



Research Article

# Preparation of $\text{TiO}_2\text{-SiO}_2$ using Rice Husk Ash as Silica Source and The Kinetics Study as Photocatalyst in Methyl Violet Decolorization

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## Abstract

Preparation, characterization and utilization of  $\text{TiO}_2\text{-SiO}_2$  as photocatalyst for methyl violet (MV) decolorization has been conducted. In this research, preparation of  $\text{TiO}_2\text{-SiO}_2$  was developed based on natural renewable silica source; rice husk ash (RHA) via a sol-gel technique. The composite was formed by the dispersing of titanium isopropoxide as titania precursor into the gel of silica followed by aging, drying and calcination. The  $\text{TiO}_2\text{-SiO}_2$  sample was characterized by powder X-ray diffraction (XRD), diffuse reflectance-UV Visible spectrophotometric analysis (DRUV-Vis), gas sorption analyzer and Scanning electron micrograph (SEM) before its utilization as photocatalyst in methyl violet photooxidation. As comparison to the physicochemical character study, the synthesis of  $\text{TiO}_2\text{-SiO}_2$  by using tetraethyl ortosilicate (TEOS) was performed as a confirmation. Result showed that prepared  $\text{TiO}_2\text{-SiO}_2$  has the character similar to  $\text{TiO}_2\text{-SiO}_2$  as synthesized by TEOS precursor. The formation of crystalline titania in anatase and rutile phase was identified with increasing surface porosity data and the value of band gap energy which sufficiently contribute to a photocatalytic mechanism. The character data are in line with the kinetic data of methyl violet decolorization. From the compared photooxidation, photolysis, photocatalysis and adsorption process, it can be concluded that  $\text{TiO}_2\text{-SiO}_2$  acts efficiently as a photocatalyst. © 2015 BCREC UNDIP. All rights reserved.

**Keywords:** photocatalysis;  $\text{TiO}_2\text{-SiO}_2$ ; photodegradation; methyl violet

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## 1. Introduction

Photocatalysis becomes important process in environmental technology as well as renewable energy researches. In these applications, some metals such as cerium dioxide (ceria), titanium dioxide or titania ( $\text{TiO}_2$ ), aurum, zinc oxide photocatalyst and those combination are reported [1-4]. Titania is commonly used because it has a high band gap energy, chemically sta-

ble, harmless to the human body, and the process is easy [5, 6]. For environmental application, the photoactivity of  $\text{TiO}_2$  can be applied in a photocatalytic degradation of organic compounds as well as photoreduction of some metal ions through a photon interaction combined with the adsorption mechanism in the process. In other side, photocatalytic activity is closely related to the formation of particles in the nanometer scale that allows the interaction of photons and the adsorption of the target compounds in the oxidation mechanism.

Key role of the photocatalytic activity is re-

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lated with the surface area and the band gap energy. Therefore, various strategies have been made to expand the surface area of the TiO<sub>2</sub>, such as mesoporous molecular sieve arrangement of TiO<sub>2</sub>. One strategy in order to improve the quantum size effect of TiO<sub>2</sub> photoactivity is attaching TiO<sub>2</sub> nanoparticles into a porous support to form a stable composite [3, 4]. Among some composites, titania-silica composite is an important combination since silica source is very abundant. Some investigations reported that the combination between titania and silica in a composite gives a synergistic activity in photocatalysis mechanism.

Considering that silica can be obtained from rice husk ash (RHA), the synthesis of TiO<sub>2</sub>-SiO<sub>2</sub> by RHA is interesting topic. The isolation of silica from RHA has been reported by some previous investigation [9-11]. The possibility to attach titania with silica framework by using sol-gel mechanism can be utilized to create nanosized TiO<sub>2</sub>-SiO<sub>2</sub>. Based on these background, the purpose of this research is to study the physicochemical character of TiO<sub>2</sub>-SiO<sub>2</sub> based on RHA and its comparison with the preparation TiO<sub>2</sub>-SiO<sub>2</sub> by previous reported method. Study focused on physicochemical characterization and the photocatalytic activity study in dye photodegradation reaction. For photocatalytic study, photodegradation of methyl violet was chosen for a reaction model.

## 2. Materials and Methods

### 2.1. Materials

Rice husk ash was obtained by firing rice husk (RHA) at 700 °C for 4 h. Some chemicals consist of titanium isopropoxide, ammonium hydroxide, isopropanol, hydrogen peroxide, and methyl violet were purchased from Merck-Millipore.

### 2.2. Method

The preparation of TiO<sub>2</sub>-SiO<sub>2</sub> was performed by diluting 3 g of RHA into 2 M of NaOH and followed by ageing for 24 h. The solution was filtered and the filtrate was titrated with hydrochloric acid of 1 M until the pH of 8.0 was obtained. The clear solution was aged for 48 h to form gel. Into the gel, titanium isopropoxide solution was dispersed at the theoretical Ti:Si mass ratio equal to 4:9 and then was added with 20 ml of NH<sub>4</sub>OH 0.1 M. The mixture was stirred for 1 h until a homogeneous sol was produced. The procedure of solvent evaporation and drying were then conducted before calcining the powder at 500 °C for 4 h. The solid

product was characterized by X-ray Diffraction, BET surface area analyzer, SEM-EDX and DRUV-Visible spectrophotometry. A XRD instrument Shimadzu X600 was utilized with Ni-filtered Cu-K $\alpha$  radiation at the range of 2-65° and step size of 4 °/min. For surface analysis and DRUV-Vis spectral analysis, a NOVA 1200e instrument and JASCO 670 instrument were used respectively while for surface morphology the analysis was performed by using SEM-EDX Seiko instrument.

Photocatalytic activity testing of as prepared TiO<sub>2</sub>-SiO<sub>2</sub> was evaluated in the photodegradation of methyl violet (MV). The evaluation consist of the comparison between dye concentration reduction over photooxidation, photocatalysis, photolysis and adsorption mechanism as well as the monitoring on the kinetics of dye photooxidation. A batch reactor with UVA and UVB lamp at around 20 cm above the reactor was used for simulation. A photooxidation treatment was the treatment with the addition of TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst and H<sub>2</sub>O<sub>2</sub> as oxidant into MV solution and under UV lamp illumination. Photocatalysis treatment was similar process with photooxidation but without H<sub>2</sub>O<sub>2</sub> while photolysis treatment was the process of UV illumination only into the MV solution without the presence of photocatalyst. As control process, adsorption was the treatment of photocatalyst addition in dark condition with neither H<sub>2</sub>O<sub>2</sub> addition nor UV light exposure.

## 3. Result and Discussion

The diffraction patterns of TiO<sub>2</sub>-SiO<sub>2</sub> and RHA are depicted in Figure 1. From the reflection refinement, amorphous silica is exist in RHA as shown by the reflection at around 22.5° while after the composite formation, TiO<sub>2</sub>-SiO<sub>2</sub>, the crystalline form was obtained [11, 12]. From the specific reflection, it is concluded that both anatase and rutile phase of TiO<sub>2</sub> are produced in the synthesis. Reflections at 2 $\theta$  of 25.0, 37.3, 47.7, 53.8, 54.5, 62.4, and 68.7 are assigned to the presence of the 101, 004, 200, 105, 211, 2014, 106, 220, 215, 312, and 224 (JCPDS No.21-1272). Another reflections at 2 $\theta$  of 26.9, 35.9, 38.0, 43.3, and 55.8 are correspond to the reflections of 110, 101, 200, 111, and 301 (JCPDS No.21-1276) [13].

Furthermore, study on the relationship between TiO<sub>2</sub> crystal formations to the photoactivity was studied by evaluating the potency of material to catch the photon energy. The character related to DRUV-Vis spectrophotometry analysis. In order to compare the ability of prepared material, the spectrum of TiO<sub>2</sub>-SiO<sub>2</sub> in

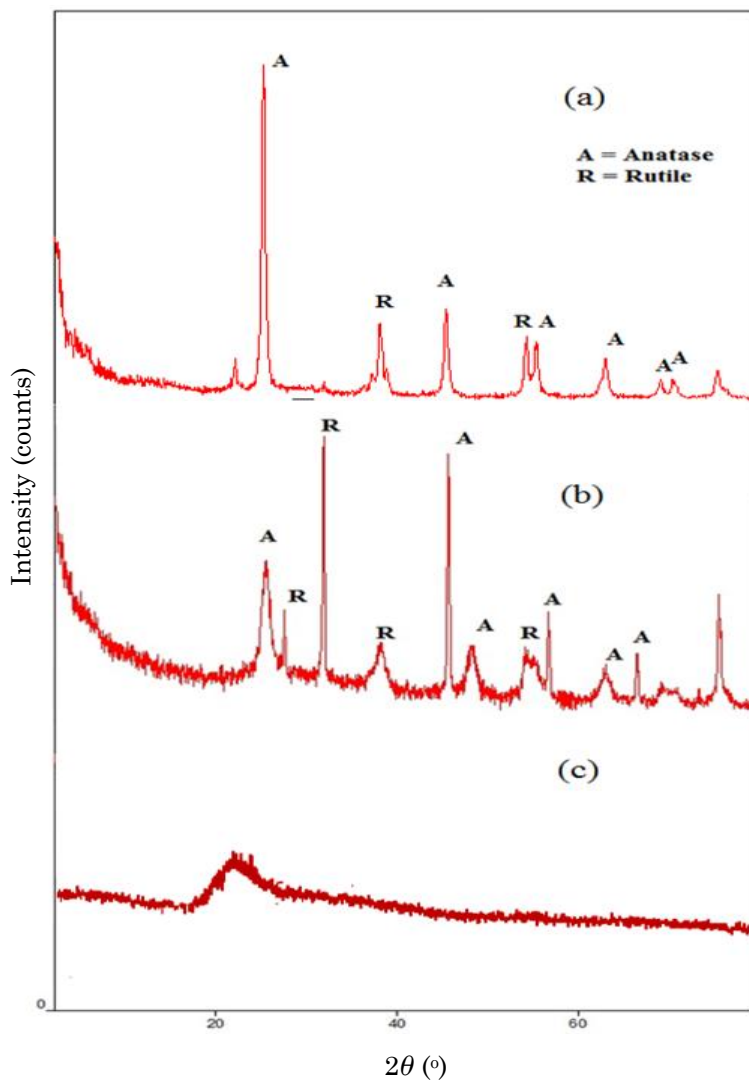


Figure 1. XRD pattern of (a) TiO<sub>2</sub>-SiO<sub>2</sub> (TEOS), (b) TiO<sub>2</sub>-SiO<sub>2</sub> (RHA), and (c) RHA

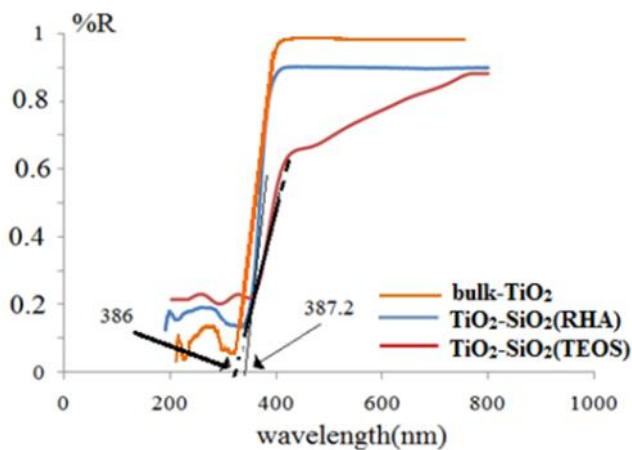


Figure 2. Diffuse reflection absorption of bulk-TiO<sub>2</sub> and prepared TiO<sub>2</sub>-SiO<sub>2</sub>

Table 1. Band gap energy of bulk TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub>

Sample	Edge wavelength / $\lambda_{edge}$ (nm)	Band Gap Energy (eV)
TiO <sub>2</sub> -SiO <sub>2</sub> (TEOS)	389.4	3.18
TiO <sub>2</sub> -SiO <sub>2</sub>	396.6	3.12

Table 2. Surface parameter of RHA and TiO<sub>2</sub>-SiO<sub>2</sub>

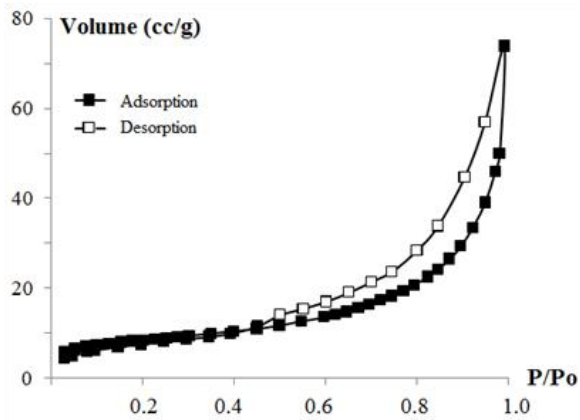
Sample	Specific Surface Area (m <sup>2</sup> /g)	Pore Volume (cc/g)
RHA	25.09	11.60
TiO <sub>2</sub> -SiO <sub>2</sub> (RHA)	91.91	15.18
TiO <sub>2</sub> -SiO <sub>2</sub> (TEOS)	59.22	14.92

comparison with the spectrum of bulk-TiO<sub>2</sub> is presented in Figure 2. From the spectra, it can be seen that the TiO<sub>2</sub>-SiO<sub>2</sub> material exhibits a little bit higher edge wavelength compared to bulk-TiO<sub>2</sub>, while the value of edge wavelength ( $\lambda_{edge}$ ) is related to the band gap energy ( $E_g$ ) by following Equation (1).

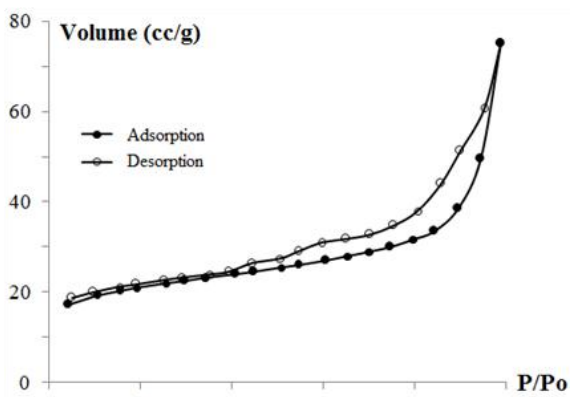
$$E_g = \frac{1240}{\lambda_{edge}} \quad (1)$$

From the obtained data, it is concluded that the prepared TiO<sub>2</sub>-SiO<sub>2</sub> has lower band gap energy than TiO<sub>2</sub>. The lower value is probably related to the titania phase contained within the material while the different phase of titania gives different value of band gap energy. The presence of rutile phase in TiO<sub>2</sub>-SiO<sub>2</sub> contributes to decrease the simultaneous band gap energy value of the composite form.

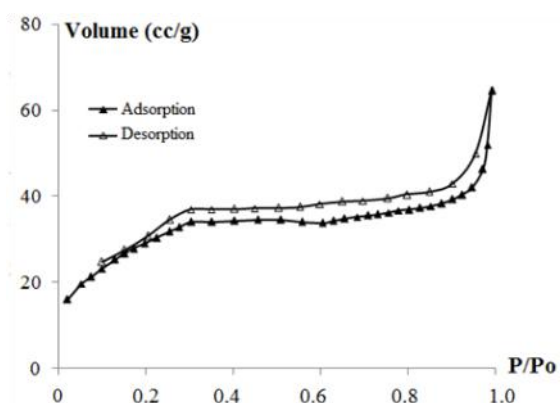
One of the aims of the formation of TiO<sub>2</sub>-SiO<sub>2</sub> composite as photocatalyst is to enhance



(a)

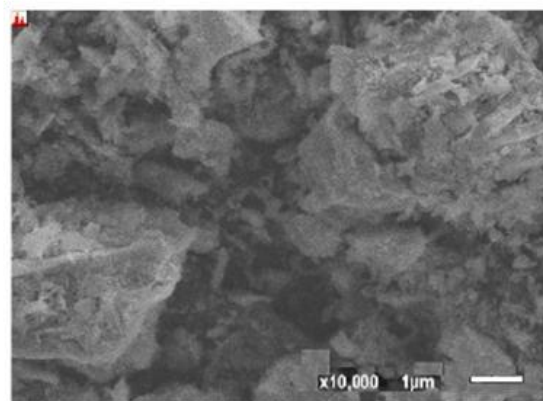


(b)

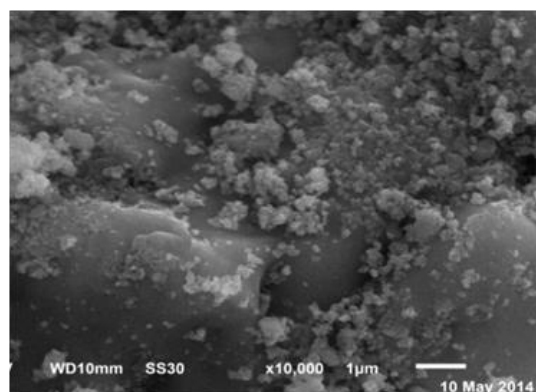


(c)

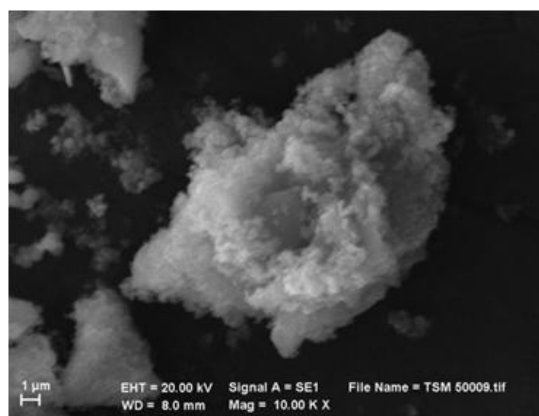
**Figure 3.** Adsorption-desorption profile of of (a) RHA, (b) TiO<sub>2</sub>-SiO<sub>2</sub>(RHA), (c) TiO<sub>2</sub>-SiO<sub>2</sub> (TEOS)



(a)



(b)



(c)

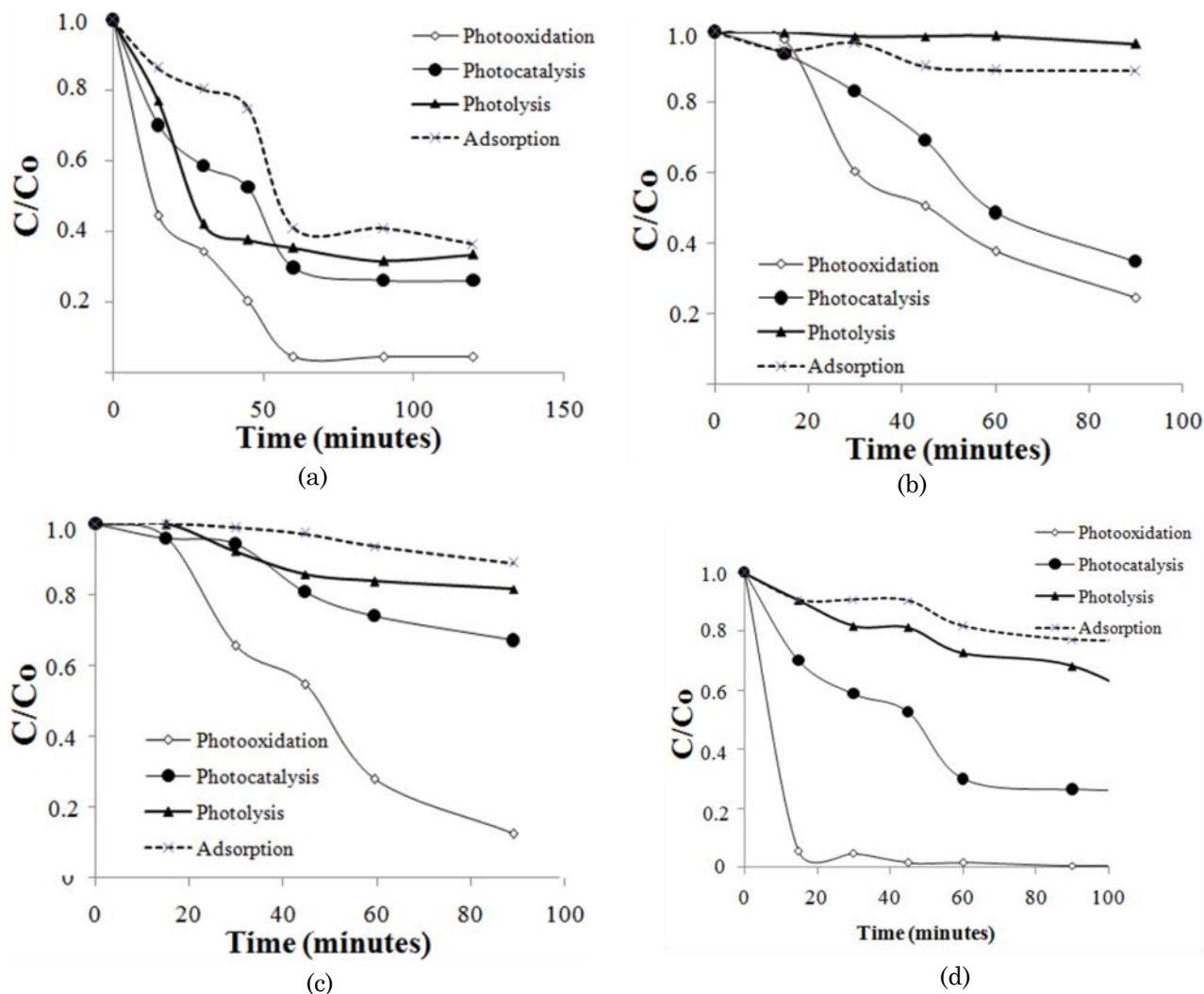
**Figure 4.** SEM photograph of (a) RHA, (b) TiO<sub>2</sub>-SiO<sub>2</sub> (RHA), (c) TiO<sub>2</sub>-SiO<sub>2</sub> (TEOS)

the photocatalysis mechanism through the formation of higher specific surface area. The N<sub>2</sub> adsorption-desorption profile presented in Figure 3 and the parameters of specific surface area, pore volume and pore radius of the prepared material is listed in Table 2.

Adsorption-desorption profiles of RHA and TS-RHA are consistence to the type IV adsorption isotherm with H3 hysteresis loop while TS-TEOS is fit to H4 refer to IUPAC classification. The type IV is associated with the presence of framework structure of mesopore and H3 hysteresis loop is identified for slit shaped mesopore [10, 14]. From Table 2, the formation of TiO<sub>2</sub>-SiO<sub>2</sub> has higher specific area and pore volume compared to RHA. It would provide more surface sites for adsorption of reactant molecules and enhance photocatalytic activity [7]. This is due to the formation of titania particles on the surface of SiO<sub>2</sub>.

The new porous structures was formed during sol-gel mechanism of the composite provides larger surface area that can be filled out by N<sub>2</sub> gas. It is shown in SEM photograph (Figure 4).

Kinetic study of MV decolorization over prepared TiO<sub>2</sub>-SiO<sub>2</sub> was performed by conducting photooxidation, photocatalysis, photolysis and adsorption treatment to the MV solution. The photooxidation treatment means the decolorization by adding prepared TiO<sub>2</sub>-SiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> as oxidant under UV light illumination while the photocatalysis treatment is the same process with photooxidation but without the addition of H<sub>2</sub>O<sub>2</sub>. Another process as control; photolysis is MV treatment with only the addition of H<sub>2</sub>O<sub>2</sub> under UV illumination and adsorption process that is the decolorization by the addition of TiO<sub>2</sub>-SiO<sub>2</sub> in dark condition. The different processes was applied to the MV solution, it was aimed to evaluate the effectiveness



**Figure 5.** Kinetics of MV removal: (a) over TiO<sub>2</sub>-SiO<sub>2</sub> (RHA) at [MV]<sub>0</sub> = 0.5 ppm, (b) over TiO<sub>2</sub>-SiO<sub>2</sub> (RHA) at [MV]<sub>0</sub> = 1.0 ppm, (c) over TiO<sub>2</sub>-SiO<sub>2</sub> (TEOS) at [MV]<sub>0</sub> = 0.5 ppm, (d) over TiO<sub>2</sub>-SiO<sub>2</sub> (RHA) at [MV]<sub>0</sub> = 1.0 ppm

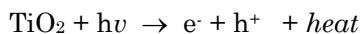


of prepared TiO<sub>2</sub>-SiO<sub>2</sub> as photocatalyst in the mechanism.

From the kinetic data presented in Figure 5, it can be concluded that all process cause decreasing MV concentration along increasing time of the treatment. Photooxidation process demonstrates the fastest MV decolorization while the photolysis process gives the slowest and both adsorption and photocatalysis lay in between both rates. MV concentration was significantly reduced after the treatment for 40 minutes and then it getting constant at increasing time while until 20 minutes the concentration was still higher compared to both photolysis and photocatalysis. Eventually, both adsorption and photocatalysis show similar reaction rate. This phenomenon comes from the indication of the contribution of oxidation mechanism in photooxidation that was more effective after initializing process.

The presence of H<sub>2</sub>O<sub>2</sub> as oxidant was included in the formation of hydroxyl radicals in the whole oxidation process of organic compound. Furthermore, from the kinetics profile of adsorption, photocatalysis, and photooxidation, it can be summarized that both adsorption and oxidation seem increase the degradation rate by simultaneous and synergistic effect. Adsorption mechanism is also involved within photocatalysis process but the degradation rate from adsorption process is not significantly different with the photocatalysis. It means that photon energy is not sufficient to preserve hydroxyl radicals to oxidize MV in the solution.

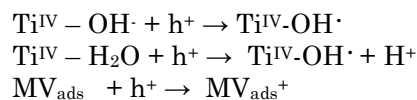
Refer to previous researches [15, 16], the generation of hydroxy radicals and its relationship with photoactivity can be figured by following reaction mechanism:



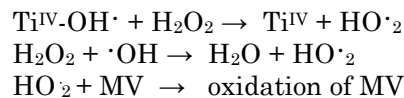
**Table 3.** Kinetics order simulation of MV photooxidation TiO<sub>2</sub>-SiO<sub>2</sub> (RHA)

[MV] o/ppm	1st order simulation	2nd order simulation	3rd order simulation
1	R <sup>2</sup> =0.9180 k= 0.0464	R <sup>2</sup> =0.6553	R <sup>2</sup> =0.5378
2	R <sup>2</sup> =0.99570 k= 0.0238	R <sup>2</sup> =0.9657	R <sup>2</sup> =0.8949
5	R <sup>2</sup> =0.9832 k= 0.0246	R <sup>2</sup> =0.9344	R <sup>2</sup> =0.8282
8	R <sup>2</sup> =0.8547 k= 0.0160	R <sup>2</sup> =0.8412	R <sup>2</sup> =0.8298

The generated holes in TiO<sub>2</sub> structure are utilized for the generation of hydroxyl radicals and direct oxidation of MV or they can be combined with the electron from a donor species:



The presence of H<sub>2</sub>O<sub>2</sub> in the system can stimulate the formation of more radicals:



Furthermore, kinetics of the MV photooxidation was evaluated for varied MV concentration. Data simulation is depicted in Figure 6. From the data presented in Figure 5, the kinetics order and kinetics constant of the data can be resumed and the data are listed in Table 3.

All kinetics data in Table 3 represent that photooxidation of MV obey first order reaction, which indicate that initial concentration of MV affects strongly to the kinetics mechanism. Langmuir-Hinshelwood simulation of the kinetics data gives no sufficient determination constant (R<sup>2</sup>= 0.7568) (Figure 3) indicate that the MV degradation is not only depend on the MV concentration. Refer to kinetics data in Figure 4, it can be concluded that H<sub>2</sub>O<sub>2</sub> as oxidant was also affect to the reaction rate. This is similar with that was reported in previous investigation [17, 18]. Due to the net neutral charge of MV and its simple chemical structure, some conditions such as pH, catalyst dosage and the presence of oxidant in the system were strongly affect the kinetic of degradation. In general by this experiment it can be found

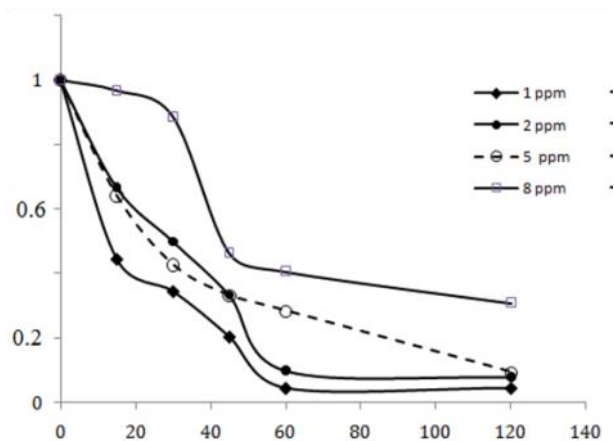


Figure 6. Kinetics simulation of MV photooxidation over TiO<sub>2</sub>-SiO<sub>2</sub> (RHA)

that TiO<sub>2</sub>-SiO<sub>2</sub> effectively catalyzes the MV degradation via photooxidation mechanism. The presence of both anatase and rutile in the composite form demonstrate the photoactivity.

#### 4. Conclusion

TiO<sub>2</sub>-SiO<sub>2</sub> was successfully prepared by sol-gel mechanism based on rice husk ash as silica source. Titania in anatase and rutile phases are presence in the prepared composite and they play role in MV photodegradation. By kinetic simulation it can be concluded that the fastest MV degradation was obtained by photooxidation mechanism.

#### Acknowledgment

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