molecular formula of $C_{16}H_{18}ClN_3S$, this is a synthetic organic dye. For the purposes of the experiment and for expected results, MB should be oxidized under the presence of solar energy with the TiO_2 and N-TiO_2 catalyzing their respective reactions at different rates [13].

A stock solution of 1.5% MB from Sigma-Aldrich was used to prepare a 20-mg/L solution of MB by serial dilution.

Most of the problems associated with this dye comes from industrial discharge of it into the waste water system. As MB is commonly used in paint, plastics, food, textile and rubber, it is abundantly found in the industries. MB is also used in the medical field to stain cells before viewing them under a microscope. It has broad applications and needs to be treated properly if disposed incorrectly.

MB has been linked with diseases such as vomiting, dermatitis, cancer and gene mutations. These are all concerns connected with colored dye effluents into the waste water system and needs to be dealt with.

MB, as mentioned previously, is a relatively abundant compound i.e. it could be easily obtained. It is cost effective as well. It was straightforward to run an experiment on a MB solution because of its relative ease of decomposition under sunlight.

MB solution (Figure 2) being an organic dye shows a specific set of characteristics. Since the objective was to measure MB concentration as a function of absorbance using a DR 5000 spectrophotometer, an absorption peak at 664 nm was identified as indicator. The experiment then monitored how the absorption of energy at the peak changed with respect to time of treatment. As it is known via literature review, the peak of absorption wavelength should not change during degradation process [7,10,11]. While it would have been more accurate to measure the total organic carbon or TOC and the amount of carbon dioxide produced by the MB after degradation, due to time constraints these could not be done in this experiment and is something that will be addressed in future experimentations.

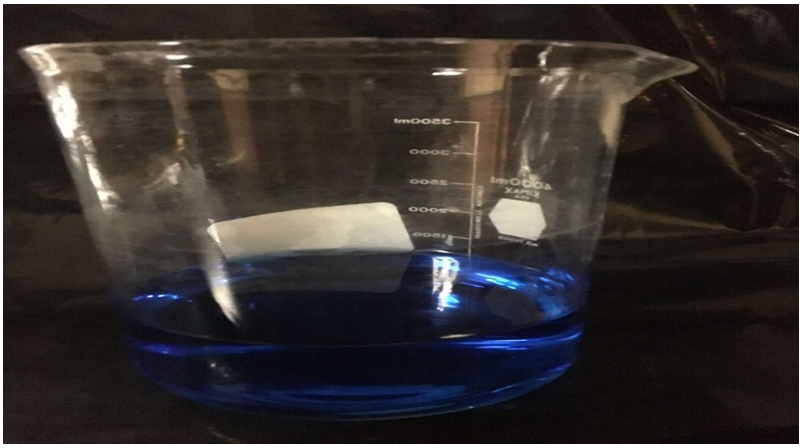

Figure 2 : Methylene Blue solution (20-mg/L)

4.2 Anatase Titanium Dioxide

TiO_2 is considered to be one of the most investigated photocatalysts. This is mainly due to the fact that it has high photo-activity, low cost, low toxicity, good chemical stability and of course good thermal stability [7] .

TiO_2 is a semi-conductor. This is one of the key characteristics that allows TiO_2 to act as a photocatalyst. A semi-conductor is capable of donating electrons and accepting protons according to the type of reaction that is taking place. It can also be doped with other metals and/or non-metals to either increase or decrease conductivity. For instance, doping changes the charge carriers in the crystal lattice of the semi-conductor. This in turn makes it possible for the semi-conductor to either form free holes known as “p-type” which are electron deficient or form electron rich “n-type” lattice structure which donates electrons. This then makes the semi-conductor a highly useful material in either oxidation or reduction reactions [11]. The free holes can then accept electrons to act as an oxidizing agent in certain reactions. The excess electrons can be donated and the material then acts as a reducing agent.

For the purposes of this experiment, according to the literature review [7,11], anatase TiO_2 was selected(Figure 3). It is white in color (Figure 4) . This is one variation of TiO_2 that can absorb up to 7% of the supplied UV rays. This is a higher absorption rate than the other forms of TiO_2 available. This is beneficial in this experiment because it can be used to compare the effect of doping this variation of TiO_2. As the TiO_2 alone is be able to perform some photocatalytic activity it is a better measure to compare how doping would enhance the photocatalytic activity especially in the visible light spectrum.

The mechanism in which the anatase TiO_2 works is interesting and is important for the purposes of the experiment. This is because of the mechanism in which this compound generates electrons is significant. As MB needs to be oxidized, electron generation is an important step in this experiment. During photocatalysis, irradiating photons of light with energy greater than the bandgap of the semi-conductor excites electron from the valence band to the conduction band. In the case of anatase, the bandgap is 3.2 eV, therefore UV light which has primarily a wavelength of less than or equal to 387 nm can be utilized. This part is vital for the purposes of this experiment.

As previously mentioned TiO_2 is a semi-conductor. This property is crucial because unlike conductors (usually metals) , the process of recombination, i.e., the process by which a conduction band electron losses energy and re-occupies the energy state of the electron hole in the valence band, is very low in semi-conductors. This means that semi-conductors remain separated into electron carriers and holes for a longer duration than conductors or insulators therefore, making them very useful as a catalyst.

The ability to be sufficiently and easily doped is the most important factor in choosing TiO_2 as the photocatalyst. While each type of doping brings specific characteristics out of the photocatalyst, doping it with non-metals are economically more feasible. Regardless, of the intended application, it is worth discussing the types of doping that can be done.

Morphological and chemical doping can be done to TiO_2. In morphological doping, the semi-conductor is doped in such a way that its chemical properties are not altered. For instance, when a compound is morphologically doped, its surface area is increased as is its porosity. This is done to increase adsorption. However, it doesn’t concern with altering the energy band gap, thus making it not useful for using solar energy to perform photocatalysis [11].

Chemical doping is done to introduce other elements in the lattice of the semi-conductor in order to overcome chemical deficiencies. It is primarily done by incorporating additional components into the lattice. By doing this, the band gap of the anatase changes, and thus the absorption range gets broadened. This, in turn, makes it possible for TiO_2 to absorb energy in a broader frequency and wavelengths, or in the visible light region i.e. $\lambda > 398$ nm [7,10,11] . This is where the nitrogen doped TiO_2 (Figure 5) comes into the fold in this experiment.

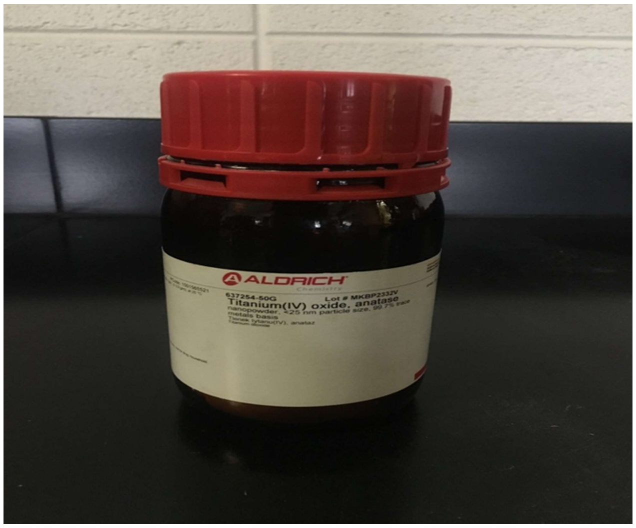

Figure 3: Titanium(IV) oxide, anatase from Sigma-Aldrich

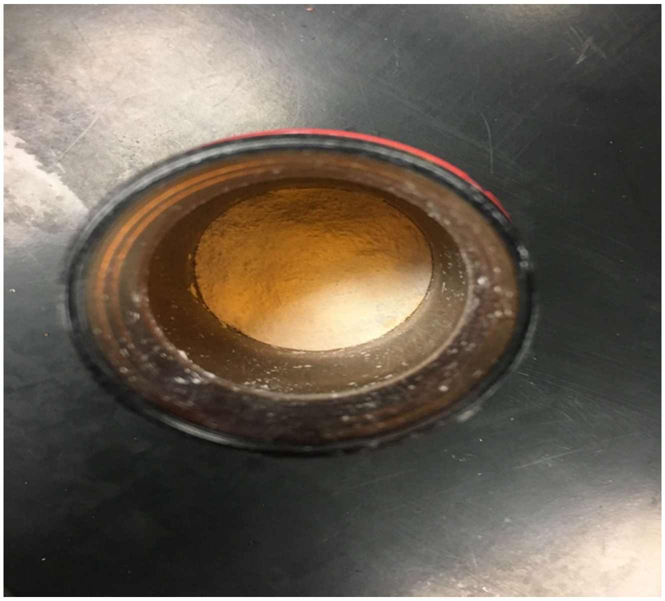

Figure 4 : TiO_2 powder (White)

Figure 5 : N-TiO_2 Powder (Yellowish Brown)

4.3 Nitrogen-Doped Anatase Titanium Dioxide (N-TiO_2)

Nitrogen doping induces a significant improvement in optical absorption of the energy from the sunlight [7,11]. It also improves the photocatalytic degradation capacity of TiO_2 in the visible light region. While it is true that the oxidizing ability of TiO_2 does get diminished after nitrogen is doped into the structure of TiO_2, there has been enough evidence to suggest that the improved efficiency in the range of absorption compensates for the lack of oxidation ability of the original compound [7,11].

N-doped TiO_2 exhibits broad absorption in the visible light region, especially in the wavelengths less than or equal to 550 nm [7,11] . Therefore, N-TiO_2 can utilize a large part of the solar spectrum rather than be restricted to simply using UV rays as is the case with TiO_2. This might be useful for environmental and energy applications, such as photocatalytic degradation of organic pollutants, solar cells, sensors and water splitting reactions.

Photocatalysis is based on the generation of electron-hole pairs upon irradiation with light, as previously mentioned. The electron then migrates from the valence band to the conduction band within the lattice structure of the semi-conductor. This leaves behind a hole in the valence band. This hole then participates in adsorbed organic species and adsorbed molecular oxygen to conduct ‘redox’ reactions i.e. reduction and oxidation.

The incorporation of nitrogen into the TiO_2 lattice leads to the formation of a new mid-gap energy state. This mid-gap state eventually decreases the band gap of TiO_2 to about 2.5eV from the original 3.2 eV and shifts the optical absorption to the visible light region. This happens due to either of the following reasons: [7,11,14]

First, the conduction band of the TiO_2 compound is usually the 3d energy level of the titanium in the compound. The valence band is consequently the 2p energy level of the oxygen. These two have a band gap of 3.2 eV as discussed previously. However, when nitrogen is incorporated into the structure, the 2p energy level from the nitrogen now acts as valence band and this band is at a higher energy level than that of oxygen, therefore reducing the band gap.

Second, the nitrogen and the oxygen 2p energy levels mix to form a hybrid energy level somewhere above that of the original oxygen 2p level which now acts as a new valance band. This new valence band is then above the original oxygen 2p level, therefore, reducing the bandgap again.

Third, the titanium in the structure is replaced by the doped nitrogen. This happens only while using the hydrothermal method discussed below. This then causes the 2p energy level of the nitrogen to act as the conduction band and thus substantially reducing the bandgap.

It is therefore possible for the electrons to migrate from the valence band to the conduction band upon absorbing visible light, which leads to the visible light activity of N-doped TiO_2.

The implications of nitrogen doping are important for this experiment. However, there are several methods of doping nitrogen onto the TiO_2. These are also described and assessed before disclosing which method of nitrogen doping was selected for this experiment.

4.4 Methods of Nitrogen Doping

Several methods of nitrogen doping into TiO_2 has been developed and studied [11] . Methods include : ball milling, sputtering, plasma or ion implantation, sol-gel method, solvo-thermal method and hydrothermal method. Among these the most commonly used and those that are proven to be most efficient are the methods that include direct synthesis of TiO_2 in a nitrogen environment or oxygen treatment of titanium nitride.

For the aforementioned methods to be successful, the sources of nitrogen that are generally used are : nitrogen dioxide, tert-butylamine, ammonia, hydrazine, triethylamine, urea and thiovrea.

Considerable number of reports have focused on doping TiO_2 thin films and powders with nitrogen by annealing TiO_2 at a very high temperature. However, this method only yielded approximately 5% doping of nitrogen into the structure of lattice [7]. Another method is thus used while making the nitrogen doped catalyst in this experiment.

Degussa P25 TiO_2 is a commercial photocatalyst with a high activity under UV irradiation. It is very significant and practical to explore the direct and simple amination method of P25 for the production of N-TiO_2. It should yield a high nitrogen concentration that has a high photocatalytic activity under solar and visible light.

For this experiment, we used precisely the aforementioned method due to its success in previous research [7]. Facile hydrothermal method is used to dope nitrogen into P25 TiO_2 with triethlyamine(TEA) as the nitrogen source. It is expected that the dopant concentration of nitrogen could reach up to 21% using this method.

5.0 METHODOLOGY :

5.1 Photocatalyst synthesis

For this experiment, the hydrothermal method of doping was used. Triethylamine (TEA) was used as the source of nitrogen. In a method adopted from [7], 1.0 gram of commercially available P25 anatase titanium(IV)oxide was added into a 80-mL solution of commercially available TEA . To disperse the mixture homogenously, the mixture was first stirred manually using a metallic stirrer. The mixture was then sonicated using a high intensity ultrasound sonicator for 30 minutes while periodically shaking the beaker containing the mixture to prevent overheating of the mixture. After the sonication, the mixture was left to cool down for about 2 minutes. After that, it was put into a Teflon-lined stainless autoclave and was heated at 140 °C for 24 hours. The resulting solution was cooled down for 12 hours for it to reach room temperature. Then, the suspension (Figure 6) was washed by de-ionized water and absolute ethanol in a separation funnel several times. The precipitate was then centrifuged for 15 minutes at high intensity. Any remaining supernatant was then disposed off and the pure precipitate was then dried in a convection oven at 200 ° C for 10 hours. The resulting yellowish brown powder (Figure 7) yielded a by-product of about 65% recovery from the original amount of TiO_2. This powder was then ground to make it as small as possible.

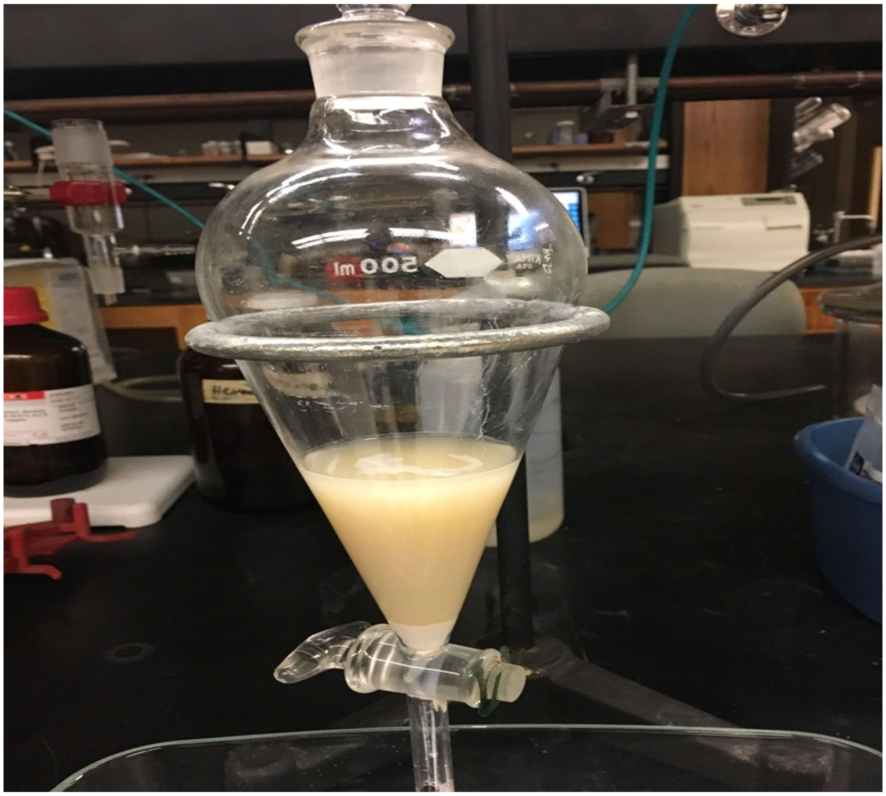

Figure 6 : Settling of the precipitate

Figure 7: N-TiO_2 Powder after thermal treatment

5.2 Preparation of the Methylene Blue Solution

A commercially available stock solution of 0.015-g/mL-MB solution was purchased from Sigma Aldrich. This solution was then serially diluted by using deionized water a concentration of 20-mg/L (Figure 2) . The serial dilution was done by equating the initial and the final concentration of the solution keeping the number of moles constant.

5.3 Preparation of Methylene Blue and photocatalyst mixture

The mixture used in the experiment is a combination of either the aforementioned MB solution and the TiO_2 powder or the MB solution and the N-TiO_2 powder. First, 100-mL of 20-mg/L MB solution is poured into a 100-mL beaker using a measuring cylinder. Then, 50-mg of the catalyst (doped or undoped depending on the experiment) is added to the same beaker. This beaker is then ultrasound sonicated for 15 minutes using a high intensity sonicator to allow the powder to thoroughly mix with the MB solution (Figure 8).

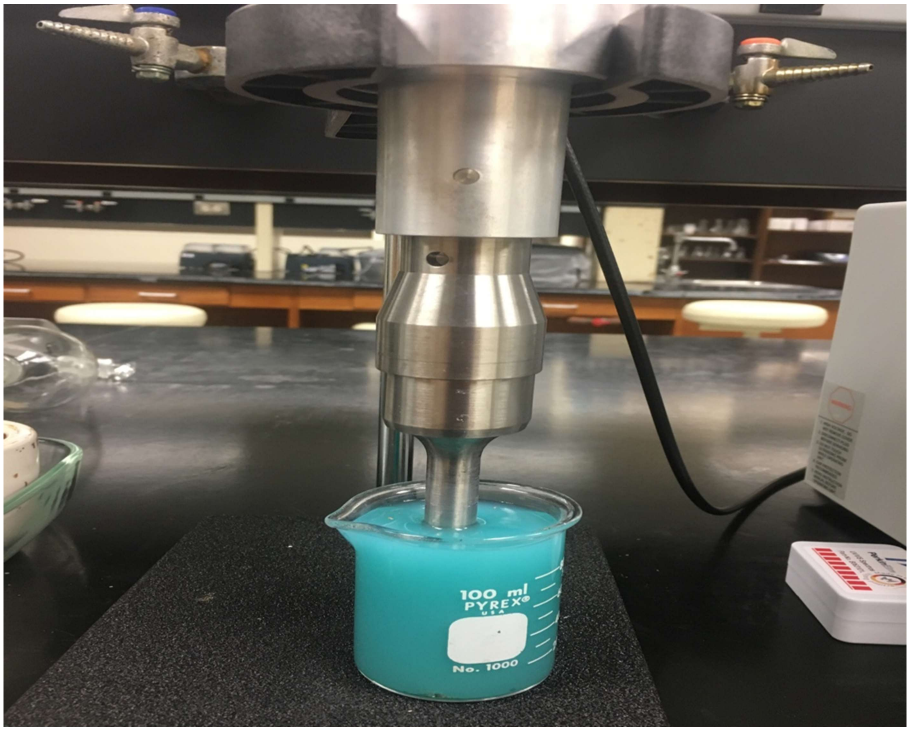

Figure 8: Sonication of Methylene Blue Solution and Catalyst

5.4 Setup of the experimental station

The experimental procedure has been adapted from previous literature [10]. However, it has been modified slightly to accommodate the needs of this experiment.

First, a large 1000-mL glass beaker was filled half way with water and placed on top of the magnetic stirrer plate. The plate is part of a grander setup in which the plate is a platform which can extend up or down and the solar light simulator lamp is placed above the plate fixed. The whole setup is framed in a wooden stage. The entire setup is shown in Figure 9.

Second, the batch reactor of 500-mL capacity is placed inside the glass beaker with water forming a moat around the reactor. This acts as a water bath. This is done so that the temperature of the reactor remains constant throughout the duration of the experiment. A magnet is then placed inside the reactor. The magnetic plate is raised so that the distance between the top of the light source and the top of the reactor is 15 cm. A thermometer is then placed in the moat portion to monitor temperature (Figure 11).

Third, the sonicated MB and catalyst mixture is poured into the reactor and the magnetic stirrer is turned on to allow homogenous mixing throughout the reaction (Figure 10). The mixture is stirred for an hour in the dark (lamp off) to ensure adsorption equilibrium. It is then turned on for the remainder of the experiment (Figure 12).

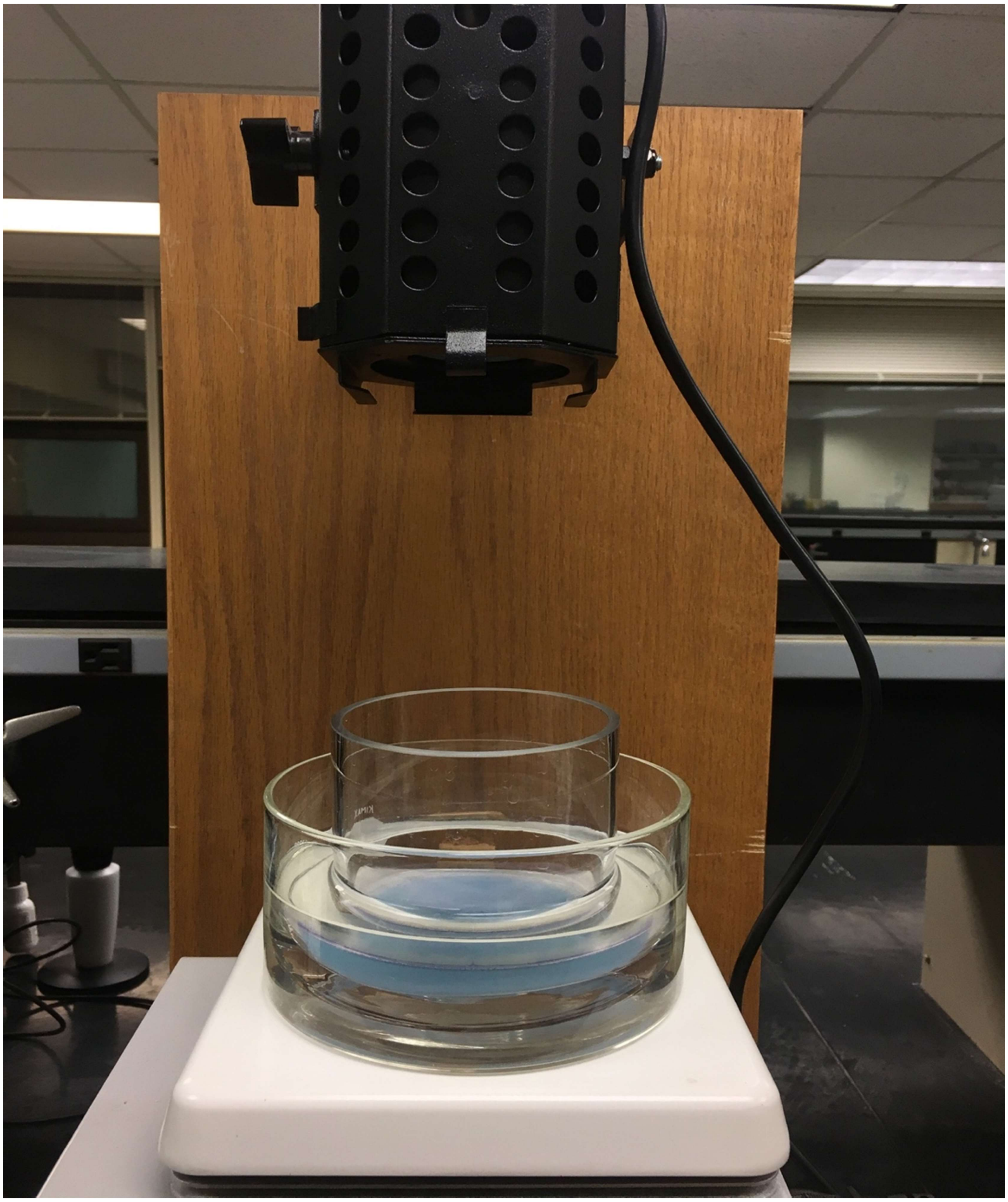

Figure 9: Photocatalytic batch reactor setup

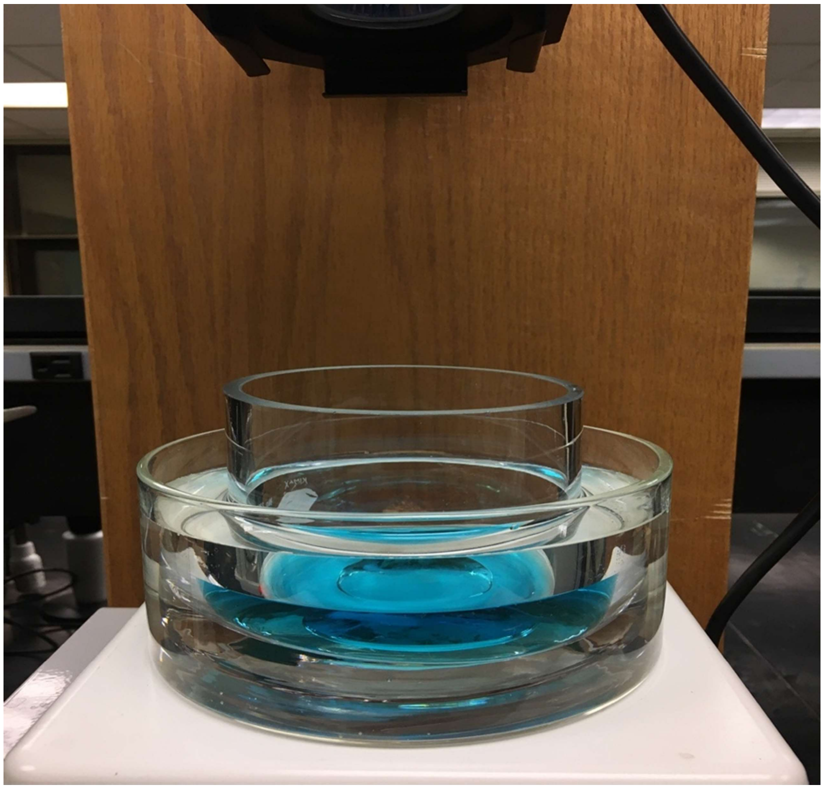

Figure 10: Setup after mixture is poured in

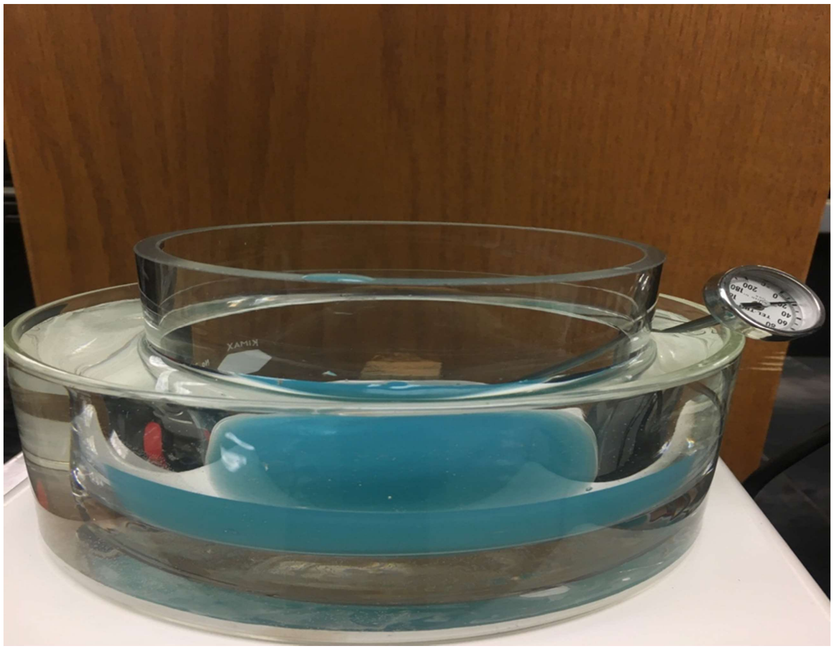

Figure 11: Setup after thermometer is placed in

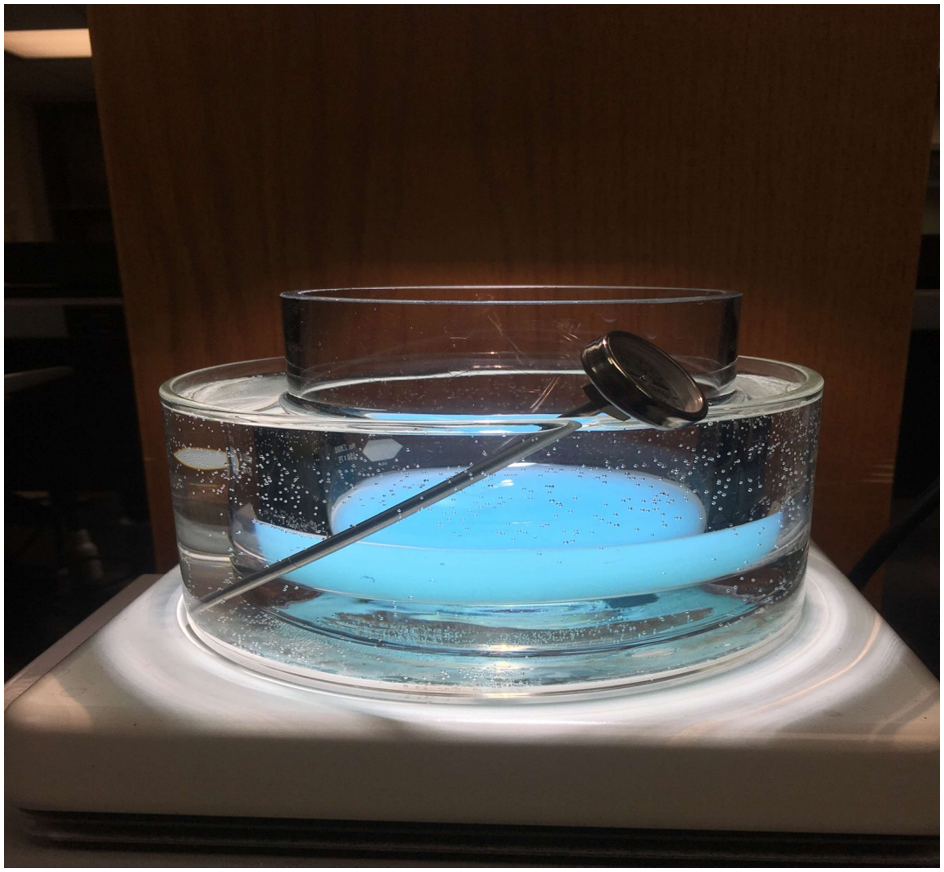

Figure 12: Reactor after the lamp is turned on

5.5 The Experiment

The setup described above was used to perform the experiment. Several types of experiments were run. The results of each experiment will be discussed in the next section.

First, the pure MB solution with a concentration of 20-mg/L was tested. This experiment was a control experiment to set a baseline. 100-mL of pure 20-mg/L-MB solution was poured onto the batch reactor. The magnetic stirrer was turned on and the temperature of the water bath was measured. For the first hour of the experiment, the light source was not turned on.

This period worked as the adsorption period when either the doped or the undoped catalyst was used. Each half hour about 2-mL sample from the reactor was extracted using a pipette and its absorption spectrum was recorded. The temperature was also measured and monitored each time the sample was extracted. After the absorption spectrum was recorded from the spectrophotometer, the extracted sample was poured back into the batch reactor to restore the original volume. For the next two hours the same steps were repeated only this time the light source was turned on. The light source was kept at 15 cm from the top the batch reactor.

Since the absorption peak of the MB is identified around 664 nm from literature and experimentation, the experiment focused on recording any changes or shifts that happened to the absorbance of the MB at 664 nm [12]. A calibration curve to establish a relationship between the absorption and the concentration of the MB at given times was obtained from these results.

Second, 100-mL of 20-mg/L MB solution mixed with 50-mg of TiO_2 was sonicated using the ultrasound sonicator for 15 minutes. This mixture was then poured into the batch reactor and the magnetic stirrer was turned on. For the first hour, the experiment was conducted in the dark to allow mixing and adsorption equilibrium between the liquid and the solid. At this time, it was expected that the rate of molecules attaching to each other would be the rate at which they were being released. Each half-hour, a 2-mL sample of the mixture would be extracted and run through the spectrophotometer. There was a small complication in this step. The original idea was to filter the powder out and run the solution only to see the change in concentration at the peak of 664 nm. However, the filtration process also reduced the concentration of the MB as the MB was absorbed in the filter paper as seen below(Figure 13).

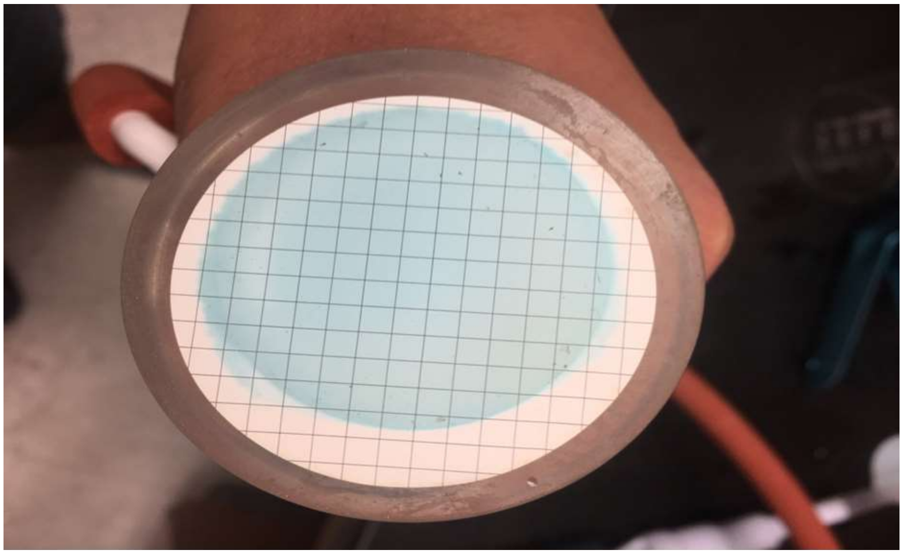

Figure 13: Filter paper showing absorbed MB

As a result, filtration was removed as a step and the spectrophotometer measured absorbance of the test on the entire mixture with the assumption that the concentration of the MB was proportional to the absorption at the 664 nm based on Beer's law. Starting from the second hour, the light was turned on and the same process was repeated, withdrawing a 2-mL sample every 30 mins and pouring the sample back in to the batch reactor after analysis. The temperature was also monitored to ensure it remained constant throughout.

Third, the exact same procedure as mentioned in the second part is followed, except this time the catalyst was the N-TiO_2 instead of the TiO_2. This is essential because the goal here is to compare the efficiency of the doped and undoped catalyst when solar light is used instead of the traditional ultraviolet intensive light sources which have been shown to have a good effect on the undoped catalyst on its own right. [7,10,11]

6.0. Results

In this section the results generated from the previously described experiments are presented. As discussed in the procedure section of the text, the absorbance spectrum ranging from 200 nm wavelength to 800 nm wavelength are plotted for each batch of sampled mixture. This range covers the UV-B (290-320 nm) and UV-A (320-400 nm) that is produced by the lamp and the visible light region (400-800nm). At 664 nm, the peak absorbance of the mixture was taken and using Beer's Law was converted into its corresponding concentration. A calibration curve was plotted for the pure MB solution to establish this relation, while proportionality was used for the mixture on the assumption that concentration should be proportional to the absorbance at the peak.

6.1 Photocatalyst characterization

50-mg each of TiO_2 and N-TiO_2 were sonicated in 100-mL deionized water for 15 minutes. 2-mL of each sample was taken after sonication to measure the absorption spectrum. This was based on previous research [7] . The absorption spectrum ranging from 300 nm to 800 nm was plotted to check whether or not nitrogen was doped into the TiO_2 powder. The absorption spectra of both mixtures are shown in Figure 14.

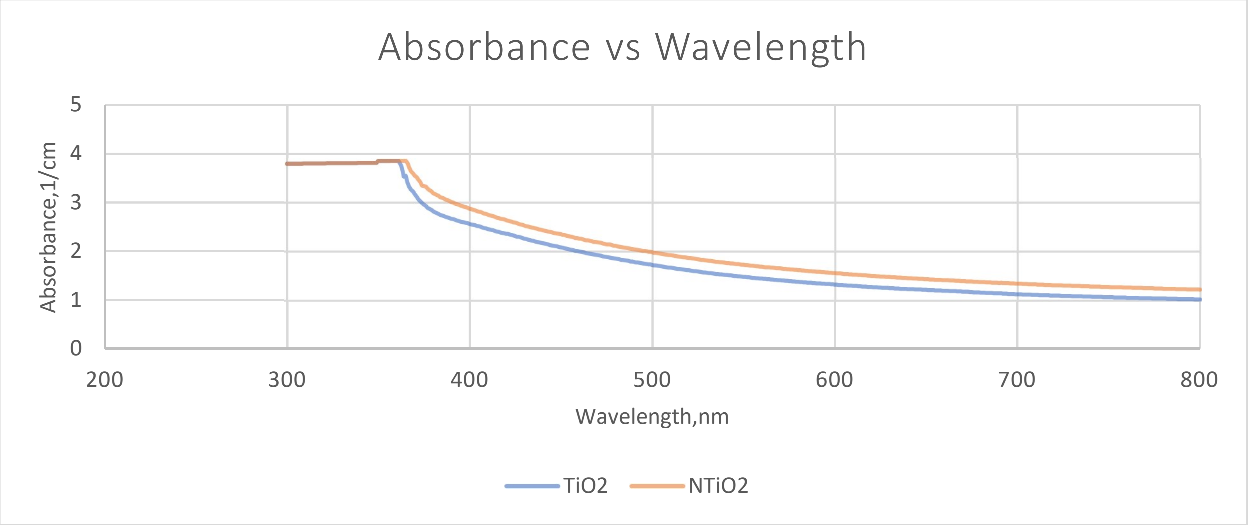

Figure 14 : Absorbance vs Wavelength for TiO_2 and N-TiO_2

The graph shows that the absorption of the N-TiO_2 increases slightly in the wavelengths above 380nm. Compared with the spectrum of pure TiO_2, N-TiO_2 presents a slightly increased absorption tail in the visible region from 380 nm to 800 nm. This is a typical feature of N-TiO_2.[10] However, as XPS and other tests to confirm these could not be performed, the exact amount of nitrogen that was doped into the catalyst is unknown.

The modification of TiO_2 with nitrogen under hydrothermal condition resulted in the shift of the absorbance region toward longer wavelength, from 400 nm onwards . This could be attributed to the incorporation of nitrogen into the TiO_2 structure as mentioned in section 4.3, owing to the substitution of titanium by oxygen or nitrogen by oxygen. The significance either type of substitution provides is also described in section 4.3 , however, light absorbance of the N-TiO_2 in the visible-light region is of great importance.

6.2 Experimental results analysis

Figures 15 through 17 show the results of the experiments described in in section 5. As shown in Figure 15, the absorbance of the MB-only solution remains more or less constant during the first hour when no light is irradiated. Then, as irradiation begins, there is a slight but not significant decrease in absorbance. This behavior is expected as MB solution does not have any catalyst in it and therefore does not degrade significantly on its own. It does degrade slightly on its own when sunlight is irradiated into it, as seen in Figure 16 and Figure 17.

Figures 15,16 and 17 show a trend. For the first hour when the mixture is left in the dark, the MB get adsorbed onto the surface of the doped and the undoped photocatalyst respectively, reducing its absorbance at the 664 nm . As the light is turned on at 1 hour, it is assumed that the catalyst has reached adsorption-desorption equilibrium, meaning any loss in absorbance of the MB happens as a result of photocatalytic activity. Although this can be seen from the graphs below as well, it will be easier to explain the exact nature of these results if explained in terms of concentration of the MB.

The concentration of the solution is assumed to be proportional to the absorbance at 664 nm, the peak of MB, from Beer’s Law .

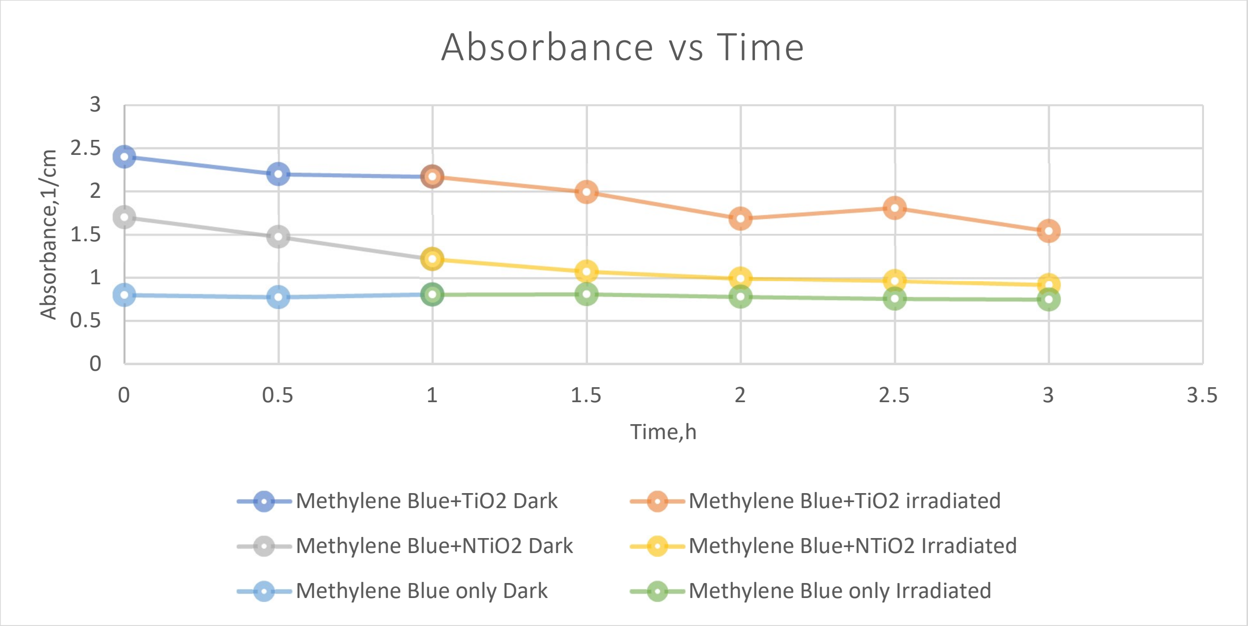

Figure 15 : Change in absorbance with time for indicated experiments

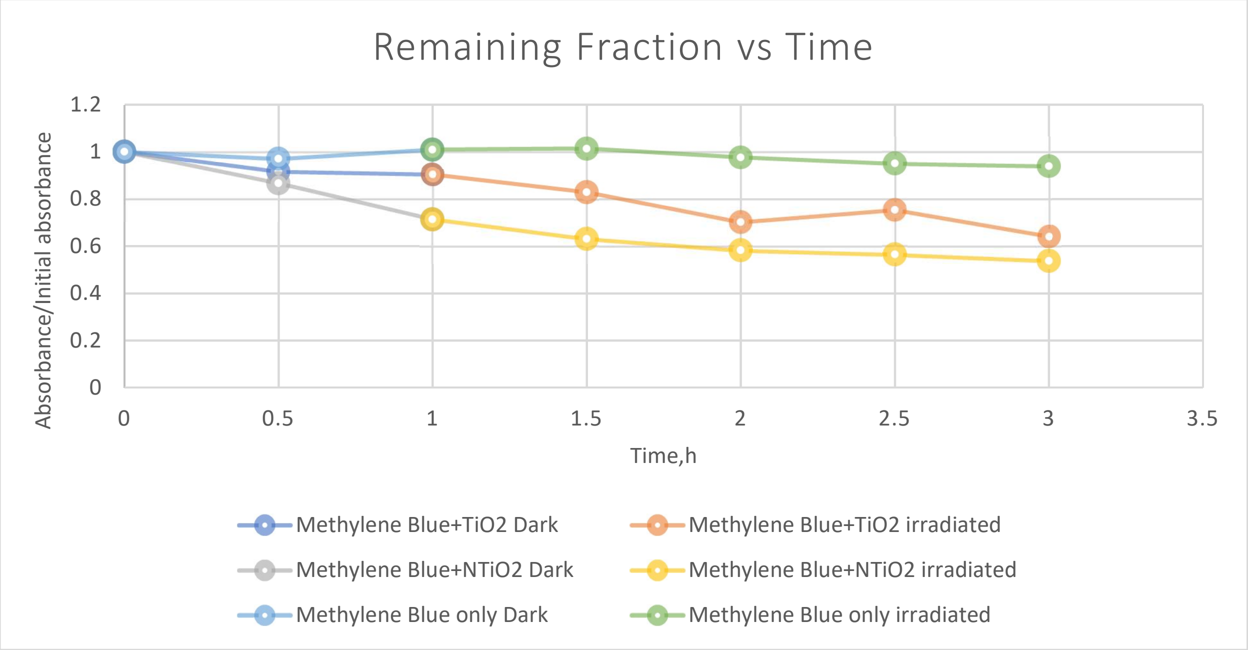

Figure 16 : Change in fraction remaining(absorbance) with time for indicated experiments

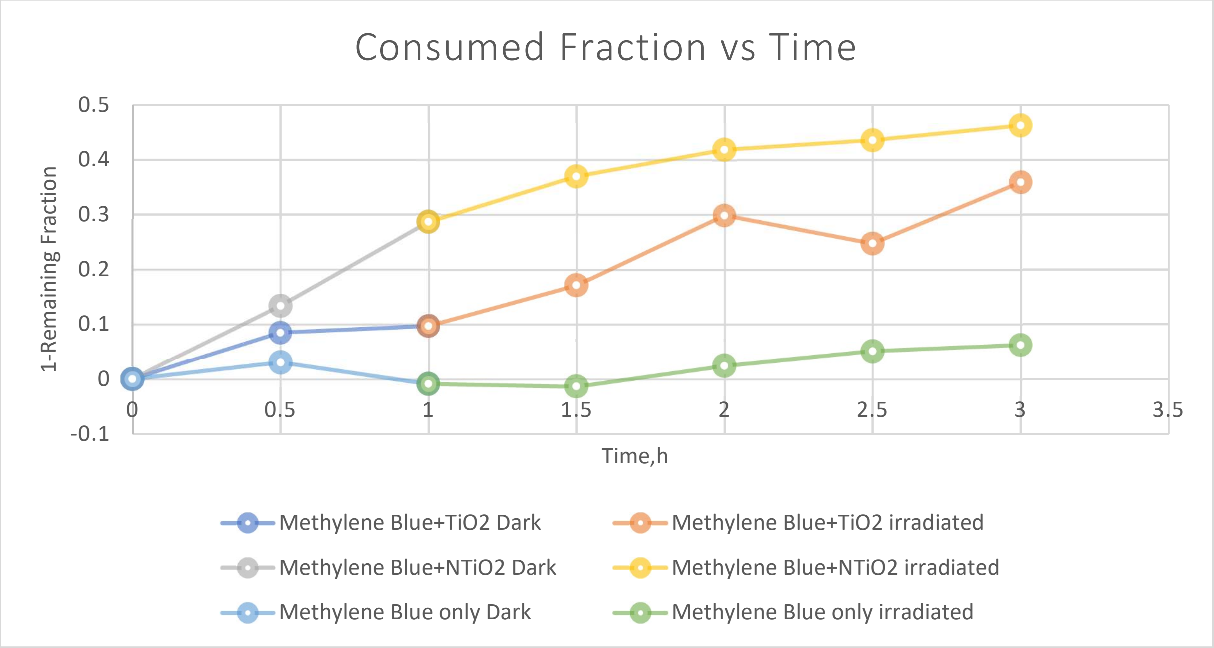

Figure 17: Change in consumed fraction(absorbance) with time for indicated experiments

A calibration curve (Figure 18) was created and plotted for the pure MB solution to determine its concentration as a function of absorbance. The range selected is narrow to recreate the concentrations that would most likely resemble the values that is expected to be obtained in the experiment. Based on this relationship, it is assumed that the absorbance would still remain proportional to the concentration even when the powder was added to the solution, from Beer’s Law. Figures 19-21 are based on this assumption.

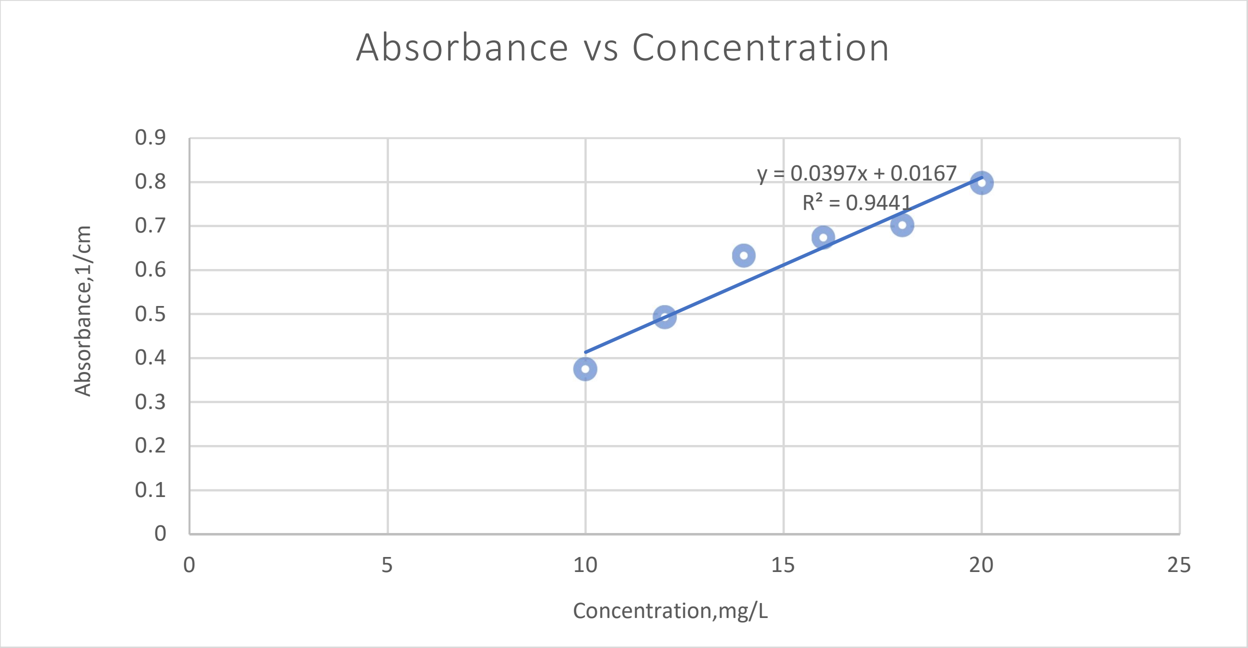

Figure 18: Absorbance-Concentration calibration curve

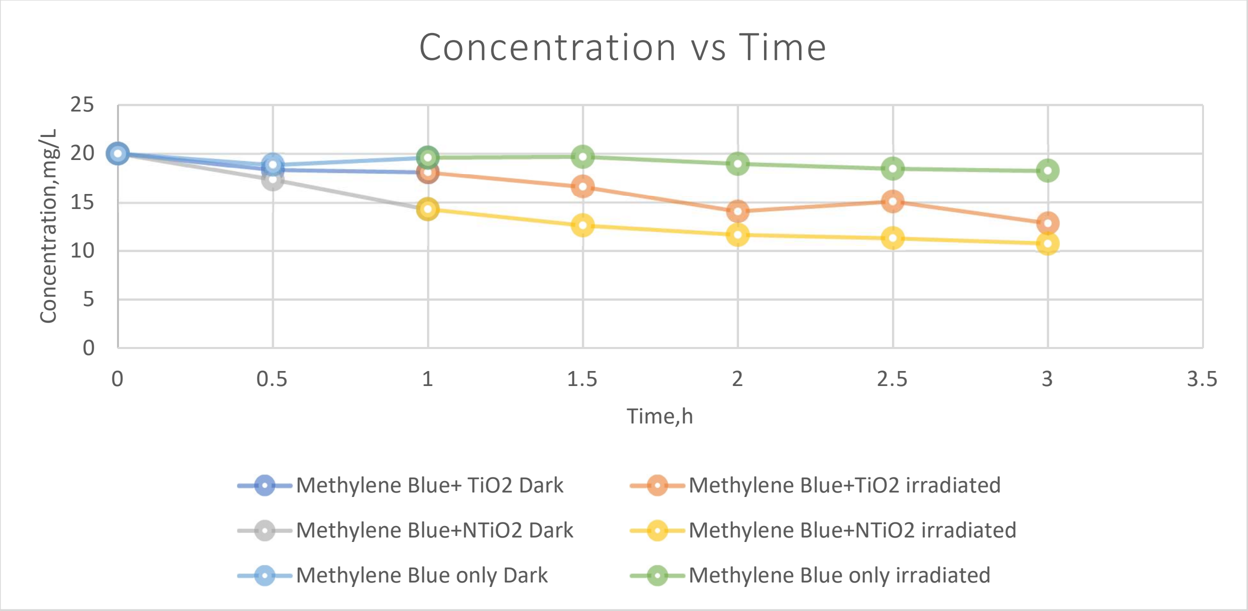

Figure 19 : Change in concentration with time for indicated experiment

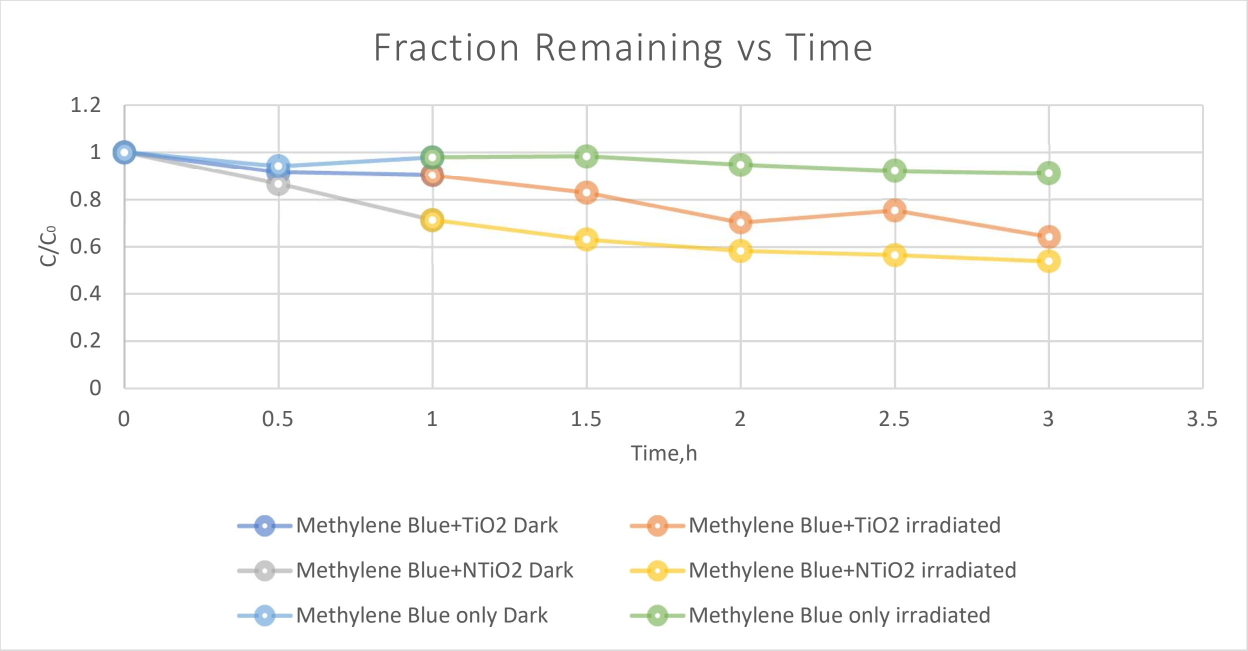

Figure 20 : Change in fraction remaining with time for indicated experiments

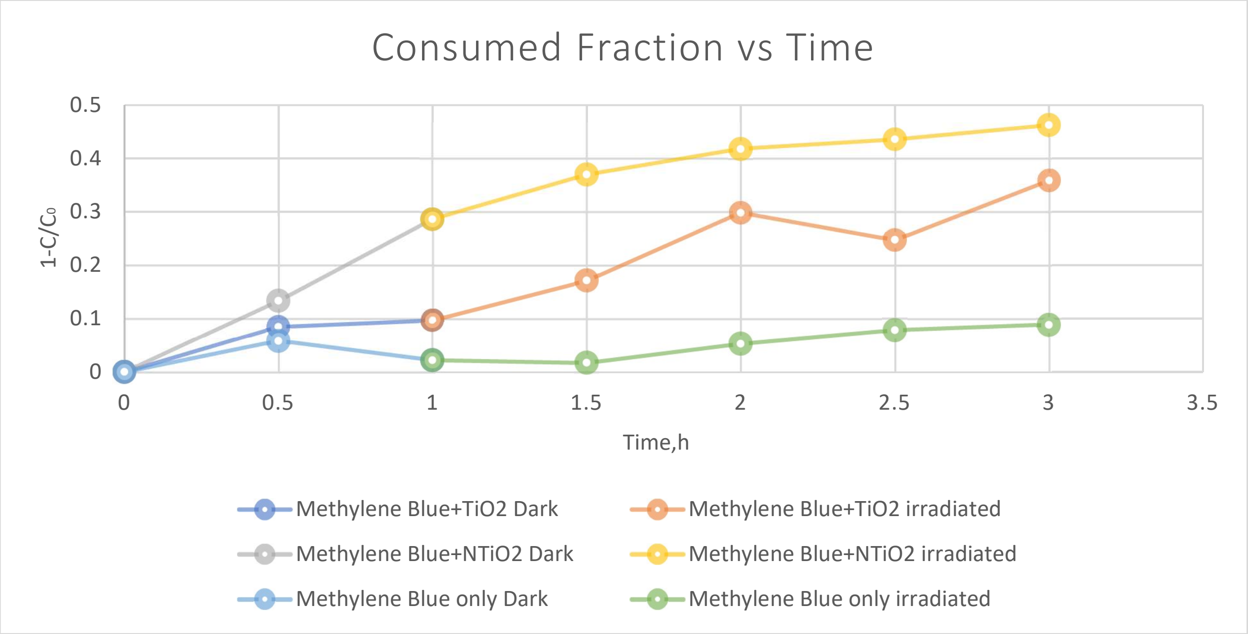

Figure 21 : Change in consumed fraction with time for indicated experiments

As seen in Figure 19, the concentration of the MB solution remains constant throughout the experiment with slight decline when the light is turned on. This is an expected behavior as MB compound is shown to degrade slightly without the presence of a photocatalyst in the presence of sunlight.

Similar trends can be seen in Figure 20 and 21 where the fraction remaining(final concentration divided by initial concentration vs time) of MB solution decreases slightly with respect to time and consumed fraction of the solution increases with respect to time concluding that without the presence of a photocatalyst, while the MB compound does degrade upon irradiation, it is a very small amount and it remains more or less constant throughout otherwise.

6.3 TiO_2 as photocatalyst:

Also from Figure 19, for the first hour when the mixture is not irradiated, the concentration of MB decreases due to the adsorption of MB onto TiO_2 surface. This causes a drop in the concentration from 20-mg/L to about 18.06-mg/L of the MB during the first hour the mixture has not been irradiated. By the end of the first hour, it is assumed that the MB and the TiO_2 have reached an adsorption-desorption equilibrium, meaning that the rate at which the titanium dioxide molecules are attaching the MB molecules to itself via adsorption is equal to the rate at which the already attached MB molecules are being released back to the mixture in the batch reactor. So, any change in activity past the first hour is due to photocatalytic activity as the light has been turned on.

Again, referring to Figure 19, for the first half hour there is a reduction in the concentration of the MB from 18.06-mg/L to 16.56-mg/L. In the next half hour, it decreases further down to 14.03-mg/L. In the next half hour, the concentration increases slightly back to 15.06-mg/L before finally reducing to 12.825-mg/L in the final half hour. These trends are seen more evidently in the fraction remaining and fraction consumed vs time graphs respectively.

Once irradiation starts, the TiO_2 gains thermal energy and the energy from UV(about 0.85% according to the manufacturer) portion of the light source to allow electrons from the valence band to gain 3.2 eV of energy and move into the conduction band.

TiO_2 during illumination acts as a strong oxidizing agent lowering the activation energy for the decomposition of organic and inorganic compounds. The illumination of the surface of the TiO_2 induces separation of the electron e^- and the hole h^+ , in the conduction and valence band respectively. The following mechanism is used by TiO_2 to conduct oxidation of organic compounds(or synthetic organic dyes) such as MB [13].

$TiO_2 + energy \rightarrow h^+ \ + e^-$;

where h^+ is the hole in the valence band and e^- is the electron in the conduction band.

$D + h^+ \rightarrow \cdot D^+$;

where D is the organic compound that is adsorbed to the TiO_2 , and $\cdot D^+$ is the oxidized form of the same organic compound.

Similarly, the following reactions may also occur to facilitate oxidation of organic compounds :

$H_2O + h^+ \rightarrow \cdot OH + H^+$;

where $\cdot OH$, is the hydroxyl radical

$O_2 + e^- \rightarrow \cdot O_2 -$;

where, $\cdot O_2 -$ is the superoxide ion.

Note, $\cdot OH$ and $\cdot O_2 -$ are strong oxidizing agents.

From the procedure discussed below(Figure 22) it can be seen how in the presence of water and dissolved oxygen the MB+ TiO2 mixture may use the light as energy to perform oxidation.

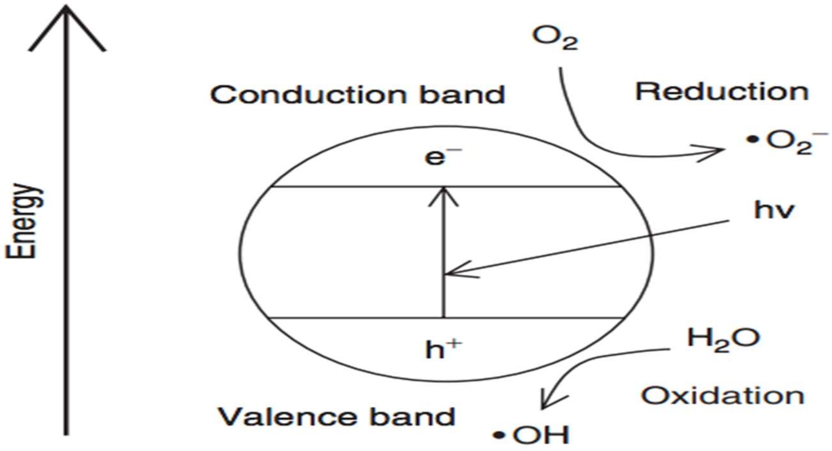

Figure 22 : Mechanism of the redox process in TiO2 [13]

Referring back to the Figures, it can be seen that the energy supplied by the sunlight is being used by the TiO2 to act as a photocatalyst in the oxidation of MB solution. It is also known that the band gap of TiO_2 is higher than the bandgap of N-TiO_2. And, although thermal energy and the presence of UV may have provided energy for the electron-hole pair to form, it is worth comparing the final yield of the TiO_2 catalyzed reaction to that of the N-TiO_2 catalyzed reaction to see the effectiveness of the two catalysts. It is seen that at the end of 2 hours of irradiation more amount of MB has been degraded by the N-TiO_2 catalyst than the TiO_2 catalyst (Figure 20). This shows that there has been a shift in the energy absorption by the catalyst if doped with nitrogen ,i.e., the simulated solar light which gives off most of its light in the visible light region 400 nm or higher is more effective.

However, it is worth noting that it is speculated [11] that the oxidative power of the visible light induced holes generated by the photoexcitation from N 2p to Ti 3d is lower than those of the O 2p to Ti 3d (Section 4.3) . This could explain why there is still significant oxidation being done by simply TiO_2 even when there is not a substantial amount of wavelengths 400 nm or less generated by the light source.

6.4 N-TiO_2 as photocatalyst:

The mechanism by which N-TiO_2 helps in degrading organic compounds is the similar to that done by the TiO_2 (Section 6.3). However, the important difference is that once the photocatalyst has been doped, the bandgap between the valence and the conduction band is smaller allowing the electrons to get excited more easily.

Thus, from Figures 19, 20 and 21 , it can be seen that the concentration of MB does decrease with time once irradiation starts. The concentration decreases linearly from 14.3-mg/L to 10.75-

mg/L ,during irradiation. The amount of adsorption is also higher than that compared to TiO_2. It can also be seen in Figure 21 that the fraction of the MB that has been oxidized is higher in each interval starting from the first half hour after the irradiation had begun in comparison the undoped catalyst.

The final concentration of MB is lower in the nitrogen doped catalyst experiment to that of the plain catalyst at 10.75-mg/L and 12.8-mg/L respectively. This confirms that doping the catalyst does make it easier for photocatalysis to work in the visible light region of the spectrum as opposed to UV intensive region which is required for the undoped catalyst.

As the simulated solar light contains wavelengths between 400 nm to 800 nm , the experiments show that doping the catalyst with nitrogen reduces the bandgap , thus, ensuring that lower energy or longer wavelengths found in the visible light region can be used for photocatalysis if the catalyst is doped. However, it is worth noting that the efficiency in the catalysts while being significant, is pretty close to each other. The efficiency was calculated by measuring the concentration of MB that remained at the end of the experiment with respect to its initial concentration. The N-TiO_2 is 46.2% efficient while the TiO_2 is 35.9% efficient.

7.0. Conclusion :

The experiments run in this project were designed to figure out whether or not nitrogen doped Titanium Dioxide(N-TiO_2) is a better photocatalyst than undoped titanium dioxide (TiO_2) in the visible light spectrum i.e. wavelengths greater than 400 nm. A solar simulator light of 120V with 0.85% UV was purchased, the photocatalyst was synthesized using methods described in Section 5.1 and photocatalytic experiments were run under this.

From experimental results, it is found that the N-TiO_2 reduced MB concentration by 46.2% while TiO_2 achieved only 35.9% reduction under the same experimental conditions. While this result shows that the Nitrogen doped catalyst is in fact a better catalyst than the undoped catalyst, there were some variables (exact of amount of nitrogen doped, evaporation and filtering of the catalyst) that this experiment couldn't account for. Also, the results in this experiment is not fully consistent with what was reported in literature [7,11]. The literature showed that there was a significant increase in the activity of N-TiO_2 in the visible light region of the spectrum. In this case, there is only a slight increase in activity of the doped catalyst in comparison to the undoped catalyst in the visible light region. This could mean that nitrogen was not doped into this catalyst in the same amount as was reported in literature [7]. This might have been a result of issues with the synthesis of the catalyst. Because the process of synthesis was very challenging to reproduce and took several failed trials before a comparable catalyst was synthesized at the UNO labs, sufficient nitrogen may not have been doped into the catalyst.

Taking all factors into considerations, while doping nitrogen into TiO_2 to perform photocatalysis under visible light does show promise and effectiveness, more research must be done in order to definitively claim this.

8.0. Appendix :

Spectrophotometer Plots

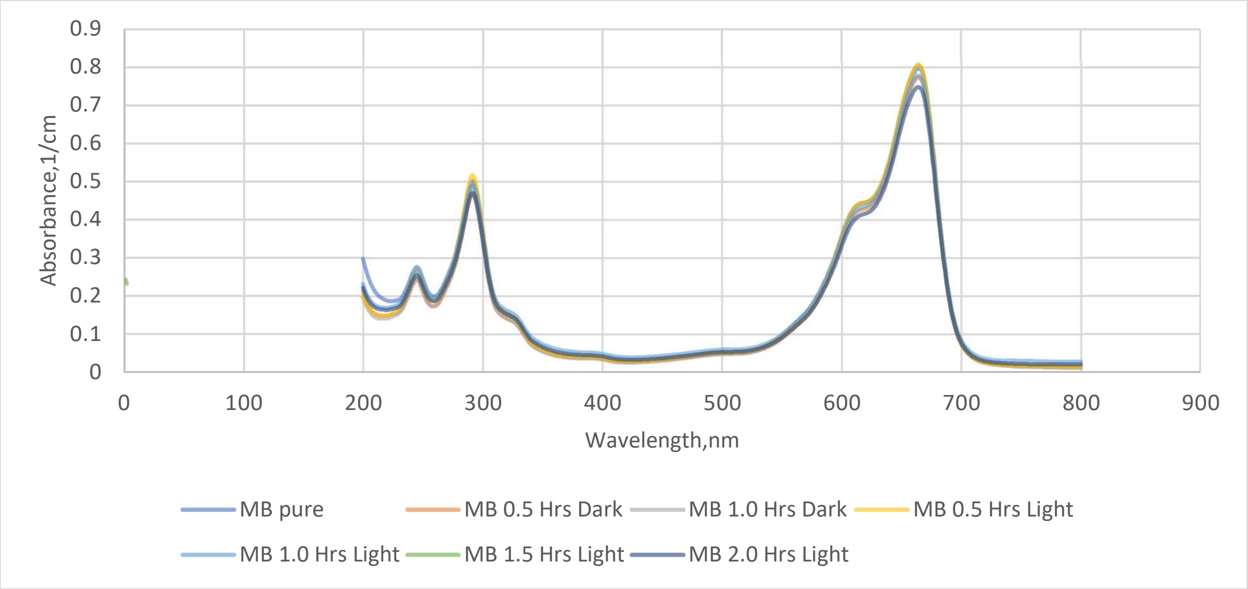

Figure 22.1 : Absorbance vs Wavelength plot of 20-mg/L MB solution

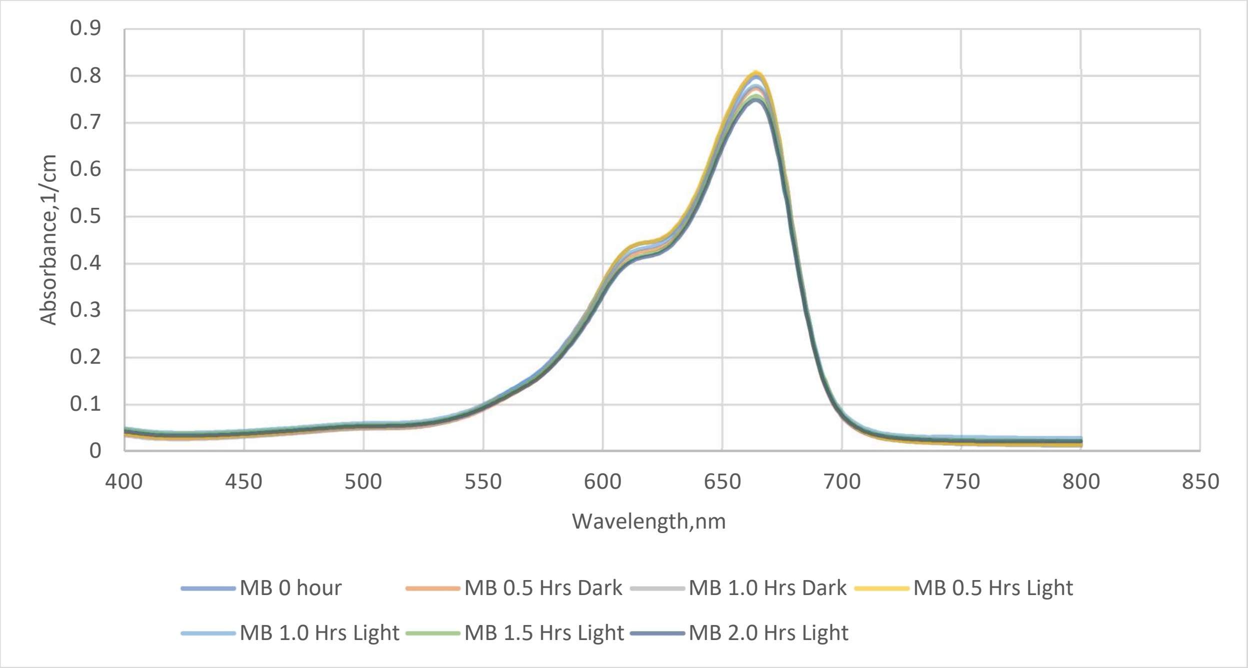

Figure 22.2 : Absorbance vs Wavelength plot of 20-mg/L MB in the visible light region

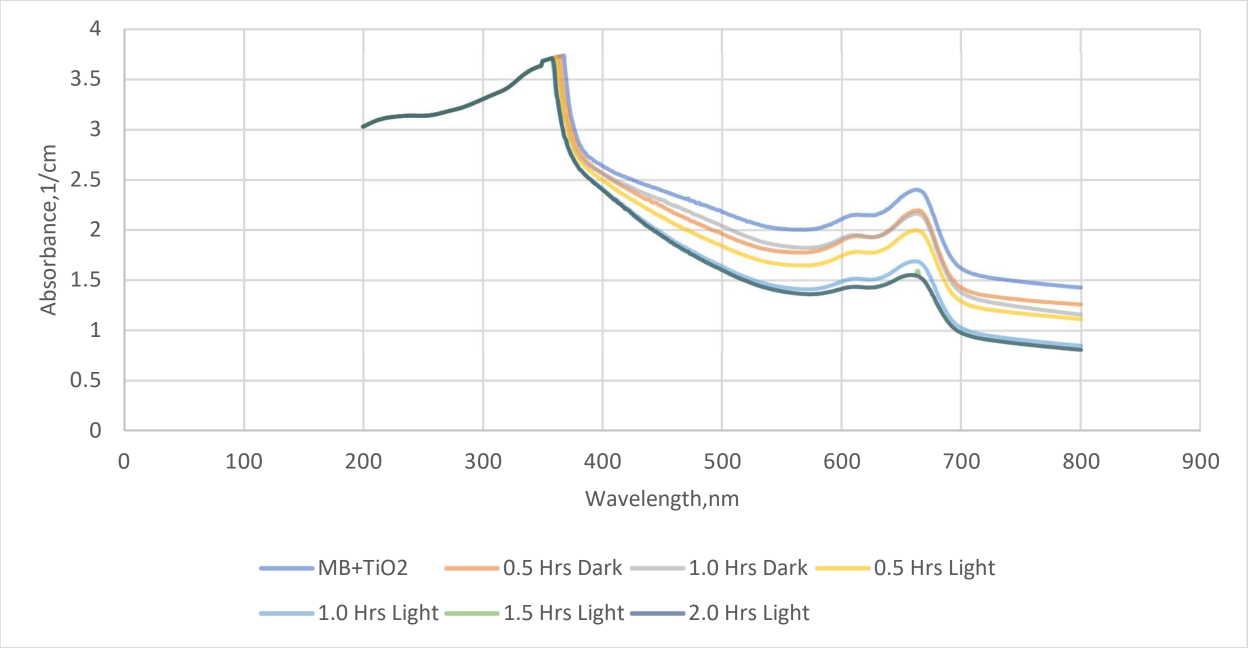

Figure 22.3 : Absorbance vs Wavelength plot of 20-mg/L MB solution + TiO_2

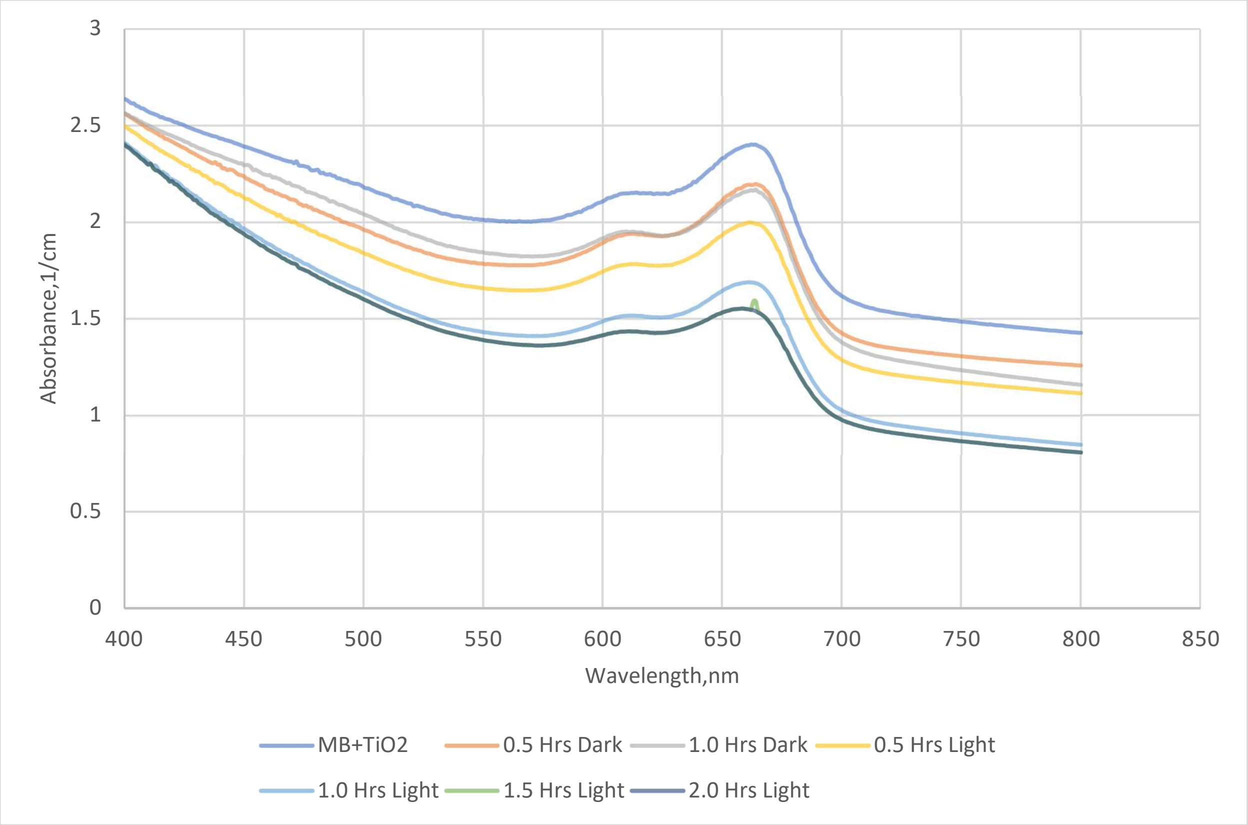

Figure 22.4 : Absorbance vs Wavelength plot of 20-mg/L MB solution + TiO_2 in the visible light region

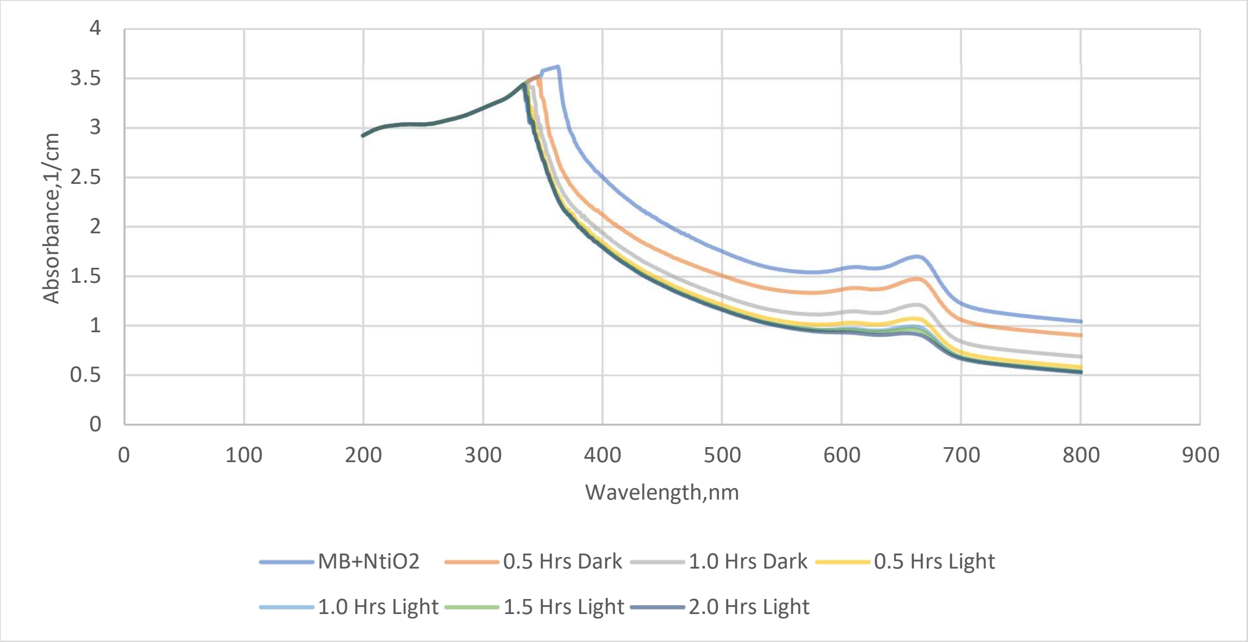

Figure 22.5 : Absorbance vs Wavelength plot of 20-mg/L MB solution + N-TiO_2

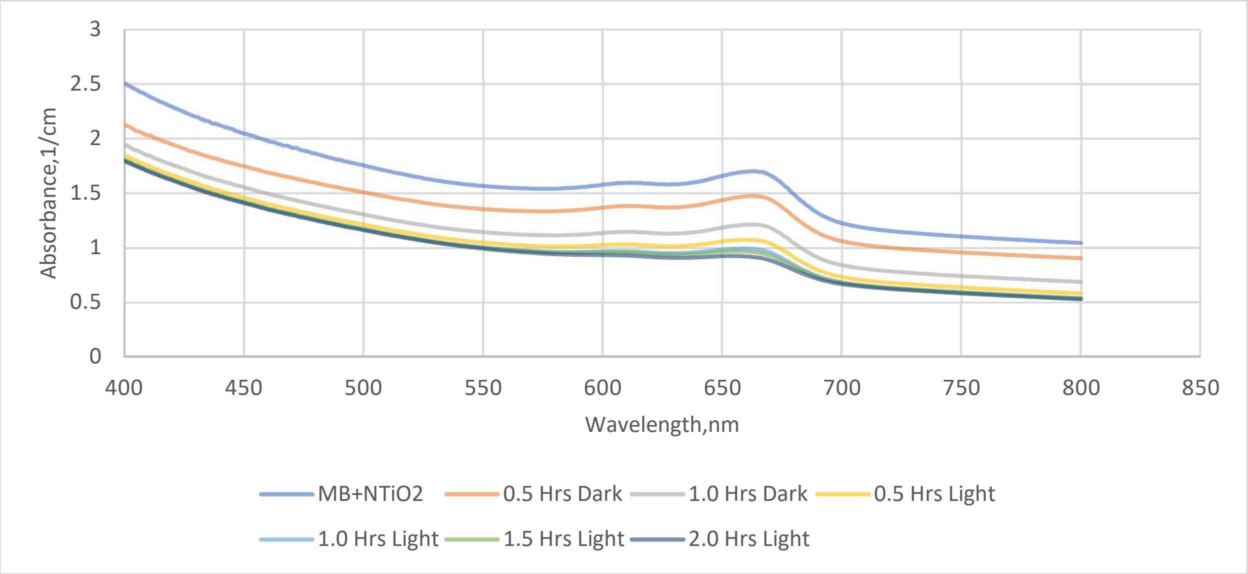

Figure 22.6 : Absorbance vs Wavelength plot of 20-mg/L MB solution + N-TiO_2 in the visible light region

9.0. References :

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