PAPER • OPEN ACCESS

TiO$_2$ Photocatalytic Degradation of Methylene Blue Using Simple Spray Method

To cite this article: F D Utami *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **599** 012026

View the article online for updates and enhancements.

TiO$_2$ Photocatalytic Degradation of Methylene Blue Using Simple Spray Method

F D Utami[1], D Y Rahman[1], D O Margareta[1], H D Rahmayanti[1], R Munir[1], E Sustini[1] and M Abdullah[1]

[1]Department of Physics, Faculty of Mathematical and Natural Sciences,
Bandung Institute of Technology, Jalan Ganeca 10 Bandung 40132, Indonesia

* Email: din@fi.itb.ac.id; fisca.dian.utami1@gmail.com

Abstract. The present work focused on the effects of TiO$_2$ in degrading organic wastewater. Technical TiO$_2$ of anatase crystalline phase was used. TiO$_2$ photocatalyst showed a powerful result in destroying organic effluent. Spray coating was conducted to immobilize the TiO$_2$ particles onto the plastic buffer followed with heat-treatment process. As a result, 30 mL of 25 mg L^{-1} methylene blue (MB) used in the photocatalyst test was sucessfully degraded after 4 hours of irradiation. Repetitive use of the TiO$_2$ films still has a great photodecomposition ability of removing 99% of the organic contaminant after 5 times use.

Keywords: Photocatalytic degradation, TiO$_2$, Spray method.

1. Introduction

Nowadays, the disposal of dyeing process in textile industries contributes to the primary causes of water contamination in the environment. Various kinds of chemicals and dyes are utilized in the textile industry. From the entire dyeing process, it is estimated that about 15 – 20 % dye is released into the environment [1,2]. Dyes are not facilely degraded due to their complex chemical structure and aromatic rings. The presence of textile dyes in water reduces light penetration, aesthetic appearance, may led water to be unsafe for drinking and may caused cancer disease due to its high toxicity. It prompts many scientists to focus on organic dye waste management. The commonly used method in the treatment of organic dye waste is employing a combination of biological oxidation and physico-chemical treatment [3]. This conventional method still leaves some obstacles, such as incomplete waste degradation, the formation of secondary products after waste treatment, and high cost. Because of these obstacles, many scientists consider photocatalyst to be a very potent method to degrade organic contaminants. The term "Photocatalyst" refers to the process that occurs in semiconductor materials when irradiated with light in a certain wavelength range inducing chemical reactions that can destroy the chain of organic contaminant compounds. It produces electron-hole, then reacts with the contaminant compounds [3,4].

Many semiconductor materials are commonly used for photocatalyst applications, such as water treatment, air purification, anti-bacterial, etc. Those semiconductors include TiO$_2$, ZnO, V$_2$O$_5$, Fe$_2$O$_3$, CdS, ZnS, ZrO$_2$ and WO$_3$ [5,6]. Among these, TiO$_2$ catalyst is mostly preferred for photocatalyst applications due to interesting properties, such as chemical stability, no secondary product, high reduction-oxidation activity, and low price [6,7]. Besides, TiO$_2$ also has thermal stability and remains stable after a repetitive catalytic process [6].

There are two types of reactors commonly used in photocatalyst-based waste treatment processes, namely slurry reactors (catalysts directly mixed in pollutant) and immobilization reactors (catalysts immobilized on transparent support surface). Slurry reactors have the advantage of a high contact area with the catalyst, but this photoreactor has several drawbacks, such as the possibility of agglomeration when using high concentration catalysts, the reduction of degradation rate due to scattered light, and high-cost of post-treatment in separating TiO_2 particles after photocatalytic process [8]. Current attention has been focused on immobilizing TiO_2 on transparent substrates to solve such obstacles. When using the immobilized reactor, we can provide reusable catalyst, reduce operating costs due to the absence of post-treatment, and minimize the occurrence of scattered light [8].

The immobilization technique can be carried out on the reactor wall, a buffer material or on the wall of the UV source. Esparza et al. and Stathatos et al. explain the superiority of TiO_2 immobilization, including the expansion of the contact surface between catalysts and pollutants, high adsorption properties and increasing the number of hydroxyl groups on the surface or reducing the risk of recombination of electron-hole pairs [9,10]. Several techniques for immobilizing TiO_2 in various buffers have been reported, including TiO_2 immobilized on a hydrogenation method [11], on Cellulose by dip coating method [12], on NTCs using the sol-gel method [13], on Al_2O_3 ceramic paper by direct spraying method [14], on silica by RF-Magnetron sputtering [15], on Borosilicate glass by spray coating [16], on Zeolite by Photodeposition and Lyophilization [17], on photoanode by heat attachment method [18], on chemically treated metal buffer by sol-gel electrospinning [19], on Polypropylene by thermal milling method [20], on Polyethylene Terephthalate by spray coating method [21-23], and so on.

Mostly, the present methods as mentioned above tend to be complicated and costly. In current work, we propose a simple spray method of immobilizing TiO_2 onto plastic to improve degradation rate. Attaching TiO_2 powder on the surface of plastic with an easier method becomes a high challenge and give distinct advantages of this study.

2. Experimental

2.1. Procedures

Methylene blue (MB) powder from Sakura (Indonesia), a cationic thiazine dye, was directly used as a pollutant model. TiO_2 technical powder of anatase crystalline structure was employed as a catalyst. As mentioned above, we focused on an easy, inexpensive, high degradation rate, and potentially applied method for large-scale application. Here, the solid buffer material used was transparent plastic (local suppliers; Indonesia).

Before the spraying process begins, the transparent substrate was cleaned using 95% ethanol from Sakura (Indonesia). TiO_2 dispersion was achieved by stirring the 5 gr of TiO_2 powder and 100 mL of deionized water at the room temperature. The cleaned transparent plastic was placed on the hot plate then coated by spraying the TiO_2 dispersion solution onto it. The spraying process was conducted using a laboratory spray gun. This spray apparatus has been illustrated in Figure 1.

During the spraying, heat treatment was conducted. The hot plate temperature was set on 27 $^\circ$C and 100 $^\circ$C. Each of these samples was labeled with sample 1 and 2, respectively. Sample 1 was dried in room condition (no heat treatment) while sample 2 was put into the electric oven then kept at the temperature of 100 $^\circ$C for 1 hour. All samples were rinsed in distilled water.

In addition, to determine the effect of spray number to the degradation rate, we varied the spray number during the spraying process, including 10, 20, and 30 times of spraying. The substrates were placed on the hot plate at the temperature of 100 $^\circ$C. All samples were placed in the electric oven then held at 100 $^\circ$C for 1 hour, with the same treatment as the sample 2. Samples 1 and 2 were then formed into cylinders and placed on a different photo-reactor. The height of the cylinder is about 5 cm and the diameter is 2 cm.

We performed a photocatalytic test with 30 mL solution with 25 mg L^{-1} MB. It is placed outside the catalyst cylinders in each photoreactor. The photocatalytic tests were investigated under solar exposure. It was performed during 5 hours.

Figure 1. Spray process apparatus set up.

To study the performance of the catalysts, different treatments were applied to each reactor (Table 1). Here, we used 4 labeled reactors: A, B, C and D. Reactor A contained sample 1 which was placed in a dark condition without irradiation. Reactor B contained the pollutant without the use of catalyst. Reactor C contained sample 1 and reactor D contained sample 2. Reactor B, C and D were investigated under solar exposure. The catalyst cylinders were put into the tubular reactor with diameter of 8 cm. The number of catalyst cylinder used were 4 cylinders for each reactor. In addition, to investigate the influence of spray number in catalyst performance toward the degradation rate, three different reactors were employed, each containing the sprayed catalyst of 10 times, 20 times and 30 times. The treatment was the same as in reactor D.

Table 1. The different treatment of each reactor

| Name	Treatment			
	Presence of Catalyst	Irradiation	Hot plate temperature (°C)	Annealing temperature (°C)
Reactor A	√	-	100	100
Reactor B	-	√	-	-
Reactor C	√	√	27	27
Reactor D	√	√	100	100

2.2. Analysis
An ocean optic USB2000 spectrometer was employed to measure the UV-Vis absorbance. The shifting and decreasing of MB absorbance peak (UV-Vis) can be used to determine the photoactivity of catalyst in MB degradation. Based on the Beer-Lambert theory related with the light absorption, the MB concentration can be measured since it shows a direct proportion to the MB absorbance. When the monochromatic spectrum surpasses a solution containing a larger number of molecules, the absorbance value also increases; it indicates a higher concentration in substance. The thicker the medium transversed by the beam, the greater the attenuation of the light intensity [24].

3. Result and Discussion
As previously described, the degradation of Methylene blue concentration which is used as the contaminant was determined by UV-Vis absorbance [25]. The maximum peak of UV-Vis absorbance is clearly described in Figure 2 ranging 663-664 nm. We used the wavelength shifting of maximum peak

to analyze the degradation of contaminants [26,27]. Figure 3 shows a decrease in contaminant concentration after irradiation. The UV-Vis absorbance measurement of MB solution was performed every hour for 5 hours. Line A shows a decrease in MB concentration due to presence TiO_2 but without irradiation (in the dark condition). This decrease is very small compared to other treatments. The degradation process is not a photocatalytic process since there is no source of TiO_2 activating photons. Instead, it is the adsorption of MB particles by TiO_2 surface [28]. This process shows a decrease in Methylene blue concentration due to its adsorption by TiO2 surface without any irradiation effects of the photon source. The corresponding degradation level C/C_0 curve tends to decrease linearly with time. The same result was also reported by Lao et al. [28].
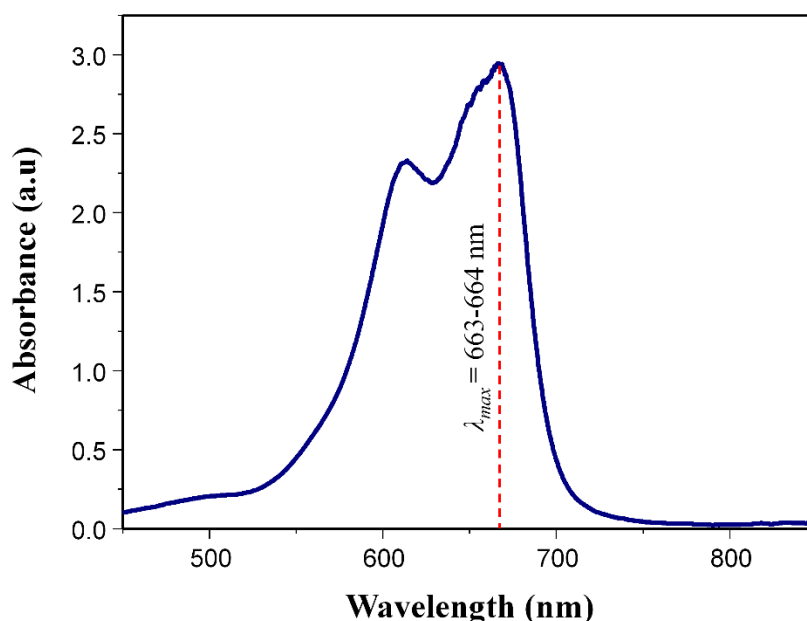
Figure 2. UV-Visible absorbance spectrum of Methylene blue.

Line B represents a decrease in methylene blue concentration due to sun exposure. This process is also not a photocatalytic process since no catalyst (TiO_2) is used. This mechanism is due to the transfer of energy from the solar photons to the catalyst. These photons excite the electrons in the molecules. This process can break the chemical chains of the organic contaminant, in this case methylene blue. This mechanism is called photolysis. It takes longer than the photocatalytic process [29]. Line B also shows a linear decrease in concentration due to the sunlight irradiation without the presence of the catalyst.

Line C and D show reduction in MB concentration due to the photocatalytic process of TiO_2 catalysts. It is activated when illuminated by a source of photons (sunlight) whose energy is higher than its bandgap; it then encourages an electron to travel from VB (valence band) to CB (conduction band) leaving a hole in VB [3,6-10]. It was found that both curves followed the pseudo-first-order decay kinetics toward the time after irradiation (Figure 3).
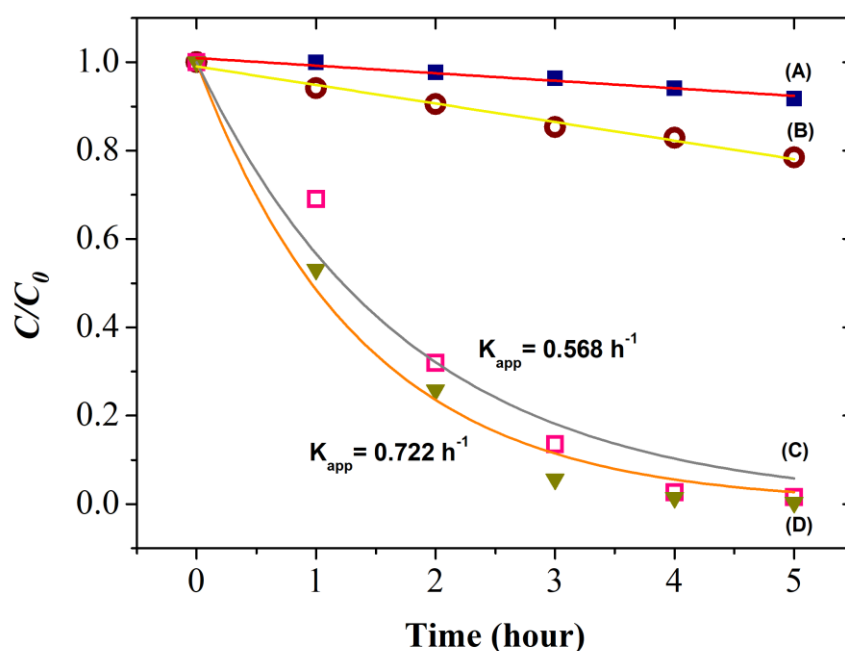
Figure 3. The degradation level of MB after treatment by (A) TiO_2 without irradiation; (B) irradiation without catalyst used; (C) TiO_2-coated plastic using spraying method without heat treatment; and (D) TiO_2-coated plastic using spraying method combined with heat treatment.

The rate of photocatalytic degradation strongly depends on the light radiation and the characteristics of the surface of the photocatalyst. The common model is the kinetic scheme of Langmuir-Hinshelwood or LH model [6]. Here the reaction rate K is directly proportional to the surface fraction covered by the catalyst. The adsorption level is determined by the value of the adsorption equilibrium constant, K, while C indicates the concentration of organic compounds at time t. Thus the first-order reaction rate constants are obtained by the equation

$$\frac{C}{C_0} = e^{-K_{app}t} \tag{1}$$

we can determine the reaction rate constants of the photocatalyst by fitting the data using the equation above [6]. It represents a photocatalyst scheme generating a curved characteristic.

There is a difference in reaction rate between lines C and D. The degradation rate of the line C is obtained at 0.568 h^{-1} while the line D is 0.722 h^{-1}. The highest reaction rate is indicated by line D at which TiO_2 was used as catalyst and coated by combined spraying and heat treatment method. It explains why the heating process when the TiO_2 nucleation took place on a plastic substrate influences the TiO_2 coating's strength to the substrate. The strength of the coating increases with the increase of adhesion strength between TiO_2 and the substrate. This is also confirmed by the washing process after the coating process: the released TiO_2 particles are less than the TiO_2 coating process without heating process (conducted at room temperature). It can be stated that the use of the heat treatment-based spraying method produces more coated TiO_2 particles. More TiO_2 particles on the substrate surface allow greater probability that TiO_2 will come into direct contact with organic contaminants, so that the degradation rate of MB is faster.

Once we see that the catalyst can work effectively, the influence of spray number on the photocatalyst performance was also investigated. The used catalyst was TiO_2-coated plastic using spraying method combined with heat treatment. From figure 4, The degradation rate of blue curve (the sprayed catalyst of 10 times) is obtained at 0.537 h^{-1}, the yellow curve (the sprayed catalyst of 20 times) is 0.723 h^{-1} while the pink curve (the sprayed catalyst of 30 times) is 0.486 h^{-1}. The reactor using the sprayed catalyst of 20 times exhibits the highest photocatalytic activity compared to the other. After 4 hours of sun exposure, 99% of the contaminants were successfully destroyed. The use of catalysts that sprayed 30 times resulted in lower photodegraded performance. When we observe the use of a sprayed catalyst of 10 times compared to the sprayed catalyst of 20 times, the reaction rate of the photocatalyst obviously increases. The increase was caused by the greater probability of catalyst surface contacted directly with the pollutant. More TiO_2 particles were attached on the substrate surface.
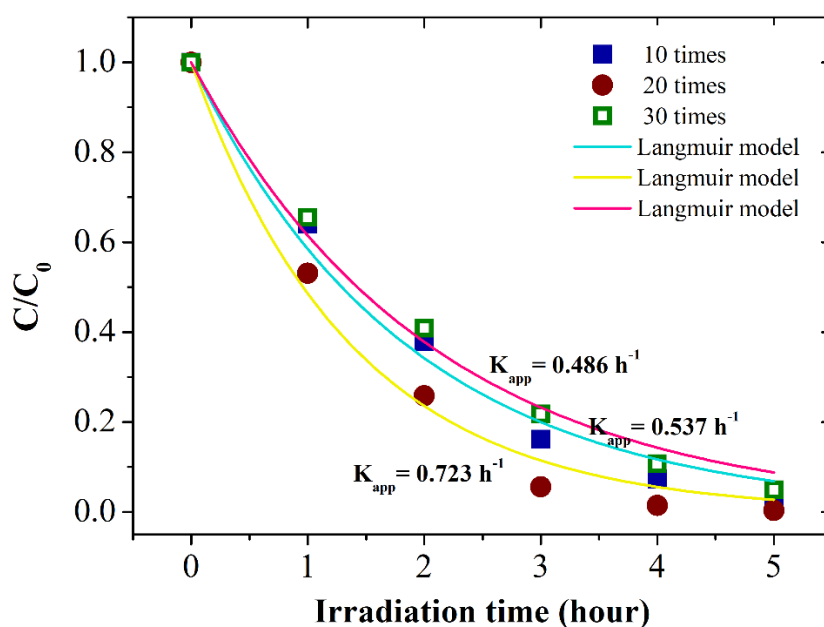
Figure 4. The effect of spray number in catalyst performance toward kinetic rate of photocatalyst activity, blue curve represents the sprayed catalyst of 10 times, yellow curve represents the sprayed catalyst of 20 times, and pink curve represents the sprayed catalyst of 30 times.

The semiconductor was activated by the photons and produced electrons and holes. The electrons will bind to oxygen generating superoxide radicals while the holes will bond to OH in water to form hydroxyl radicals. These radical agents will break the chain of contaminants and promote mineralization in H_2O and CO_2 [3]. The two main parts are playing the role here, i.e. the photon energy and the amount of catalyst present on the surface substrate. Both are the essential parts that play a prominent role in the photocatalytic process and can be applied to the treatment of organic contaminants [30,31]. The higher the light intensity of the photon source, the more surface of TiO_2 generating electron-hole pairs that can be in direct contact with the pollutant so that the organic pollutant degradation process will be faster. These explained why the photo-activation reached the optimum condition with the use of sprayed catalyst of 20 times and returned down when using the sprayed catalyst of 30 times. The coming light can't penetrate effectively when using the sprayed catalyst of more than 20 times, in this case the sprayed catalyst of 30 times, which makes the electron-hole recombined.
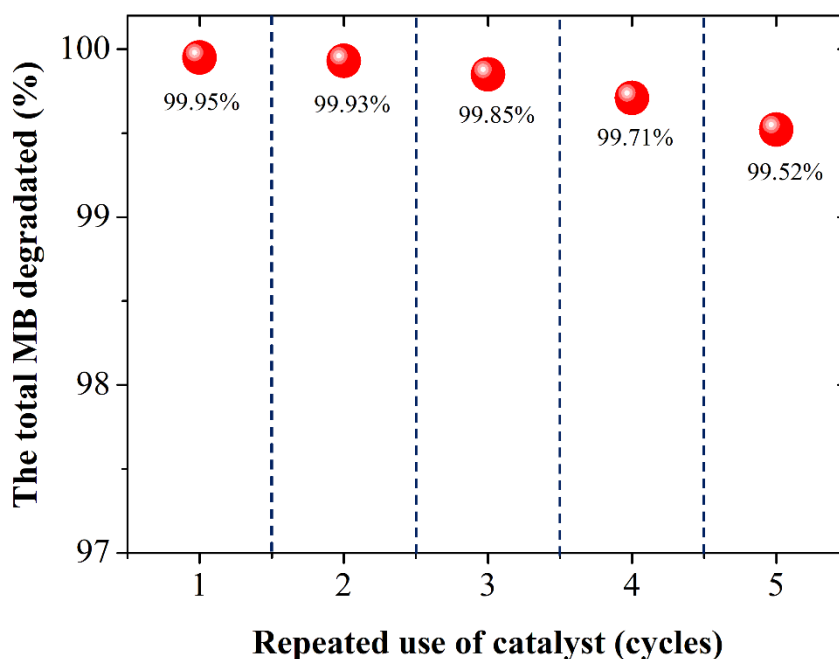
Figure 5. The repetitive usable of catalyst for MB degradation process.

One of the interesting properties of TiO_2 is its stable characteristic after repeated use. In this study, catalyst performance was investigated through repeated use of TiO_2 films. The film was repeatedly used for 5 times sequentially. Each cycle of repetition is carried out for 5 hours of irradiation. After the photocatalytic test, it was found that the film still has a great ability of decomposition by degrading 99% of the MB concentration. Only about 0.5% was reduced from the first use.

4. Conclusion

We have successfully coated TiO_2 on transparent plastic substrate using simple spray method. The excellent performance of the catalyst was achieved with TiO_2 coated plastic made by a combined spraying and heat treatment process. The method produced more coated TiO_2 particles. It allows greater probability that TiO_2 will come into direct contact with organic contaminants, so that the degradation rate of MB is faster. Since this method is adequate easy and affordable price, it is worthy to be promoted as a forthcoming photocatalyst technology.

5. References

[1] Zhu H Y, Xiao L, Jiang R, Zeng G M, and Liu L 2011 *Chemical engineering journal* **172**(2-3) 746-753
[2] Clarke C E, Kielar F, Talbot H M, Jouhnson K L 2010 *Environ. Sci. Technol.* **44** 1116–1122
[3] Fujishima A, Rao T N and Tryk D A 2000 *J. Photochem. Photobiol. C: Photochem. Rev.***1** 1-21
[4] Ameta R, Solanki M S, Benjamin S, and Ameta S C 2018 Photocatalysis. In Advanced oxidation processes for waste water treatment (pp. 135-175). Academic Press
[5] Tayade R J, Natarajan T S, and Bajaj H C 2009 *Ind. Eng. Chem. Res.* **48** 10262-10267
[6] Chong M N, Jin B, Chow C W K, and Saint C 2010 *Water Res.* **44** 2997-3027
[7] Atout H, Álvarez M G, Chebli D, Bouguettoucha A, Tichit D, Llorca J, and Medina F 2017 *Mater. Res. Bull.* **95** 578-587
[8] Vaiano V, Sacco O, Pisano D, Sannino D, and Ciambelli P 2015 *Chem. Eng. Sci.* **137** 152-160
[9] Esparza P, Borges, M E, Diaz L, Alvarez-Galvan M C, and Fierro J L G 2010 *Appl. Catal. A* **388** 7–14

[10]   Stathatos E, Papoulis D, Aggelopoulos C A, Panagiotaras D, and Nikolopoulou A 2012 *J. Hazard. Mater.* **211** 68–76

[11]   Wang W, Ni Y, Lu C, and Xu Z 2014 *Appl. Surface Sci.* **290** 125–130

[12]   Ortelli S, Blosi M, Albonetti S, Vaccari A, Dondi M, and Costa A L 2013 *J. Photoch. Photobio. A* **276** 58– 64

[13]   Dong Y, Tang D, and Li C 2014 *Appl. Surf. Sci.* **296** 1-7

[14]   Vereb G, Ambrus Z, Pap Z, Mogyorosi K, Dombi A, and Hernadi K 2014 *React. Kinet. Mech. Catal.* **113** 293-303

[15]   Barrocas B, Serio S, Rovisco A, Nunes Y, and Jorge M E M 2016 *Appl. Surf. Sci.* **360** 798-806

[16]   Yadini A El, Saufi H, Dunlop P S M, Byrne J A, Azzouzi M El, and Hajjaji S El 2014 *J. Catal.* **2014** 1-8

[17]   Jansson I, Yoshiiri K, Hori H, García-García F J, Rojas S, Sanchez B, Ohtani B, Suarez S 2016 *Appl. Catal. A Gen.* **521** 208-219

[18]   Lee S L, Ho L N, Ong S A, Wong Y S, Voon C H, Khalik W F, Yusoff N A, and Nordin N 2017 *Chemosphere* **166** 118-125

[19]   Ray S, and Lalman J A 2016 *Mater. Today Proc.* **3** 1582-1591

[20]   Aliah H, Aji M P, Masturi, Sustini E, Budiman M, and Abdullah M 2012 *Am. J. Environ. Sci.* **8** 280-290

[21]   Utami F D, Rahman D Y, Sustini E, and Abdullah M 2019 *J Phys. Conf. Ser.* **1171**(1) 012030

[22]   Utami F D, Rahman D Y, Sutisna, Kamirul, Margaretta D O, and Abdullah M 2019 *J Phys. Conf. Ser.* **1204**(2019) 012086

[23]   Margaretta D O, Permadi K W, Rahman D Y, Utami F D, Viridi S, and Abdullah M 2019 *J Phys. Conf. Ser.* **1204**(2019) 012051

[24]   Aarthi T, Narahari P, and Madras G 2007 *Journal of Hazardous Materials* **149** 725-734

[25]   Tseng K H, Chung M Y, and Chang C Y 2017 *Nanomaterials* **7** 133

[26]   Slimen H, Houas A and Nogier J P 2011 *J. Photochem. Photobiol. A Chem.* **221** 13-21

[27]   Wang F, Min S, Han Y, and Feng L 2010 *Superlattices Microstruct.* **48**(2) 170-180

[28]   Thao L, Dang T, Khanitchaidecha W, Channei D, and Nakaruk A 2017 *Materials* **10**(2) 122

[29]   Wong C C, and Chu W 2003 *Chemosphere* **50**(8) 981-987

[30]   Rajeswari R and Kanmani S 2009 *Iran J. Environ. Health. Sci. Eng.* **6** 61-66

[31]   Zangeneh H, Zinatizadeh A A L, Habibi M, Akia M and Isa M H 2015 *J. Ind. Eng. Chem.* **26** 1-36