

Degradation of Paraquat in Gramoxone Pesticide with Addition of ZnO

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ABSTRACT

Paraquat is the most toxic herbicide, the main agricultural crops and plantations that use them are cloves, cocoa, oil palm, rubber, coffee, and pepper. Therefore, it is necessary to study to degrade paraquat compounds by photolysis method with using ZnO. Photolysis is a process of UV irradiation with a wavelength of 200-400 nm. In this study Photolysis method used UV light with $\lambda = 365$ nm. Degradation of paraquat compound was done with the influence of variation of time without the addition ZnO, the influence of ZnO additional variations, and the effect of combination between variations of time and optimization of ZnO addition. The result of the study shows that photolysis degradation product without the addition of ZnO for 120 minutes has been degraded by 12.56%. While the optimum addition of 0.1 grams ZnO increased the percentage of degradation which is about 57.64%. This is proved that the addition of ZnO with photolysis method can degrade more paraquat compounds.

Keywords : degradation, herbicides, paraquat, photolysis, ZnO

INTRODUCTION

In Indonesia, paraquat has been marketed under the brand name Gramoxone by Syngenta Corporate and by different manufacturers sold under different names as well (Dyson, Js. 2002). Paraquat is the most toxic herbicide, the third most widely used herbicide in the world, almost more than 120 countries and used for more than 50 plants. The main crops and plantations that use them are cloves, cocoa, oil palm, rubber, coffee, and pepper. Paraquat chemical name based on IUPAC is 1,1-dimethyl-4,4-bipyridinium dichloride. It is a green liquid with a boiling point 175 – 180 °C and is easily soluble in water. Paraquat is relatively stable at normal temperature, pressure, and pH, allowing the paraquat to stay longer in the soil.

Therefore, an appropriate handling of the pollutant processing of the herbicide is required. Advanced Oxidation Process (AOP) shows a very interesting development compared to conventional processing that is often inadequate to treat high concentrations of pollutants or toxic pollutants (Toor, A. P, A. Verma, C. K. Jotshi, P. K. Bajpai, 2006). Degradation of pollutant compounds can be done in various ways, among others through the process: Steam Methane Reforming (SMR), thermochemistry, electrolysis, and photolysis. The SMR process requires an expensive cost. The thermochemical process of

high temperature heating can be used from nuclear sources for the process of separating pollutants. Afterwards, the electrolysis process is one of the basic methods passing an electric current on water then it will decompose the toxic compounds pollutants. The electrolysis technology used nowadays requires an enormous amount of electricity. This shows that the energy consumed for the electrolysis process compared to the chemical energy produced is not economically balanced. One simple way that can be used for the degradation of these pollutant compounds is through photochemical processes using photocatalysis methods.

Photocatalysis is one of the processes of degradation of substances assisted by the presence of light. When the photocatalyst material is exposed to light, it absorbs the photon energy which causes various chemical reactions. This chemical reaction can degrade toxic compounds. The advantages of this photocatalytic technology are that the process can take place at room temperature so that its energy needs are much lower. Also, photocatalytic requires only very few chemicals and is relatively cheaper.

Metal complexes and semiconductor are known as photocatalyst materials. The ZnO semiconductor catalyst was tested for its activity as a photocatalyst in the dyestuffs degradation process (J. Zhao and L.wang, 2011). Zn is a type of transition metal, reacting

with oxygen at high temperatures in the air to produce oxides in the form of ZnO. This compound is amphoteric, which is soluble in acids and bases. As with other metal oxides such as TiO₂, ZnO is also a semiconductor. ZnO has a band gap of 3.37 eV. Electronic properties such as the band gap play an important role for a semiconductor photocatalyst. With this band gap, ZnO can be used in UV light photolysis.

The ZnO powders which have been studied extensively over the years. ZnO compared with TiO₂ has larger quantum efficiency. There are many researchers have reported the ZnO has higher photocatalytic activities than TiO₂ in some conditions (F. Xu, P. Zhang, A. et al). Further more, one dimensional ZnO structures are widely been prepared, which can easily been filtered out after the photocatalytic process, while there has not been much success in the synthesis of TiO₂ (D.L. Jian, p.X. Gao, W.J. Cai, et al).

Given the high level of paraquat toxicity, research was needed to be done to degrade the compound. In this study, paraquat would be degraded by photolysis method with additional ZnO. The degraded paraquat solution was measured uptake with a UV-Vis spectrophotometer to determine the amount of paraquat successfully degraded. This study aimed to provide information on the conditions needed to degrade pesticide paraquat so it could be converted into compounds that are not harmful to the environment.

EXPERIMENTAL SECTION

In this study was laboratory scale research where the herbicide paraquat used was Gramoxone herbicide with active ingredient 276 g/L (PT Syngenta Indonesia). The result of paraquat degradation was observed by inspecting the change in absorbance obtained after photolysis using a UV-Vis spectrophotometer.

The tools used were UV-Vis Spectrophotometer (S.1000 Secoman, Sarcelles, France), 10W 365nm UV LED (Germicidal CE G13. Base 8FC11004), magnetic stirrers, analytical balance (Kern, ALJ 220-4m), membrane filter (advanced membrane filters, polymers: cellulose mixed esters 0.45 µm, 25 mm), heating, erlenmeyer and other glassware. The materials used were compounds in paraquat pesticides Gramoxone with 276 g active ingredient/L (PT Syngenta

Indonesia), powdered ZnO catalysts, and distilled water. The method used in this research was photolysis method with the addition of ZnO catalyst.

Paraquat dichloride solution with a concentration of 276 g/L was taken about 1 ml then diluted in a 100 ml measuring flask with distilled water to the marked limit. So, the paraquat solution with the concentration of 2760 mg/L was obtained. Then, the paraquat solution with 2760 mg/L concentration was taken about 7.2 ml and diluted in a 100 ml measuring flask with distilled water to the marked limit, so that the paraquat solution with 200 mg/L concentration was made. Preparation of paraquat with various concentration 2 mg/L; 4 mg/L; 6 mg/L; 8 mg/L; and 10 mg/L in the 100 ml. The five variations in the concentrated solutions were respectively measured by the UV-Vis spectrophotometer at 200 - 400 nm wavelength.

Preparation of 20 ml solution with optimum concentration 4 mg/L. The effect of time toward paraquat degradation had been photolysis at various times of 30 minutes; 60 minutes; 90 minutes; and 120 minutes. And degradation process with optimum concentration 4 mg/L had been photolysis on various ZnO catalysts of 0.02 g, 0.04 g, 0.06 g, 0.08 g and 0.1 g for 60 min. The 20 ml solution with optimum concentration was fed into the petri dish. The solution had been photolysis at various times of 30 minutes; 60 minutes; 90 minutes; and 120 minutes with additional ZnO catalyst according to the result of the optimum degradation percentage from the previous experiment. The results of photolysis were filtered by the filter membranes. The respective absorbance spectra of each solution were measured by a UV-Vis spectrophotometer at the optimum wavelength.

RESULTS AND DISCUSSION

Measurement Absorption Spectrum of Paraquat

Paraquat absorption spectrum measurements at 2 mg/L; 4 mg/L; 6 mg/L; 8 mg/L; and 10 mg/L in a solvent of distilled water were using UV-Vis spectrophotometer. This UV-Vis spectrophotometer was an analysis method based on the measurement of monochromatic light absorption of a solution lane in visible and ultraviolet rays. Electromagnetic radiation UV-Vis has a wavelength ranging from 200 to 800 nm.

Adsorption of radiation will cause electron excitation. Atoms or molecules would absorb at wavelength regions whose energy corresponds to the energy difference between the ground state and the excited state of the atom or molecule and were specific to each of the compounds.

For quantitative measurements, the UV-Vis spectrophotometer method was used to determine the concentration of the solution where the absorption of light by the solution was a function of concentration. At concentration of 2 mg/L, it was obtained absorbance of 0.235, while at concentration of 4 mg/L; 6 mg/L; 8 mg/L; and 10 mg/L respectively obtained the absorbance value of 0.454; 0.642; 0.882; and 1,120. Under optimum conditions, a linear relationship can be made directly between the absorption of the solution and the concentration of the solution. The linear relationship between concentration and absorbance is represented in the standard paraquat calibration curve in **Figure 2**.

The calibration curve of paraquat standard for paraquat range from 2 mg/L concentration to 10 mg/L concentration, the solution for standardized regression with the equation of $y = 0.1109x$ was used to determine the concentration of paraquat herbicide. Based on Lambert-Beer's law, molar absorption coefficient (ϵ) paraquat absorption spectrum for each solution concentrations, the solution with a concentration of 4 mg/L had a value above the molar absorption coefficient level of the respective absorption spectra of each other solution. For further research, 4 mg / L paraquat solution had been used as the optimum condition for the solution to be photolysis. In determining the absorption spectra pattern of paraquat solution between 200 – 800 nm, it was obtained the maximum wavelength data of the solution which was 258 nm. This maximum wavelength determination was used for subsequent measurements of the paraquat absorption spectrum solution.

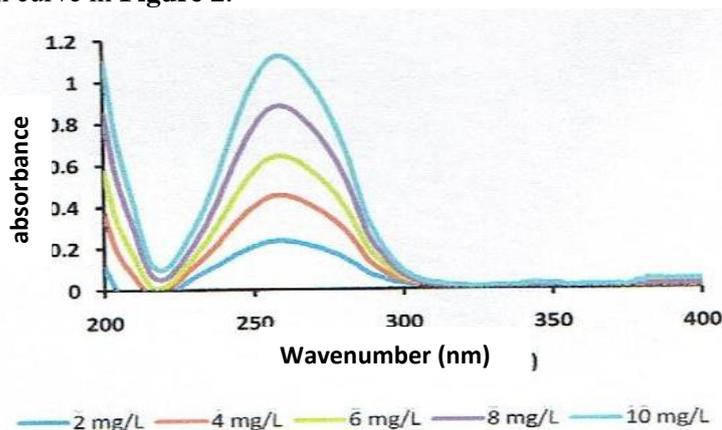


Figure 1. Paraquat absorption spectrum

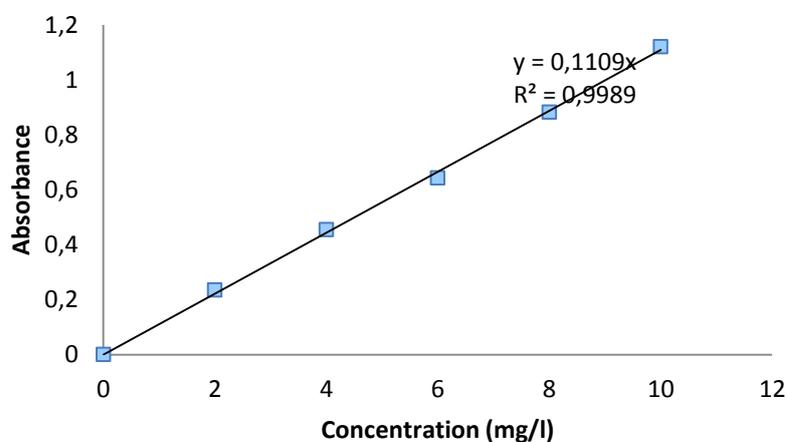


Figure 2. Calibration curve of paraquat standard

To evaluate the effect of UV irradiation on paraquat degradation was done with some variation of times. The variation of UV irradiation times were 30 minutes; 60 minutes; 90 minutes; and 120 minutes. Photo-degradation of paraquat was performed on a maximum absorption spectrum of 258 nm with an optimum concentration of 4 mg/L without the addition of ZnO catalyst. **Figure 3** shows degradation percentage of paraquat with the variation of time.

Degradation percentage at 30 minutes reached 9.69%, while with 60 minutes variation reached 10.03% and 10, 57% degradation percentage in 90 minutes. While at irradiation of 120 minutes, degradation percent could reach 12.56%. It can be seen that the percentage rate of paraquat degradation was not too large, this indicates that the photolysis of the paraquat might occur even though the percentage of paraquat degradation was not very large. The percentage of paraquat degradation increased with increasing

irradiation time, as the longer the irradiation time the greater the amount of OH radicals that were formed to degrade the paraquat compound.

Paraquat solution with optimum concentration of 4 mg/L was added by ZnO catalyst with weight variation of 0.02 g; 0.04; 0.06 g; 0.08 g; and 0.10 g. The solution would be photolysis for 60 minutes. During the process of photolysis, there was an ongoing activity of solution stirring with magnetic stirrer. The purpose of this stirring was to equalize the ZnO particles throughout the paraquat solution portion. The stirring process helped the balance of absorption process on the catalyst surface and helped the process of dissolving oxygen into the suspension. Stirring caused an interaction, when the solution was subjected to the light the reaction that occurs between ZnO semiconductor photocatalysts and paraquat molecules became more perfect. So it can degrade more paraquat compounds.

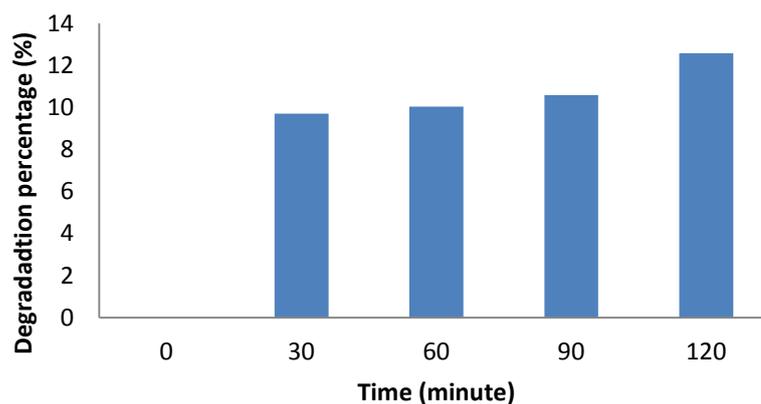


Figure 3. Effect of exposure time photolysis toward percent degradation of paraquat

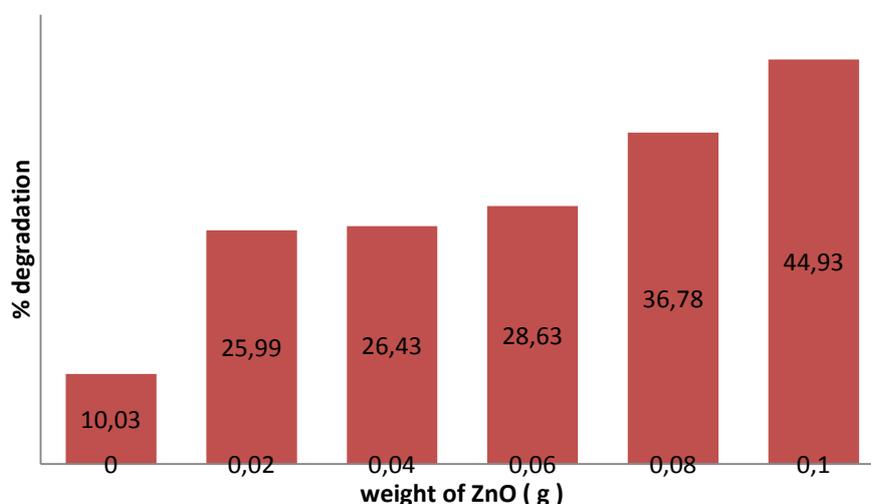
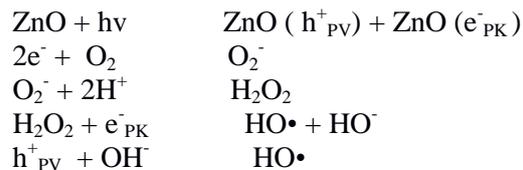


Figure 4. The effect of ZnO on percent paraquat degradation

The results of the photolysis of paraquat solution with the addition of ZnO semiconductor catalyst can be seen in **Figure 4**. Where this photolysis degradation of paraquat has been added ZnO catalyst as much as 0.02 g, it could degrade the paraquat by 25.99%, whereas with ZnO 0.04 g catalyst weight degradation became 26.43%. For the addition of ZnO catalysts of 0.06 g and 0.08 g respectively yielded the degradation percentage of 28.63%, and 36.78%. Viewing from the graph, the paraquat degradation increased every additional number of ZnO catalysts. Although the increment of degradation was not too sharp, for the addition of 0.10 g catalyst could degrade paraquat almost 50% which was equal to 44.93%.

Degradation of paraquat using this ZnO photocatalyst was occurred through the process of paraquat absorption to the surface of catalyst particles simultaneously accompanied by a photocatalytic oxidation (PCO) process against paraquat. When ZnO was exposed to UV irradiation, in the photocatalyst would occur electron excitation from the valence band to the conductive band which would produce e^- , and caused vacancies or holes (h^+_{pv}). Positive hole (h^+_{pv}) which would react with hydroxide that formed hydroxyl radical which is a strong oxidizing agent to oxidize paraquat. For electrons present on the semiconductor surface would be trapped in the hydroxide and could react with the capture of electrons present in the solution. For example, H_2O or O_2 form a hydroxyl or superoxide radical ($O_2^{\bullet-}$) that will oxidize paraquat.

The mechanism of semiconductor photocatalysis is as follows:



Radical (HO^{\bullet}) played a role in degrading chemical compounds. This radical would be formed continuously as long as ZnO was still subjected to UV rays and attacked the paraquat so it could be degraded more.

Paraquat solution of 4 mg/L was added with ZnO semiconductor catalyst as much as 0.10 g. The addition of 0.10 g catalyst was the optimum result of prior paraquat degradation percentage. Photolysis would then be done with variations of time ie for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. During the course of photolysis, the paraquat solution would be accompanied by stirring. **Figure 5** shows that the UV irradiation time of 30 minutes obtained a percentage of paraquat degradation of 38.98%, UV irradiation time of 60 minutes resulted in 44.93% and UV irradiation for 90 minutes had degradation percent 50.22%. After 120 minutes of percent paraquat degradation, it became 57.70%. With further increase of time, the degradation rate started to increase, and the ZnO catalysts were completely increased their catalytic activity. The paraquat was easily to absorb on the surface ZnO, thereby speeding up the degradation. Another reason contributing to the enhancement of the photocatalytic activity with the rise of time is that the concentration of hydroxyl ions have more chance to react with the holes to form oxidizing hydroxyl radicals (OH^{\bullet}).

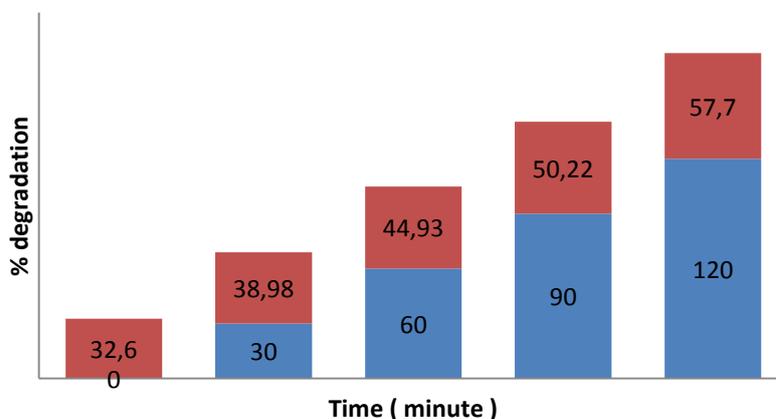


Figure 5. The effect of time toward paraquat percentage degradation.

CONCLUSION

Based on the results of research that have been done, it could be concluded that the paraquat degradation obtained by the optimum condition at the concentration of 4 mg/L with maximum wavelength of the solution was 258 nm. Degradation of 4 mg/L concentration paraquat solution by photolysis that was irradiation for 120 minutes without addition of ZnO catalyst could degrade paraquat as much as 12.56%. UV irradiation for 120 minutes with the addition of 0.10 g ZnO catalyst (optimum catalyst) paraquat could be degraded by 57.70%. The ZnO serves as a catalyst that helped to increase the efficiency of photocatalysis the paraquat more faster than without ZnO.

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