The Effects of Titanium Dioxide Nanotubes on the Photodegradation of Methyl Orange for Wastewater Decontamination

Tracy Wan

Bergen County Academies

Abstract

Titanium dioxide nanotubes have demonstrated significant potential in the photodegradation of organic dyes due to its increased surface area than titanium dioxide nanoparticles. The photocatalyst accelerates the decomposition of dye molecules under ultraviolet radiation. As an organic dye, methyl orange is expelled from various textile plants as wastewater. Methyl orange, as part of the azo group, is carcinogenic. In addition, when wastewater containing organic dyes goes into the stream system, it could potentially harm the aquatic organisms residing in the stream by altering the chemical composition of its habitat. In this experiment, titanium dioxide nanotubes were synthesized through the anodization of titanium foil in ethylene glycol and ammonium fluoride at different voltage. The prepared titanium dioxide nanotubes was viewed under a scanning electron microscope to confirm its structure. The photodegradation rate of titanium dioxide nanotubes is compared with that of titanium dioxide nanoparticles. The efficiency of the titanium dioxide nanoparticle turns out to be higher than that of titanium dioxide nanotubes. This could be due to the insufficient amount of titanium dioxide nanotubes present on the surface of the titanium foil. Titanium dioxide nanomaterial has the potential to be used to further decompose other harmful organic molecules from wastewater.

Introduction

Decontamination of wastewater, utilization of environment-friendly chemicals, and adaptation of sustainable energy sources are a few of the most prominent issues that green chemistry is trying to deal with (Mathes, 2014, p. 2). In recent years, there had been an increasing number of applications using photocatalyst such as titanium dioxide nanoparticles to treat wastewater (Lachheb et al., 2014). Titanium dioxide as a semi-conductor is composed of a conduction band and a valence band according to the band theory. Between these two bands, there exists a band gap where no electrons can exist. When the titanium dioxide is irradiated with ultraviolet light with a wavelength shorter than 375 nm, the cut-off wavelength of titanium dioxide, the high energy of the light causes the electron from the valence band to jump to the conduction band.

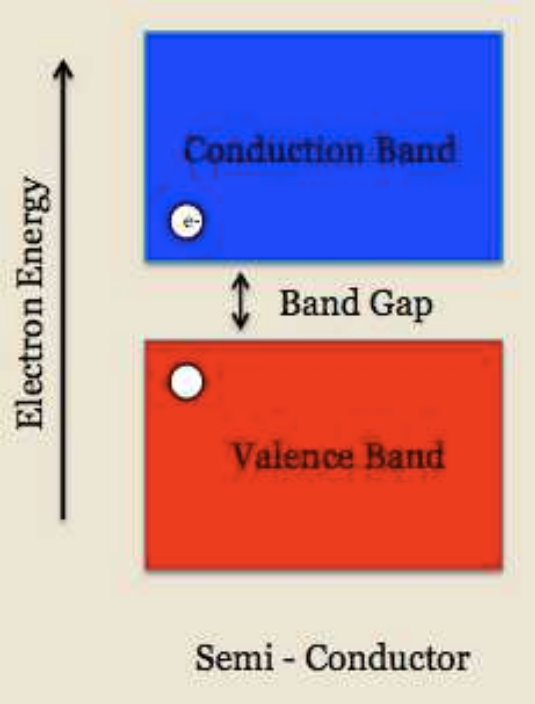

Figure 1. A schematic diagram illustrating the excitation of electrons where the electrons jump form the valence band to the conduction band

This leaves an electron hole in the valence band, which allows the creation of more activated species used to decompose organic dye molecules. As different pathways for various reaction mechanisms are created, the activation energy is lowered thereby increasing the speed of the overall reaction.

Electron Hole Pair Formation:

$$TiO_{2(s)} + hv \rightarrow TiO_{2\,(aq)}{}^{-} + OH^{*}{}_{(aq)}\ (\text{or } TiO_2{}^{+})$$

Oxidation of Organic Molecules:

$$OH_{(aq)}{}^{*} + C_nO_mH_{(2n-2m+2)(aq)} \rightarrow\rightarrow\rightarrow nCO_{2\,(g)} + (n-m+1)H_2O_{(l)}$$

Nonproductive Radical Reactions

$$2OH_{(aq)}{}^{*} \rightarrow H_2O_{2(aq)}$$

$$2HO_{2(aq)} \rightarrow H_2O_{2(aq)} + O_{2(g)}$$

Table I. Mechanism of photocatalytic process on irradiated Titanium Dioxide (Blake, 2014, p. 7)

Compared with titanium dioxide nanoparticles, titanium dioxide nanotubes have a greater surface area available for reaction to take place. With the same outside radius, the surface area of titanium dioxide nanotubes is about twice that of titanium dioxide nanoparticles due to its hollow nature. The hypothesis is that if titanium dioxide nanotubes are used as photocatalysts instead of titanium dioxide nanoparticles to accelerate the photodegradation of methyl orange, then the efficiency of titanium dioxide nanotubes will be higher than that of titanium dioxide nanoparticles.

To synthesize the titanium dioxide nanotubes used in the experiment, an electrolytic cell is set up such that electrical energy are converted to chemical energy to drive the non-spontaneous reaction. At the cathode end, there is a platinum plate and at the anode end there is a titanium foil. As current is passed through the system, oxides start to deposit on the surface of the titanium foil, forming titanium dioxide. The electrolyte containing ammonium fluoride provides fluorine ion that bonds to titanium ion and dissolves titanium dioxide. As the titanium dioxide corrodes away, nanotubes are formed. After the titanium dioxide nanotubes are formed, it is submerged in methyl orange under ultraviolet radiation, providing the sample with enough energy to catalyze the reaction. Then the sample is analyzed using a spectrometer for peak absorbance. The results are compared with that of titanium dioxide nanoparticles for efficiency (Sohn et al., 2014, p. 373).

Methyl orange is a commonly used dye in the textile industry. However as part of the azo group derived from benzidine, it has been demonstrated that it has carcinogenic effect on humans. A study done by Golka et al. on the exposed factory workers showed that the azoreduction of benzene-based dyes occurs in humans. Through metabolic activity, benzidine-, 3,3□- dimethylbenzidine- and 3,3 - dimethoxybenzidine-based dyes are converted to its carcinogenic amine precursors. Several epidemiological studies have showed that the use benzidine based dye could cause bladder cancer in humans. In addition, the expelled wastewater from textile factories could easily get into the river system. A small amount of methyl orange could cause coloration in large areas of the river. Algae and other aquatic plants rely on energy from the sun to perform photosynthesis. The pigmentation of the river water has a direct effect on the wavelength of light aquatic plants are able to absorb. A decrease in the amount

of producers will significantly affect the entire river ecosystem. Therefore to prevent such disaster it is important to filter out these organic dyes using environmentally friendly method.

Experimental Description

Titanium dioxide nanotubes were prepared through electric chemical methods.

First a 0.127 mm thick, annealed, 99% metal basis purity titanium foil was obtained from Sigma-Aldrich. Next it was immersed into an acetone bath for thirty minutes of sonication to clean off the possible debris on the surface of the foil. Then one side of the foil was labeled with diamond-tip marker as to distinguish the side where the most amount of titanium dioxide nanotube grew on. This concluded the preparation of titanium foil. Similar cleaning procedure was also applied to platinum foil also obtained from Sigma-Aldrich.

Next 2cm × 5cm segments of titanium foil and platinum foil were clipped with alligator clips, respectively. These alligator clips were taped to stirring rods 2 cm apart. 0.8% distilled water and 0.8% ammonium fluoride, 98.4% ethylene glycol was be poured into a beaker at 20 ℃. Ammonium fluoride and ethylene glycol are common lab chemicals that could also be obtained from Sigma-Aldrich. After half-submerging the foil into the solution, Consort DV265 sent 50V at 405 mA to the solution. After the two hours, the nanotubes were formed on the surface of the titanium foil that was facing the platinum foil.

Completed nanoparticles are characterized under FEI Quanta 200 3D scanning electron microscope for length and diameter. Before putting the sample under the scanning microscope, it was coated in gold in an ion-sputter coater for 30 seconds to ensure conductivity. Afterwards, the image was zoomed to 2000x magnification.

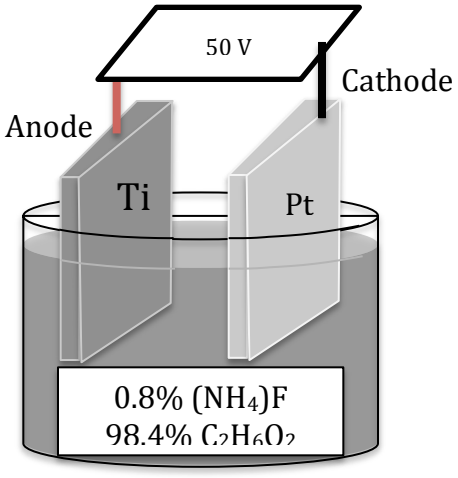

Figure 2. A schematic diagram of titanium dioxide nanotube synthesis set up

Titanium dioxide nanoparticles were obtained from Sigma-Aldrich. A calibration curve of methyl orange was made with absorbance versus concentration using spectrometer. Later using the measured absorbance, the concentration of the solution could be determined.

The mass of titanium dioxide nanotubes was estimated using its volume and density. The same amount of 0.0319 grams of titanium nanoparticles and nanotubes are applied to 40 uM of methyl orange under ultraviolet-light. A SPARK thermometer is used to track the temperature of the sample during the experiment. After each 10 minutes interval, a sample is taken out of the methyl orange solution. By the end of the hour, these samples are centrifuged at 2000 rpm for 10 minutes and analyzed under the spectrometer.

From the graph produced by the spectrometer, it was evident that the concentration of the titanium dioxide nanotubes did not change as seen from the constant absorbance value and peak. The graph of the titanium dioxide nanoparticles is used for further analysis. Using the calibration curve made previous, the concentration of methyl orange was determined. Graphs of concentration versus time, the reciprocal of concentration versus time and the natural log of concentration versus time is plotted using Microsoft Excel to determine the order of the reaction.

Results

A calibration curve of methyl orange was created with absorbance versus concentration.

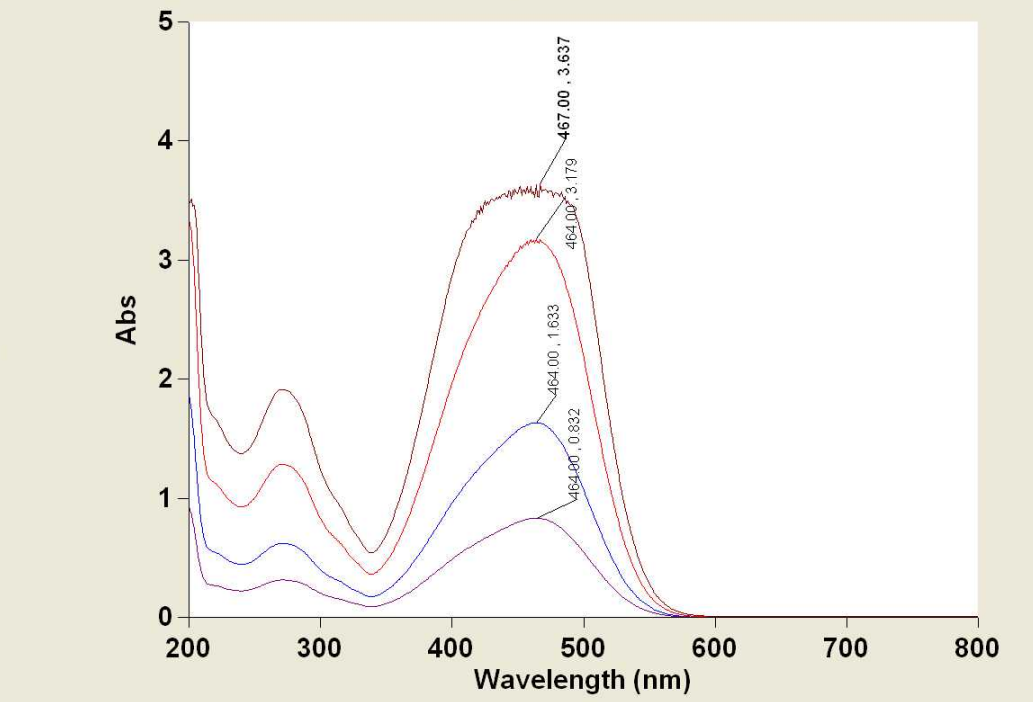

Figure 3. The absorbance of methyl orange at various concentrations. Purple represents 5 µM, blue represents 10 µM, red presents 20 µM and maroon represents 40 µM.

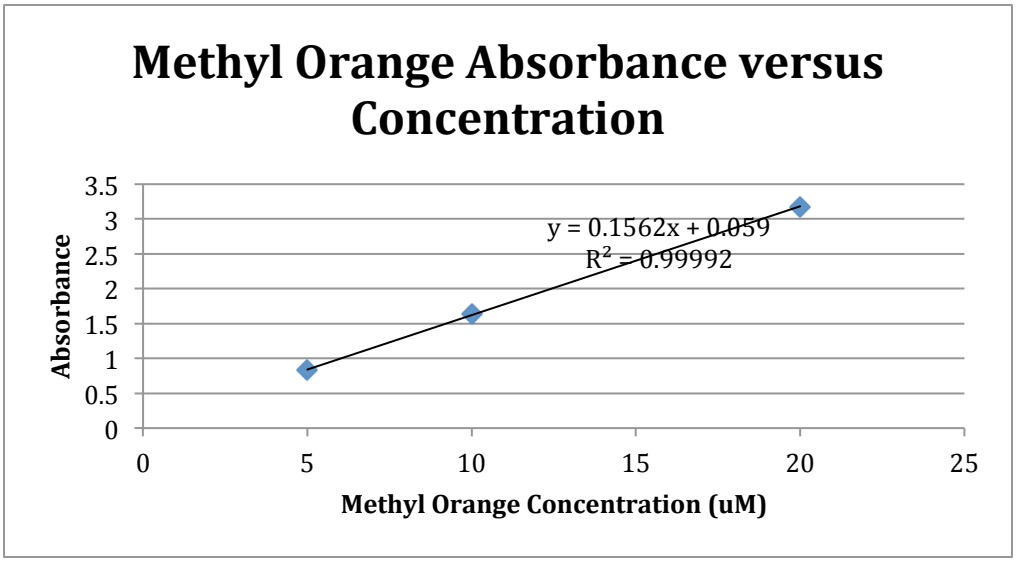

Figure 4. The calibration curve of methyl orange's absorbance versus concentration. 40 µM was omitted due to UV spectrometer's cut-off.

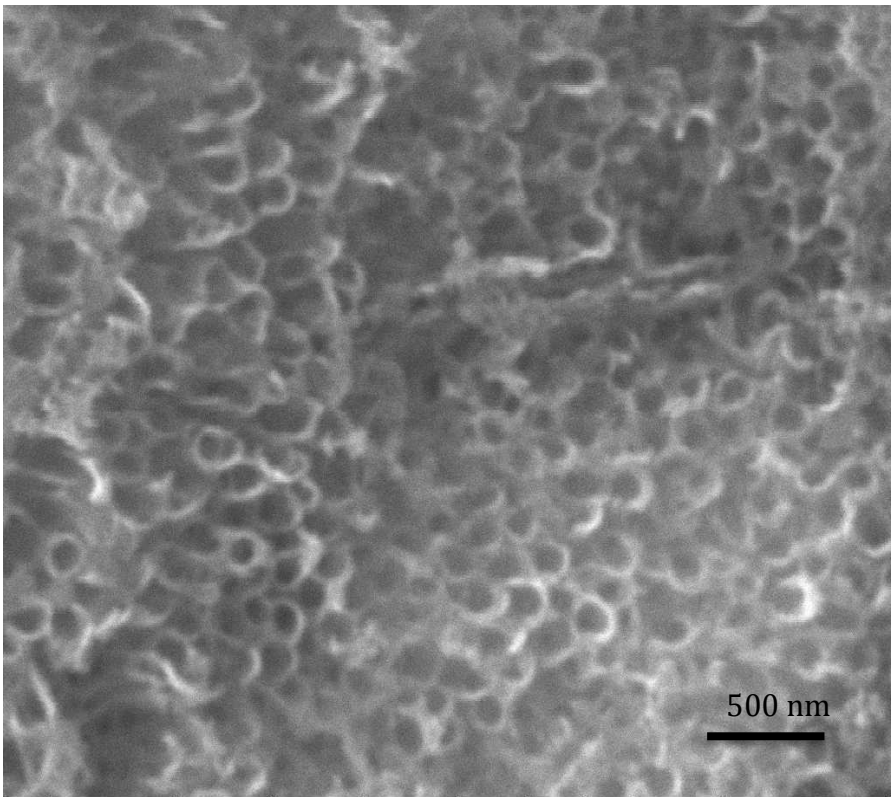

Figure 5. Image of titanium dioxide nanotubes under scanning electron microscope with 40,000 times magnification

When titanium dioxide nanotubes were added to methyl orange under ultraviolet radiation, no observable phenomena occurred after the first thirty minutes. The absorbance of the sample methyl orange changed after the first thirty minutes. The calculated concentration according to the calibration curve of methyl orange went from 20 µM to 18.2 µM. From thirty minutes to fifty minutes, there was no significant change in the absorbance of methyl orange.

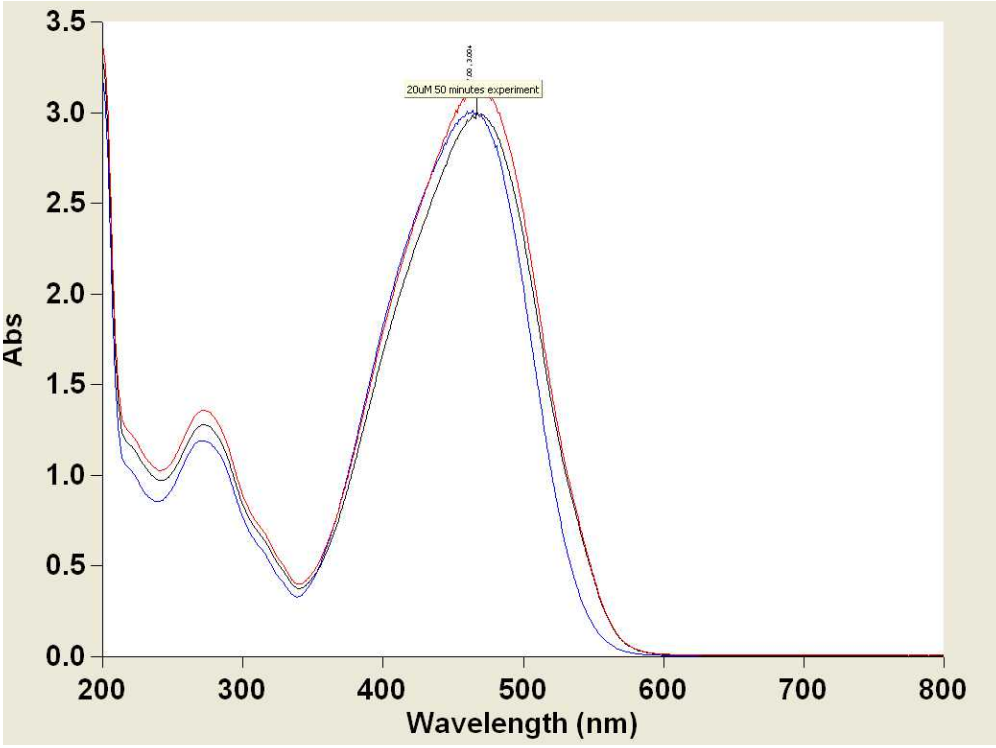

Figure 6. Ultraviolet absorbance graph of titanium dioxide nanotubes reacting with methyl orange. Red represents control. Green represents 30 minutes and blue represents 50 minutes.

When titanium nanoparticles were added to methyl orange, the absorbance of the sample decreased significantly.

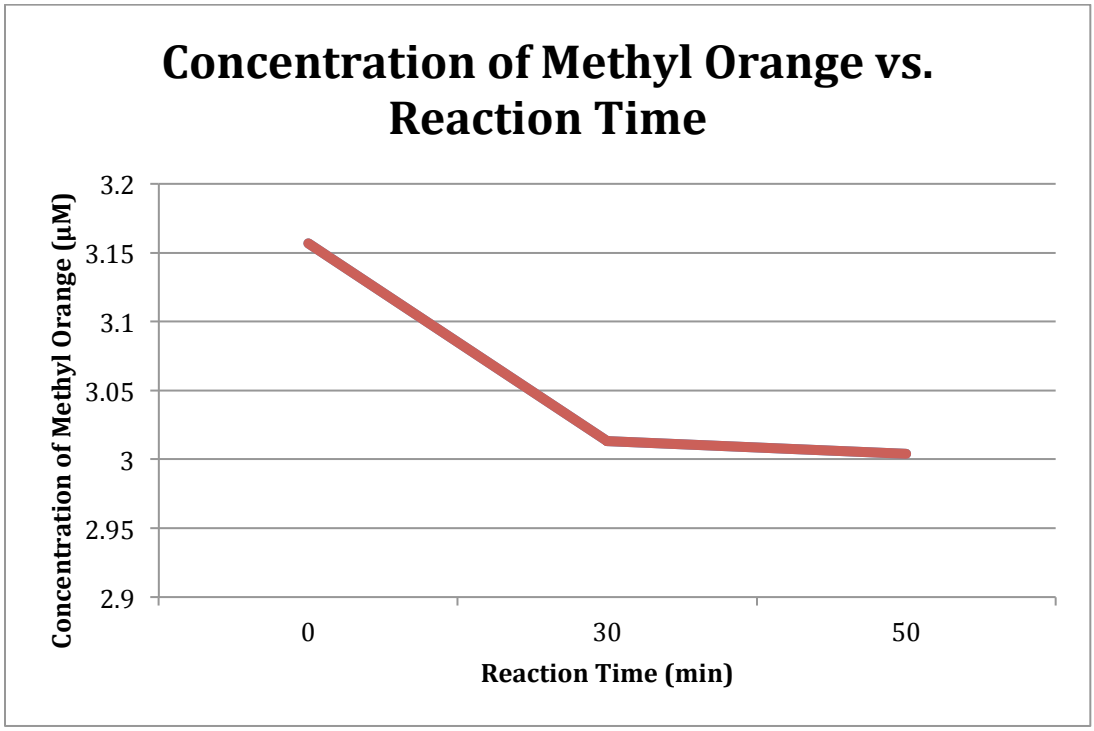

Figure 7. The concentration of Methyl Orange over reaction time

When the concentration of Methyl Orange against reaction time, the graph shows that there was an initial dip in concentration after the first 30 minutes. However by 50 minutes, the reaction has stopped proceeding.

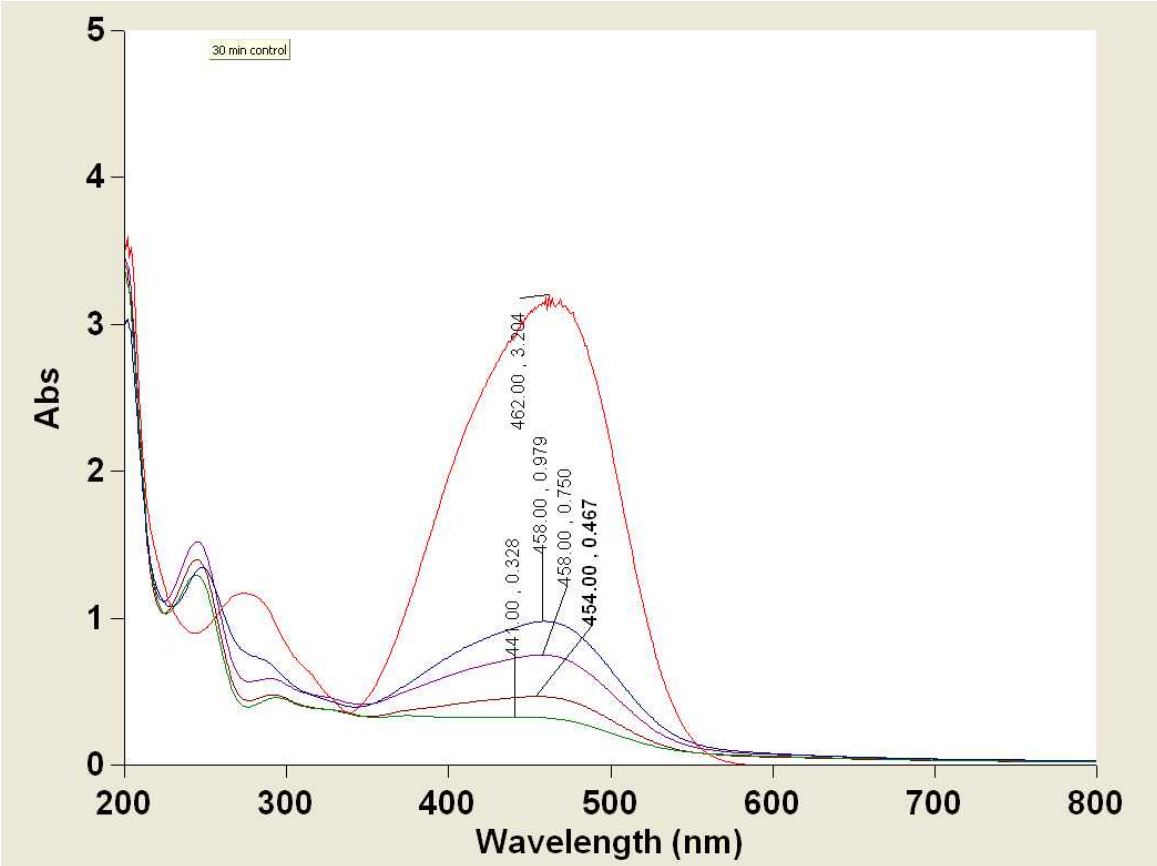

Figure 8. Ultraviolet absorbance graph of titanium dioxide nanoparticles reacting with methyl orange. Red represents control, blue represents after 30 minutes, purple represents after 40 minutes, orange represents after 50 minutes and green represents after 60 minutes.

Applying beer□s law to the absorbance of the product of the reaction between methyl orange and titanium dioxide nanoparticles, the estimated concentration of each sample is obtained. After further analysis of data by plotting the absorbance versus time graph on Microsoft Excel in Figure 8-10, it was determined that the reaction involving titanium dioxide nanoparticles is a first order reaction. The R^2 value of ln of reaction versus absorbance is closest to 1 in Figure 10, meaning that the trend line is closest to a line. According to the graph, the k value for the reaction is 0.0007. From that, the half-life of the reaction is calculated to be 16.5 minutes.

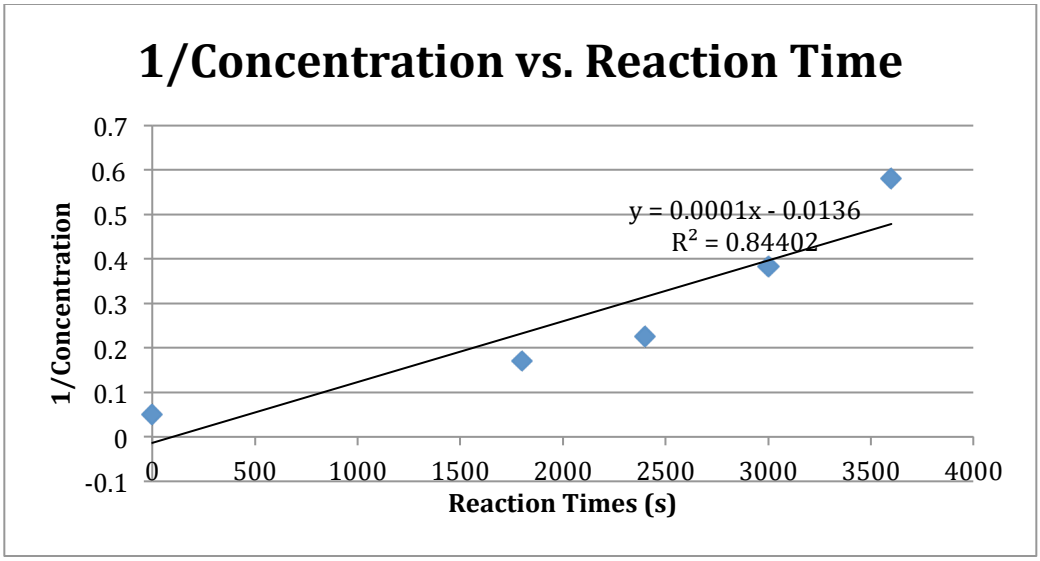

Figure 9. The graph of the reciprocal of the concentration of methyl orange versus reaction time with a R^2 value of 0.84. This demonstrates that the integrated kinetics of this reaction is not zeroth order, rate = k.

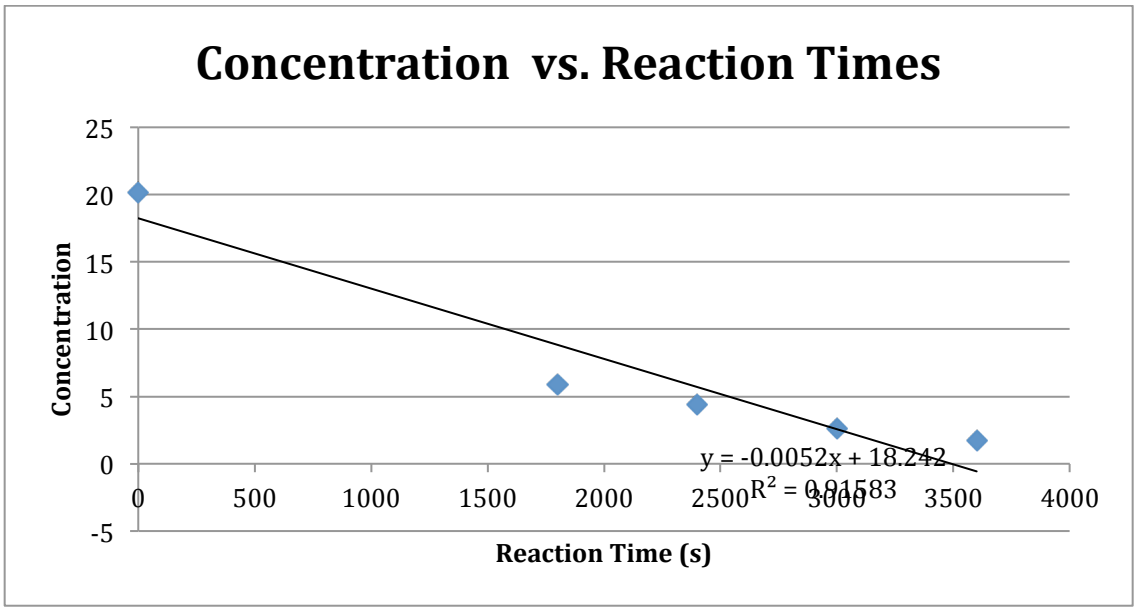

Figure 10. The graph of concentration of methyl orange versus reaction time with a R^2 value of 0.915. This demonstrates that the integrated kinetics of the reaction is not second,

rate = k[Methyl Orange]^2.

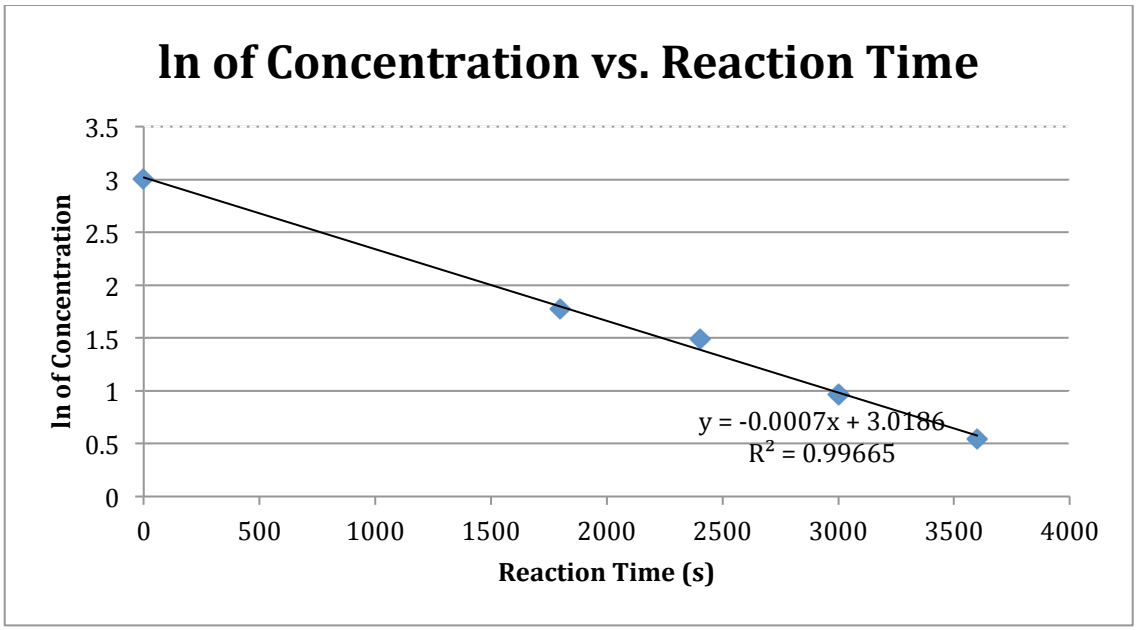

Figure 11. The graph of the natural log of the concentration of methyl orange versus reaction time with a R^2 value of 0.99. This demonstrates that the integrated kinetics of the reaction is first order, rate = k [Methyl Orange].

The results of my work did not support the initial hypothesis. The initial hypothesis stated that if titanium dioxide nanotubes were used as photocatalysts instead of titanium dioxide nanoparticles to accelerate the photodegradation of methyl orange, then the efficiency of titanium dioxide nanotubes would be higher than that of titanium dioxide nanoparticles. The results rejected the hypothesis and showed the exact contrary.

The reason why the titanium nanotubes did not react with methyl orange could be due to the structure of nanotubes present. After the electrolysis has completed, the titanium foil was covered in a thin translucent film of titanium dioxide nanotubes. When measuring the efficiency of methyl orange degradation, the amount of titanium dioxide nanoparticles used was the same as the estimated amount of titanium dioxide nanotubes. Under the scanning microscope, the structure of the titanium nanotubes seems irregular with patches clumped together. Compared to the regular shape of titanium dioxide nanoparticles, the uneven shape of the titanium dioxide nanotubes could have contributed to the low efficiency.

To address this issue in further experimentation, titanium dioxide nanotubes could be synthesized at different voltage to modify the morphology. The titanium nanoparticles and nanotubes could also be tested at different concentrations. To be more environmentally friendly, the titanium dioxide nanotubes could be synthesized using chlorine ions instead of fluorine ions. Other organic dye, such as methyl blue at different concentration could also be used to test for the efficiency of the titanium material. The final

goal of this experiment would be to modify titanium dioxide nanotubes such that it has the ability to filter most organic molecules.

Conclusions

In this study, titanium dioxide nanotubes are synthesized using electric chemical methods. Its structure is confirmed under the scanning electron microscope and its photodegradation rate is compared with that of titanium dioxide nanoparticles. Because of increased surface area, it is hypothesized that titanium dioxide nanotube will be more efficient than titanium dioxide nanoparticles. Unlike predicted in the hypothesis, the results demonstrated that titanium dioxide nanotubes are less efficient than titanium dioxide nanoparticles. This could be due to the relative low concentration of titanium dioxide nanotubes and its random distribution on the surface of the titanium foil. For future studies, titanium dioxide nanotubes could be synthesized at different voltage to modify its morphology and concentration. The procedure could also be modified so that chlorine ions are used instead of the more harmful fluorine ions. By further modifying the procedure, it is possible to find a more efficient method for filtering out harmful organic dye from wastewater.

Reference

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