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Article

Modification of ZnO/Perlite for Methylene Blue Photodegradation

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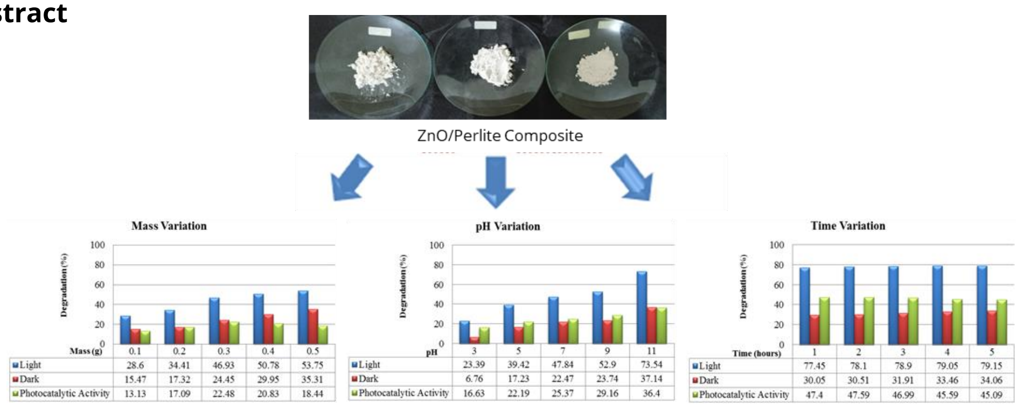
Abstract

Waste disposal in the growing industry causes pollution caused by pollutants. One of them is liquid waste from the textile industry which contains toxic dyes such as methylene blue which is difficult to decompose in the environment. Therefore, efforts are needed to overcome these problems by using photocatalysis. Photocatalyst materials that are often used are semiconducting metal oxides such as ZnO. However, ZnO semiconductors still have limitations in their application. To overcome these limitations, the ZnO catalyst will be modified with supporting materials such as perlite which is a lightweight and porous material. The synthesis method used in this research is impregnation. Impregnation is one of the methods in catalyst preparation which is done by adsorbing the active component of the metal in solution to the solid of the carrier. The purpose is to fill the pores of the carrier with a metal salt solution of a certain concentration. This research aims to test the effectiveness of ZnO/Perlite in degrading methylene blue. ZnO/Perlite composite with 20% composition showed the highest photocatalytic activity compared to ZnO/Perlite composite with 10% and 30% composition. The optimum condition of 20% ZnO/Perlite in degrading methylene blue was achieved at a mass of 0.3 g under pH 11 conditions, and stirring for 2 hr with ultraviolet light irradiation, and produced a photocatalytic activity of 47.59% and combined adsorption and photocatalytic activity of 78.1%. XRD analysis shows the characteristic wurtzite-structured ZnO crystal peaks at (100), (002), (101), (102), (110), (103), and (112), while the 2θ diffraction angle (10°−30°) indicates the amorphous nature of perlite. DRS results show 20% ZnO/Perlite which has a band gap value of 3.21 eV.

Keywords: *: Floating photocatalyst, Semiconductor, Methylene blue; ZnO/Perlite*

Graphical Abstract



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Introduction

Waste disposal in the growing industry causes pollution by various kinds of pollutants that are harmful to organisms and the environment. One of the pollutants that pollute the environment is liquid waste from the textile industry which still contains various dyes that have toxic effects on humans [1]. Textile dyes usually use synthetic dyes, one example is methylene blue which is often used in the textile industry. Figure 1 shows the structure of methylene blue which is a type of cationic heterocyclic aromatic complex compound that has a benzene structure that is difficult to break down in the environment [2]. Therefore, it is necessary to make an effort to overcome the problem of dye waste pollution.

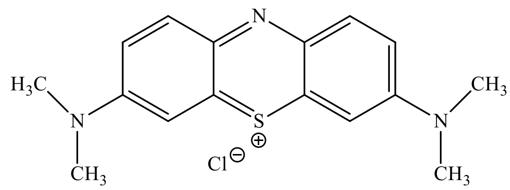


Figure 1. Chemical structure of methylene blue [3]

One way that can be done to overcome dye waste is by using photocatalysis. Photocatalyst materials have the ability to degrade organic compounds and pollutants contained in industrial wastewater. A photocatalyst material is able to accelerate the rate of oxidation and reduction reactions through photochemical reactions. Photocatalyst materials that are often used are metal oxide semiconductor materials [4]. Examples of metal oxide semiconductor materials include TiO_2, CuO, ZnO and Fe_2O_3. In this study, ZnO received great attention because of its role as a photocatalyst so that it can be applied to the dye photodegradation process.

Research by Bemis et al. [5] has proven that ZnO photocatalyst modified with activated carbon can degrade rhodamine B dye by 86.838%. Although modified ZnO semiconductor is widely used for its high photocatalytic activity, non-toxicity and cheapness, current interest is much more focused on the synthesis of new photocatalysts to overcome its limitations in applications. Some of those limitations are modified ZnO is always in powder form, it always sinks or gets suspended into the solution which decreases the light utilization rate, ZnO powders are difficult to recycle, easily agglomerate, and cause separation problems from the solution. To overcome these limitations, much attention has been paid to developing modified ZnO catalysts [6].

Recently, several studies have developed a new concept of "floating photocatalyst" which is a photocatalyst synthesized on the surface of a floatable substrate. One of the substrates that can float and can be used as a supporting material for ZnO catalysts is perlite. Perlite is a lightweight and porous material that is expected to increase adsorption power. In addition, perlite also has the ability as a floating substrate that can overcome the problem of separation in photocatalyst results so that it is expected to increase the photocatalytic activity of ZnO. Research by Ngaha et al. [7] has proven that TiO_2 photocatalyst supported with perlite is able to degrade thiamethoxam in aqueous solution by 87% for 270 minutes. Therefore, in this study, ZnO photocatalyst is used which will be modified with perlite so that it can be applied to the degradation of methylene blue dye.

Material and Methods

Materials and Instrumentations

Perlite, methylene blue, distilled water (ddH_2O), ZnO powder, ethanol (C_2H_5OH) absolute for analysis, nitric acid (HNO_3) 1 M, hydrochloric acid (HCl) 1 M, and sodium hydroxide (NaOH) 1 M. Spectrophotometer UV-Vis type UV-1601 SHIMADZU, X-Ray Diffration (XRD) type PANalytical Xpert MPD, and Diffuse Reflectance Spectroscopy (DRS) type Perkin Elmer UV-Vis Lambda 365.

Methods

Preparation of Pertile. Perlite preparation refers to research [8]. The perlite was weighed as much as 50 g then washed with 1 L of distilled water and stirred for 12 hr at room temperature with the help of a magnetic strirrer. Furthermore, perlite was filtered using filter paper with the help of a vacuum pump. After that, the filtered perlite was dried in an oven at 105ºC for 8 hr. After the perlite is dry, it is sieved using a 120-mesh sieve and the sieve results are stored in a polypropylene container.

Synthesis and Activation of ZnO/Perlite Composite. The synthesis of ZnO/Perlite composites refers to research [8]. ZnO/Perlite composites will be synthesized with 10, 20 and 30% composition. The synthesis was carried out by dispersing ZnO powder in ethanol. Then HNO_3 with pH 3.5 was added to the solution. Furthermore, the solution was sonicated for 15 min, then stirred using a magnetic stirrer for 30 min, in the process added perlite that has been prepared in the previous stage gradually as much as 10 g. After that, the mixture obtained was filtered using a magnetic stirrer. After that, the mixture obtained was filtered and allowed to evaporate at room temperature for 20 min to evaporate excess ethanol. Furthermore, the results of the filtration process were calcined at 450 ^oC for 30 min using a furnace. After that, the powder obtained was cooled and washed using distilled water. Then the results obtained were dehydrated at 120^oC in the oven for 24 hr, after the synthesis results were obtained, they were immediately packaged and stored in polypropylene containers. To synthesize 10, 20 and 30% ZnO/Perlite composites require 1, 2 and 3 g of ZnO powder. Ethanol required 36, 72 and 108 mL, while HNO_3 required 3, 6 and 9 mL..

Determination of The Maximum Wavelength of Methylene Blue. Determination of the maximum wavelength is done by measuring the absorbance of methylene blue solution. The first step is to make a standard solution of methylene blue 1000 ppm from methylene blue powder dissolved in 100 mL of distilled water. Then made a standard solution of methylene blue with a concentration variation of 0; 0.5; 1.0; 1.5; 2.0; 2.5 and 3.0 ppm by diluting the standard solution of methylene blue 1000 ppm. Methylene blue standard solution with a concentration of 3.0 ppm was measured for absorbance in the range of 400 – 800 nm. The wavelength with the highest absorbance will be used in this study.

Determination of Methylene Blue Calibration Curve. The calibration curve is made by plotting between the concentration (x) and absorbance (y) so as to obtain a linear regression equation y = bx + a. The value of "a" shows the constant or cut-off point of y, while the value of "b" shows the coefficient of regression. This regression equation will be used to determine the concentration of the degraded methylene blue sample. The process of making a calibration curve is done by measuring the absorbance of the methylene blue standard solution with a concentration variation of 0; 0.5; 1.0; 1.5; 2.0; 2.5 and 3.0 ppm using a UV-Vis spectrophotometer at the maximum wavelength.

Determination of Optimum Mass of ZnO/Perlite Composite. ZnO/Perlite that has been synthesized with different compositions, each weighed with a mass variation of 0.1; 0.2; 0.3; 0.4; and 0.5 g. Then put into an erlenmyer containing 50 mL of methylene blue solution with a concentration of 10 ppm. Furthermore, the solution was stirred using a magnetic stirrer for 5 hr with each in the dark and in a state illuminated by an ultraviolet lamp with a power of 20 Watts. Then the suspension was centrifuged at 3000 rpm for 15 minutes and the supernatant obtained was measured for absorbance with a UV-Vis spectrophotometer at the maximum wavelength of methylene blue. Then the percentage value of degradation for each treatment was calculated. The following formula was used to calculate the percentage degradation value (Equation 1).

$$\%D = \frac{C_o - C}{C_o} \times 100\% \quad \text{..(1)}$$

Description:
%D = Percent degradation
C_O = Initial concentration of methylene blue
C = Methylene blue concentration at t hr

Determination of Optimum pH of ZnO/Perlite Composite. ZnO/Perlite was put into an erlenmyer containing 50 mL of methylene blue solution with a concentration of 10 ppm using the optimum mass on the composite that has the highest photocatalytic work activity. Furthermore, HCl or NaOH solution was added to adjust the pH point with pH variations of 3, 5, 7, 9, and 11. Then the solution was stirred using a magnetic stirrer for 5 hr with each in the dark and in a state illuminated by an ultraviolet lamp with a power of 20 Watts. Then the suspension was centrifuged at 3000 rpm for 15 min and the supernatant obtained was measured for absorbance with a UV-Vis spectrophotometer at the maximum wavelength of methylene blue. Then the percentage value of degradation was calculated according to formula (1) for each treatment.

Determination of Optimum Time of ZnO/Perlite Composite. ZnO/Perlite was put into an erlenmyer containing 50 mL of methylene blue solution with a concentration of 10 ppm using the optimum mass on the composite that has the highest photocatalytic work activity and optimum pH conditions. Furthermore, the solution was stirred using a magnetic stirrer with each in the dark and in a state illuminated by an ultraviolet lamp with a power of 20 Watts for a time variation of 1, 2, 3, 4, and 5 hr. Then the suspension was centrifuged at 3000 rpm for 15 minutes and the supernatant obtained was measured for absorbance with a UV-Vis spectrophotometer at the maximum wavelength of methylene blue. Then the percentage value of degradation was calculated according to formula (1) for each treatment

Results and Discussions

Synthesis and activation of ZnO/Perlite composite.

The synthesized ZnO/Perlite composites can be seen in Figure 2, where the three composites are powdered and white in color, indicating that the synthesis of ZnO/Perlite composites has been successfully carried out. ZnO/Perlite composites that have been synthesized at the previous stage will be characterized using XRD and DRS instruments.

10%	20%	30%

Figure 2. ZnO/Perlite composites (10%, 20%, 30%)

The 20% ZnO/Perlite composite gives optimal results compared to 10 and 30%, so it needs to be further characterized to know that the ZnO/Perlite photocatalyst has been successfully synthesized. In the Figure 2 presented the results of the characterization of the 20% ZnO/Perlite composite.

Characterization of XRD. The 20% ZnO/Perlite composite was characterized using XRD to determine the crystal phase formed through the diffractogram with the appearance of specific 2θ diffraction angle peaks. Figure 3 shows the XRD diffractogram pattern of the 20% ZnO/Perlite composite.

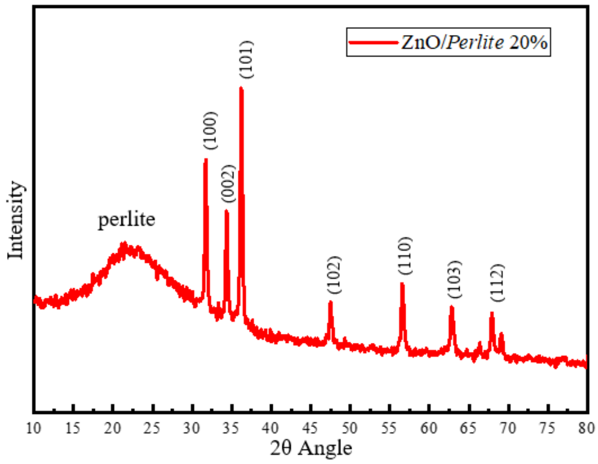


Figure 3. XRD diffractogram of 20% ZnO/Perlite composite

The diffractogram pattern (Figure 3) of 2θ diffraction angles from 10° to 30° shows the characteristics of perlite as an amorphous material. According to research by Almeida et al. [9], states that these characteristics when the calcination process at high temperatures is able to maintain the characteristics of the material without the crystallinity process. The diffraction peaks at 2θ values of 31.68° (100), 34.35° (002), 36.23° (101), 47.45° (102), 56.58° (110), 62.75° (103), dan 67.97° (112) are the most intense XRD peaks, which indicates the characteristics of ZnO crystals which have a wurtzite structure or a structure that has a hexagonal shape. This is in accordance with the research of Kumar et al. [10], which states that these peaks are in accordance with the results mentioned in the literature [11] that ZnO has a wurtzite structure. Thus, the results of the analysis can be concluded that the ZnO/Perlite composite has been successfully synthesized.

Characterization of DRS. The 20% ZnO/Perlite composite was characterized using DRS to determine the band gap energy of ZnO. The amount of band gap energy produced will affect the performance of the ZnO material in exciting electrons from the valence band to the conduction band. Figure 4 shows the DRS spectrum of the relationship between wavelength and absorbance of the 20% ZnO/Perlite composite. The spectrum that has been obtained is then calculated using the Tauc Plot method to determine the band gap energy of the 20% ZnO/Perlite composite. Figure 4 shows the graph of the relationship between hv and $(Ahv)^2$.

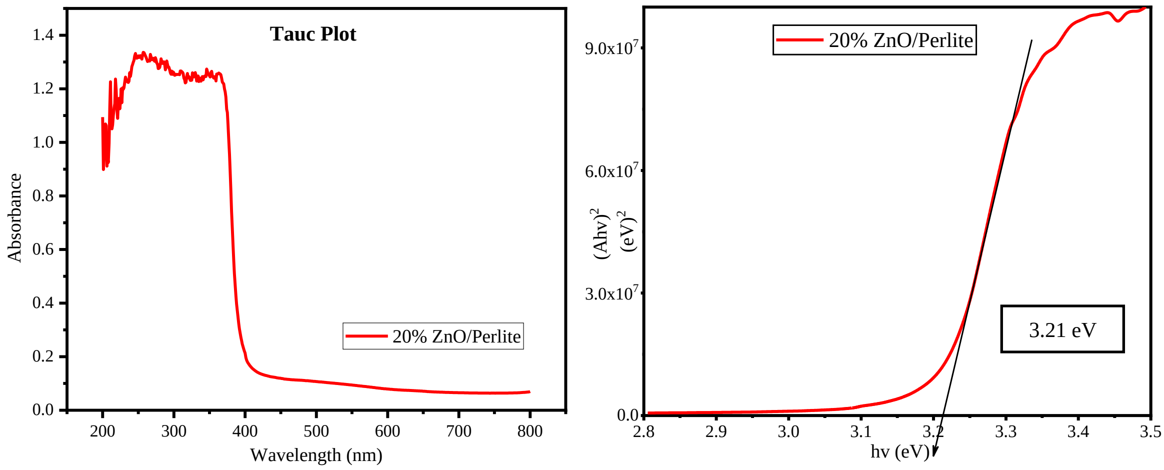


Figure 4. The graph of Tauc Plot calculation of 20% ZnO/Perlite composite

Based on the analysis method, the band gap energy of the 20% ZnO/Perlite composite is 3.21 eV. The band gap energy obtained has decreased compared to the band gap energy of the pure ZnO sample which is 3.37 eV [12]. This is due to the addition of perlite material in the ZnO structure so as to form a new band gap energy that will give the ability of ZnO to absorb light at a smaller energy. The smaller the band gap energy value, the ability to excite electrons from the valence band to the conduction band becomes easier [13]. Based on the results of this analysis, it can prove that the ZnO/Perlite composite has been successfully synthesized.

The maximum wavelength of methylene blue. The maximum wavelength is obtained from the relationship curve between wavelength and absorbance [14]. Determination of the maximum wavelength is done to determine the specific maximum wavelength where the dye can absorb light radiation optimally.

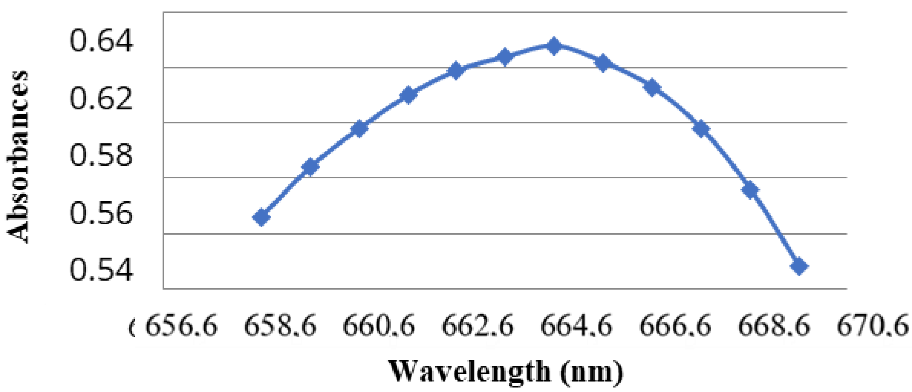


Figure 5. Maximum wavelength graph of methylene blue

Based on the graph in Figure 5, the maximum wavelength of methylene blue is 664.6 nm. The maximum wavelength of the methylene blue solution obtained will be used to measure the absorbance of the degradation of methylene blue solution.

Methylene blue calibration curve.

The calibration curve is a relationship curve between the concentration and absorbance of the solution. The process of making a methylene blue solution calibration curve is done by measuring the absorbance of methylene blue standard solution at various concentrations, namely 0; 0.5; 1.0; 1.5; 2.0; 2.5 and 3.0 ppm at a maximum wavelength of 664.6 nm.

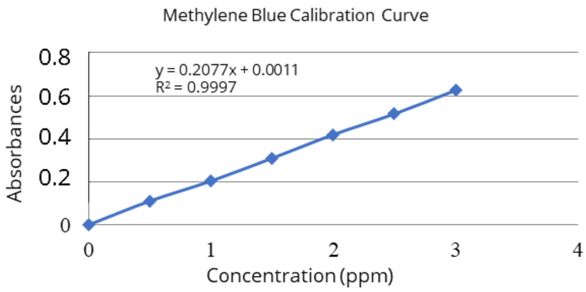


Figure 6. Calibration curve of methylene blue standard solution

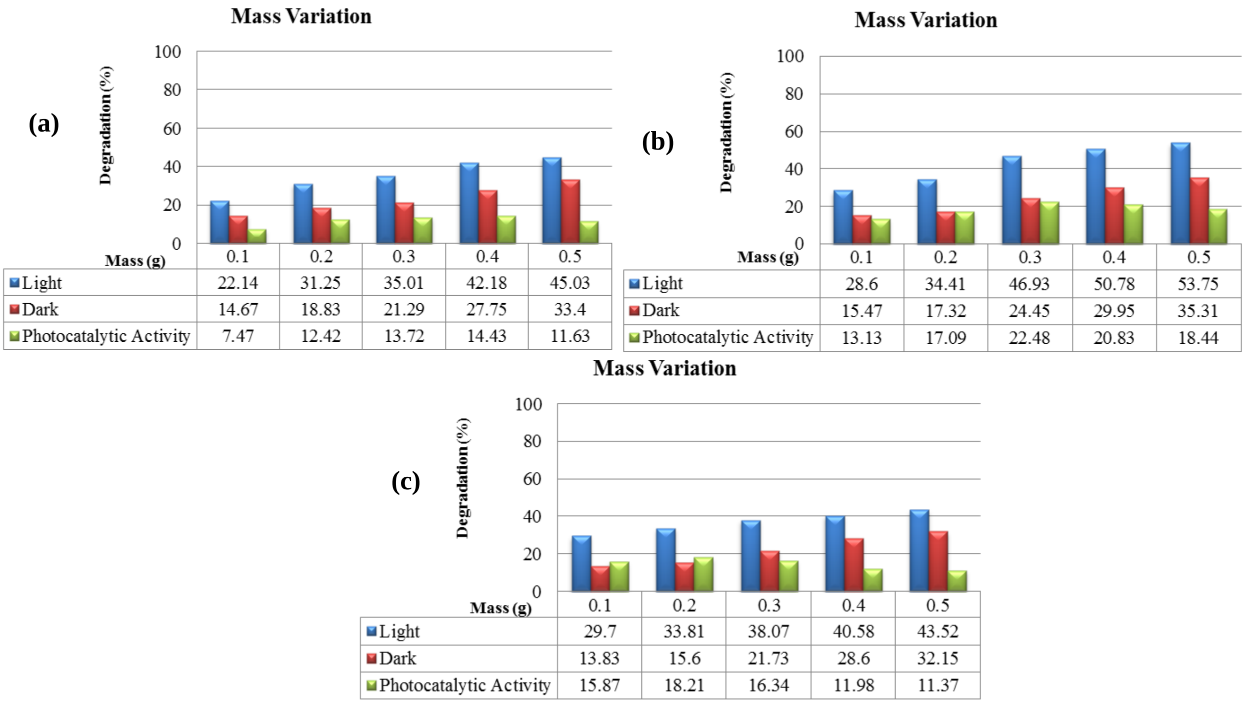
Based on Figure 6, the calibration curve of methylene blue standard solution shows a straight line with a correlation coefficient (R^2) value of 0.9997 which is close to the value of 1. There is a linear relationship between the concentration and absorbance of the solution. The linear regression equation obtained is y = 0.2077x + 0.0011.

The optimum mass of the ZnO/Perlite composite.

Based on the observation (Figure 7), the optimum photocatalytic activity of 10; 20; and 30% ZnO/Perlite composites were 14.43; 22.48; and 18.21%, respectively. While the optimum mass obtained in each composite is 0.4; 0.3; and 0.2 g, respectively. The difference in the results of determining the optimum mass is related to the difference in the composition of ZnO used in each composite. This is because ZnO functions as a catalyst in the degradation process of methylene blue compounds, the greater the composition of ZnO used, the smaller the optimum mass that will be obtained in the degradation process [15]. Among the three composites that have been tested, it can be seen that the 20% ZnO/Perlite composite has the highest photocatalytic activity.

These results are slightly different from research conducted by Silva et al. [8] on different composites, which states that the 30% TiO_2/Perlite composite gives better results than the 10% TiO_2/Perlite composite, because it is able to degrade remazol red by 100%. The difference in results is due to the different masses used in the study. Based on the observation (Figure 7), it can be seen that the degradation activity value of photocatalytic activity in each composite increases with the increase in the number of ZnO/Perlite composites. This is because ZnO/Perlite as a photocatalyst helps the methylene blue degradation process and causes the degradation process to take place faster.

However, as the mass of ZnO/Perlite composite added increases, it causes a decrease in the activity of photocatalytic activity after reaching its optimum mass. This is due to the unbalanced amount of ZnO/Perlite composites with the energy of the UV light provided so that it causes not the maximum electron excitation process from the valence band to the conduction band so that it affects the reduced number of products in the form of hydroxyl radicals (OH•) which act as degrading agents [5].



(a)

Mass (g)	0.1	0.2	0.3	0.4	0.5
Light	22.14	31.25	35.01	42.18	45.03
Dark	14.67	18.83	21.29	27.75	33.4
Photocatalytic Activity	7.47	12.42	13.72	14.43	11.63

(b)

Mass (g)	0.1	0.2	0.3	0.4	0.5
Light	28.6	34.41	46.93	50.78	53.75
Dark	15.47	17.32	24.45	29.95	35.31
Photocatalytic Activity	13.13	17.09	22.48	20.83	18.44

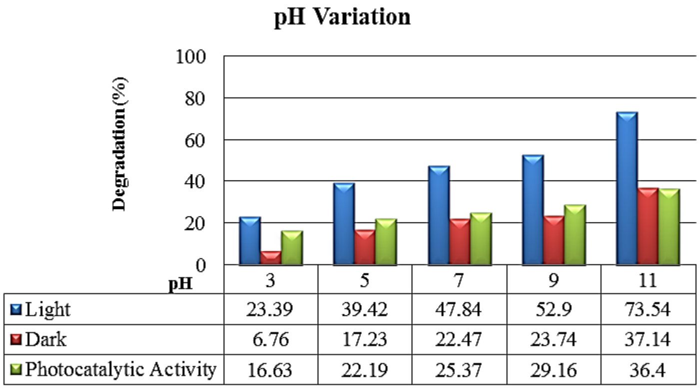
(c)

Mass (g)	0.1	0.2	0.3	0.4	0.5
Light	29.7	33.81	38.07	40.58	43.52
Dark	13.83	15.6	21.73	28.6	32.15
Photocatalytic Activity	15.87	18.21	16.34	11.98	11.37

Figure 7. Graph of mass effect of (a) 10% (b) 20% (c) 30% ZnO/Perlite on methylene blue degradation

The optimum pH of the ZnO/Perlite composite.

Based on the observation (Figure 8), it can be seen that the value of photocatalytic activity on the 20% ZnO/Perlite composite increases as the pH value increases. This is because the increase in the pH value of the solution causes the concentration of OH^- ions, to increase so that OH^- ions that react with holes (h^+) in the valence band form more and more hydroxyl radicals (OH•). The more hydroxyl radicals (OH•) that are formed, the more methylene blue is degraded [16]. Hydroxyl radicals (OH•) are strong oxidizers which in this study are useful for oxidizing methylene blue dye into NH_4^+, SO_2^-, CO_2, and H_2O compunds [17].



pH	3	5	7	9	11
Light	23.39	39.42	47.84	52.9	73.54
Dark	6.76	17.23	22.47	23.74	37.14
Photocatalytic Activity	16.63	22.19	25.37	29.16	36.4

Figure 8. Graph of pH effect of 20% ZnO/Perlite on methylene blue degradation

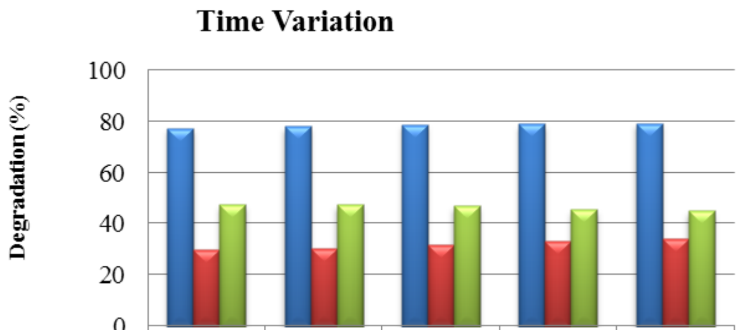
In theory, the surface of ZnO above pH 9 (alkaline conditions) is negatively charged so that positively charged dyes will be more easily adsorbed on the ZnO surface during alkaline conditions [18]. Here is the reaction equation 2 that occurs when ZnO is in alkaline conditions.

$ZnOH + OH^- \rightarrow ZnO^- + H_2O$ .... (2)

Based on the reaction equation (2), it can be seen that the ZnO surface is deprotonated under alkaline conditions so that the product is ZnO which has a negatively charged surface [19]. In this study, methylene blue is one of the positively charged dyes (cation) so that the methylene blue photodegradation process using 20% ZnO/Perlite composite is effective in alkaline conditions, namely at pH 11 with a photocatalytic activity of 36.4%. This result is different from the research conducted by Silva et al. [8] on a different composite, which states that the 30% TiO_2/Perlite composite can degrade remazol red by 100% at pH 5 conditions. The difference in these results is due to the different dyes used in the study.

The optimum time of the ZnO/Perlite composite.

Based on the observation (Figure 9), it can be seen that the value of degradation activity in light conditions on the 20% ZnO/Perlite composite increases with increasing radiation time. This is because the longer the radiation causes the longer the contact time between photons and the ZnO/Perlite photocatalyst. The more electrons that experience excitation from the valence band to the conduction band, the more superoxide radicals ($O_2\bullet^-$) will be formed which function as reductants and hydroxyl radicals (OH•) which function as oxidizers in the methylene blue degradation process [20]. However, as time increases, the value of photocatalytic activity in each composite decreases when it has reached its optimum time. This occurs due to the electron recombination process in which the electrons that have been excited to the conduction band will return to the valence band so that no species or pair of holes (h^+) and electron (e^-) is produced as a trigger for the hydroxyl radical (OH•) formation reaction [5].



Time (hours)	1	2	3	4	5
Light	77.45	78.1	78.9	79.05	79.15
Dark	30.05	30.51	31.91	33.46	34.06
Photocatalytic Activity	47.4	47.59	46.99	45.59	45.09

Figure 9. Graph of time effect of 20% ZnO/Perlite on methylene blue degradation

Based on the test results from the determination of the optimum time that has been carried out, it shows that the optimum time used in the 20% ZnO/Perlite composite is 2 hr with a photocatalytic activity of 47.59%. This result is similar to research conducted by Silva et al. [8] on a different composite, which states that the 30% TiO_2/Perlite composite can degrade remazol red by 100% within 2 hr. The similarity of these results is likely due to TiO_2 and ZnO having the same band gap energy.

Conclusions

The 20% ZnO/Perlite composite has the most optimum photocatalytic work activity in degrading methylene blue with a mass of 0.3 g under pH 11 conditions for 2 hr of stirring under ultraviolet irradiation with a photocatalytic activity of 47.59% and a combined adsorption and photocatalytic activity of 78.1%. XRD results indicate the characteristics of ZnO crystals which have a wurtzite structure, as well as the characteristics of perlite as an amorphous material. Supported by DRS results show that it has a band gap value of 3.21 eV.

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Author Contibutions

Conceptualization, B. and T.S.; Methodology, B.; Validation, B., T.S. and K.R.; Formal Analysis, B.; Investigation, B.; Resources, T.S. and K.R.; Data Curation, B.; Writing – Original Draft Preparation, B.; Writing – Review & Editing, B.; Visualization, B.; Supervision, T.S. and K.R.; Project Administration, B.; Funding Acquisition, T.S. and K.R.

Conflict of Interest

There are no significant conflicts

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