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ZNO-ZEOLITE NANOCOMPOSITE APPLICATION FOR PHOTOCATALYTIC DEGRADATION OF PROCION RED AND ITS ADSORPTION ISOTHERM

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Abstract. In this paper, the photocatalytic degradation of procion red dye, one of the most frequently used dyes in the textile industry, was studied. The objective of the research is to study the ZnO-Zeolite nanocomposite application to degrade procion red dye by using different irradiation sources. The adsorption isotherm was also investigated. The ZnO-Zeolite nanocomposite was prepared by a sol-gel process. Photodegradation test was applied under the sunlight irradiation, ultraviolet (UV) lamp, and in a darkroom. The dye degradation was also examined by the synthetic zeolite and ZnO for a comparison. Another objective of this study is to analyse the appropriate adsorption isotherm to describe the degradation process of procion red dye by using ZnO-Zeolite nanocomposite. The adsorption ability of the nanocomposite was described by Langmuir and Freundlich isotherms. The adsorption of the nanocomposite was reported to depend on the degradation time. The highest photodegradation result of 98.24 % was achieved by irradiating 50 mg/l of procion red dye under the sunlight for 120 minutes. The result showed that the Langmuir adsorption isotherm was the appropriate adsorption equation for the degradation process of procion red dye by using ZnO-Zeolite nanocomposite with R^2 value of 0.995.

Keywords: Nanocomposite, ZnO, zeolite, adsorption isotherm, photocatalytic degradation, procion red.

1. Introduction

The growing textile industry, in addition to producing commercial products, also produces byproducts in the form of dye wastewater. Procion red is one of most often used synthetic dye that is hard to decompose and is present in the wastewater. One of the most important aspects of water treatment technology is the process to remove the organic compounds in the wastewater [1]. Based on previous research, there are several conventional methods used to degrade textile dye wastewater. However, the photodegradation process and the use of photocatalyst is the best and most suitable method for wastewater treatment.

The photocatalytic oxidation process combines UV irradiation with a catalyst; TiO_2, CdS, ZnO [2]. The photocatalytic reaction produces hydroxyl radicals as an oxidator to break down the pollutant gradually in a stepwise process [3]. ZnO is the most suitable and is often used as a photocatatalyst [4]. In photocatalytic applications, semiconductor ZnO is cheaper than the other nanosized metal oxides and ZnO is also better due to its environmental stability. The adsorption capacity of the photocatalyst is still weak, and the combination of photocatalyst and adsorbents will solve this problem [5].

This combination is carried out in order to maximize the dye pollutants' contact with photocatalysts [6]. The adsorbent used also does not need to be regenerated because the photocatalyst will immediately degrade the pollutants that have been absorbed in the adsorbent in situ so that the adsorbent is not easily saturated.

Zeolite has good adsorption properties and has a large surface, so it is used as an adsorbent and helps the adsorption-catalytic process [7]. The activation of zeolite aims to increase its purity [8]. However, synthetic zeolite, which has physical properties is much better than natural zeolite; the pore size of the synthetic zeolite is uniform, and it maximizes the adsorption results. This is the basis for selecting the synthetic zeolite adsorbents to be combined with the ZnO photocatalysts.

The zeolite adsorbent also has a good adsorption ability. The adsorption capacity can be determined by the adsorption isotherm equation, generally by the Freundlich or Langmuir equation [9]. Among the several adsorption isotherms, the equations proposed by Freundlich and Langmuir are most frequently used and are very useful for a mathematical description of adsorption from aqueous solutions [10].

Therefore, this study will use the photodegradation process as a method of removal of red procion textile colour substances using composites consisting of photocatalyst ZnO and synthetic zeolite adsorbent.

In this study, the sol-gel process is used for the formation of ZnO-Zeolite nanocomposites, the process will produce metal oxides using alcohol or water [11]. Based on several researches that have been carried out, the ZnO-Zeolite nanocomposite was applied for the photodegradation process of procion red dye, and the effect of the irradiation source in the photodegradation process should also be seen.

Therefore, in this study, the determination of the adsorption isotherm that is suitable for the degradation process of the procion red dye by using ZnO-Zeolite nanocomposites was also considered, to study the adsorption mechanism and the interaction between the adsorbent and the absorbed substance, and to determine the maximum adsorption capacity [12].

2. Materials and methods

Zinc acetate, zinc oxide, ethanol, NaOH, and HCl were obtained from Sigma Aldrich and synthetic procion red powder dye was obtained from dyestuff store (Fajar Setia, Jakarta). Commercial synthetic zeolite of A-Type ($Na_2O.Al_2O_3.2SiO_2.4.5H_2O$) was purchased from PT. Phy edumedia, East Java.

Synthetic zeolites with a 400 mesh size have been activated by heating in oven at 110 °C for 2 hours, then washed with 0.4 M HCl for 60 minutes, and finally, washed with distilled water. The synthetic zeolite was dried in an oven at 110 °C for 2 hours [13].

2.1. Synthesys and characterisation of ZnO-Zeolite nanocomposite

ZnO-synthesis zeolite nanocomposite is produced by sol-gel method, as referred to in [13]. The reason for using the precursor weight of Zinc acetate and zeolite 2:1 is because the ratio produces the highest degradation of colour substances, as it was discovered in previous research [14] which has also compared the influence of ZnO and zeolite photocatalyst ratios and the 2:1 weight ratio is the best ratio.

Zinc acetate as precursor is added with active synthetic zeolite in the precursor and synthetic zeolite ratio of 2:1, then dissolved in 80 ml of 99 % ethanol. The precursor and zeolite mixture was heated in a reflux flask to 76 °C for 2 hours. Then, 225 ml of 2 M NaOH was added to the solution and stirred for 60 minutes. The mixture was stood for 12 hours and then it was filtered. Next, the precipitate obtained was heated at 60 °C for 24 hours and then stored in a desiccator to keep it dry [13]. The ZnO-Zeolite nanocomposites were analysed by SEM-EDX, BET, and XRD.

2.2. ZnO-Zeolite nanocomposite application for photocatalytic degradation

ZnO-Zeolite nanocomposite have been tested for the degradation of 50 mg/l of procion red dye. Dye photodegradation was applied in three ways, by using sunlight, ultraviolet (UV) lamp and dark conditions. The use of only zeolite and only ZnO was also tested for the photodegradation process. Before the degradation process, the maximum wavelength of procion red solution was measured. A 100 mg of ZnO-Zeolite nanocomposite, mixed with 25 ml of 50 mg/l procion red, was stirred and placed directly under the sun. Experiments using sunlight were carried out at noon between 11.00 am–1.00 pm. The light intensity at that time was measured by a luxmeter.

Samples were tested in several time variations from 5–120 minutes; first, they were filtered and then the colour degradation was analysed. The experiments were also carried out with ultraviolet light irradiation [14] by using UV lamp (Evaco 254 nm) and in dark conditions. The experiments in dark conditions were carried out without turning on the UV lamp and closing the reactor using a black plastic coated box.

The final dye's absorbance and dye's concentration were measured by using a UV-Vis spectrophotometer. The maximum wavelength of procion red solution is 470 nm. The degradation percentage of procion dye and the adsorption percentage formulas are shown in Equations (1) and (2).

$$Degradation\ Percentage = \frac{A_0 - A_1}{A_0} \times 100\,\% \quad (1)$$

Equation (1) explains how to find the dye degradation percentage, A_0 is the value of the initial absorbance of the dye and A_1 is the value of the final absorbance.

$$Adsorption\ Percentage = \frac{C_0 - C_1}{C_0} \times 100\,\% \quad (2)$$

Equation (2) shows the adsorption percentage calculation, C_0 is the value of the initial concentration of the dye and C_1 is the value of the final concentration.

2.3. Determination of ZnO-Zeolite nanocomposite adsorption isotherm type

The adsorption process in dark conditions with ZnO-Zeolite nanocomposite provides data on the photodegradation results of procion red dye in the form of adsorption values and the final concentration of the dye. The data analysis weas performed by determining the final content of the procion red dye after the adsorption process.

Calculations of the Langmuir and Freundlich equations are carried out to determine the pattern or type of adsorption isotherm suitable for the absorption process of procion red dye by ZnO-Zeolite nanocomposites. The calculation results of each type will be plotted on the graph, and the most suitable ZnO-Zeolite nanocomposite adsorption isotherm will be

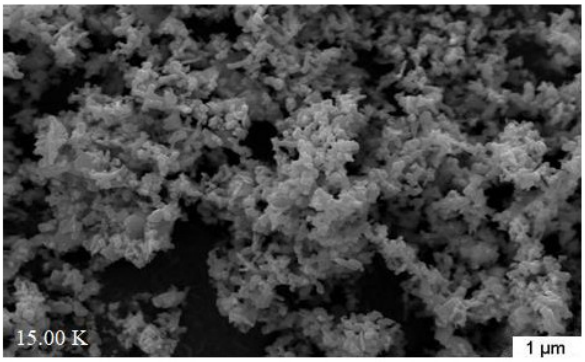

Figure 1. SEM image of ZnO.

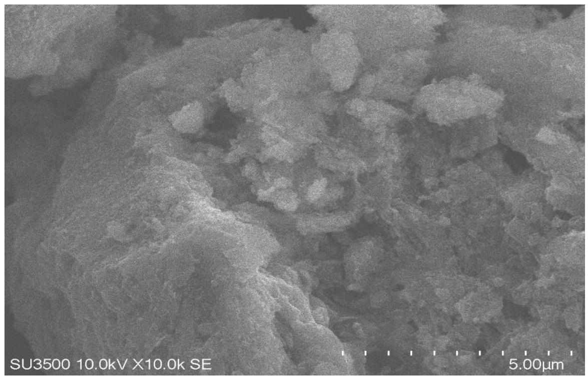

Figure 2. SEM image of Activated Synthetic Zeolite.

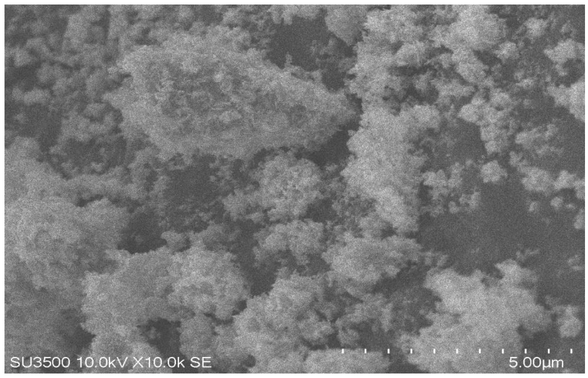

Figure 3. SEM image of ZnO-Zeolite nanocomposite.

determined. A good linearization of the line on the graph and the coefficient of determination $R^2 \geq 0.9$ (close to 1) are parameters for determining the corresponding adsorption isotherm equation to describe the degradation process of procion red dye using the ZnO-Zeolite nanocomposite.

The Langmuir isotherm model in Equation (3) assumes that a single particle will be adsorbed by each site and a monolayer on the surface of adsorbent will be formed by the adsorbate,

$$\frac{C_e}{q_e} = \frac{1}{a.b} + \frac{1}{a}C_e. \tag{3}$$

The Freundlich isotherm in Equation (4) explains the adsorption on heterogeneous surfaces and microporous adsorbent [2].

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{4}$$

3. Results and discussion

3.1. ZnO-Zeolite nanocomposite characters

Figure 1 shows the SEM image of ZnO with a magnification of 15 000. The image shows a uniform distribution of the particle shape. Figure 2 presents the SEM image of activated synthetic zeolite with a magnification of 10 000. The active synthetic zeolite has a smoother structure and has a more regular shape and size than before the activation process. The EDX results of ZnO-Zeolite nanocomposites showed that ZnO and zeolite components are present in the ZnO-Zeolite nanocomposite with a Zn content of 56.13 % and an oxygen content of 22.42 % weight percent. The other components are carbon content of 12.61 %, aluminium of 2.75 % and silica of 6.09 % weight percent [13]. The silica and aluminium contents indicate the presence of zeolite in the nanocomposites. SEM image result of the nanocomposite, with a magnification of 10 000, is showed in Figure 3. The nanocomposite particle distribution and particle size look smooth and uniform.

Based on a previous study, the surface area of the nanocomposite that consists of ZnO and synthetic zeolite also has a significant impact on the photodegradation process. The results of BET characterisation showed that the surface area of the activated synthetic zeolite was 47.192 m^2/g, for ZnO, it was 19.192 m^2/g, and for ZnO-Zeolite nanocomposite, it was 95.981 m^2/g. The ZnO-Zeolite nanocomposite has the highest surface area. These BET results have also been discussed in previous research by [13].

The XRD of ZnO-Zeolite nanocomposite confirmed and proved that the nanocomposite consisted of zinc oxide (ZnO) and synthetic zeolite components as shown in Figure 4. The XRD pattern of the nanocomposite shows the diffraction peaks at 2θ of 31.43°, 34.51°, 36.37°, and 54.99° that are identical to hexagonal ZnO peaks [15]. The other peaks found at $2\theta=$ 10.01°, 22.12°, 26.11°, and 29.98°, represent the presence of synthetic zeolite [16], [13].

3.2. The photodegradation results of procion red

Overall, the highest dye photodegradation was achieved by using the ZnO-Zeolite nanocomposite for the longest time period of 12 minutes. Research by [17] showed similar results where ZnO photocatalysts with natural zeolites were the most effective and resulted in the highest degradation of dyes. The percentage rate of dye removal increases by increasing the time up to 120 minutes, because the nanocomposite has a high photocatalytic activity and produces more hydroxyl radicals to degrade the dye, moreover, the

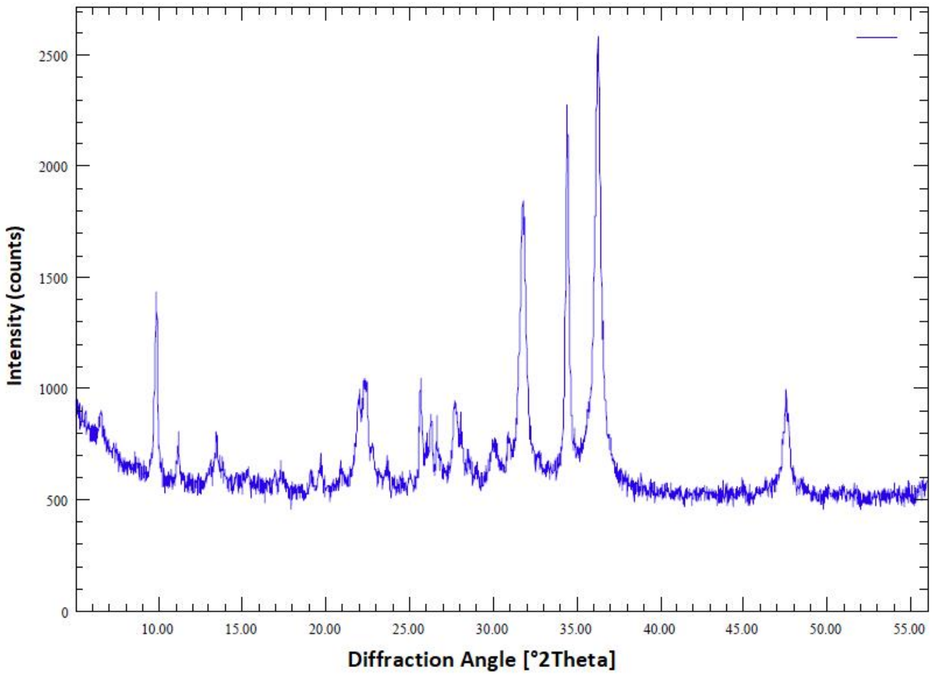

Figure 4. XRD of ZnO-Zeolite nanocomposite.

ZnO photocatalysts will directly degrade pollutants on the surface of the zeolite adsorbent.

The photodegradation process was applied by using three different materials in different irradiation conditions. Figures 5–7 below shows a graph comparing the decrease in the procion red dye concentration by using nanocomposite of ZnO-Zeolite, ZnO, and synthetic zeolite under three different exposure conditions, the sunlight, UV light, and in dark conditions.

The results of the photodegradation using nanocomposite and ZnO under the sunlight showed the highest photodegradation percentage of procion red as compared to the photodegradation application under the UV light and dark conditions. As shown in Figure 5, the procion red dye showed the highest degradation rate by using nanocomposites under the sunlight.

During 5 minutes of degradation by using nanocomposites, the concentration of procion red dye under sunlight has decreased by 24.5 %, by 18 % under the UV lamps, and in the dark conditions, the concentration decreased by 17 %. During 15, 25 and 30 minutes of degradation, it was seen that the degradation of procion red under the UV light was higher than that of sunlight, this was due to the intensity of sunlight that was changing over the time, due to this, it was possible that the sun's intensity was decreasing or lower so the removal of colour substances also decreased.

After degrading under the sunlight for 30 minutes, the percentage of degradation was 70 % and had reached 91 % at 60 minutes of degradation. Degradation under the sunlight for 120 minutes resulted in the highest percentage of degradation of procion red, 98.24 %, meanwhile, in the case of the UV lamp, the degradation percentage was 90.42 %. The lowest degradation percentage of only 28.56 % was obtained in the dark conditions. As can be seen in the Figure 5, the degradation of procion red in the dark conditions by using ZnO-Zeolite nanocomposite showed no significant increase after 60 minutes, indicating the possibility that the zeolite adsorbent could have become saturated over time.

Degradation by using only ZnO also showed a similar result. Based on Figure 6, it can be noticed that the highest decrease in procion red concentration was obtained with radiation from the sunlight. However, for 20, 25, and 30 minutes, the UV lamp degradation shows higher results than under the sunlight, this is also due to the intensity of sunlight, which is not constant changes over time and at that time, the intensity of sunlight was low, thus reducing the degradation process. For 120 minutes, the percent degradation of procion red under the sun has reached 97.65 %, for UV lamp, it reached 80.64 %, and in the dark conditions it was still low, only 35.57 %.

ZnO-Zeolite nanocomposite and ZnO can decompose procion red dye using either a direct exposure to the sunlight or by using the UV lamp. This is because the ZnO-Zeolite nanocomposite and ZnO only, work based on the photocatalytic mechanism. These results are also reported from the research conducted by [18], which states that the differences in light sources also have an impact on the photocatalytic process. The photocatalytic process occurs under ultraviolet light (UV lamp) and the sun as the light source.

The sunlight can produce the highest percentage of degradation because the intensity of the light produced is very high. The sun's intensity is much greater than the UV rays. Energy from the sunlight produces the highest percentage not because it is better than

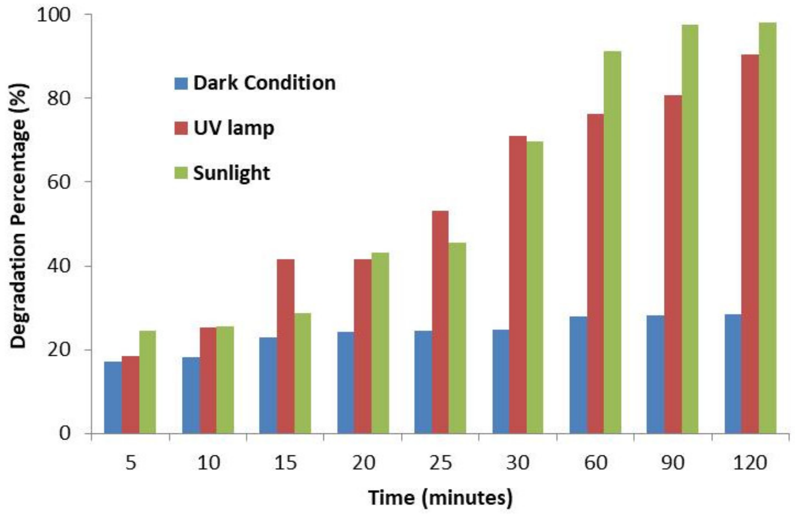

Figure 5. Effect of irradiation sources on degradation percentage of 50 mg/l procion red by using ZnO-Zeolite nanocomposite.

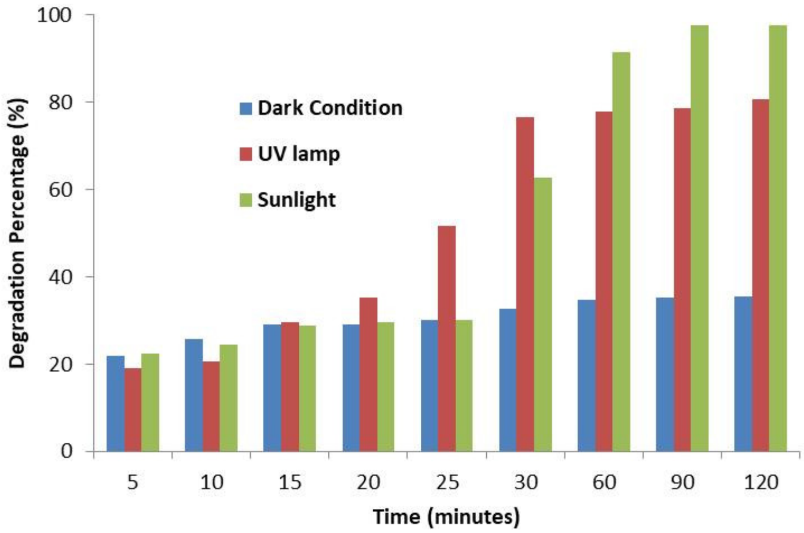

Figure 6. Effect of irradiation sources on degradation percentage of 50 mg/l procion red by using only ZnO.

the UV light, but because the energy from the sunlight is much higher than from the UV light installed in the reactor. The wavelength of sunlight is polychromatic, the sunlight has a wide range of wavelengths from ultraviolet light to infrared light, while the UV light is monochromatic, meaning that the range of wavelengths is narrower.

The photocatalytic process is yields better results using sunlight as a light source as compared to UV lamps. This is due to the fact that the sunlight has more energy than ultraviolet light, meaning a higher electron excitation takes place [18]. The sunlight has a greater light intensity than the UV light. The sunlight also has a wider wavelength, resulting in the highest reduction in dye concentration [17].

Research by [2] also reached similar results, namely that the percentage of dye degradation in the sunlight was higher than for the ultraviolet light, or the conditions without any light. The greater the sunlight intensity, the easier the photocatalytic process runs, so the percentage of dye degradation will be higher as well. The sunlight causes an even greater rate of decomposition of the dye. Electrons can be excited to a higher energy level due to the energy emitted by light both by sunlight and UV rays [19].

In this study, photodegradation was carried out between 11.00 am–1.00 pm, during hot conditions, or when the measurement results of light intensity by the luxmeter are very high. In that time frame, the highest light intensity measurement results were obtained, around or more than 100 000 lux. The results have shown that the highest average light intensity is at 12.00 am–1.00 pm. The large number of active photocatalysts exposed to visible light enhances the formation of hydroxyl radicals for the photodegradation process [20].

The photodegradation mechanism of sunlight and UV rays is different, the percentage degradation of

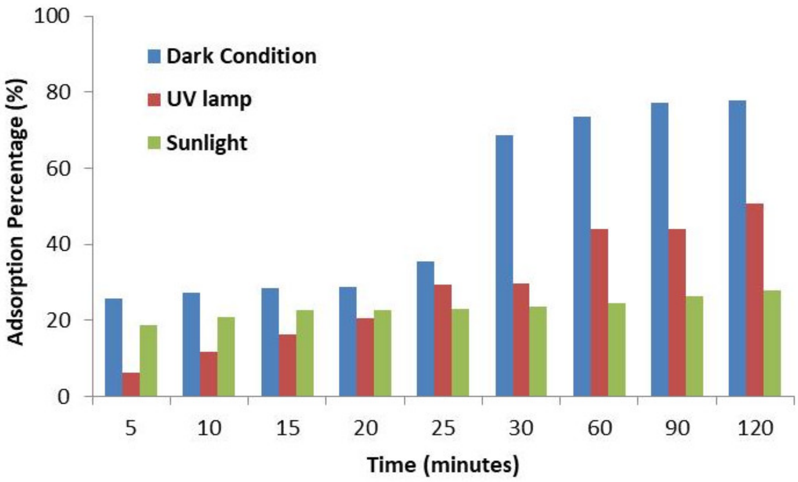

Figure 7. Effect of irradiation on adsorption percentage of 50 mg/l procion red by using synthetic zeolite.

the sun is higher than that of UV light. The sunlight provides a lot of visible light irradiation and its photodegradation uses the ultraviolet light mechanism and the visible light mechanism, whereas the UV light only uses the ultraviolet light mechanism [21]. Photon energy from the UV light makes the percentage of degradation increase, this is also due to the excitation of electrons and the formation of hydroxyl radicals.

The results of degradation in dark condition are not significant, because in dark conditions, there are no photons that can activate the ZnO or ZnO-Zeolite nanocomposite, so there were no hydroxyl radicals formed which are strong oxidizers for the photodegradation process of procion red. When it is dark, the degradation process happens only due to the entrapment process carried out by zeolite particles.

In dark conditions, there is no light that will help the ZnO photocatalysts to produce hydroxyl radicals that can degrade dyes, so the photocatalytic process does not run optimally, this is the reason why the degradation results of using nanocomposite and ZnO in the dark conditions are so unsatisfying. The ZnO-Zeolite nanocomposite can still degrade procion red dye even in dark conditions due to the dye adsorption process carried out by synthetic zeolite, but the results are still not optimal because they are not assisted by the ZnO photocatalytic process.

In the ZnO-Zeolite nanocomposite degradation, the ZnO photocatalyst plays a more important role as well, because in terms of its sustainability, the catalyst can be used continuously, and its sustainability is more guaranteed than that of the adsorbent. When using zeolite adsorbent, after the dye is absorbed, the adsorbate can become saturated and can no longer serve as an adsorbent. A longer degradation time will result in the zeolite getting saturated and the semiconductor photocatalyst ZnO itself then becomes responsible for the degradation of the dye.

Figure 7 shows the effect of irradiation on the adsorption percentage of procion red dye by using only synthetic zeolite. The adsorption of procion red showed that the highest yield was obtained in dark conditions. Meanwhile, the percentage of dye removal by using UV lamp and under the sunlight were 29.73 % and 23.74 %, respectively.

After 120 minutes, the adsorption in dark conditions reached an adsorption percentage of 78 %, 50.64 % for the UV lamp, and 27.91 % for the sun. After 90 minutes, the percent adsorption by synthetic zeolite did not increase anymore, this was due to the adsorption process of procion dye was only made by synthetic zeolite adsorbent, so which could have become saturated.

The adsorption percentage by using the synthetic zeolite under the sunlight and the UV light is lower than in the dark conditions because the adsorption process of procion red dye, unlike in the case of ZnO and nanocomposites, works based on the photocatalytic method that requires the light. The dye concentration decreasing was due to the adsorption process of the dye by the synthetic zeolite. The adsorption percentage by using the synthetic zeolite is quite low due to the fact that the adsorption process is only made by the zeolite adsorbent, for which the adsorption process occurs only at the surface. Meaning the larger the surface area of the zeolite is, the more dye is adsorbed [22].

The ZnO-Zeolite nanocomposite gave the highest photodegradation percentage as compared to using ZnO and synthetic zeolite, this is because they not only use the dye adsorption process by synthetic zeolite, but are also aided by the ZnO semiconductor presence in the ZnO-Zeolite nanocomposite. The effect of zeolite is also increased under the sunlight or UV light.

3.3. Types of adsorption isotherm for degradation of ZnO-Zeolite nanocomposite

The adsorption process carried out in dark conditions by using ZnO-Zeolite nanocomposite provided data

	C_e [mg/l]	q_e	$\ln q_e$	$\ln C_e$	C_e/q_e
50	33.56	4.11	1.41	3.51	8.18
100	81.31	4.67	1.54	4.44	18.21
150	128.12	5.47	1.69	4.91	24.77
200	176.53	5.87	1.77	5.24	32.14
250	227.25	5.69	1.73	5.47	41.69

TABLE 1. Calculation of the values of q_e, C_e/q_e, $\ln q_e$, and $\ln C_e$ for Freundlich and Langmuir Isotherms.

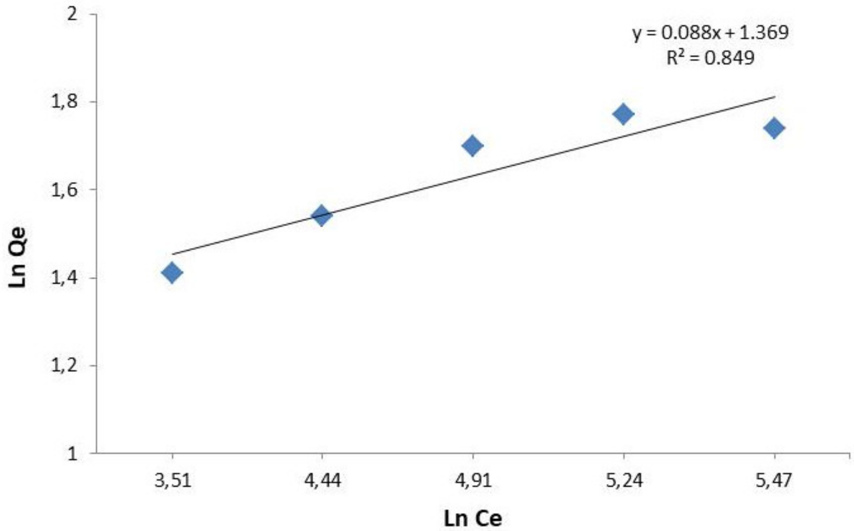

FIGURE 8. Freundlich Isotherm Graph.

on the degradation results of the procion red dye in the form of the adsorption value and the final concentration of the dye. Experiments in dark conditions were carried out without turning on the UV lamp and closing the reactor using a black plastic coated box.

The interaction between the adsorbent and the adsorbate was described in several types of adsorption isotherms. This adsorption isotherm will show the maximum capacity of the adsorbent [23]. The results were then analysed using the adsorption isotherm equation. The suitable type of adsorption isotherm for the adsorption process of procion red dye by ZnO-Zeolite nanocomposite was determined using the Langmuir and Freundlich equations. These equations are very well known and applicable [23].

In wastewater treatment, Freundlich and Langmuir isotherm equations are the most used. The calculation results of each type were plotted on the graph and the most suitable ZnO-Zeolite nanocomposite adsorption isotherm was be confirmed. The adsorption process of the adsorbent against the adsorbate and the maximum capacity of the adsorbent can be specified by determining the appropriate type of adsorption [24].

The adsorption process of ZnO-Zeolite nanocomposite was applied by varying the dye concentration during the degradation time of 60 minutes. The value of procion red dye concentration was set to 50, 100, 150, 200, and 250 mg/l.

The values of q_e, C_e/q_e, $\ln q_e$ and $\ln C_e$ were calculated to be included in the Langmuir and Freundlich isotherm equations and are presented in Table 1. The q_e value is obtained from the following Equation (5):

$$q_e = \frac{(C_0 - C_e) \times V}{W}. \tag{5}$$

Plotting the values for C_e/q_e and C_e will yield the Langmuir equation and plotting $\ln q_e$ versus $\ln C_e$ will yield the Freundlich equation.

3.4. FREUNDLICH ISOTHERM

A good linearization graph and the value of the coefficient of determination $R^2 \geq 0.9$ (close to 1) show the corresponding adsorption isotherm equation. Figure 8 demonstrates the relationship between $\ln q_e$ and $\ln C_e$ in the Freundlich isotherm equation. Based on the graph, an equation in the form of a linear equation $y = 0.088x + 1.369$ and the value of $R^2 = 0.849$ were obtained. The linear equation of the Freundlich isotherm graph fulfils Equation (6) and gives a constant K_f value of 3.933, a value of $1/n$ of 0.088 and an n value of 11.403.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \tag{6}$$

K and $1/n$ are Freundlich constants indicating the rate of adsorption and heterogeneity factors. Freundlich described a heterogeneous adsorption system.

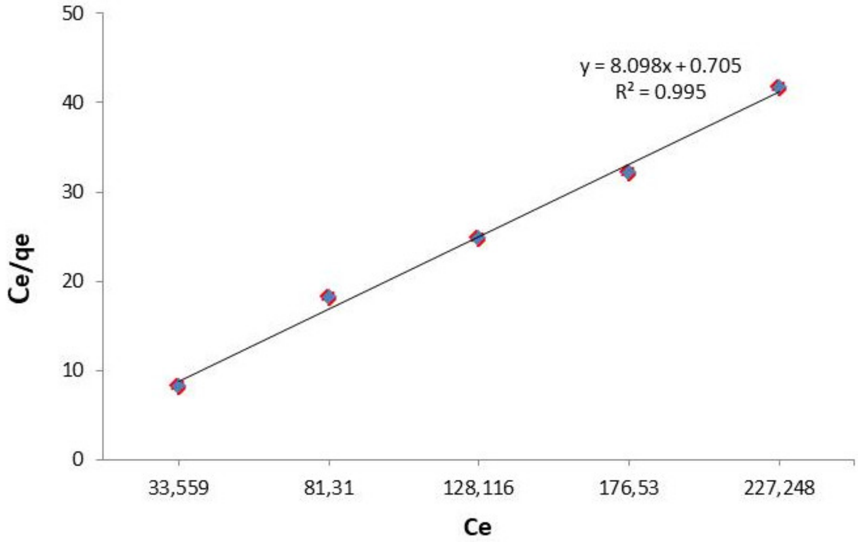

FIGURE 9. Langmuir Isotherm Graph.

The value of K_f (mg/g) also indicates the power or the maximum adsorption capacity of the material. The value of $1/n > 1$ explains that the saturation of the adsorbent is not achieved; on the contrary, when $1/n < 1$, the adsorbent has been saturated by the adsorbate molecules, this happens more in the adsorption system [24].

Isoterm Langmuir	Isoterm Freundlich
$R^2 = 0.995$	$R^2 = 0.849$
$b = 11.488\,\mathrm{L/mg}$	$n = 11.403$
$a = 0.124\,\mathrm{mg/g}$	$K_f = 3.933\,\mathrm{mg/g}$

TABLE 2. Adsorption Isotherm Parameters.

3.5. LANGMUIR ISOTHERM

The Langmuir isotherm equation is illustrated in Figure 9, which shows the C_e/q_e and C_e relationship curves for the Langmuir isotherm. The Langmuir graph produces the linear equation of $y = 8.098x + 0.705$ an $R^2 = 0.995$.

$$\frac{C_e}{q_e} = \frac{1}{a.b} + \frac{1}{a}C_e. \tag{7}$$

The linear equation of the Langmuir isotherm graph follows the Equation (7) and gives a constant value of b of 11.488 l/mg and a of 0.124 mg/g. The value of b is the Langmuir equilibrium constant or constant (l/mg) and the value of a is the maximum concentration value in the solid phase (mg/g), which can also indicate the maximum adsorption capacity of the material.

Table 2 shows the adsorption isotherm parameters for both types of adsorption isotherms. Based on the Langmuir and Freundlich graphs, the adsorption isotherm equation that is suitable for the process of degradation of the procion red dye with ZnO-Zeolite nanocomposites is the Langmuir adsorption equation with an R^2 value of 0.995, while the Freundlich isotherm equation does not meet the requirements, because the coefficient of determination R^2 is 0.849.

This is also similar to [2] research, where the dye adsorption isotherm pattern carried out by the ZnO-Zeolite composite follows the Langmuir isotherm, and from the graph, it can be seen that it produces a coefficient of determination R^2 that is close to 1 (0.94) as compared to the isotherm. Freundlich does not comply because the value of $R^2 = 0.1$. The research of [24] also conducted a similar study and obtained the highest correlation coefficient (R^2) value found in the Langmuir isotherm, this indicates that the adsorption of liquid waste follows a Langmuir isotherm approach.

This shows that the adsorption of procion red dye by using ZnO-Zeolite nanocomposite is more appropriate and in accordance with the Langmuir adsorption isotherm type, as evidenced by the value of the correlation coefficient (R^2) which is closer to 1 as compared to the Freundlich isotherm type, so it can be assumed that the adsorbed dye or adsorbates are adsorbed in a single form (monolayer) and the adsorption process of procion red dye by using ZnO-Zeolite nanocomposite is a homogeneous one. However, Freundlich isotherm type describes a multilayer adsorption process and involves more physical interactions [3].

4. CONCLUSIONS

Photodegradation application by using ZnO-Zeolite nanocomposite produced a higher decomposition percentage of the procion red dye under the sunlight as compared to UV light and in the dark condition. The highest degradation percentage was 98.24 % by irradiation under the sunlight for 120 minutes. The photodegradation process of procion red dye using the ZnO-Zeolite nanocomposite followed the Langmuir adsorption isotherm pattern with the linear equation $y = 8.098x + 0.705$, the coefficient of determination $R^2 = 0.995$, Langmuir constant value b of 11.488 l/mg, and a maximum adsorption capacity a of 0.124 mg/g.

List of symbols

C_e Equilibrium concentration [mg/l]
C_o Concentration of initial pollutants [mg/l]
q_m The adsorption capacity at maximum
q_e Amount of adsorbate at equilibrium [mg/g]
V Volume of sample [l]
W Adsorbent weight [g]
a Maximum adsorption capacity [mg/g]
b Langmuir constant
K_f, n Freundlich's empirical constant

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References

[1] P. Zawadzki, E. Kudlek, M. Dudziak. Kinetics of the photocatalytic decomposition of bisphenol a on modified photocatalysts. *Journal of Ecological Engineering* **19**(4):260–268, 2018. https://doi.org/10.12911/22998993/89651.

[2] P. Zawadzki, E. Kudlek, M. Dudziak. Titanium(IV) oxide modified with activated carbon and ultrasounds for caffeine photodegradation: Adsorption isotherm and kinetics study. *Journal of Ecological Engineering* **21**(8):137–145, 2020. https://doi.org/10.12911/22998993/126985.

[3] M. Ahda, S. Sutarno, E. S. Kunarti. Sintesis silika MCM-41 dan uji kapasitas adsorpsi terhadap metilen biru. *Pharmaciana* **3**(1), 2013. https://doi.org/10.12928/pharmaciana.v3i1.414.

[4] M. T. Adiwibowo, M. Ibadurrohman, Slamet. Synthesis of ZnO nanoparticles and their nanofluid stability in the presence of a palm oil-based primary alkyl sulphate surfactant for detergent application. *International Journal of Technology* **9**(2):307–316, 2018. https://doi.org/10.14716/ijtech.v9i2.1065.

[5] D. A. Wismayanti, N. P. Diantariani, S. R. Santi. Pembuatan komposit ZnO-arang aktif sebagai fotokatalis untuk mendegradasi zat warna metilen biru. *Jurnal Kimia (Journal of Chemistry)* **9**(1):109–116, 2015. https://doi.org/10.24843/JCHEM.2015.v09.i01.p18.

[6] S. Naimah, S. Ardhanie A., B. Jati, et al. Degradasi zat warna pada limbah cair industri tekstil dengan metode fotokatalitik menggunakan nanokomposit TiO_2 – Zeolit. *Jurnal Kimia dan Kemasan* **36**(2):225–236, 2014. https://doi.org/10.24817/jkk.v36i2.1889.

[7] M. O. Ruliza, T. E. Agustina, R. Mohadi. Impregnation of activated carbon-TiO_2 composite and its application in photodegradation of procion red synthetic dye in aqueous medium. *IOP Conference Series: Earth and Environmental Science* **105**:012024, 2018. https://doi.org/10.1088/1755-1315/105/1/012024.

[8] D. A. Wulandari, N. Nasruddin, E. Djubaedah. Selectivity of water adsorbent characteristic on natural zeolite in cooling application. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* **55**(1):111–118, 2020.

[9] Jasmal, Sulfikar, Ramlawati. Kapasitas adsorpsi arang aktif ijuk pohon aren (arenga pinnata) terhadap Pb^{2+}. *Sainsmat : Jurnal Ilmiah Ilmu Pengetahuan Alam* **4**(1):57–66, 2015. https://doi.org/10.35580/sainsmat4112842015.

[10] A. Puszkarewicz, J. Kaleta. Adsorption of chromium (VI) on raw and modified Carpathian diatomite. *Journal of Ecological Engineering* **20**(7):11–17, 2019. https://doi.org/10.12911/22998993/108640.

[11] P. Laokul, V. Amornkitbamrung, S. Seraphin, S. Maensiri. Characterization and magnetic properties of nanocrystalline $CuFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ powders prepared by the aloe vera extract solution. *Current Applied Physics* **11**(1):101–108, 2011. https://doi.org/10.1016/j.cap.2010.06.027.

[12] M. Murtihapsari, B. Mangallo, D. D. Handyani. Model isoterm Freundlich dan Langmuir oleh adsorben arang aktif bambu andong (G. Verticillata (Wild) Munro) dan bambu ater (G. Atter (Hassk) Kurz Ex Munro). *Jurnal Sains Natural* **2**(1):17–23, 2012. https://doi.org/10.31938/jsn.v2i1.31.

[13] R. Gayatri, T. E. Agustina, R. Moeksin, et al. Preparation and characterization of ZnO-Zeolite nanocomposite for photocatalytic degradation by ultraviolet light. *Journal of Ecological Engineering* **22**(2):178–186, 2021. https://doi.org/10.12911/22998993/131031.

[14] A. Salam, T. E. Agustina, R. Mohadi. Photocatalytic degradation of procion red synthetic dye using ZnO-Zeolite composites. *International Journal of Scientific & Technology Research* **7**(8):54–59, 2018.

[15] A. C. Mohan, B. Renjanadevi. Preparation of zinc oxide nanoparticles and its characterization using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). *Procedia Technology* **24**:761–766, 2016. https://doi.org/10.1016/j.protcy.2016.05.078.

[16] E. Nyankson, J. K. Efavi, A. Yaya, et al. Synthesis and characterisation of zeolite-A and Zn-exchanged zeolite-A based on natural aluminosilicates and their potential applications. *Cogent Engineering* **5**(1):1440480, 2018. https://doi.org/10.1080/23311916.2018.1440480.

[17] T. E. Agustina, E. Melwita, D. Bahrin, et al. Synthesis of nano-photocatalyst ZnO-natural zeolite to degrade procion red. *International Journal of Technology* **11**(3):472–481, 2020. https://doi.org/10.14716/ijtech.v11i3.3800.

[18] A. Rahman, M. Nurjayadi, R. Wartilah, et al. Enhanced activity of TiO_2/natural zeolite composite for degradation of methyl orange under visible light irradiation. *International Journal of Technology* **9**(6):1159–1167, 2018. https://doi.org/10.14716/ijtech.v9i6.2368.

[19] R. Fraditasari, S. Wardhani, M. M. Khunur. Degradasi methyl orange menggunakan fotokatalis TiO_2-N : Kajian pengaruh sinar dan konsentrasi TiO_2-N. *Jurnal Ilmu Kimia Universitas Brawijaya* **1**(1):606–612, 2015.

[20] A. Charanpahari, S. S. Umare, S. P. Gokhale, et al. Enhanced photocatalytic activity of multi-doped TiO_2 for the degradation of methyl orange. *Applied Catalysis A: General* **443-444**:96–102, 2012. https://doi.org/10.1016/j.apcata.2012.07.032.

[21] D. Windy Dwiasi, T. Setyaningtyas. Fotodegradasi zat warna tartrazin limbah cair industri mie menggunakan fotokatalis TiO_2 - sinar matahari. *Molekul* **9**(1):56–62, 2014. https://doi.org/10.20884/1.jm.2014.9.1.150.

[22] I. Kustiningsih, D. K. Sari. Uji adsorbsi zeolit alam bayah dan pengaruh sinar ultraviolet terhadap degradasi limbah methylene blue. *Teknika: Jurnal Sains dan Teknologi* **13**(1):25–32, 2017.

[23] M. Ghosh, K. Manoli, X. Shen, et al. Solar photocatalytic degradation of caffeine with titanium dioxide and zinc oxide nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry* **377**:1–7, 2019. https://doi.org/10.1016/j.jphotochem.2019.03.029.

[24] D. Darmansyah, S. Ginting, L. Ardiana, H. Saputra. Mesopori MCM-41 sebagai adsorben: Kajian kinetika dan isotherm adsorpsi limbah cair tapioka. *Jurnal Rekayasa Kimia & Lingkungan* **11**(1):10–16, 2016. https://doi.org/10.23955/rkl.v11i1.4228.