Effect of Hydrogen Peroxide on the Degradation of Methylene Blue in a UV Photocatalytic Reactor

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Abstract

Photocatalysis has emerged to be an important technique to remove pollutants in water treatment process. This study investigates the photocatalytic degredation of methylene blue using TiO_2 as a catalyst, ultraviolet light as an energy source and H_2O_2 as an oxidizer; varying the H_2O_2 concentrations to see its effect on rate of reaction. Higher concentrations of H_2O_2 generally increases rate of reaction due to increased production of hydroxyl radicals (•OH), which is consistent with the results of the experiment. However, inconsistencies in the data were observed, particularly for 0.5 mL and 1 mL of H_2O_2 added, where the rate of reaction were unexpectedly lower than in trials without H_2O_2. These inconsistencies were due to experimental errors, specifically the use of degraded TiO_2 pellets in one of the two reactors. By separating the data from the different reactors, a clearer comparison between H_2O_2 concentrations was shown, revealing a positive correlation between H_2O_2 concentration and rate of reaction. Future work could focus on other variables affecting rate of reaction such as oxidizer type or temperature to find the optimal reaction condition.

1 Introduction

Photocatalysis has emerged to be one of the most widely used approach to degrade and remove a wide variety of chemicals and pollutants in water treatment process. As the world further industrialize, the release of chemical pollutants into our water system is becoming a problem. As a result, industrial waste water treatment has become an important part of keeping Earth green.[1] Textile dyes in particular is a major source of water contamination due to its extensive production and chemical stability. Additionally, they pose a strong ecological risk as even in small concentrations, these dyes can put strong colours to bodies of water and are toxic to living things.[2]

Photocatalytic degradation has gained traction in recent years as a method for water treatment. This method uses light-activated catalyst to break down harmful pollutants into less harmful byproducts.[2] Photocatalysis has advantages compared to other water treatment approaches, such as using minimal chemicals to degrade the pollutants, being more cost effective due to using sunlight as main source of energy and producing minimal harmful byproducts. However, it does have some disadvantages, such as its reliance on light to work, they are relatively inefficient in real-world scenario and there is a limited number of pollutants that can be degraded by photocatalysis.[3]

Photocatalysis facilitated by TiO_2 as the catalyst, H_2O_2 as the oxidizer and ultraviolet light as energy source has gained popularity in recent years due to its relatively high efficiency and non-toxicity. The process involves exciting TiO_2 with ultraviolet light to form free radicals, which then oxidizes the pollution, leading to its degradation.[4]

The different variables that affects photocatalysis such as the type of catalyst, the amount of oxidizer, and environment conditions can be experimented on to improve our understanding on this topic. Understanding the fundamental concept of photocatalysis will help in the application in the real world and can provide insight to improving efficiency.

2 Background

Water pollution caused by organic and industrial contaminants are major contributors to environmental and public health concerns. As such, advanced oxidation processes (AOPs) have gained much attention for their abilitiy to effectively degrade persistent organic pollutants. Among these processes, UV photo catalysis has emerged as a potential technique due to its capability to mineralize organic compounds into harmless byproducts such as CO_2 and H_2O without producing hazardous secondary pollutants.[5]

Photocatalysis is based on light-driven chemistry using semiconductor materials. Primarily titanium dioxide (TiO_2) is used to produce reactive oxygen species (ROS) such as hydroxyl radicals (•OH), which helps degrade pollutants.[6] When TiO_2 is exposed to UV radiation, electrons from the valence band to the conduction bad are excited, generating electron- hole pairs and thus initiating the process. These charge carriers will then interact with water and oxygen molecules in the system, producing ROS that oxidize organic that breaks down organic pollutants.

In spite of its advantages, UV/TiO_2 photocatalysis faces challenges that limit scalability in industrial applications: low limited visible-light absorption, low quantum efficiency, and rapid charge recombination.[7] Strategies such as doping TiO_2 with other elements, coupling with other semiconductors to form heterojunctions, and optimizing reaction parameters, oxidant addition, and catalyst loading, are being explored to increase photocatalysis efficiency.[8]

Here we show how the photocatalytic degradation rate of methylene blue (MB) is increased by the addition of hydrogen peroxide (H_2O_2). The rate law for this reaction is typically influenced by the role of H_2O_2 as an electron acceptor and an additional source of ROS such as hydroxyl radicals. By initially developing a calibration curve between the absorbance of the MB solution, and the time it takes for the dye to degrade, we can relate the rate of MB breakdown against time. Furthermore, leveraging the radical chemistry of H_2O_2, we were able to plot rate laws for different concentrations of H_2O_2 used. This analysis showed that the rate of photocatalytic breakdown for MB was significantly increased with increasing amounts of

H_2O_2, indicating a need to further investigate how similarly based chemistry can be optimized for scalability.

3 Theory

Photocatalysis is a process that utilizes a semiconductor material, usually titanium dioxide (TiO_2), to accelerate the degradation of organic compounds under ultraviolet (UV) light. When exposed to UV light with energy greater than its bandgap, TiO_2 undergoes electronic excitation, producing electron-hole pairs. These charge carriers accomodate redox reactions that lead to the formation of ROS, such as (•OH) and superoxide anions ($O_2 \bullet ^-$). These species are highly effective in breaking down organic pollutants such as MB. The fundamental reaction mechanism follows:

$$\mathrm{TiO_2} + \mathrm{h}\nu \longrightarrow \mathrm{e}^- + \mathrm{h}^+ \tag{1}$$

where h, ν, e^-, and h^+ represent Planck's constant (6.626×10^{34}), the excited electron in the conduction band and the generated hole in the valence band, respectively. These charge carriers interact with water and oxygen to produce hydroxyl radicals, as shown in the following reactions:

$$\mathrm{H_2O} + \mathrm{h}^+ \longrightarrow \bullet\,\mathrm{OH} + \mathrm{H}^+ \tag{2}$$

$$\mathrm{O_2} + \mathrm{e}^- \longrightarrow \mathrm{O_2} \bullet ^- \tag{3}$$

where the radicals initiate the oxidative breakdown of MB, leading to its complete mineralization into carbon dioxide and water.

To quantify the photocatalytic degradation of MB, spectrophotometric analysis is performed using Beer-Lambert's Law:

$$A = \varepsilon C l \tag{4}$$

where A is the absorbance, ε is the molar absorptivity coefficient, C is the concentration of MB, and l is the optical path length. A calibration curve is developed to establish the relationship between absorbance and concentration, allowing for the determination of MB concentration at different time intervals.

The kinetics of MB degradation can often be described by a pseudo-first-order rate law:

$$\frac{dC}{dt} = -k_{\text{app}} C \tag{5}$$

where k_{app} is the apparent rate constant. Integrati thisng this equation produces:

$$-\ln\left(\frac{C}{C_0}\right) = k_{\text{app}} t \tag{6}$$

where C_0 is the initial MB concentration and C is the concentration at time t. According to this relationship, a plot of $\ln C$ vs. t should be linear, with k_{app} as the value of the slope.

Hydrogen peroxide (H_2O_2) is often introduced into the system to enhance degradation efficiency. As an additional electron acceptor, H_2O_2 can suppress electron-hole recombination and generate further hydroxyl radicals through:

$$\mathrm{H_2O_2 + e^- \longrightarrow OH^- + \bullet OH} \tag{7}$$

in this redox reaction. However, excessive H_2O_2 can act as a scavenger for hydroxyl radicals, leading to the formation of hydroperoxyl radicals ($HO_2\bullet$) by the reaction,

$$\mathrm{H_2O_2 + \bullet OH \longrightarrow HO_2 \bullet {}^{+} H_2O} \tag{8}$$

where these $HO_2\bullet$ radicals have lower oxidation potential. This suggests the presence of an optimal H_2O_2 concentration, beyond which further addition leads to a decrease in the degradation rate.

4 Methods

A photocatalytic reactor was set up by placing TiO_2 into an ultraviolet reactor. Methylene blue was placed in a container with a stirrer and a pump was used to circulate the liquid into the reactor and back into the container. Concentration was measured using UV-Vis spectroscopy, so a calibration curve was produced using five known concentrations of methylene blue.

A solution of 10 ppm methylene blue was made and 2 mL of H_2O_2 was added. The absorbance was then measured. The pump was turned on to let the methylene blue react in the photocatalytic reactor and the absorbance of the solution was measured every 5 min up to 50 min. This was repeated with 1 mL, 0.5 mL and 0 mL of H_2O_2 added into the methylene blue solution.

5 Results and Discussion

All solution samples in Fig. 1, Fig. 2a, Fig. 2b, Fig. 3, Fig. 4a, and Fig. 4a were initially measured for their absorbance and then calibrated for methylene blue concentration (in ppm) using Fig. 5 to determine how much remained in the solution. All solutions use the basis of 1 L H_2O.

At the conclusion of the experiment, it was noted that the catalytic TiO_2 semiconductor pellets inside the UV reactor associated with data in Fig. 2a and Fig. 4a had darkened significantly and were much more gray than unused white pellets and those of the other reactor, of which the data are isolated in Fig. 2b and Fig. 4b.

Firstly, The degradation of methylene blue over time based on our data yielded an approximately linear relationship at the low concentrations of 6% hydrogen peroxide used, which is consistent with Eq. (5). Additionally, adding H_2O_2 to the solution does increase the rate of reaction, as opposed to its absence in the solution, as shown in Fig. 2b. This is consistent

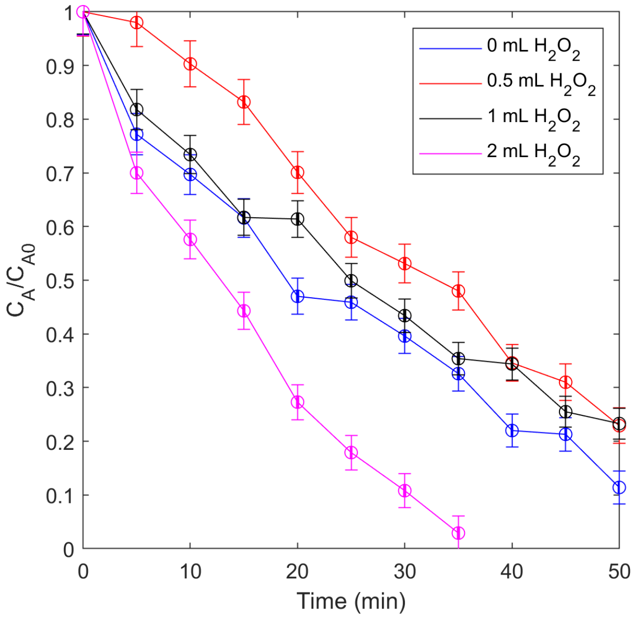


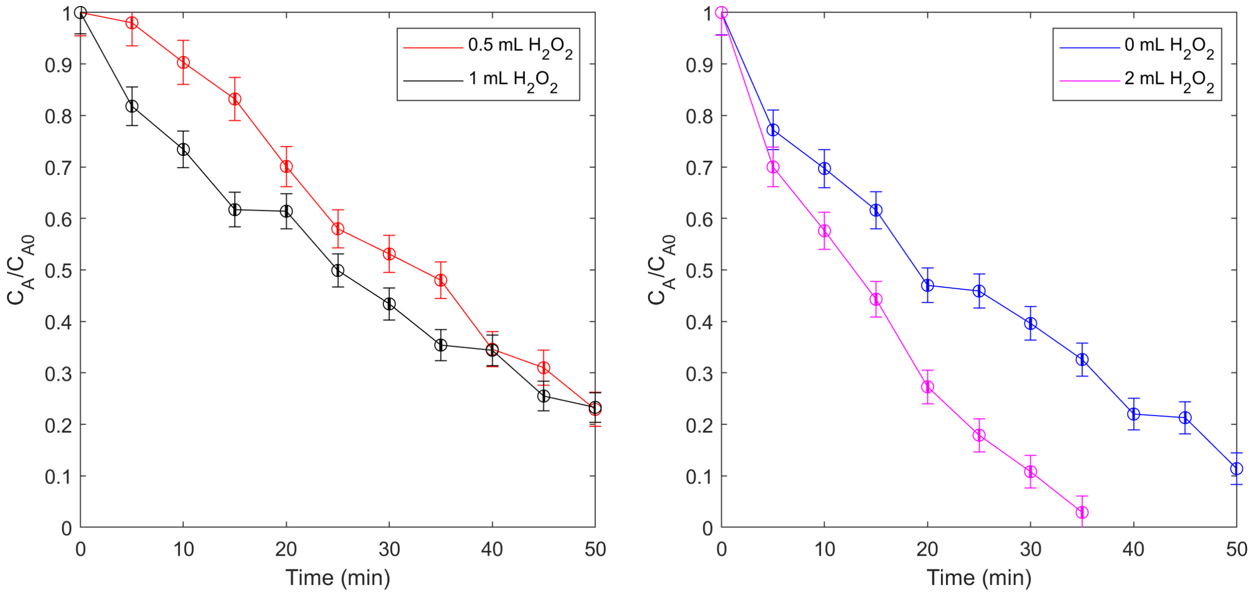
Figure 1: Ratio of methylene blue concentration to its initial concentration in solution of approximately 10 ppm methylene blue, 1 L water, and varying amounts of H_2O_2. Horizontal error bars represent a 5 second uncertainty in sampling time. Vertical error bars combine digital spectrophotometer uncertainty and propagated spectrophotometer calibration uncertainty.

with theory based on Eq. (7), as the hydrogen peroxide should create more hydroxyl radicals to degrade the methylene blue faster.

Notably, the degradation of methylene blue was significantly slower and the final relative concentrations (C_A/C_{A0}) were much smaller for both the 0.5 mL and 1 mL H_2O_2 trials shown in Fig. 2a than 0 mL and 2 mL H_2O_2 trials shown in Fig. 2b, despite being the middle two trials. As such, regression on the linearized rate law equation (Eq. (6)) expectedly resulted in larger

Table 1: Apparent rate constants and their uncertainties for solutions with different H_2O_2 concentrations based on Eq. (6) by linear regression shown in Fig. 3, Fig. 4a, and Fig. 4b.

Volume of H_2O_2, V (mL)	Rate Constant, k_{app} (s^{-1})	Rate Constant Uncertainty, u_k (s^{-1})
0	0.0366	0.0015
0.5	0.0247	0.0014
1	0.0288	0.0005
2	0.0797	0.0062



(a) (b)

Figure 2: Datasets are split from Fig. 1 depending on which reactor the data came from. The left plot shows data from the reactor with over-saturated TiO_2 pellets; the right plot shows data from a reactor functioning as expected.

slopes for the 0 mL and 2 mL datasets, with the slopes representing the apparent rate constant of the reaction, as shown in Tab. 1. This was unexpected and is a very unlikely outcome, as more H_2O_2 should always produce more hydroxyl radicals and a faster degradation rate due to the reaction shown in Eq. (7). Instead, data for degradation and methylene blue concentration in Fig. 1 and the rate constant derived from the slope linear regression in Fig. 3 for the 0.5 mL and 1 mL H_2O_2 trials should fall in between data for 0 mL and 2 mL H_2O_2 at similar timeframes. However, if the two reactors' results are isolated, it can be noted that the higher amount of H_2O_2 added in both Fig. 4a and Fig. 4b show increasing reaction rates, which was expected, though, without more trials and a wider range of H_2O_2 concentrations tested, there is not enough data to suggest this (or any) trend is conclusive.

Overall, the data do not show a particular trend or relationship between H_2O_2 volume and the apparent rate constant shown in Tab. 1 and Fig. 3, which is contrary to theory based on Eq. (6) and Eq. (7), through which it can be inferred that adding H_2O_2 to the solution generates

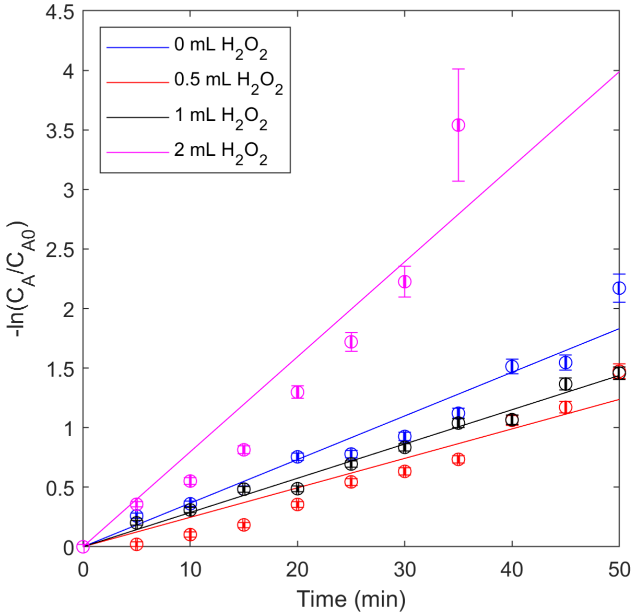
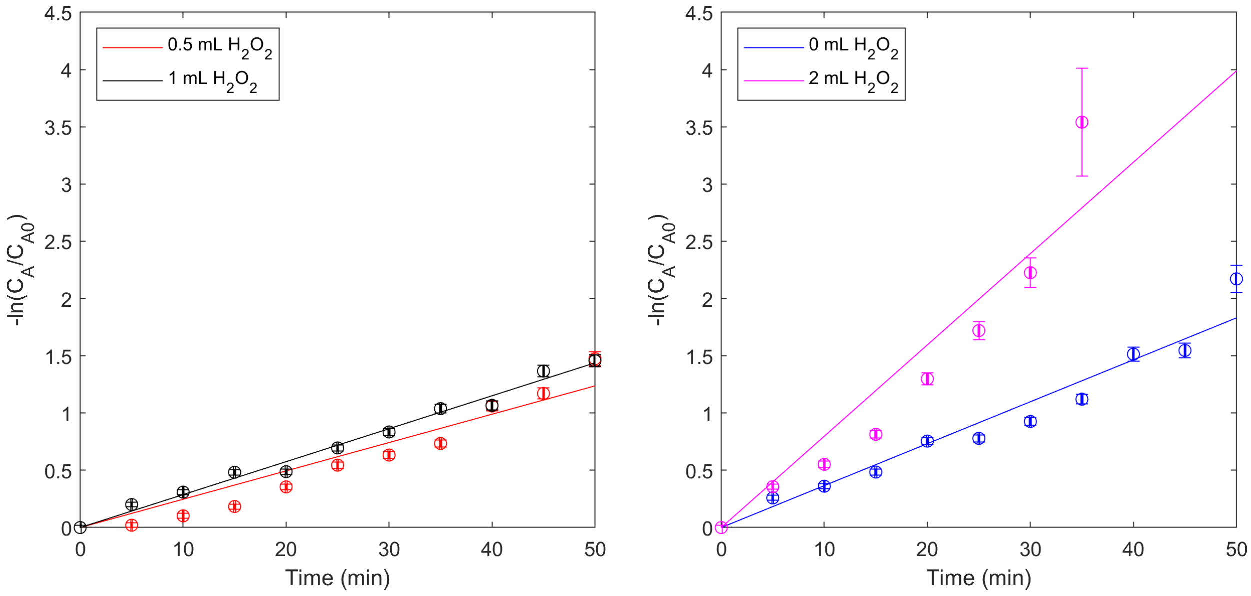


Figure 3: Rate law for the degradation of methylene blue in the form of Eq. (6), a linearized relation between time and concentration. Horizontal error bars remain a 5 second uncertainty in solution sampling, and vertical error bars are propagated from those in Fig. 1 through Eq. (6). Linear regression used to approximate rate laws for each solution, dependent on their H_2O_2 concentration.

more hydroxyl radicals, which then react with methylene blue to degrade it faster. The lack of a consistent overall trend can be attributed to a low sample size and a narrow range of H_2O_2 volumes tested as previously mentioned, but it is more likely related to the gray, over-saturated TiO_2 pellets present in the reactor producing the data in Fig. 4a. These TiO_2 pellets should be catalyzed by UV light to create charge carriers, as noted in Eq. (1), which in turn should have no problem reacting with water to create the necessary hydroxyl radicals to degrade the methylene blue (Eq. (2)). Instead, because the TiO_2 pellets had likely not been replaced after previous experiments, portions of the pellets' surface areas were saturated, leaving reaction sites for water to attach to TiO_2 through adsorption limited, creating less hydroxyl radicals than expected, therefore leaving significantly more methylene blue in the solution over time.



(a)

(b)

Figure 4: Like Fig. 2a and Fig. 2b, datasets are split from Fig. 3 dependent on which reactor the data came from. The left plot shows data taken while using the reactor with over-saturated TiO_2 pellets; the right plot shows data from a properly functioning reactor.

6 Conclusions

This experiment investigated the degradation of methylene blue using TiO_2 under ultraviolet light with different concentrations of H_2O_2. The data indicated that a higher concentration of H_2O_2 will lead to a faster degradation of methylene blue as shown in Fig. 4a and Fig. 4a, which is consistent with (Eq. (7)) and (Eq. (8)) where more H_2O_2 produce more radicals to degrade methylene blue faster. However, there were inconsistencies in the data, particularly the data for 1 mL and 0.5 mL of H_2O_2 added, where the rate of reaction is lower than when no H_2O_2 is added as shown in Fig. 3 and Tab. 1. This was due to an error made during the set up of the experiment, where old and darkened TiO_2 catalyst pellets were used for one of the two reactors, rendering the catalyst ineffective.

The data was split between the two reactors to show the comparison between the different concentrations of H_2O_2 as seen in Fig. 2a, Fig. 2b, Fig. 4a, and Fig. 4a. Doing this eliminates the error from the faulty catalyst, showing the true comparison between concentrations of H_2O_2.

The low data sample also contributes to the inconsistencies, which is especially true when the data was split, causing even less data sample per reactor.

Future experiments on photocatalysis with TiO_2 under ultraviolet light can focus on other variables affecting pollutant degradation such as oxidizer type or temperature to find an optimal condition for this reaction. A wider range of H_2O_2 concentration should also be used to see the true trend between rate of reaction and oxidizer concentration. Future studies could also focus on finding more stable catalysts to prevent catalyst degradation, which can slow down rate of reaction. These improvements could improve efficiency of the reaction, which could increase its effectiveness in the real world and contribute to a more economic and efficient method of water treatment using photocatalysis.

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Appendix

1. Titanium Dioxide Photocatalysis
   - Author(s): Fujishima, A.; Rao, A. N.; Tryk, D. A.
   - Year published: 2000
   - Journal name: Journal of Photochemistry and Photobiology C: Photochemistry Reviews
   - 1-3 major accomplishments of this paper:
     (a) Provided a comprehensive review of titanium dioxide ($TiO2$) photocatalysis, summarizing its applications in environmental remediation and water splitting.
     (b) Discussed the fundamental reaction mechanisms of $TiO2$ photocatalysis, including charge carrier dynamics and the formation of reactive oxygen species (ROS).
     (c) Highlighted the challenges and future directions for improving photocatalytic efficiency, such as bandgap engineering and material modifications.
2. Principles of Photocatalysis on TiO_2
   - Author(s): Linsebigler, A. L.; Lu, G.; Yates, J. T.
   - Year published: 1995
   - Journal name: Chemical Reviews
   - 1-3 major accomplishments of this paper:
     (a) Established a detailed theoretical framework for $TiO2$ surface chemistry and its photocatalytic properties.
     (b) Investigated electron-hole recombination dynamics and their effect on photocatalytic efficiency.

    (c) Provided a systematic review of reaction intermediates and surface interactions involved in $TiO2$ photocatalysis.

3. Heterogeneous Photocatalytic Degradation of Organic Contaminants
   - Author(s): Gaya, U. I.; Abdullah, A. H.
   - Year published: 2008
   - Journal name: Journal of Photochemistry and Photobiology C: Photochemistry Reviews
   - 1-3 major accomplishments of this paper:
     (a) Reviewed the heterogeneous photocatalytic degradation of organic contaminants using TiO_2, emphasizing real-world applications.
     (b) Examined factors affecting photocatalytic efficiency, such as pH, catalyst loading, and light intensity.
4. Fourth main reference
   - Author(s): M. Saquib, M. Abu Tariq, M. M. Haque, M. Muneer
   - Year published: 2008
   - Journal name: Journal of Environmental Management
   - 1-3 major accomplishments of this paper:
     (a) Demonstrated the effectiveness of the UV, TiO_2, and H_2O_2 process for the degradation of methylene blue.
     (b) Provided kinetic insights into the photocatalytic reaction, showing its potential for wastewater treatment applications.

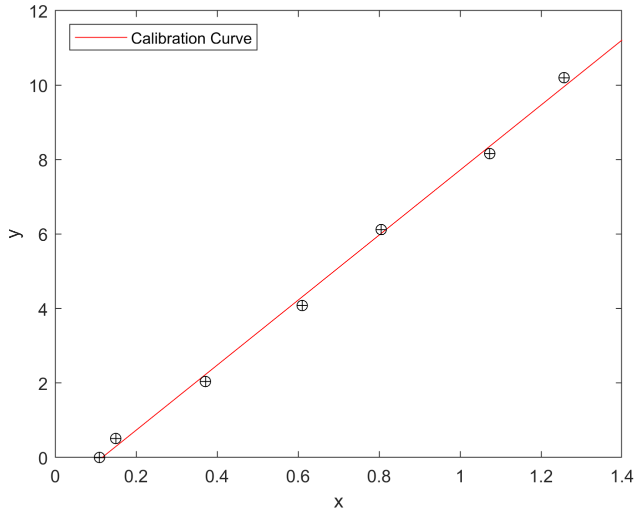

Figure 5: Spectrophotometer calibration curve relating AU to methylene blue concentration in solution, in ppm. Linear regression based on set methylene blue concentrations and their respective absorbance.