Photocatalytic Degradation Of Procion Red Synthetic Dye Using ZnO-Zeolite Composites

Abdis Salam, Tuty Emilia Agustina, Risfidian Mohadi

Abstract: Textile industry consumes the most amounts of dye lots in the production process which have a non-biodegradable in nature. It is necessary to do the dye wastewater treatment before discharging to the environment. Photodegradation is a process of decomposition of organic compounds with the aid of photon energy, in which oxidation and reduction reactions occur on the surface of the semiconductor. One of the good semiconductors used is ZnO. Furthermore, adding a matrix or dopants is expected to assist ZnO photocatalysts so that dye degradation is more optimal. Zeolite is a good solid support for dispersing ZnO semiconductors because zeolite has large surface area and uniformity of pore size. Procion Red was used as a model of synthetic dye wastewater. The objectives of the study are to synthesize ZnO-zeolite composites by impregnation method and to study the effects of irradiation time (30-120 minutes), type of composites used, and light conditions (dark room, UV light, and sunlight) on Procion Red degradation. ZnO-zeolite composites are made by weight ratio (1:2), (1:1) and (2:1). ZnO-zeolite composites that have been synthesized were characterized by using SEM-EDX. The degradation of procion red dye produced was characterized by using UV-Vis Spectrophotometer. The results showed that Procion Red degradation by using sunlight exposure was greater than UV lamp and dark room for Procion Red concentration of 150 mg/L. From the three ZnO-zeolite composites synthesized, the composite (2:1) showed the best degradation percentage of 83.96% for 120 minutes under sunlight irradiation.

Index Terms: photocatalytic, degradation, ZnO-zeolite, composites, procion red.

1 INTRODUCTION

Many types of industries in Indonesia use dye role in the production process. Manufactures of furniture, paint, varnish, household appliances to textiles require the dye to further improve production results. Among some of the mentioned industries, the textile industry is the kind of industry that consumes the most amounts of dye lots in the production process. The rapid growth of the textile industry in Indonesia resulting dye needs to be increased **[1]**. The synthetic dyes are often used in the textile industries which have a non-biodegradable in nature, such as procion, erionyl and auramin. The dye is used for several reasons, such as cheaper and more durable than natural dyes, easily obtained in a variety of colors, and easy to use. However, the waste generated provides a striking color and difficult degradable in the environment. If the levels are excessive then it will disrupt the ecosystem environment. Wastewater from the textile industry if directly discharged into the water body will reduce the amount of dissolved oxygen needed by living things in the waters, because the dissolved oxygen is actually used to oxidize various pollutants including organic compounds such as synthetic dyes **[2].**

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Besides, it also reduces the aesthetic value of the marine environment, especially on the color and quality of water. The liquid waste is a major problem in controlling the environmental impact of the textile industry because it provides the most extensive impact, both in terms of physical and chemical **[1]**. The textile industry produces wastewater with parameters of Color, BOD, COD, suspended solids, and others depending on the dye used. Therefore, it is necessary to do a series of dye wastewater treatment before discharging to the environment in order to meet the quality standards of textile industry waste in accordance with Minister of Environment of Indonesia's Decree No.5 of 2014.

Table 1. *Maximum Level and Samples of Textile Industry Wastewater*

Parameter	Maximum Level (mg/L)*	Wastewater on Jumputan Cloth (mg/L)**	Wastewater on Stamped Batik of Palembang (mg/L)***
COD	150	385	4.230,36
TSS	50	165	535
Total Phenol	0,5	not tested	0,008
Total Chrome (Cr)	1,0	not tested	0,1385
Color	-	282 (Pt-Co)	not tested
pH	6,0-9,0	8,0	6,0
Maximum waste discharge	100 m^3/ton of products	not tested	not tested

** Minister of Environment Regulation No. 5 Year 2014 on Wastewater Quality Standard* ***[3]***
*** Agustina, T. E., Bakri, M.A., and Sufra, R. (2013)* ***[4]***
**** Agustina, T. E. et al,. (2011)* ***[5]***

In Table 1, it can be seen the samples of textile industry wastewater with some parameters. It is necessary to set up waste treatment technology so that the effects of pollution can be prevented and controlled. Efforts to tackle the problem of environmental pollution have been carried out in various ways. Starting from the conventional methods, such as adsorption using activated carbon or zeolite to cutting-edge methods, such as biodegradability, chlorination, ozonation, ionizing radiation, or plasma technology. However, both methods have their own weaknesses. The conventional method is not effective enough to degrade environmental pollutants, while the cutting-edge method is not efficient enough because it requires a relatively high cost **[6]**. Photodegradation is a process of decomposition of organic compounds with the aid of photon energy, in which oxidation and reduction reactions occur on the surface of the semiconductor **[7]**. Photodegradation is an alternative method that has several advantages, which are able to mineralization of the organic pollutants, low cost, the process is relatively fast, and have the ability to be used in long-term **[6]**. The success of photodegradation method based on photocatalysts, which are solids that have semiconductor properties. For example, ZnO, TiO_2, CdS and Fe_2O_3. When the material is affected by UV light, it will be able to decompose organic compounds through photocatalytic reactions **[7]**. One of the good semiconductor used is ZnO. Research conducted **[8]** showed that the efficiency of photodegradation of methylene blue dye can be increased up to four-fold by using ZnO as a photocatalyst. According to **[9]**, Semiconductor ZnO has an advantage compared to TiO_2 because it was able to absorb the solar spectrum and the quantum of light more than the TiO_2. Kansal et al. **[10]** examined the rate of photodegradation of methyl orange using ZnO photocatalyst by varying the concentration of MO 5 to 200 mg/L. The optimum concentration was obtained at concentrations of 5 and 10 mg/L with almost 100% degradation occurring between 60 and 120 minutes. Furthermore, the semiconductor photocatalytic activity should be increased by adding a matrix or dopants. The dopants can be used are natural minerals, such as bentonite and zeolite **[11]**. Zeolite is a good solid support for dispersing ZnO semiconductors because zeolite has large surface area and pore volume and uniformity of pore size and channel size **[12]**. In this study, ZnO photocatalysts will be combined with zeolite, so it is expected to degrade the procion red dye more optimally. ZnO-zeolite composites that have been synthesized will be characterized using SEM-EDX. After that, testing photodegradation activity of procion red dye with three conditions (darkroom, UV light, and sunlight). The degradation of procion red dye produced will be characterized by using UV-Vis Spectrophotometer.

2 Experimental Section

2.1 Materials

Natural Zeolite obtained from Central Kimia Store in Palembang. The procion red dye obtained from Fajar Setia Dyestuff in Jakarta and used without further purification. The other chemicals were supplied from Merck such as Zinc Oxide (ZnO) solid, Hydrogen Chloride (HCl), and Ethanol. Equipments used in this research are; Evaco 15W UV lamp with wavelength 254 nm of 2 pieces, Light Meters UNI-T UT383, Scanning Electron Microscope (SEM-EDX) ZEISS EVO® MA 10 and UV-Vis Spectrophotometer.

2.2 Methods

a. Zeolite Activation

Natural zeolite as much as 100 g crushed until smooth using mortar and sifted gradually with 60, 120 and 170 mesh sieve. The zeolite which left in a 170 mesh sieve then washed with 600 mL of distilled water. The washing zeolite was filtered off and dried in an oven at 110°C for 2 hours. A total of 75 g of washed zeolite added 500 mL of 0.4 M HCl were then shaken with shaker for 1 hour. Zeolites are filtered and washed with distilled water so that the filtrate is free of Cl^- ion. The zeolite residue in filter paper is then dried in an oven at 110°C for 2 hours. After that weighed so that the mass is constant.

b. Impregnation of ZnO Catalyst on Zeolite

Synthesis of zeolite is done by mixing zeolites that have been activated with ZnO solid. In ZnO-Zeolite synthesis there are 3 variations with weight ratio ZnO:Zeolite, i.e (1:2); (1:1) and (2:1). The ratio of 1:2 is made by mixing 4 g of ZnO with 8 g of activated zeolite. The ratio of 1:1 is made by mixing 6 g of ZnO with 6 g of activated zeolite. The ratio of 2:1 is made by mixing 8 g of ZnO with 4 g of activated zeolite. Each mixture was added ethanol 100% as much as 25 mL and diluted with aquadest until the solution become 100 mL, stirred using a magnetic stirrer for 4 hours. Then the mixture is exposed to ultrasonic waves for 30 minutes. ZnO-zeolite was dried in an oven for 5 hours with a temperature of 120^{o}C until dry. Then, calcined at a temperature of 400°C for 2 hours. Composites of ZnO-zeolite characterized by using SEM-EDX to determine the morphology of the composites.

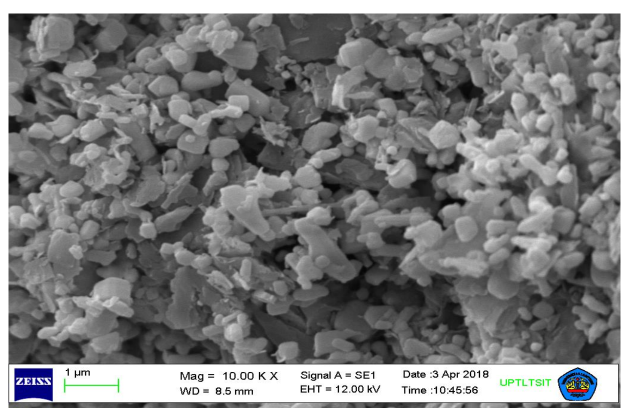
c. Degradation of Procion Red

Procion red solution of 25 mL with a concentration of 150 mg/L was added with 100 mg of ZnO-zeolite composites [(1:2), (1:1), (2:1)] at a contact time of 30 minutes, 60 minutes, 90 minutes and 120 minutes with 3 different conditions, with darkroom, UV light, and sunlight. The mixture is then separated by centrifugation to separate the solids from procion red waste. Procion Red has been degradated by ZnO-zeolite composites was measured absorbance value using a UV-Vis spectrophotometer at the maximum wavelength. From these absorbance values, can be calculated the concentration of procion red, as well as the percentage of procion red degradation.

3 Results and Discussion

3.1 Characterization of ZnO-Zeolite Composites

ZnO-zeolite composites were characterized using SEM-EDX. SEM analysis is used to determine particle morphology (surface) and particle size whereas EDX analysis result is used to determine composition of compound from a sample. The SEM results of ZnO-zeolite composites with the weight composition ratio of ZnO and Zeolite are presented in Figure 1.



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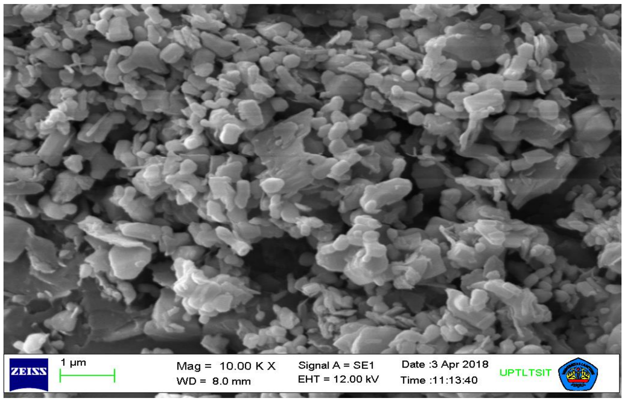

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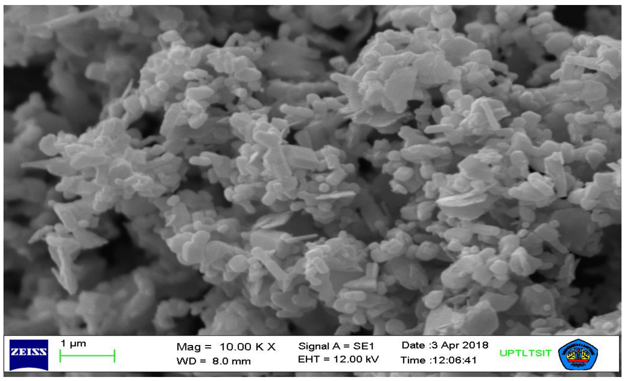

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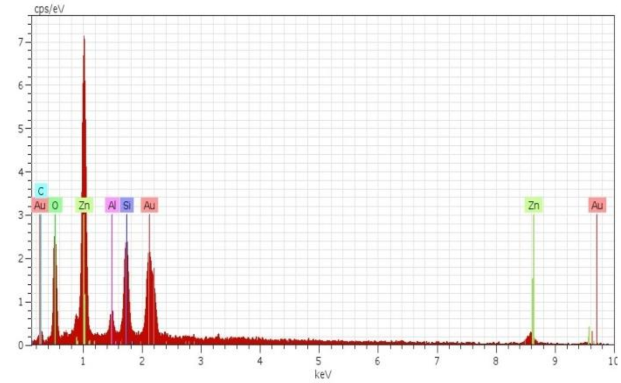
Figure 1. *SEM results of ZnO-zeolite composites with weight ratio: (a) ZnO-Zeolite (1:2), (b) ZnO-Zeolite (1:1), and (c) ZnO-Zeolite (2:1)*

From Figure 1, it can be seen the ZnO-Zeolite composites surface with 10,000x magnification. There are 2 types of material with different colors and stick together. Dark color is thought to be a Zeolite material because it has a larger size while bright colors are suspected ZnO powder material that is nano-sized. In composite (1:2), Zeolite seen more than with ZnO powder, this is in accordance with the composition of the composite weight made of 8 grams of Zeolite and 4 grams of ZnO. In the composite (1:1), it is seen that ZnO and Zeolite are in a balanced amount, according to the composition made, ie 6 grams of Zeolite and 6 grams ZnO. While the composite (2:1), it appears that ZnO is more dominant than Zeolite, this is because ZnO composition more than zeolite, which is 8 gram ZnO and 4 gram Zeolite. The SEM results of activated ZnO-Zeolite composites are then compared with the results of another researcher. The research of **[13]** showed similarity on the surface of the ZnO-Zeolite composites in this research. This means that the ZnO-Zeolite composites have been successfully synthesized.



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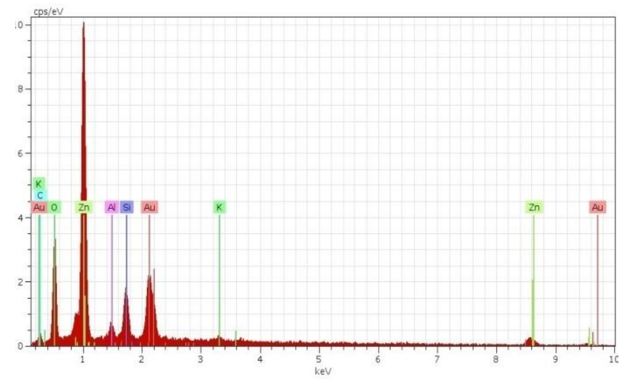

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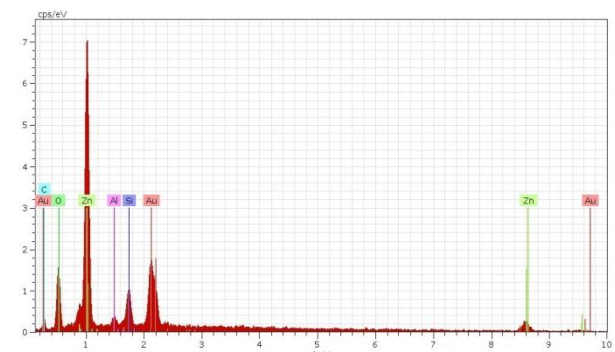

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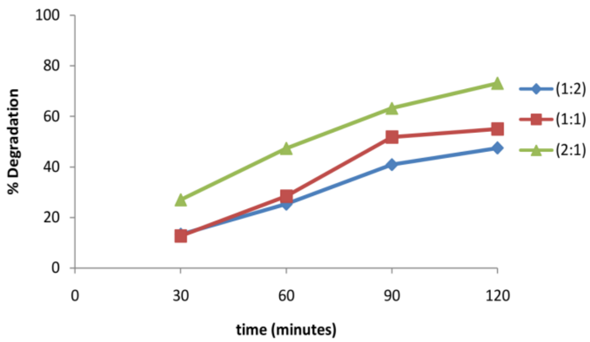
Figure 2. *EDX results of ZnO-zeolite composites with weight ratio: (a) ZnO-Zeolite (1:2), (b) ZnO-Zeolite (1:1), and (c) ZnO-Zeolite (2:1)*

Figure 2 shows the result of EDX analysis of ZnO-Zeolite composites. The EDX analysis was used to determine which chemical elements are present in the composite. The EDX Spectra shows the peaks of Zn and O. It means the composite comprise of ZnO photocatalyst.

3.2 Degradation of Procion Red by ZnO-Zeolite Composites

Degradation of 150 mg/L of Procion Red by using ZnO-zeolite composites with various irradiation conditions has been studied. ZnO-zeolite composites used with weight ratio (1:2), (1:1), and (2:1).



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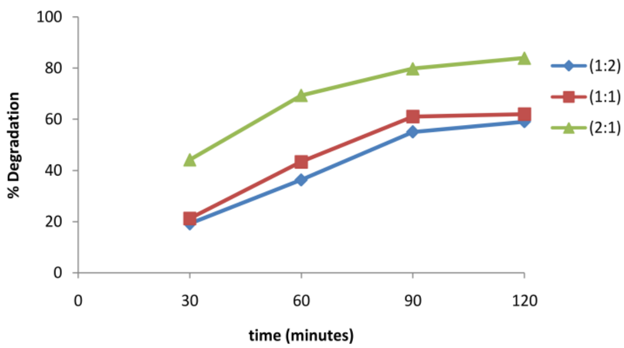

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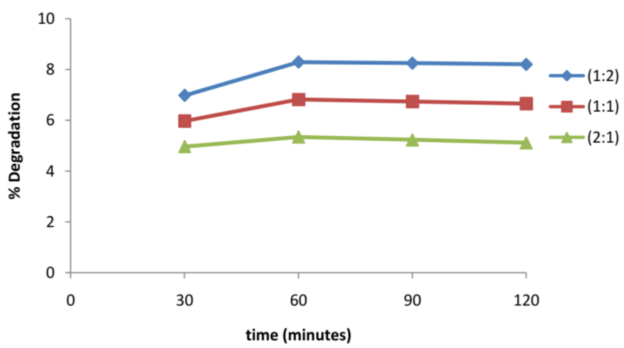

(c)

Figure 3. *Relationship between time and percentage of rocion red degradation at concentration 150 mg/L by various composites with conditions: (a) UV Light, (b) Sunlight, and (c) Darkroom*

Figure 3 (a) showed the effect of time and composites used on procion red degradation under UV light irradiation. The degradation of procion red will increase with increasing time of irradiation. This applies to all composites used. In composites (1:2), (1:1), and (2:1), the highest degradation percentage was obtained at the same irradiation time, 120 min, with degradation percentage of 47.43%, 55.01%, and 73.08% respectively. The composite (2:1) has a higher degradation value because the composite composition contains more ZnO, so with the help of UV light occurs photodegradation process. In addition, the content of Zeolite in the composite has less functional in absorbing the dyestuff, so the degradation percentage of procion red in the composite containing a lot of zeolites is relatively low. Figure 3 (b) showed the effect of time and composites used on procion red degradation under sunlight irradiation. In composites (1:2), (1:1), and (2:1), the highest degradation percentage was obtained at the same irradiation time, 120 min, with degradation percentage of 59.05%, 62.03%, and 83.96% respectively. Degradation of procion red with sunlight irradiance tends to be similar to UV light irradiation. However, sunlight is more effective in the dyestuff degradation process because it has a higher light intensity and wavelength compared to UV lamps. This causes the photon energy to be absorbed more in the photodegradation process so that the degradation process runs faster and more optimum. Research from Fraditasari **[14]** showed similar results, which in her study used methyl orange as a dye. Degradation of methyl orange using TiO_2-N photocatalyst by studying the effect of UV lamp and sunlight. From the research conducted, radiation with the sunlight produces dye degradation greater than the UV lamp. Photocatalytic Degradation occurs when ZnO absorbs light energy equal to or greater than the band gap energy there will be a charge separation or photo excitation in the semiconductor **[15]**. When the ZnO catalysts exposed to the sunlight or UV light, resulting in a strong oxidation hole and form a radical OH•. The radical OH• degrade the Procion Red into a simpler compounds. The ZnO catalysts were subjected to the photon energy will experience the excitation of electrons to form pairs of electrons and holes. The electrons react with O_2 molecules on the surface of ZnO to form superoxide anion radical ($\bullet O_2^-$). The anions will react with the adsorbed water molecules (H_2O) to produce hydroxide ions. Then the hydroxide ions (OH^-) will react with a hole to form OH• which is a strong oxidizing agent **[16]** that is helpful in the process of procion red degradation. Based on **[15]** below are the proposed mechanism in dyestuff degradation process with ZnO catalyst:

$$ZnO + h\nu \longrightarrow ZnO\ (e^- + h^+) \quad (1)$$
$$h^+ + H_2O \longrightarrow H^+ + OH\bullet \quad (2)$$
$$h^+ + OH^- \longrightarrow OH\bullet \quad (3)$$
$$e^- + O_2 \longrightarrow \bullet O_2^- \quad (4)$$
$$OH\bullet + \text{dye} \longrightarrow \text{Oxidation of the dye compound} \quad (5)$$
$$\bullet O_2^- + \text{dye} \longrightarrow \text{Reduction of the dye compound} \quad (6)$$

Figure 3 (c) showed the effect of time and composites used on procion red degradation without irradiation (darkroom). In the ZnO-zeolite composites that were not exposed to UV light and sunlight, the photodegradation process does not occur. The photodegradation process does not occur because there is no light or energy on the surface of the catalyst so that the catalyst can not release electrons and the formation of holes. This causes the failure of the formation of radical OH• as well as superoxide anion radical $\bullet O_2^-$ which can decompose the dye into simpler components. Therefore, in darkroom only occurs the adsorption process. Adsorption of Procion red is dominated by zeolite contained in the composites. It can be proven on the highest degradation percentage value obtained on the composite (1:2) that is 8.29%. While the degradation percentage of procion red of composite (1:1) and (2:1) were respectively 6.82% and 5.35%. In darkroom conditions, the optimum time is obtained at 60 minutes. After 60 minutes, degradation percentage of procion red is constant, even tending to decrease. This shows the ability of the composite in absorbing dye less than optimal. Composites consisting of ZnO powders and zeolites are bonded together. The pores of the zeolite are expected to absorb the dye, but are covered by a nano-sized ZnO powder, thereby reducing the ability of zeolite absorption. In addition, continuous stirred ZnO photocatalyst powder causes stability of the suspension in the dyestuff mixture, which would complicate the ZnO separation process from the clear substance even when centrifugation is done. A stable suspended solid causes the light passing through the cuvette to be scattered, so the intensity of the light received and transmitted by the spectrophotometer detector will be less than the intensity of its occurrence and result in a greater absorption readability **[17]**. The quality of the zeolite used also affects the composite's ability to absorb dyes. This can be caused by the process of making the activated zeolite is not good so it does not match the expected results. ZnO-zeolite composites have good ability in degradation of procion red dyes, especially on photodegradation. Comparison of light conditions to degradation percentage of procion red based on the highest value of the composite used can be seen in Fig. 4.

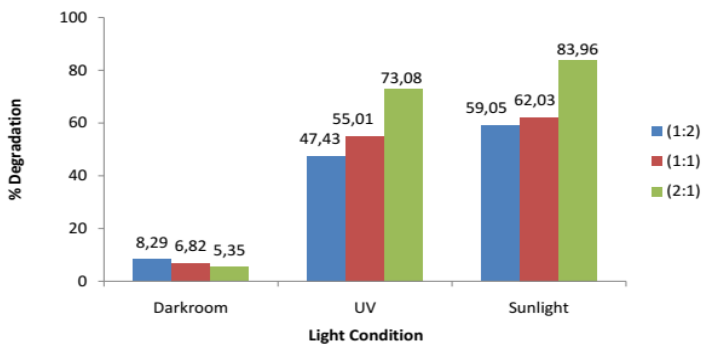

Figure 4. *Relationship between light conditions and percentage of procion red degradation at concentration 150 mg/L by various composites*

In Figure 4, in the darkroom conditions, the highest degradation percentage of procion red was obtained from composite (1:2), i.e 8.29%, while for composites (1:1) and (2:1) each of 6.82% and 5.35%. Optimal time is obtained at 60 minutes for each composite. In dark conditions no photodegradation process occurs, only the adsorption process that is influenced by the content of zeolite in the composite. Under UV light irradiation conditions, degradation percentage of procion red is much better. This is due to the photodegradation process of the ZnO catalysts contained in the composite. The highest value obtained from the composite (2:1), i.e 73.08%, while the composite (1:2) and (1:1) were 55.01% and 47.43% respectively with an optimum time of 120 minutes. In the case of irradiation with sunlight, it has the same pattern as UV light irradiation, but the degradation percentage of procion red is better than UV light irradiation, because sunlight has greater light intensity and wavelength compared to UV lamps so that the absorption of photon energy by composite more optimal. The highest degradation was obtained by using composite (2:1), i.e 83,96% while composite (1:2) and (1:1) were 62,03% and 59,05% respectively with optimum exposure time 120 minutes.

4 Conclusion

ZnO powder and activated zeolite were successfully impregnated with various compositions of ZnO-zeolite (1:2), (1:1) and (2:1) according to composite characterization test using SEM-EDX. Degradation of procion red in darkroom condition is influenced by zeolites that can adsorb dyes, whereas ZnO does not occur photodegradation process. The optimum condition was obtained at composite (1:2), i.e 8.29% in 60 min. Degradation of procion red under UV light and sunlight conditions are more influenced by the presence of ZnO as the photocatalyst. The optimum condition was obtained at composite of (2:1), i.e 73,08% for UV light irradiation and 83,96% for sunlight irradiation with the optimum contact time of 120 min.

Acknowledgment

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