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PHOTOCATALYTIC DEGRADATION OF VIOLET-RR WITH SOLAR IRRADIATION USING TIO$_2$ CATALYST

Safni[1*], Fatma Yuka Desri[1], Zulhadjri[2], Khoiriah[1], Reza Audina Putri[1]
Universitas Andalas
fatmadesri@yahoo.com

Abstract.

Violet-RR ($C_{34}H_{14}Cl_2O_2$) is one of the most common classes of Vat dyes used in the textile industry. These dyes are stable, toxic and can inhibit solar-light penetration into the waters system. In this study, Vat Violet-RR dye was degraded by using TiO_2 as a catalyst under UV and solar-light irradiation. Some parameters i.e., irradiation time, catalyst mass and energy sources were studied. The reduction of dye concentration was measured by UV-Vis spectrophotometer at a wavelength 554 nm. The optimal catalyst mass obtained was 9 mg. Degradation percentage of Vat Violet-RR dyes obtained by photolysis without catalyst under UV and solar-light irradiation were 4.09% and 13.51%, respectively. The presence of TiO_2 catalyst increased the degradation percentage to be 35.15% and 81.15% for 300 minutes irradiation. Based on the results, solar-light irradiation gives better results on Vat Violet-RR degradation than UV-light.

Keywords: Degradation; Photolysis; Vat; Violet-RR; TiO_2

1. INTRODUCTION

Violet-RR (**Figure 1**) is a synthetic dye in the Vat group that is widely used in the textile industry, especially in West Sumatra. This dye has an organic characteristic structure with a stable heterocyclic aromatic ring. Its continuous use will cause its concentration increase in the environment. This dye is categorized as a dangerous and poisonous compound and the color of this substance can inhibit the penetration of sunlight into the water. This will have a negative impact on the photosynthesis of water population like microorganisms [1] . So we need an effective method to reduce the concentration of Violet-RR dye in the waters.

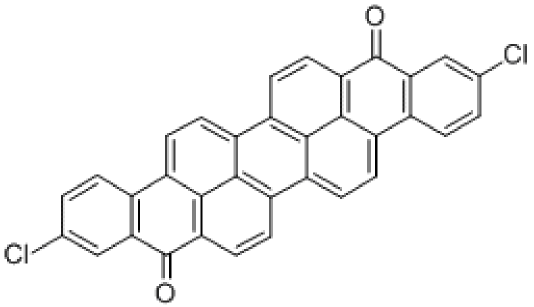

Figure 1. Structure of Violet-RR

One of potential method for degradation of dyes is photocatalysis, which generates and uses highly reactive hydroxyl radical (•OH) species to oxidize organic pollutants into environmentally friendly compounds. Photocatalysis has been reported to be effective in the degradation of dyes [2-4] and pesticides [5,6] . This method combines the roles of a semiconductor catalyst and light as a source of photons. The catalyst electrons will be excited from the valence band to the conduction band in the presence of a photon energy equal or greater than the catalyst bandgap

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energy. This process produces *holes* and reactive species (OH radicals) which act as strong oxidizing agents to oxidize the target compounds. The end products expected from this method are simpler and more environmentally friendly compounds such as CO_2 and H_2O [5] .

Titanium Dioxide (TiO_2) is the most commonly used semiconductor catalyst in the photocatalytic process with several advantages. It is semiconductor, non-toxic, inexpensive, and has high stability [7,8] with a large band gap of 3.2 eV and active in UV light. Band gap means the difference energy between conduction bond (CB) and valence bond (VB) [xx]. TiO_2 can use in UV light an also with sunlinght because there is UV in sunlight. There are so many research has reporte using this TiO2 as catalyst ie : rhoamin B [xxx], orange G, amido black, eosin Y, safranine O [xxxx] and no reports using TiO_2 catalyst on the degradation of Vat Violet-RR dye. Therefore, this study carried out the degradation of the Vat Violet-RR dye by photolytic Degradation using a TiO_2 catalyst by studying several parameters, namely; the effect of the initial concentration of the dye, the effect of the mass of the catalyst, the effect of the type of light source and the effect of the irradiation time.

2. EXPERIMENTAL METHODS

2.1 Materials and Equipments

The materials used in this research were Violet-RR ($C_{34}H_{14}Cl_2O_2$; Fig.1), TiO_2 (Ishawara), distilled water and acetonitrile (*HPLC Grade, Merck*). The equipment includes UV lamps (Sankyo Denki Black light blue lamp 10 W, λ = 245 nm), radiation black box, analytical balance (Kern & Sohn GmbH), centrifuge (Nasco, 2000-8000 rpm), oven and *furnace* and other beaker equipment.

Quantitative analysis of the dye solution before and after the degradation process was carried out using spectrophotometer UV-Vis (Shimadzu-02587, Japan), while for qualitative analysis the High Performance Liquid Chromatography apparatus was used with the HPLC column used was an ODS-Hypersyl (Thermo Scientific) measuring 150 mm ×4.6 mm x 5 µm. The detector used will be a visible light lamp with a wavelength of 554 nm.

2.2 Experiment

2.2.1 Preparation of the solution Violet-RR dye and determining the optimum concentration of the Violet-RR dye

Violet-RR dyes with concentrations of 10, 20, 30, 40 and 50 mg/L were prepared by diluting the main solution 100 mg/L using distilled water. The solution was measured using spectrophotometer UV-Vis at the wavelength of 400-800 nm.

1.2.2 determination of initial concentration of Violet-RR

The dye with variation of concentrations (10, 20, 30 40 and 50 mg/L) was degraded under UV lamp for 120 minutes to determine the optimum initial concentration of the dye. The concentration of dyes before and after degradation is measured by spectrophotometer UV-Vis .

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2.2.3 Effect of catalyst mass on the degradation of the Violet-RR dye

The 30 mg/L dye solution with a volume of 20 mL was put into the petridish and added catalyst (3, 6, 9, 12, and 15 mg). The suspension solution was irradiated with UV light for 120 minutes. The degradation solution was centrifuged at a speed of 3000 rpm to separate the catalyst. The dye concentration that changed was detected using spectrophotometer UV-Vis at a wavelength of 554 nm .

2.2.4 Effect of time and light source on the degradation of the Violet-RR dye

30 mg / L dye solution was added to the petridish. The solution was added with the optimal mass of catalyst and then exposed to UV light for (60, 120, 180, 240 and 300) minutes. The TiO_2 catalyst was separated by centrifuge at 3000 rpm for 30 minutes. Changes in the dye concentration were detected using spectrophotometer UV-Vis at a wavelength of 554 nm. The degradation of the dye without a catalyst by photocatalytic and adsorption was also carried out as a control. The Violet-RR dye was also degraded under sunlight to see the effect of the light source on the photolysis process. The experiment was carried out under direct sunlight at 10.30 - 15.30 in bright sunny conditions without clouds with an intensity (9000 *lux*) of temperature (27 ° C to 33 ° C). The intensity is measured by a luxmeter application on a smartphone .

2.2.5 Analysis of the degraded violet-RR dye

The most degraded violet-RR dye solution was also analyzed using HPLC to determine whether new compounds were formed in the degradation process. **.** The analysis was carried out with the stationary phase using silica and the mobile phase was a mixture of distilled water and acetonitrile at a ratio of 75/25, v / v, a flow rate of 0.6 mL / minute with a Photo Diode Array (PDA) detector , and the volume of dye injection equal to 20 µL .

3. RESULTS AND DISCUSSION

3.1 Absorbance of Violet-RR solution using spectrophotometer UV-Vis

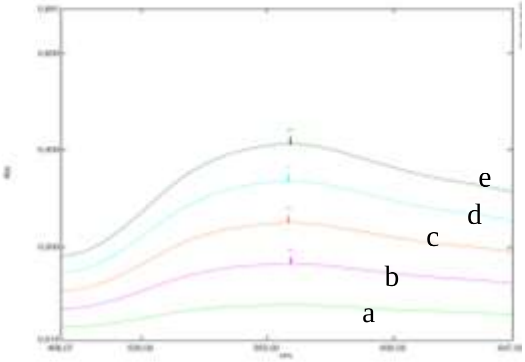

Fig 2. Absorbance of Violet-RR dye with various concentration (10 – 50 mg/L) using spectrofotometer UV-Vis

The absorbance of Violet-RR dye solution with concentrations : 10, 20, 30, 40 and 50 mg/L were measured by a spectrophotometer at wavelength of 800-400 nm. The maximum wavelength of violet-RR is at 554 nm as shown in **Figure 2**. These results also show that the absorbance of the dye increases with increasing concentration of the dye. The linearity between the dye concentration and the absorbance resulted in a coefficient

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of determination almost to 1 (0.9961) with a regression equation y = 0.0103x - 0.0902 (**Figure 3**).

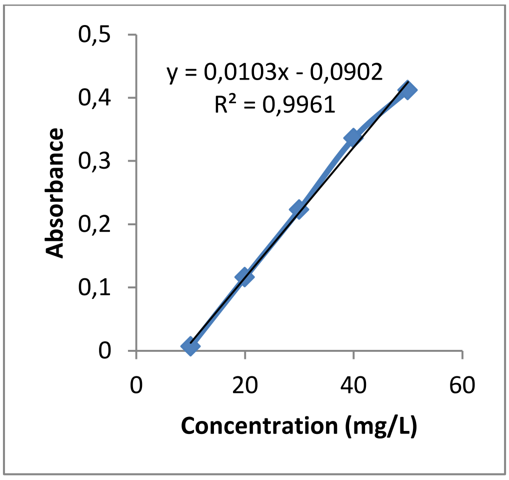

Figure 3. Calibration curves of Violet-RR with concentration 10-50 mg/L

3.2 Effect of Initial Concentration Violet-RR dye

One of the important factors affecting the degradation process is the initial concentration of organic pollutants [12] . In determining the effect of concentration in the degradation of this dye solutions of 10, 20, 30, 40 and 50 mg/L of the Violet-RR dye were irradiated under UV light 254 nm. The percentage of degradation shown below in **Figure 4**.

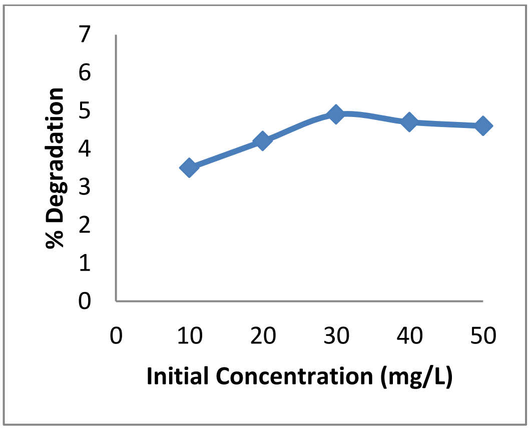

Figure 4. Effect of the initial concentration of the dye to photolytic degradation using UV light for 120 minutes

The results showed that the amount of violet-RR dye degraded increased from 3.2% to 4.9% at concentrations of 10 mg/L to 30 mg/L. The optimal concentration found was 30 m/L. However, there was a decrease in the degradation of the dye with a concentration of 40 - 50 mg/L. This is due to the high number of dye molecules in the system, blocking the light from reaching the solution. In addition, a constant level of UV light is not proportional to the number of violet-RR molecules to be degraded so that the photolysis ability of UV light to degrade is ineffective [13] . Therefore, the initial 30 mg/L solution of the dye was chosen as the initial concentration for further experiments.

3.3 The effect of the amount of catalyst

The effect of the amount of TiO_2 catalyst was carried out by adding the catalyst mass of 3, 6, 9, 12, 15 mg to a 30 mg / L violet-RR solution and irradiated with a UV lamp

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for 120 minutes. Figure 5 shows that the percentage of degradation increases with increasing the number of catalysts because the active side of the catalyst as a source of hydroxyl radicals increases. The optimum amount of catalyst was obtained in the addition of 9 mg with a degradation percentage of 28.09% and there was a decrease after added 12 and 15 mg of catalyst.

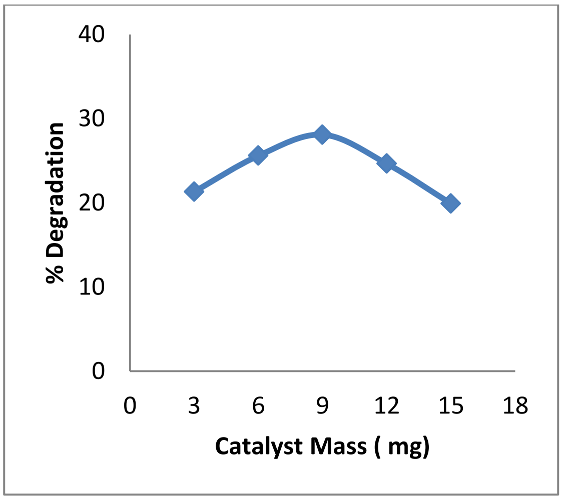

Figure 5. Effect of catalyst mass (3,6,9, 12 and 15 mg) to Violet-RR degradation by photolysis for 120 minutes

The decrease in the percentage of degradation occurs because the catalyst given in the large quantities will make the solution saturated and high turbidity so that the amount of kight reaching the dye solution is redused. This of course will affect the process of electron excitation due to the minimal number of photons from the light, as a result of which less hydroxyl radicals are formed and the efficiency of degradation decreases .

The effect of the presence of catalyst on the degradation of dyes by photolysis was carried out under UV light. The comparison of the results of the degradation without and with the addition of 9 mg of catalyst can be seen in Figure 6. Dyes degraded by 4.05% - 8.56% without a catalyst ann increased to 16.97 – 40.36 with addition of 9 mg TiO_2.

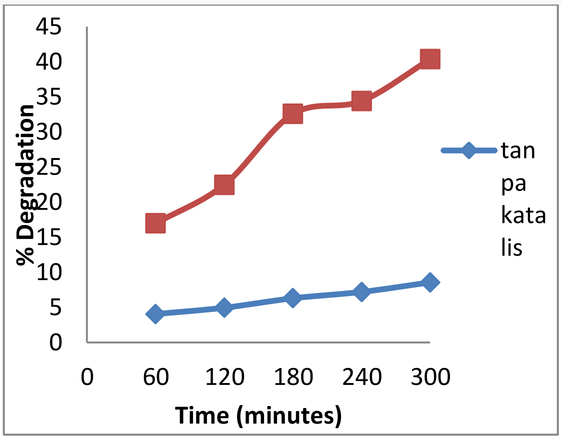

Figure 6. Effect of catalyst mass to degradation of Violet-RR with Photolysis using UV light 120 minutes

The dye is degraded directly by UV light in the photolysis system without a catalyst and in this system, the dye degrades without the contribution of hydroxyl radicals, while the presence of a TiO_2 catalyst in the photolysis system increases the percentage of degradation significantly. When a semiconductor catalyst such as TiO_2 is irradiated with a photon energy equal to or greater than it's band gap energy, electrons from the titania will be excited from the valence to conduction band. This process will produce *holes* *(h^+)* in the valence band and electrons in the conduction band. *The hole* will react with water and form

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hydroxyl radicals $(^{\cdot}OH)$ [5]. Both $^{\cdot}OH$ radicals and *holes* play a role in oxidizing violet-RR dye so that its efficiency is higher than UV photolysis.

3.4 Effect of light source to the degradation of violet-RR by photolysis

The degradation of Violet-RR by photolysis with and without a catalyst was carried out under two types of light sources (UV and solar) to investigate the effect of the energy source on degradation. The largest percentage of degradation was in sunlight with of 33.89% without and 90.67% with the addition of a catalyst during 300 minutes of photolysis as shown in **Figure 7**. Similar results were also reported by several researchers in photolytic degradation of dyes using catalysts TiO_2 [13] , Ag @ TiO_2 [14] .

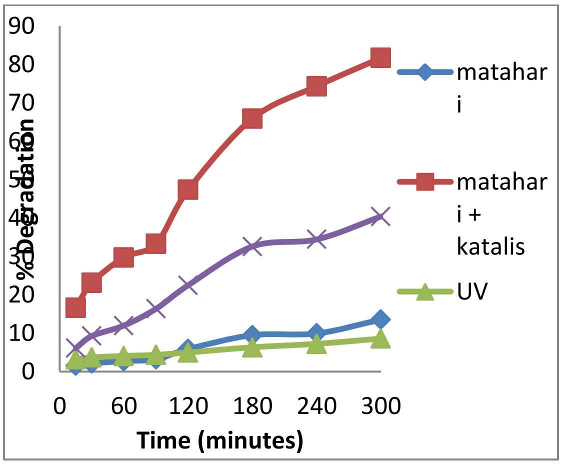

Figure 7. Effect of light sources to degradation of Violet-RR by photolysis 300 minutes

Figure 7 also shows the effect of time on degradation. The amount of Violet-RR dye that was degraded increased with increasing irradiation time in both the photolysis system without a catalyst or with a catalyst. The percentage of degradation without a catalyst is 3.15% - 8.56% and 1.47% - 13.51% to 6.07% - 40.36% and 16.07% - 81.68% with catalyst under UV light and sunlight for 15 - 300 minutes of irridiation. The length of time radiation will increase the interaction of the catalyst and the dye molecule and will slow down the possibility of the recombination process of electrons to the valence band, as a result of which the resulting hydroxyl radical increases and the Violet-RR dye is degraded more than before [5 , 10] . The same result was also obtained by Ahmed in degrading the dye methyleneblue and indigocarmine [15] .

3.5 Analysis by High Performance Liquid Chromatography (HPLC)

The HPLC chromatogram of the Violet-RR dye solution before degradation is shown in **Figure 8a**. Violet-RR appeared at a retention time of 1.34 minutes with an area of 37076 and decreased in peak area to 1614 after being degraded by photolysis under sunlight using TiO_2 catalyst for 300 minutes as shown in **Figure 8b**. A decrease in the area of the chromatogram peak indicates that Violet-RR dye has degraded.

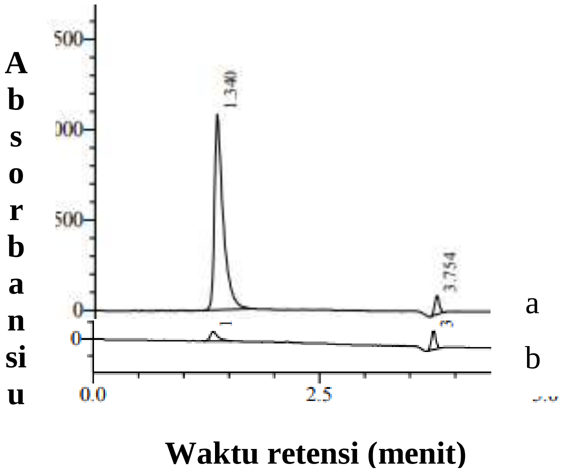

Figure 8. HPLC Chromatogram of Violet-RR (a) before and (b) after degraded by photocatalytic with sunlight using 9 mg TiO2 catalyst for 300 minutes

4. CONCLUSION

The violet-RR dye was successfully degraded by photolysis both under UV light and sunlight. The degradation of Violet-RR was significantly affected by the mass of the catalyst, the energy source and the irradiation time. The violet-RR solution with an initial concentration of 30 mg / L was degraded by 8.56% and 13.51% respectively under UV light and sunlight for 300 minutes. Under the same conditions, the degradation efficiency significantly increased to 40.36% and 81.86% with the addition of 9 mg TiO_2 catalyst .

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