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ZnO-Mn nanoparticles synthesized by pulsed laser ablation in liquid for photocatalytic degradation of Rhodamine B

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Abstract

Rhodamine B is a synthetic dye in the form of a powder, generally used for the purpose of changing colors in textile and paper factories. Rhodamine B is a chemical that is dangerous, absolutely should not be mixed in food, beverages and cosmetics, besides that rhodamine also has toxic properties so it must be degraded to reduce its toxicity. This research uses ZnO/Mn material which is synthesized using laser ablation in liquid (PLAL) technique as the degradation of rhodamine B waste. ZnO/Mn photocatalyst against rhodamine B dye. The results of the FE-SEM show that with the addition of Mn doping, the bond between the particles is getting better. ZnO/Mn with a variation of 0.1 mM obtained the best results for degradation, namely 89.474%, and the energy gap was 3.3196 eV.

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1. INTRODUCTION

Environmental pollution is a problem that is very difficult to deal with. Both environmental pollution is donated from plastic waste and textile industry waste. Industrial wastewater is a major cause of water pollution. The use of certain chemicals without proper handling can threaten the safety of the environmental network in the global scope.

Organic dyes in industrial waste have the potential to produce serious environmental pollution. Rhodamine B is a synthetic dyestuff in the form of powder, commonly used for the purpose of changing colors in textile and paper factories, for example, from white to red, whose use pollutes the environment [1- 2]

Rhodamine B has toxic properties that must be degraded to reduce its toxicity to the environment. Besides causing pollutants in water and the environment, Rhodamine B is very dangerous because it can cause cancer, skin diseases and visceral red staining [1],[3]. One method of Rhodamine B degradation is photocatalytic. In this process, semi-conductors activated by ultraviolet (UV) light are used as catalysts to destroy organic contaminants. Photocatalytic is able to degrade toxic compounds that cannot be degraded by biological processes [1]. Because the reason has been done a lot of research on the use of chemical compounds for waste treatment to be more easily degraded as in the research conducted by Nan Guo, et.al [4] in this journal which discussed the design of photocatalysts based on Fe2O3 nanoparticles with In2O3, which was used to degrade rhodamine B.

Fe2O3 nanoparticles will be doped with In2O3 to see the degradation performance of rhodamine B also reviewed from exploration of photocatalyst doses, H2O2 and PH levels [4-8], in research conducted by H. Lahmar et, al. [9], who discusses methyl orange (MO) which was degraded by photocatalytic using sunlight and obtained in 60 minutes in the heterotype system II 1NiO4 / ZnO, prepared by the impregnation method [8-9], and also in the research of Muhammad Tariq, et.,al [10] which discusses the degradation of Rhodamine B using photofentone and photocatalytic heterogeneous processes with Ni-Cu.

For this reason, a study was conducted to improve the degradation process of chemicals in this case in the form of Rhodamin B by utilizing ZnO which is one of the semiconductors in the photocatalytic process which is widely used because it is environmentally friendly, non-toxic, high redox potential, and inexpensive , and has better photocatalytic performance. With the addition of Mn as doping it is hoped that it can be activated not only by UV light but also by visible light.

2. RESEARCH METHOD

Materials

The materials used in this study were aquades, Mn (manga-

nese) solution, ZnO plate, Rhodamine B. The tools used in this research are Nd YAG Laser, magnetic stirrer, beaker glass, measuring cup, stirring rod, ultrasonic bath, hotplate, thermometer, thermometer, UV-VIS, XRD, FESEM.

Synthesis of Mn Dopped ZnO Solution

Mn (manganese) solution was diluted to 1mM concentration; 0.1 mM; 0.1mM; 0.05 mM. ZnO plate surface using sandpaper. Synthesis was carried out by firing a laser on a ZnO plate inserted in an Mn solution and placed in a beaker that was heated at 70 degrees Celsius with a concentration of 0.1 mM each; 0.1mM; and 0.05 mM. the laser is fired with energy λ = 1064 nm with ablation time t = 10 minutes in each solution.

Photocatalytic Experiments

Preparation is done by dripping Zno solution as much as 1.5 mL (control) and Mn-ZnO as much as 1.5 mL, with a concentration of 0.1 mM each; 0.1mM; and 0.05mM, on a glass plate heated on a holplate. The sample solution and the control are dropped gradually as much as 0.5 mL each time the glass plate dries.

The photocatalytic test was carried out by placing a pre-repaired glass plate in a petri dish given three kinds of treatment, namely by UV light (ultra-violet), Visible Light, and No Light by adding 10 mL Rhodamin B solution for 3 hours for each treatments. Observations were carried out every 1 hour by observing the color changes due to the reaction and measuring the absorbance value of the solution by the UV-VIS method.

3. RESULTS AND DISCUSSION

The FE-SEM image shows the morphology of the pure Zno and Zno sample particles by doping. The Figure 1 shows (a) ZnO, (b) ZnO / Mn 0.05 mm, (c) ZnO / Mn 0.1 mm, (d) ZnO / Mn 0.2mm.

The results of the FE-SEM show that with the addition of Mn doping, the bond between the particles is getting better and the shape of the particle is becoming clearer, that is, it is spherical from what was originally elliptical [11-13]. ZnO without doping shows spindle-shaped particles and some spherical-shaped particles are distorted [14].

As it is known that photocatalytic is a fusion reaction between photochemistry and catalyst, in this study ZnO / Mn acts as a catalyst that will degrade Rhodamine B which is a pollutant. The results of photocatalytic ZnO / Mn nanoparticles are shown in Figure 2 in the form of UV-Vis characterization results with a time of 1 hour to 3 hours and each treatment. From the treatment carried out namely degradation with visible light, ultraviolet and no-light conditions, it can be concluded that the longer the radiation time, the absorbance value will also decrease, this applies to each activation treatment.

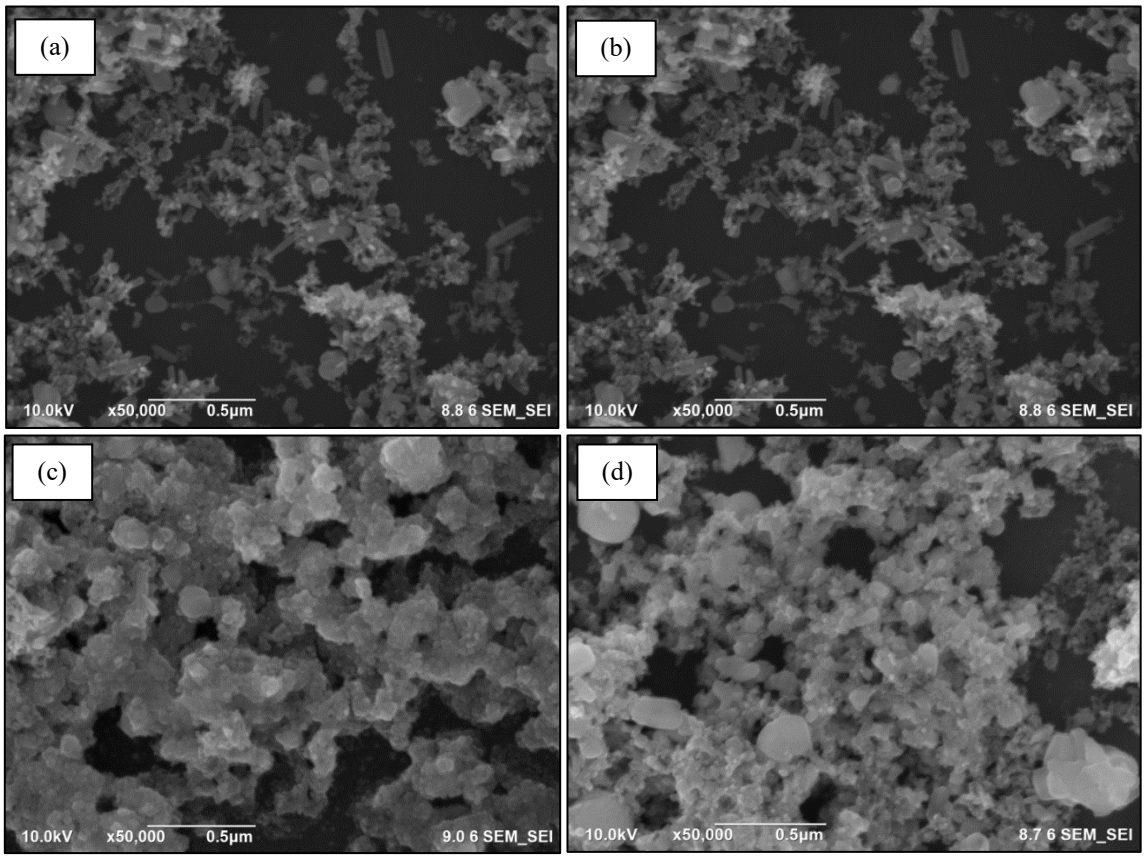

Figure 1. FE-SEM micrograph of a) ZnO, b) ZnO / Mn 0.05 mm, c) ZnO / Mn 0.1 mm, d) ZnO / Mn 0.2 mM

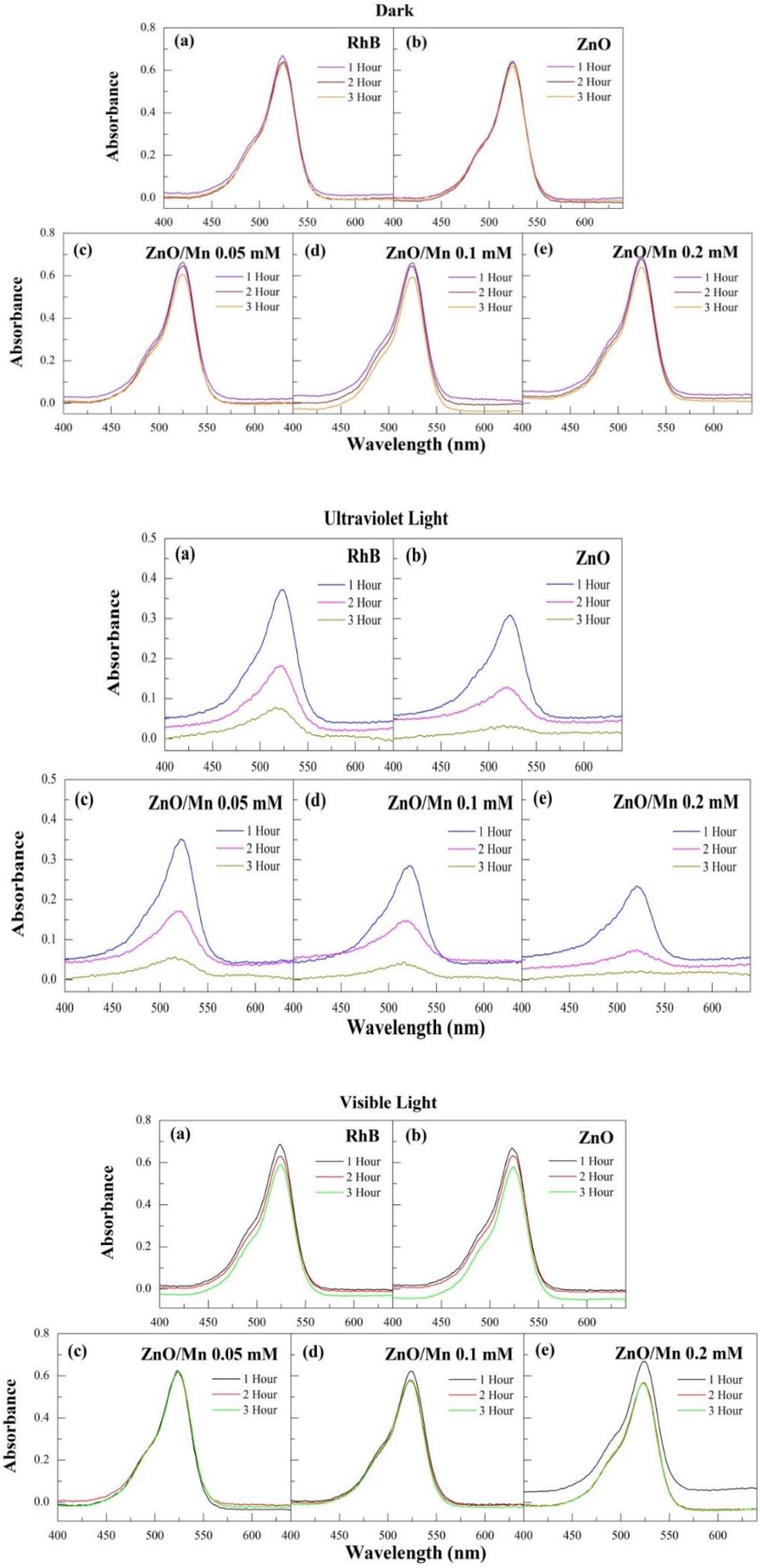

Figure.2 UV-VIS data for photocatalytic performance with three dark conditions (Dark, Visible Light and Ultraviolet Light) (a) Rhodamine B (b) ZnO (c) ZnO-Mn 0.05 mM (d) ZnO / Mn 0.1 mM (e) ZnO / Mn 0.2mM

The curve above shows that the absorbance value of the activation without light and visible light is greater than the activation using ultraviolet light. This is due to ZnO compound which has high bandgap energy and excitone energy so that ZnO is able to be activated well by UV light [3], And therefore also ZnO is modified to expand the spectrum of light that can be absorbed by adding additional manganese compounds [3]. The process of photocatalysis occurs due to the presence of photon energy from UV light irradiation causing the excitation of electrons from the valence band to the conduction band which creates an electron-hole pair. An OH radical on the surface of the ZnO photocatalyst is formed due to the loss of valence band electrons which will be positively charged where the OH radical is one of the oxidizing agents that is quite strong. Whereas the electrons originating from the valence band cause the conduction band to be negatively charged so as to reduce the oxygen molecule [15, 16]

The presence of manganese doping is expected to provide a trapping effect on the excited electrons towards the conduction band. The Mn + ion will act as an acceptor of the excitation electron. This will impact on preventing the recombination of electron-holes formed as a result of electron excitation. If recombination occurs, the hole (h +) that is created will react again with electrons and disappear then this results in the absence of a reaction between h + with water molecules that produce OH radicals. When there is no OH radical, the photocatalytic degradation process also cannot occur. It can be said that the presence of manganese metal doping will increase the chance of radical OH formation in the ZnO photocatalyst

The percentage degradation of ZnO / Mn nanoparticles is shown in Figure 3 which is the result of the characterization of UV-Vis. Based on this curve, the highest percentage of degradation was contributed by the 0.1 mM ZnO / Mn ultraviolet light activation process, which is 89,474%, it can be seen that the addition of ZnO / Mn affects the process of degradation of compounds faster than those without ZnO / Mn. even with visible light. The addition of ZnO / Mn affects the degradation process because it functions as a catalyst that plays a role in helping the degradation process of rhodamin B [1]. The result of degradation in inconsistent samples might be affected due to the formation of intermediates from Rhodamin B compounds and the reaction between intermediates and oxidants so that it affects the reaction process between active substances and oxidants [2].

Figure 3 also shows other data that the percentage of addition of manganese metal shows lower photocatalysis activity compared to photocatalysis without manganese doping. R. Ullah, et. al., [15] reported that ZnO photocatalysts doped with manganese metal have a high level of electron-hole pair recombination. Manganese metal doping in photocatalysts is intended to create an electron trap aimed at minimizing the recombination. S. Sentikhumar, et. al., [16] reported that the addition of this amount could not compensate for the high level of recombination because the level of traps formed was low.

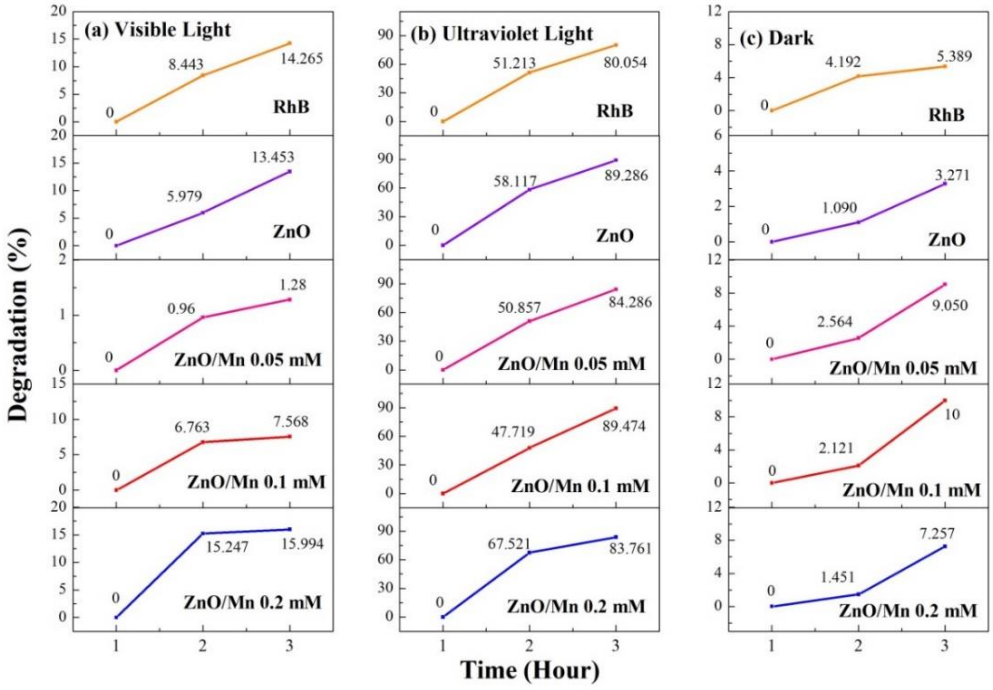

Figure 3. Percentage of degradation of each photocatalytic test sample (RhB, ZnO, ZnO-Mn 0.05 mM; ZnO-Mn 0.1 mM; ZnO-Mn 0.2 mM) with each different treatment (a) Visible Light (b) Ultraviolet Light (c) Dark

Figure 4 shows the results of the bandgap calculation with the equation $Eg = \frac{h\upsilon}{\lambda}$ obtained energy bandgap values respectively of 3.3510 eV for ZnO without doping, 3, 3224 eV for ZnO / Mn 0.05 mM, 3.3196 eV for ZnO / Mn 0.1 mM and 3, 3282 eV for ZnO / Mn 0.2 mM and showed that the best bandgap values were obtained in ZnO doped Mn 0.1 mm samples. this can be attributed to the highest degradation yield in the same Mn addition composition. The addition of manganese which has less impact on the sample may be influenced by the mixing of the solution which is not good, besides the addition of 0.1 mM Mn may be the most doping manganese which is the best condition for the application of degradation in rhodamine B [17-19].

Semiconductor material requires minimum energy for the excitation process outside the conduction band. This energy dependence results in widening of the gap between the valence band and conduction which results in an increase in the energy value of the phytocatalyst material. the addition of doping in the form of certain metals such as manganese makes it possible to form additional gaps that have an impact on decreasing the width of the band gap for. excitation process [20].

This will be different when there is a doping of certain metals in a semiconductor. The decrease in band gap energy will occur when the width of the band gap is smaller. The presence of manganese metal doping is thought to cause the formation of an additional band gap which results in a decrease in the band gap width for electron excitation.

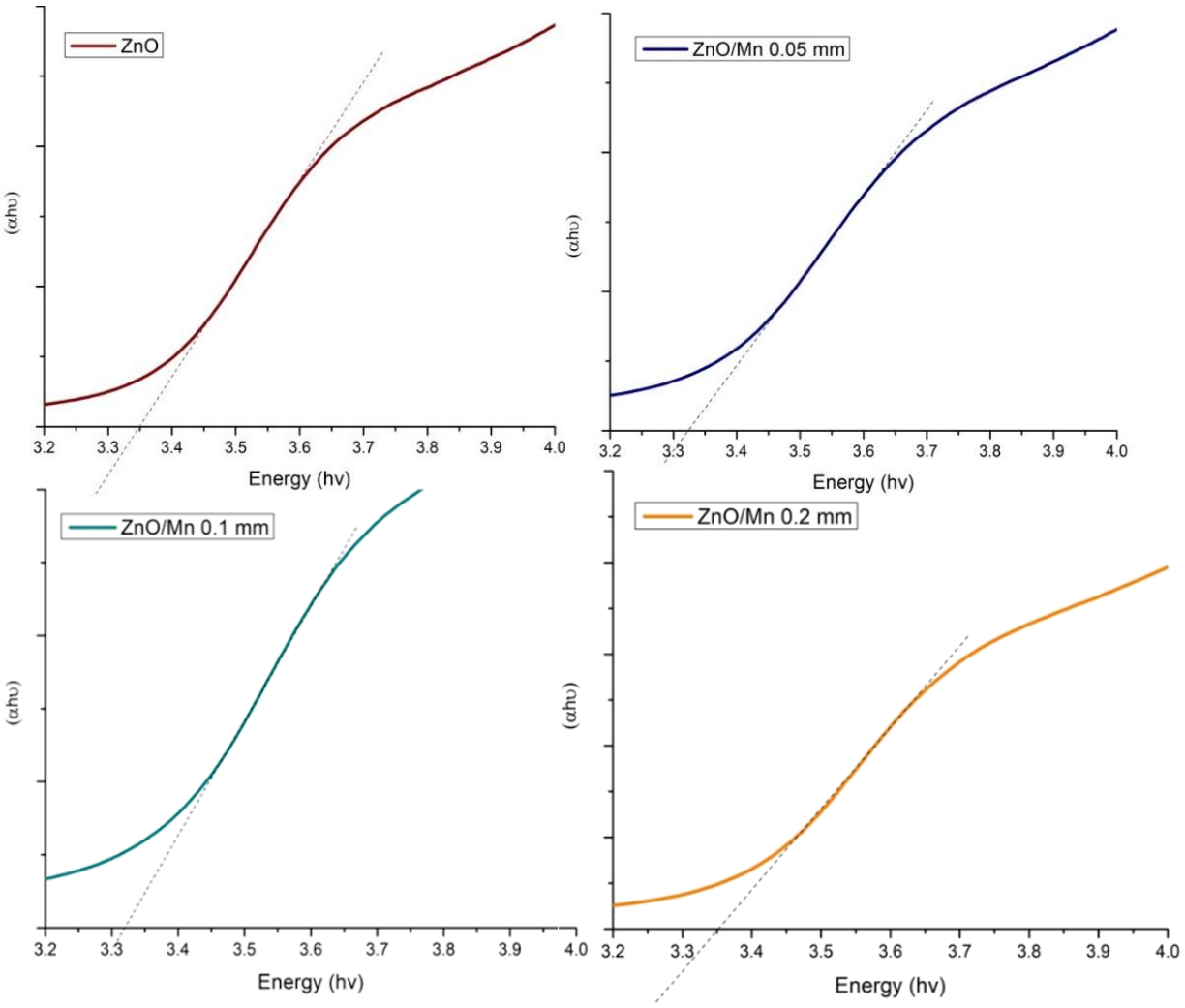

Figure 4. Energy Gap of Sample ZnO, ZnO-Mn 0.05 mM, ZnO-Mn 0.1 mM, ZnO-Mn 0.2 mM)

Figure 5 is the relationship between the degradation rate (k) and the correlation coefficient (R2), where the constant rate (k) is measured by the slope equation to measure the constant rate and the value of the correlation coefficient. Based on the picture above, it can be seen that the degradation rate constant (k) and the correlation coefficient (R2) with and without the addition of ZnO / Mn are shown in the table.

The best correlation is shown in the activation of ultraviolet light for all variations of the composition marked by the degradation rate (k) and the correlation coefficient (R2) higher than the others. It can be seen that based on the table for the activation of ultraviolet light with the composition of ZnO / Mn 0.1 mM the degradation rate is very high even though the correlation coefficient has decreased, it is caused by doping of manganese metal in this photocatalyst is intended to trap electrons aimed at minimizing the occurrence of electron-hole recombination contained on ZnO. Ruh Ullah, et. al., [15] states that the addition of manganese metal doping concentrations of such magnitude cannot compensate for the high level of recombination in ZnO because the level of traps in manganese doping formed is low.

This was also reported by Ruh Ullah, et. al., [15] and S.Sentikhumaar et. al [16] which states that manganese doping in the ZnO semi conductor causes the formation of additional bands, called tail states, in the valence band which causes excitation to occur at lower photon energy levels and decreases the band gap energy value of the material. This is also observed in other metal doping, namely Fe in the TiO2 semiconductor. Based on these results it is expected to be an alternative that can be used to improve the degradation process of liquid waste such as Rhodamin B, which impacts the environment.

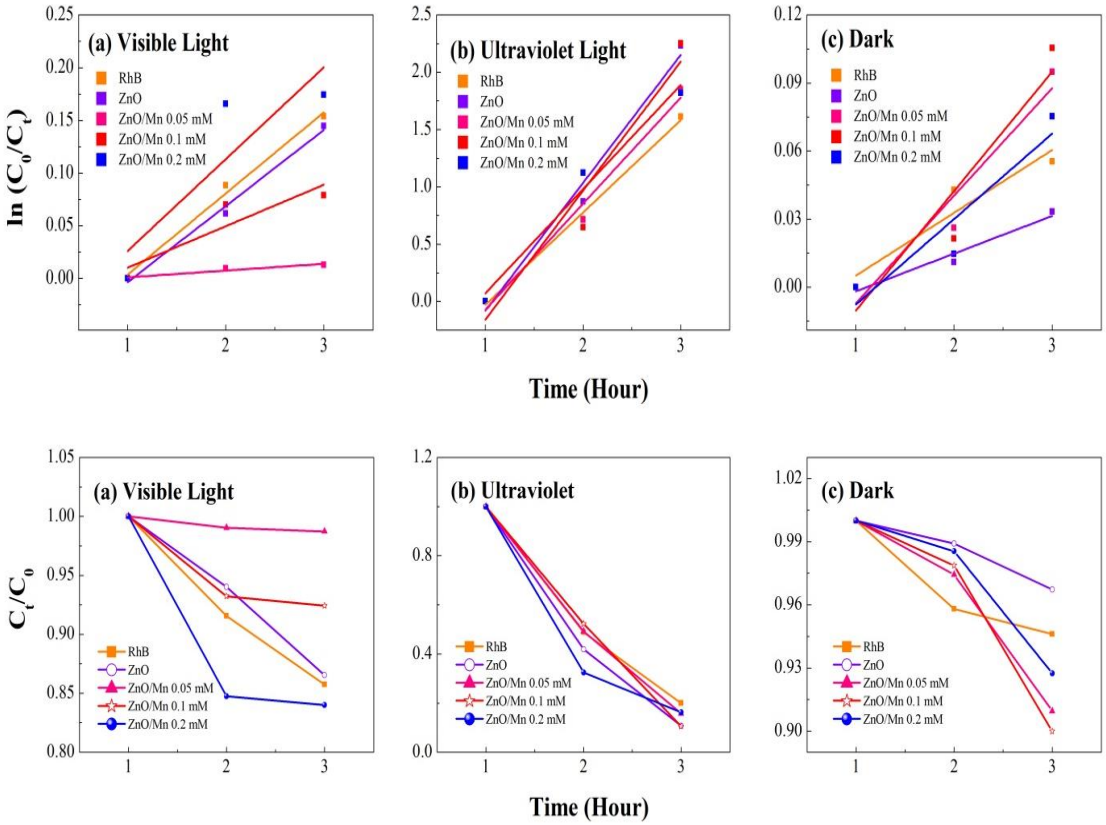

Figure 5. Ct/Co and Ln Ct/Co curves of photocatalytic degradation samples (RhB, ZnO, ZnO-Mn 0.05 mM; ZnO-Mn 0.1 mM; ZnO-Mn 0.2 mM) with each different treatment (a) Visible Light (b) Ultraviolet Light (c)) Dark.

Tabel 1. Kinetic Constant Rate (Kr) and Correlation Coefficient Value (R^2) Sample (RhB, ZnO, ZnO-Mn 0.05 mM; ZnO-Mn 0.1 mM; ZnO-Mn 0.2 mM) with each different treatment (a) Visible Light (b) Ultraviolet Light (c) Dark

Sampel	Visible Light		Ultraviolet Light		Dark	
	k_r	R^2	k_r	R^2	k_r	R^2
RhB	0.077	0.986	0.806	0.992	0.028	0.819
ZnO	0.072	0.986	1.117	0.968	0.017	0.925
ZnO/Mn 0.05 mM	0.006	0.848	0.925	0.965	0.047	0.872
ZnO/Mn 0.1 mM	0.039	0.663	1.126	0.887	0.053	0.790
ZnO/Mn 0.2 mM	0.087	0.576	0.909	0.963	0.038	0.778

4. CONCLUSION

The ability of ZnO/Mn nanoparticles to degrade Rhodamine B as a pollutant with various treatments such as visible light, ultraviolet and no light conditions is affected by the addition of Mn and ZnO itself. The best absorbance value was obtained in the activation treatment with Ultraviolet light. Based on the results, it can be concluded that the longer the degradation time, the lower the absorbance value so that the percentage of degradation also increases, which is about 89.474%, and this applies to each activation treatment. The addition of ZnO/Mn affects the degradation process because it functions as a catalyst that plays a role in helping the degradation process of rhodamine B, besides that ZnO compounds also have an energy gap and high exciton energy so that ZnO can be well activated especially by UV light. In addition to the addition of ZnO, the addition of Mn affects the formation of OH radicals to prevent electron-hole recombination that is formed as a result of excitation which will have an impact on the photocatalyst degradation process.

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