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TiO_2 nanostructure coated glass-tube for degradation of methylene blue: an experimental and design of column photocatalytic reactor

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ABSTRACT

This work presents the successfully of TiO_2 nanostructure synthesis using manual grinding combined hydrothermal method for photocatalyst. XRD confirmed that TiO_2 was arranged by anatase and rutile phase with crystal size of 18.54 nm. Characterization of digital microscope shows the spread of catalyst on the glass tube surface, which can be observed furthermore using interactive 3D surface plot. Band gap energy determination from UV-Vis spectroscopy scanning shows the minimum energy that is required to facilitate electron-hole generated. In 20 min of irradiation, TiO_2 existence can completely decompose MB (100%) that can be presented by TiO_2 absence. Degradation of MB is higher effective in acidic condition which optimum pH of 5. Using first order reaction, glass tube-coated TiO_2 has rate constant of 0.2102 min^{-1}, 1.5 times faster than bare glass tube. This enhancement proves that the designed reactor has good prospect for organic pollutant treatment. Moreover, compared with other reported study, this system provides relatively more effective of MB photodegradation.

1. INTRODUCTION

The design of photodegradation reactor is one of the important parameters on the methylene blue (MB) photodegradation. In laboratory scope, many researchers just put the dye into the glass then irradiating with the lamp (batch or column method) which is hard to apply in industry immediately. The design of an efficient photocatalytic reactor is crucial to enhance the photocatalytic activity of photocatalyst and improve the overall efficiency of the process. The design of a photocatalytic reactor is influenced by several factors, such as the type of reactor, reactor geometry, reactor material, and photocatalyst immobilization technique. Therefore, it is important to investigate and optimize the design of a photocatalytic reactor to achieve efficient degradation of pollutants in wastewater. Commonly, industry requires both automatic and fast technique, thus a development of reactor needs to develop. Abdellah et al. (2018) has studied MB decomposition using flow method with air additional in the system that improves decomposition efficiency because of more oxygen molecules presence [1]. The photocatalytic spinning disc reactor has successfully performed for

disrupting MB using thin film coated by TiO_2 as photocatalyst which is easily adjustable the flowrate [2]. The reactor structure can determine the effectivity of catalyst because it plays role as interaction medium between photocatalyst and dye molecules. Flow-based method needs to optimize the degradation condition, such as flowrate, lamp energy, design, and capacity. This technique is promising for applying at industrial scale although various parameter require optimization.

Titanium dioxide (TiO_2) as photo redox semiconductor has been widely applied in environmental photocatalytic such as decomposition of organic pollutant or dyes [3, 4], molecule splitting [5], Li-ion battery [6], etc. The popularity of TiO_2 is based on its high stability, good photoelectric properties, and less expensive fabrication [7]. In 1972, Fujishima and Honda firstly reported TiO_2 as semiconductor electrode for water splitting under ultraviolet (UV) irradiation [8]. Afterwards, the engineering of TiO_2-based is started and still continuously until now not only for environmental but also energy field. The extraordinary modification on size, Nanotechnology, attracts more attention on many researchers because of excellent properties from the resulted material. TiO_2 have been engineered through nanotechnology using top-down or bottom-up approach [9]. The size dependent effect is popular principle in nanomaterial study. The decrease of size to nano scale could enhance surface to volume ratio of material. Their shape, size, surface area, high surface to volume ratio, and high porosity also become notable specification to overcome environmental issues [10]. Besides, the crystalline parameter of TiO_2 is also the important variable that effects on its performance. Anatase, brookite, and rutile are three crystal phases of TiO_2 that could be adjusted to the aims. For photocatalytic activity, anatase results best performance among them. However, more amount of material in similar weight provides higher interaction between catalyst and substrate. The various methods have been used for obtaining TiO_2 nanostructures, such as ball milling, sol-gel, electrospinning, hydrothermal, solvothermal, and template-assisted [11].

TiO_2 nanostructure have been broadly utilized for decomposing synthetic dye such as methylene blue (MB). As an aromatical cationic dye, MB is harmful not only for human health but also environment. The certain MB accumulation on body has been reported that gives badly complication illness on digestion and respiratory [12]. MB is one of the primary colors which is often used on the textile industry because of the affordable [13]. MB needs to treat before releasing for minimizing negative effect. Here, TiO_2 could be role through photocatalysis degradation supported suitable light energy. Hamed et al. (2022) reported catalyst morphology, surface defects, and active species also influence photocatalytic activity of dye. TiO_2 has negative charge on its surface which can arrange electrostatic interaction with cation MB so pH condition is important thing [12]. In other study, Tichapondwa et al. (2020) investigated the effect of different phases, initial concentration, catalyst loading, and pH on MB decomposition under UV irradiation. The results confirm that MB removal strongly depends on its condition. Photocatalysis includes the Advanced Oxidation Processes (AOP's) technique for environment remediation that can occur economically at industrial scale [14]. This technique generates free radical molecules which can break the dye structure into intermediate compounds or simple molecule (CO_2, H_2O or O_2) directly through perfect decomposition [15].

In this study, we design a photodegradation reactor with flow and batch system combination using commercial TiO_2 which has been improved to nanoparticle through top-down approach as photocatalyst. TiO_2 nanoparticle is produced for glass-tube coating in semi-automatic reactor. Reactor performance is evaluated for decomposing MB under UV lamp irradiation. The designed reactor can enhance the efficiency of MB degradation besides providing simplicity and low-cost application. This work purpose to give an alternative technique of wastewater treatment in wider scale.

2. EXPERIMENTAL METHOD

2.1 Materials

Commercial TiO_2 powder was purchased from marketplace with purity of $\geq$98% (seller claim).

Nanoparticle TiO_2 synthesis was performed using sodium hydroxide (NaOH) from Merck, 35% hydrochloride acid (HCl), ethanol (≥99%), and MB ($C_{16}H_{18}ClN_3S \cdot 3H_2O$) as pollutant dye with purity of ≥98.5% from Nacalai Tesque Inc., then deionized water from Merck Millipore apparatus. All reagents were analytical grade without further purification.

The material was characterized using FTIR spectroscopy from Shimadzu (ATR FT-IR IR affinity-1s) to observe the functional groups, powder x-ray diffraction (XRD) to determine crystal parameter of material from Rigaku XRD instrument, digital microscope for surface morphology scanning from Olympus Biological Microscope (CX23-LED-L1), then UV-Vis spectroscopy (Shimadzu UV-1280) is utilized to evaluate degradation efficiency and electronic properties of TiO_2.

2.2 Synthesis of catalyst

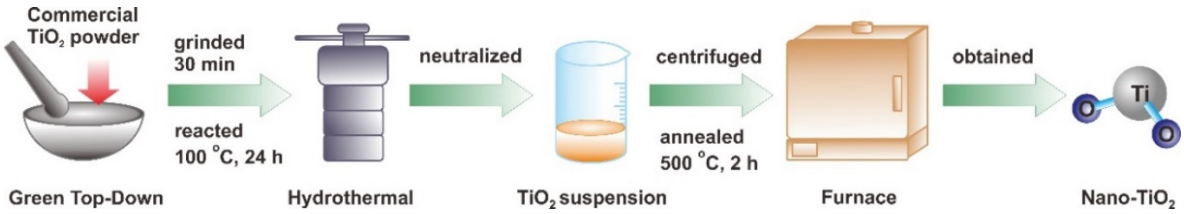

Figure 1. Illustration of nanostructure TiO_2 synthesis pathway

Commercial TiO_2 was synthesized using manual milling and basic hydrothermal combination as shown in Figure 1. The white powder of TiO_2 was grinded for 30 min to crush the structure into smaller size. Afterwards, basic hydrothermal using NaOH 12M was performed to control shape and morphology of TiO_2 structure rearrangement for 24 h at 100 ºC. White suspension was cooled down before neutralizing with HCl 0.1M until reach pH of 7 or similar with DI water pH. The precipitate was separated from the solution using centrifugation, then sol-gel was dried under atmospheric condition at 100 ºC for a night.

2.3 Design of column photocatalytic reactor

The development of photodegradation reactor aims to obtain the optimal performance of MB degradation. Figure 2 provides the reactor design of photodegradation in this study which is arranged semi-flow condition. A pump was paired with a valve that can be opened and closed for injecting dye (5 mL/s) into the glass-tube coated catalyst. The mercury (Hg) lamp from Analamp (30 μW/cm^2) with wavelength of 254 nm was used for UV energy source located inner of tube. After interaction, valve was spined for taking out the decomposition product so the water can be released to the environment safely.

2.4 Photocatalysis test

The MB solution after decomposing with designed reactor was calculated using UV-Vis spectrophotometer at wavelength of 662 nm. Initial MB solution has concentration of 10 ppm. Influence of irradiation time was observed on the decreasing of MB at 0, 2, 4, 6, 8, and 20 min. The study of pH effect was also evaluated to determine the optimal condition of solution pH (2, 5, 7, and 10). Degradation activity was performed by comparing with and without catalyst existence. The amount of degraded MB (%) was calculated using Eq. 1, whereas the degradation rate constant was determined as slope value of Eq. 2 (t vs -ln C_t/C_0) following first-order reaction.

$$Deg.(\%) = \frac{C_0 - C_t}{C_0} \; x \; 100 \qquad \text{Eq. 1}$$

$$-ln\frac{C_t}{C_0} = kt \quad \text{Eq. 2}$$

C_0 is initial concentration of MB (ppm), C_t is relative amount of MB at certain time t (min) which is length of irradiation time, and k is rate constant of degradation reaction (min^{-1}).

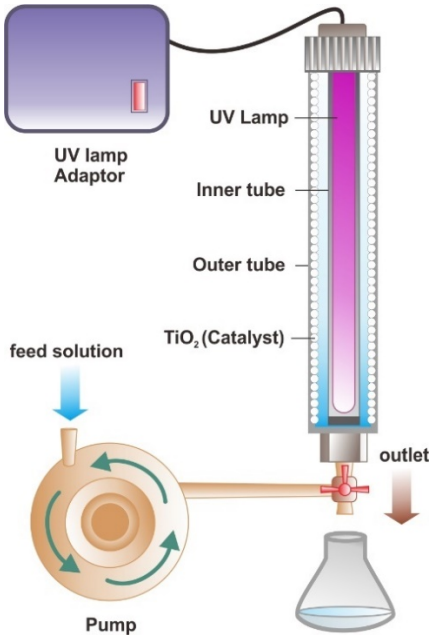

Figure 2. Design of decomposition reactor with catalyst

3. RESULTS AND DISCUSSIONS

3.1 Catalyst characterization

In this work, TiO_2 nanoparticle was produced by top-down approach from commercial powder using combination of manual grinding and hydrothermal method. The grinding process breaks the structure and changes the material size. Then, the morphology of TiO_2 is rearranged during hydrothermal under basic condition. Figure 3(a) shows the FTIR spectrum pattern of TiO_2 commercial compared with post-treatment recorded in wavenumber range of 500 to 4000 cm^{-1}. The characteristic peak of both materials at around 700 cm^{-1} is corresponded to Ti-O stretching vibration [16]. There is no intensive peak provided commercial TiO_2 on the spectrum. But at the post-treatment TiO_2, many peaks appear that indicate molecules contain in TiO_2 material such as O—H (~3400 cm^{-1}), C—H (~2900 cm^{-1}), and C—O (~1200 cm^{-1}). Actually, the existence of these functional groups gives an advantage on the interaction between catalyst and substrate, so the oxidation processes more intense.

Crystalline characteristic from post-treatment TiO_2 is presented by powder-XRD analysis. Figure 3(b) demonstrates diffractogram pattern TiO_2 after annealing at 500 ^oC for 2 h. Pattern confirms that anatase and rutile crystal phase is arranged together. Anatase peaks is ascribed by 2θ of 25.38^o and 48.13^o, respectively correspond to (101) and (202) planes. Rutile phase is shown by highest dominant peak at 2θ of 27.54^o and 54.39^o assigned to the (110) and (211) crystal planes. Combination of manual grinding and hydrothermal damage the TiO_2 structure, after that the new crystal orientation and remainder phase grow along heating treatment therefore a mixture crystal phase is re-structured. Furthermore, the size dimension of TiO_2 can be determined from diffractogram

using Debye-Scherrer equation, $D = k\lambda / \beta \cos \theta$ where D is crysallite size (nm), k is Scherrer constant or shape factor (0.9 – 1), λ is wavelength of X-ray energy source (Cu Kα = 0.1542 nm), β is FWHM (full-width at half-maximum), and θ is diffraction peak. From calculation, TiO_2 has crystallite average size of 18.54 nm indicating the synthesized material in nanostructure scale.

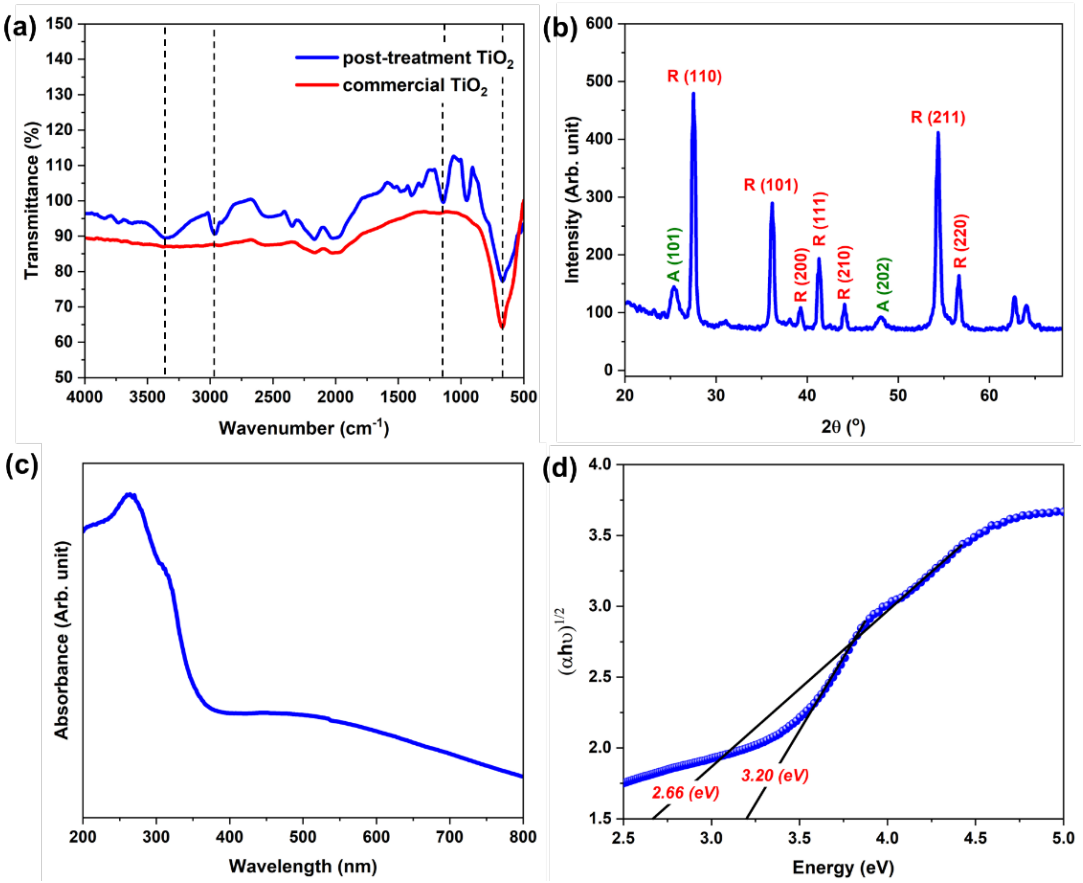

Figure 3. (a) FTIR spectrum of commercial and post-treatment TiO_2, (b) X-ray diffraction pattern of post-treatment TiO_2, (c) UV-Vis spectrum of post-treatment TiO_2, and (d) Band gap energy calculation from catalyst.

Afterwards, Figure 3 (c) and (d) reveal electronic properties of TiO_2 using UV-Vis spectroscopy scanning. The band gap energy (Eg) is obtained from this measurement then calculating with Tauc's plot method. After plotting, it shows two types of Eg 2.66 and 3.20 eV which are attributed to rutile and anatase, consecutively. Ansari and Cho (2016) reported that their material has two different band gap energy. The lower band gap can appear from the impurity or doping effect that causes widely shifting of minimum conduction band [17]. Two band gap at the same material means two direct transition on the band gap [18]. This confirms synergetic result with crystallinity observation that material is arranged by crystalline nanocomposite. The narrow band gap is preferred in photodegradation because of lower energy need (visible responsive). Actually, anatase is best known for photocatalytic than rutile and brookite phase. However, the synergic effect of mixed phase composition enhances the charge separation that more facilitate increasing of oxidative molecule [9].

The morphology of TiO_2 on the glass substrate is compared with bare glass using digital microscope combined image-J software. Figure 4 shows original capture of surface without coating (a) and with TiO_2 coating, then interactive 3D surface plot from (b) glass tube and (c) coated glass-tube. TiO_2 is non-uniformly spreading on the glass tube surface, but mostly substrate surface is covered by catalyst. However, the oxidation is initiated on the surface of catalyst which intersects with dye molecule, not only in ahead of material but also in all of side. From the image is also known

that catalyst can adhere to the surface of glass tube perfectly.

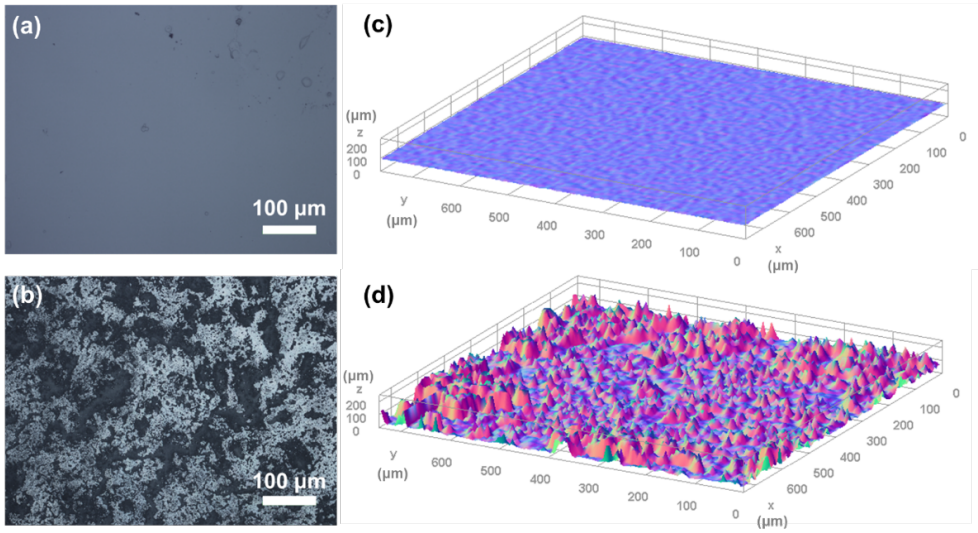

Figure 4. Morphology image using microscope of (a) bare glass and (b) TiO_2-coated glass, then interactive 3D surface plot using Image-J software of (c) bare glass and (d) TiO_2-coated glass (TiO_2 is indicated as purple-red peaks).

3.2 Photocatalytic efficiency test

The photodegradation study was investigated with comparing the reactor performance using catalyst and without catalyst. Figure 5(a) provides the decreasing of MB using TiO_2 that verifies only in 8 min irradiation the MB degradation until >98%, and then MB specific absorbance totally disappear under 20 min. The different activity was shown by reactor without TiO_2 (only UV lamp). Figure 5(b) shows that in 8 min irradiation is achieved around 82% of MB degradation which is similar with 4 min irradiation with catalyst. Without TiO_2, the MB degradation is still 98% in 20 min irradiation, not entirely degrading. Figure 6(b) exhibits the evaluation of decomposition rate between catalyst and without TiO_2. The presence of TiO_2 can improve the degradation rate almost 1.5 times quickly. Although MB can degrade by UV only, but the TiO_2 in the reactor provides much better photocatalytic performance.

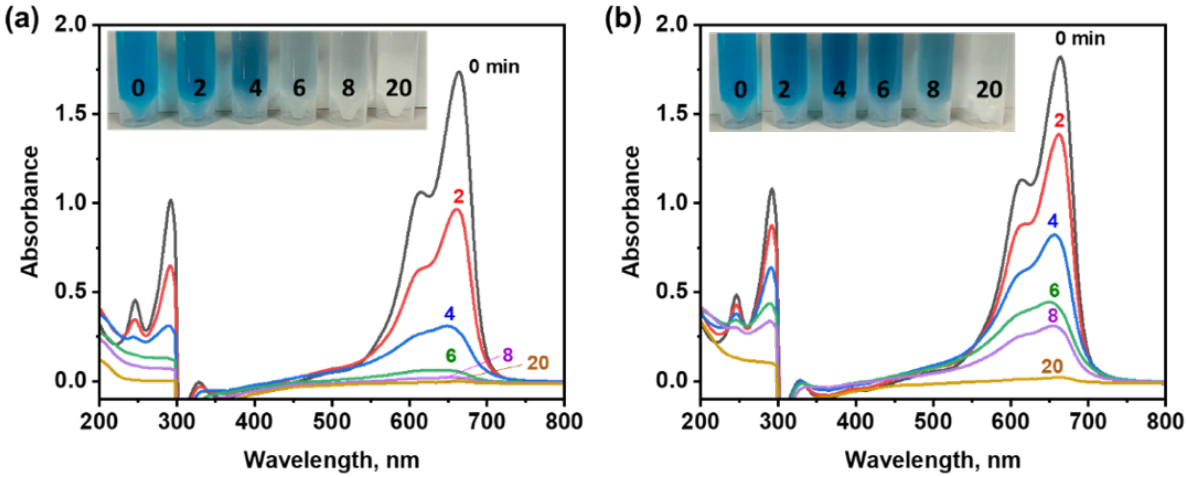

Figure 5. MB photo-decomposition activity in 20 minutes under UV irradiation of (a) with catalyst and (b) without catalyst calculated at wavelength of 662 nm.

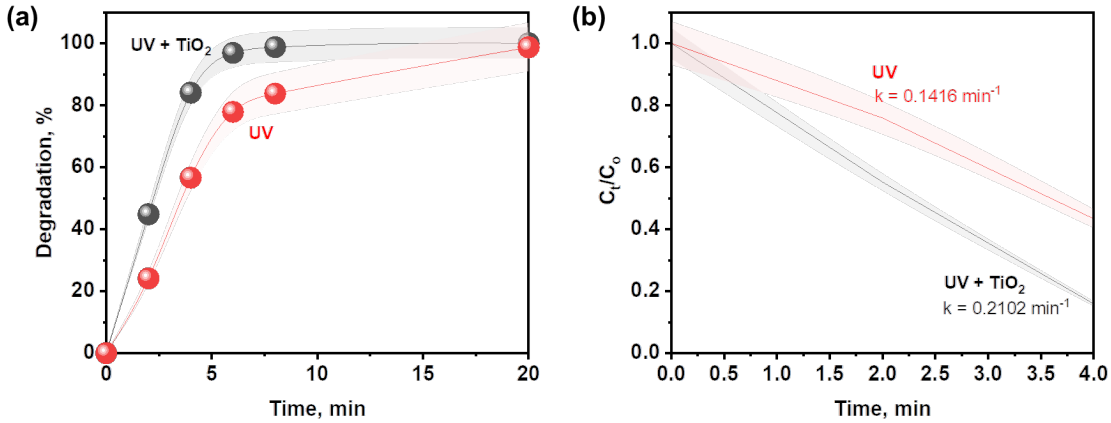

Figure 6. (a) Effect of catalyst using on MB decomposition efficiency compared with the catalyst absence and (b) decomposition rate between TiO_2 and UV only including degradation rate constant.

The effect of pH is shown in Figure 7 that display the degradation of MB in 8 min. At pH of 5 or slight acidic, degradation reach optimal performance. After increasing acidity level to pH of 2, the degradation percentage is slowly down. The degradation efficiency also extremely decreases with increasing pH level (higher alkalinity) because of hydroxy molecule. The result also similar with previous study from Dessie et al. (2017) and Pang et al. (2018) that the alkalinity inhibits the photodegradation activity of MB. The MB has positive charge that is preferred by OH so the structure can be stabilized. In acidic condition triggers a dissociation of methyl groups of MB due to the diethylamino group protonation [21].

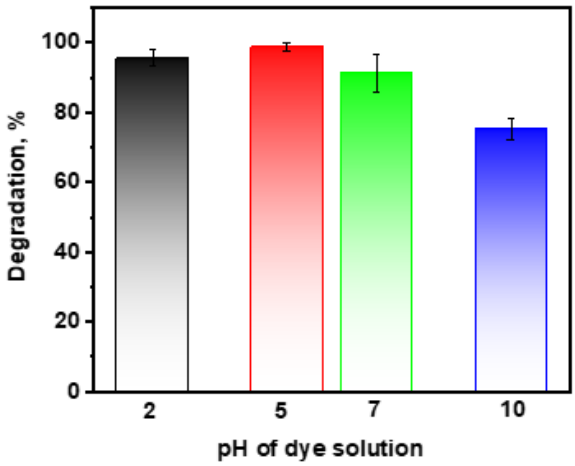

Figure 7. Performance of MB degradation on various pH of dye solution.

In addition, Figure 8 is illustrated the proposed mechanism of MB photodegradation in this study using designed reactor. The positive charge of thiol from MB interacts with negative charge from TiO_2 surface simplifying the oxidation process because of close distance. After turning on the UV lamp, electron is excited from valence band (VB) to conduction band (CB) generating hole (h^+) and electron (e^-). These molecules react with oxygen and water molecule in the solution to produce the radical molecules. Radical molecules will be oxidizing the MB resulting simple product decomposition and decolorization of MB from blue becoming clear solution.

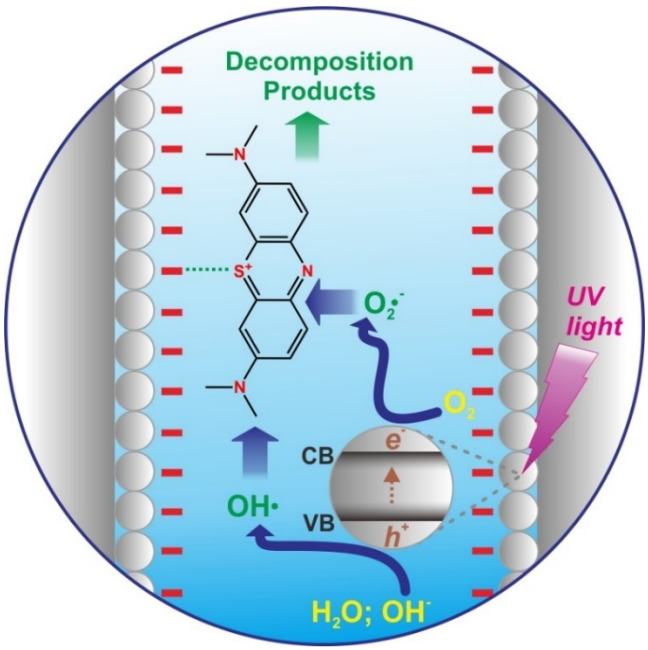

Figure 8. Proposed mechanism of MB decomposition using reactor in this study.

3.3 Theoretical comparison of reactor design

Photocatalytic processes have been widely developed with various reactor models, such as batch and continuous column reactors. A batch photocatalytic reactor is a type of reactor in which the reactants are added all at once, and the reaction continues until it is complete until the product decomposes into low molecular weight. Meanwhile, column reactors are generally carried out continuously where reactants are continually added to the reactor and products are flowed periodically. Both methods have advantages and disadvantages, but the batch reactor system is considered more straightforward and easier to operate on a large scale. The authors have studied using a TiO_2 catalyst in a batch system, but the material is coated on a glass reactor tube. Coating glass tubes with a catalyst such as TiO_2 shows a better advantage when compared to using a powder catalyst. This system offers high stability, effectiveness, and durability as a catalyst material. Furthermore, the TiO_2 coating on the glass provides good durability and resistance to catalyst reuse because the material is easy to separate and does not require special treatment for catalyst material purification.

Studies regarding the use of TiO_2 as a material photocatalyst for MB degradation have been extensively studied. Tseng et al. (2017) evaluated the batch reactor system using TiO_2 material for the degradation of MB [27]. They found that the maximum degradation efficiency under optimum conditions was around 56.9%. Another study reported by Ehrampoush et al. (2011), the authors reported the degradation of MB using tubular reactor with TiO_2/UV-C photocatalytic process [28]. At a concentration of 15 mg/L MB using a tubular reactor, the effectiveness of degradation can reach up to 98%, but the time required is quite long, namely 56 minutes. The surface area and the number of active sites the catalyst uses to adsorb pollutants play an essential role in the degradation rate. With a tubular flow reactor system, the interaction between the catalyst material and the impurity is lower, which causes the required degradation time to be longer. Compared with this study, the degradation rate at the same concentration of 10 mg/L resulted in greater efficiency. In this study, MB degradation efficiency reached 99% in a shorter time of around $\pm$ 8 min. The developed reactor system in this study offers many advantages, especially in photocatalyst activity. In this system, the surface area of the catalyst is more significant because the trigger is homogeneously dispersed on the glass surface. In addition, TiO_2-coated glass has a high surface area to volume ratio, so it is very effective for degrading organic compounds such as MB dye.

TABLE I. Various degradations of MB using TiO_2-based catalyst under UV irradiation.

Reactor model	Initial conc. of MB (mg/L)	Catalyst	Time (min)	Degradation (%)	Ref.
Batch	10	TiO_2	60	55.02	[22]
		TiO_2/RGO	60	91.48	
Batch	10	P25 Degussa	100	81.40	
		TiO_2-doped Cu	100	95.80	[14]
Batch	10	SiO_2-TiO_2	30	85	[23]
Flow	10	TiO_2	30	100	[1]
Batch	20	α-Al_2O_3-supported TiO_2	60	65	[24]
Batch	$3.14x10^{-5}$	MNP@SiO_2@TiO_2	30	95	[25]
Batch	20	TiO_2-coated membrane	480	97.2	[26]
Flow-Batch	10	Glass-coated TiO_2 NPs	20	100	This work

4. CONCLUSION

A highly effective photodegradation of MB was provided the designed reactor in this study. TiO_2 nanostructure was successfully achieved through blend method of manual grinding and hydrothermal technique using commercial powder. Anatase-rutile crystal was deposited well on glass tube surface by dip-coating with crystal size at nano scale. Because of crystal phase composite, the synthesized material has Eg range of 2.66 until 3.20 eV. Then, degradation of MB was confirmed in quick term which needs below 20 min to decompose 100% with constant rate of 0.2102 min^{-1}. This reactor is potentially applied for larger needed for environmental remediation.

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