Wetted Wall Photocatalytic Reactor for Methylene Blue Degradation

Amornpon Boonying, Artith Kasempremsak, Supunee Junpirom*, Aroonsri Nuchitprasittichai
School of Chemical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
*E-mail: supunnee@sut.ac.th

Abstract. Titanium dioxide (TiO$_2$) is generally known a good potential of photocatalyst to synthesis hydrogen peroxide (H$_2$O$_2$). The aim of this work is to generate the H$_2$O$_2$ via photocatalysis for further application in a sterilization system. Wetted wall photocatalytic reactor (WWPR) was particularly designed as a prototype for carrying out the experiments of photocatalytic reaction. An advantage of WWPR is a high contact surface area of feed and catalyst mixture with UV light to enhance a high efficiency to produce the H$_2$O$_2$. The TiO$_2$ photocatalyst was prepared via sol-gel method and mixed with rice husk based silica dioxide (SiO$_2$). Properties of photocatalyst were investigated by XRD, SEM and surface area and its photocatalytic performance was tested by methylene blue degradation with reaction measurement using the UV/Vis instrument. Variation of the catalysts loading and methylene blue initial concentration were studied in photocatalytic experiments. In the batch of 0.25 g of photocatalyst with 80 mg/L methylene blue solution, the results showed that the percentage of methylene blue removal is at 89.52% within 2 hours of reaction. This removal efficiency of methylene blue is resulted from both mechanisms of degradation by photocatalytic reaction and adsorption by the function of SiO$_2$ modification and the trap-hole of crystallized anatase structure.

Keywords: Photocatalyst; Methylene blue degradation; Sol-gel method; Titanium dioxide; Wetted wall photocatalytic reactor

1. Introduction
Titanium dioxide (TiO$_2$) or titania is well known as semiconductor material which has known a good potential of photocatalyst. Once TiO$_2$ activated by light which specific wavelength, energy from light convince electron (e$^-$) to release from valance band and leave positive hole (h$^+$) on photocatalyst surface. Both of reactive ion is capable to converts surround water and oxygen into hydrogen peroxide which is sterilant agent by deform itself into superoxide radical (O$_2^-$) and hydroxyl radical (OH$^-$) to disinfect microorganism. Both radical has capability to decompose and disinfection organic pollutant. Physical properties of photocatalyst such as specific area, particle size, crystalize structure phase composition influence to its activity and efficient to transfer electron ion. Many research articles study about photocatalytic mechanism. Which are categorized by photocatalytic activity and modification method of photocatalyst.

Fumihide Shiraishi (2003) and coworkers [1] described photocatalytic mechanism of the decomposition of HCHO and formation of H$_2$O$_2$ on Pd/TiO$_2$ photocatalyst. Irradiation source light create energy that release electron from valance band of photocatalyst to convert the surrounding molecules into radicals which has potential to convert other molecules to other product in further reaction. Jinfeng Zhang (2014) et al. [2] found the difference crystal structure of TiO$_2$ resulting to difference band gaps energy which affect to its activity and lifetime of photogenerated electrons. Tim Luttrell (2014) et al. [3] also found that higher activity of anatase resulting to higher decomposition of organic pollutants than other structure. Yusuke Kakuma (2015) et al. [4] studied the influence of difference in two polymorphs of TiO$_2$ structure between rutile and anatase affect to photocatalytic mechanism using the detection of various radicals and H$_2$O$_2$ from photogeneration on photocatalyst.
It was revealed that the formation of $\text{H}_2\text{O}_2$ and $\cdot\text{O}_2^-$ for rutile was significantly higher than that for anatase. Even photocatalytic activity of anatase is higher than rutile, but TiO$_2$ bond separation distance on anatase is wider than rutile. They discussed that atomic separation distance affected to result of photocatalytic mechanism. The length of TiO$_2$ separation plays a role as trap-hole which traps and decomposes the surrounding radicals and $\text{H}_2\text{O}_2$. They also suggested that the photocatalytic activity not only be attributed to the photocatalytic induced process. From previously knowledge providing photocatalytic activity and adsorption capability is important factor for photocatalytic mechanism. Modification method of photocatalyst has been represented from many literatures to enhance the performance of photocatalyst, both of photocatalytic activity and adsorption. Ewelina Kusiak-Nejman (2011) et al. [5] aimed to modify TiO$_2$ by carbon in case of dye decomposition application, synergistic effect between these two compounds is expected. In the result of methylene blue degradation showed that the modified TiO$_2$ has higher reaction rate constant than unmodified TiO$_2$. The presence of carbon and amount of hydroxyl group cause higher photocatalytic activity. Rachanon Klondon (2013) [6] introduced modification method for TiO$_2$ with SiO$_2$ from rice husk in difference preparation condition. SiO$_2$ plays a role to increase pollutants adsorption and change TiO$_2$ anatase/rutile structure ratio, which enhances photocatalytic efficiency better than unmodified TiO$_2$. Result of CO gas elimination by photocatalytic process after coated on DAN KWIAN Pottery which consider from previous study prove that TiO$_2$ capable to eliminate pollutants in both gas and liquid phase. Modification of TiO$_2$ indeed develop performance and increase boundary of application. Daijiro Tsukamoto (2012) et al. [7] studied on H$_2$O$_2$ generation on TiO$_2$ with variation of Au-Ag bimetallic alloy loading particles (AuAg/TiO$_2$). The experiment is observed the influence of Au and Ag alloy affecting to photocatalytic activity, but modification of Au-Ag proves that higher effective on H$_2$O$_2$ synthesis than modification of one metallic material. They discussed that H$_2$O$_2$ is generated and decomposed at the same time. Bimetallic Au-Ag does support each other in photocatalytic generation and adsorption mechanism. When Au enhances the photocatalytic activity to generate H$_2$O$_2$ from reaction. However, the H$_2$O$_2$ is likely to being adsorbed to Ag than Au. The lower activity of Ag results in reducing of H$_2$O$_2$ decomposition when it is adsorbed on Ag.

In literature, many researches have been studied on photocatalyst mechanism, however there are few studies to focus on the development of photocatalytic instrument. From the previous research, it is found that photocatalytic reaction is driven by contacting of photocatalyst and activated light. Thus, the increasing in available contact area would increase the efficiency of reaction. This work aims to study and apply photocatalytic reaction on the prototype instrument, wetted wall photocatalytic reactor (WWPR). According to Soochnul Kwon (2008) et al. [8], they’ve reviewed the improvement of photocatalytic efficiency by operating the mixing of photocatalyst and solution in the form of suspended solution. This idea is used to apply for this work in order to increase the efficiency of photocatalytic reaction.

![Figure 1. Conceptual design for wetted wall photocatalytic reactor (WWPR)](image-url)
2. Materials and Methods

2.1. SiO\textsubscript{2} preparation.

A 100 g of rice husk was rinsed in water, then soaked in 1 L of sulfuric acid solution with concentration of 0.5 M at 80 °C for 2 hours. Rice husk was taken to rinse again with water until obtain pH 7. After rinsing, rice husk was taken to dry at 120 °C for 12 hours and burned the dried sample in a furnace at 500 °C, heating rate 10 °C/min for 2 hours.

2.2. Photocatalyst preparation.

Amorphous TiO\textsubscript{2}/SiO\textsubscript{2} powder was prepared via sol-gel method [6]. Solution A was obtained by combination of titanium (IV) n-butoxide 17 ml with absolute ethanol 40 ml. Solution B was obtained by combination of HNO\textsubscript{3} 3 ml, DI water 15 ml and absolute ethanol 35 ml. Solution A, B and 2 g of SiO\textsubscript{2} were combined and stirred for 60 minute, then left it settle for 24 hours to achieve gel solution. The gel solution was taken into oven to dry it at 110 °C for 12 hours, then calcined it in the furnace at temperature 500 °C for 2 hours using heating rate at 10 °C/min. The amorphous TiO\textsubscript{2}/SiO\textsubscript{2} powder was achieved. For pure TiO\textsubscript{2} was produced by the same method without SiO\textsubscript{2} addition.

The crystal structure and external surface of prepared photocatalyst was obtained by using X-ray diffractometer (XRD) and scanning electron microscope (SEM), respectively.

2.3. Experiment of methylene blue degradation by photocatalysis.

2.3.1. Batch experiment. A batch of 200 mL of methylene blue solution with initial concentration of 80 mg/L was mixed with 0.25 g of photocatalyst. The light source of UV with 10W (Philips UV lamp G10T8) was irradiated in sample which put in a black box. During the reaction testing, the sample was stirred by using the magnetic bar, the experimental setup is shown as Figure 2(a).

![Figure 2](image-url)

**Figure 2.** Batch methylene blue photocatalytic reaction setup (Left) and Wetted wall photocatalytic reactor (WWPR) prototype diagram (Right)

2.3.2. Circulating batch experiment in a WWPR. The experiments were carried out in a WWPR. The circulating feed was prepared from the 200 mL of methylene blue 80 mg/L initial concentration mixed with 0.25 g of photocatalyst. The suspended solid solution was fed into wetted-wall reactor by peristatic pump with a flow rate 1.5 L/min. 10W UV light source was installed inside the reactor, following Figure 2(b). Experimental series were run with variation of time to observe the degradation of methylene blue. The sample were collected every 15 minutes within the range of time 2 hours. UV/Vis instrument was used to determine the absorbance of methylene blue solution to indicate its degradation efficiency. There was one experiment test without light irradiation for being a blank test.

3. Results and Discussion

3.1. Structural properties of TiO\textsubscript{2}/SiO\textsubscript{2} photocatalyst.

In general, the crystalize structure occur in TiO\textsubscript{2} is classified to anatase structure, rutile structure and brookite. XRD result is shown that prepared TiO\textsubscript{2}/SiO\textsubscript{2} was found 100% TiO\textsubscript{2} anatase structure, follow Figure 3(a). Anatase structure is highest stability structure compare with other type of structure due to cubic closed packing (CCP). In general, anatase crystal structure has higher bandgap energy than rutile\textsuperscript{4} that influence to capability of photocatalytic phenomena. Band gaps energy value also affect to its photocatalytic activity and photogenerated electron while activated by UV light. SEM image of external
surface of the photocatalyst is shown in Figure 3(b). It is observed that the porous structure occurring on the surface of photocatalyst. This porous structure occurring will increase in the efficiency to adsorb the surrounding molecules onto the surface of photocatalyst.

![Figure 3](image1.png)  
**Figure 3.** XRD pattern (a) and SEM image (b) for TiO$_2$/SiO$_2$ photocatalyst

3.2. Methylene blue degradation.  
The first experiment was carried out to compare the overall efficiency of photocatalytic activity for the differentiation of the reactor, circulating batch WWPR and a normal batch which is shown in Figure 4. The tests were operated for 2 hours with keeping the same for all reaction parameters. It is found that the circulating batch WWPR gave the 89.5% of methylene blue degradation and 59.7% from batch reactor. It is clearly proving that circulating batch WWPR has higher efficiency than batch reactor in methylene blue degradation.

This result is proving that the configuration of reactor, circulating batch WWPR, in which creating the falling film of photocatalyst suspended solution around the reactor wall providing the increasing of contact area of three main components in photocatalysis, e.g. photocatalyst, chemical agent (solution), and light. Thus, the designing concept of circulating batch WWPR is further implemented for experimental series.

![Figure 4](image2.png)  
**Figure 4.** Comparison of photocatalytic methylene blue degradation between circulating batch WWPR and batch

The effect of SiO$_2$ addition photocatalyst was studied by comparing the methylene blue degradation in WWPR, as displayed in Figure 5. The overall trends are the same for both TiO$_2$/SiO$_2$ and TiO$_2$ photocatalyst. However, the TiO$_2$/SiO$_2$ photocatalyst gave the higher efficiency in methylene blue degradation at different reaction time. The effect of SiO$_2$ can be seen in the first point of collecting data, implying that the SiO$_2$ plays a major role to increase the adsorption capacity. When
the photocatalytic reaction ran for longer time, the differences of methylene blue degradation between the TiO$_2$/SiO$_2$ and TiO$_2$ seem to be nearly constant at approximately 9%. From this observation, it can be explained that the SiO$_2$ does not affect to the kinetic reaction of photocatalysis.

![Figure 5](image)

**Figure 5.** Percentage of methylene blue degradation with variation of time and phototocatalyst type

The experiment series of TiO$_2$/SiO$_2$ photocatalyst in methylene blue degradation with and without UV irradiation was tested in order to investigate the role of SiO$_2$ in adsorption, as exhibited in Figure 6. It is found that the degradation of methylene blue rapidly increased to 70.2% within 15 min for without UV irradiation and then slightly increased to 79.9% at 120 min. This quantity is indicated to the adsorption mechanism of TiO$_2$/SiO$_2$ photocatalyst. Thus, in overview explanation of this work can be concluded that there are two main mechanisms of adsorption and photocatalysis reaction in methylene blue degradation. The adsorption may firstly take place due to the porous structure of photocatalyst. This mechanism enhances the photocatalytic reaction. Since the adsorbed molecules on the catalyst surface is more easily to be reacted with the generated free radicals.

![Figure 6](image)

**Figure 6.** Percentage of methylene blue degradation comparison with/without UV irradiation

The methylene blue degradation due to the photocatalytic reaction occurred from radiation by specific wave length of light that affected to release the electron from photocatalyst. An isolated electron convert surrounding O$_2$ and H$_2$O into radical OH$^-$ [9], then radicals can break the S$^+$ functional group in methylene blue as shown in Figure 7., in which induces the opening of the central aromatic rings. The loss of aromatic ring and structure lead to decolorize of methylene blue.
4. Conclusion

Photocatalytic degradation of methylene blue by using TiO$_2$/SiO$_2$ as a photocatalyst was carried out in circulating batch wetted wall photocatalytic reactor in which creating the falling film of photocatalyst suspended solution around the cylindrical reactor wall. This reactor gave a higher efficiency than that in a normal batch reactor approximately 29%. There are two main mechanisms of adsorption and photocatalytic reaction of methylene blue degradation. Addition of SiO$_2$ in photocatalyst plays a major role in increasing adsorption capacity of the photocatalyst.

References

[1] Fumihide Shiraishi, Tsugunori Nakasako, and Zhaozhe Hua, 2003, J. Phys. Chem. A, 107, 11072-11081.
[2] Jinfeng Zhang, Peng Zhou, a Jianjun Liu and Jiaguo Yu, 2014, Phys.Chem.Chem.Phys., 16, 20382.
[3] Tim Luttrell, Sandamali Halpegambarage, Junguang Tao, Alan Kramer, Eli Sutter, and Matthias Batzill, 2014, Sci Rep., 4, 4043.
[4] Yusuke Kakuma, Atsuko Y. Nosaka, and Yoshio Nosaka, 2015, Phys.Chem.Chem.Phys., 17, 1-8.
[5] Ewelina Kusiak-Nejman, Magdalena Janus, Barbara Grzmil, Antoni W. Morawski, 2011, Journal of Photochemistry and Photobiology A: Chemistry, 226, 68–72.
[6] Rachanon Klondon, 2013, Removal of air pollutants by photocatalytic process using TiO$_2$-SiO$_2$ coated dan kwian pottery, Retrieved Oct. 15, 2018, http://sutir.sut.ac.th:8080/sutir/handle/123456789/4751.
[7] Dajiro Tsukamoto, Akimitsu Shiro, Yasuhiro Shiraishi, Yoshitsune Sugano, Satoshi Ichikawa, Shunsuke Tanaka, and Takayuki Hirai, 2012, ACS Catal., 2, 599-603.
[8] Soonchul Kwon, Maohong Fan, Adrienne T. Cooper & Hongqun Yang, 2008, Critical Reviews in Environmental Science and Technology, Volume 38, Issue 3.
[9] Ranfang Zuo, Gaoxiang Du, Weiwei Zhang, Lianhua Liu, Yanming Liu, Lefu Mei, and Zhaohui Li, 2014, Advances in Materials Science and Engineering, Volume 2014, Article ID 170148, 7 pages.

Acknowledgement

This work was supported by Center of Excellent in Biomechanics Medicine, Suranaree University of Technology