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Synthesis and Application of ZnO/SiO_2 Composite for Methylene Blue Degradation by Photocatalyst Process and Its Kinetics

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Abstract
Methylene blue is considered a persistent organic pollutant due to the presence of a benzene group that resists degradation, making it difficult to break down. One source of SiO2 is volcanic ash from volcanic eruptions, which accounts for more than 50% of the total mixture of compounds. The abundant SiO2 in volcanic ash can be utilised and converted into silica gel by forming potassium silicate through the chemical interaction between the SiO2 present in volcanic ash and potassium hydroxide. The ZnO/SiO2 composite has been used as an adsorbent to degrade methylene blue artificial dye. This study aims to determine the composition that gives maximum results in MB dye degradation. ZnO/SiO2 composite with volume ratio of 1:1, 1:2, 1:3. In this study, the dye degradation under sunlight and UV light exposure was investigated and the effect of various factors such as mass, time, concentration and pH to achieve the highest possible degradation of MB dye was also studied. The results showed that the most effective reduction in MB dye concentration occurred when using a ZnO/SiO2 composite with a 1:3 ratio, using 100 mg of adsorbent, subjecting it to UV irradiation for 60 minutes, and working with a dye concentration of 10 g/l at a relatively neutral pH of 6. The dye degradation efficiency obtained under these conditions was 97.63%.
Keywords: *methylene blue, photodegradation, volcanic ash, ZnO/SiO_2 composite*

Abstrak
Metilen biru dianggap sebagai polutan organik yang persisten karena adanya gugus benzena yang tahan terhadap degradasi, sehingga sulit untuk diurai. Salah satu sumber SiO_2 adalah abu vulkanik dari letusan gunung berapi dengan kadar lebih dari 50% dari total campuran senyawa. SiO_2 yang melimpah yang ditemukan dalam abu vulkanik dapat dimanfaatkan dan diubah menjadi silika gel dengan menghasilkan kalium silikat melalui interaksi kimiawi antara SiO_2 yang ada dalam abu vulkanik dan kalium hidroksida. Komposit ZnO/SiO_2 diaplikasikan sebagai adsorben untuk mendegradasi pewarna buatan metilen biru. Penelitian ini bertujuan untuk menentukan komposisi yang memberikan hasil maksimal dalam degradasi pewarna MB. Komposit ZnO/ SiO_2 dengan perbandingan volume 1:1, 1:2, 1:3. Dalam penelitian ini, kami mengeksplorasi degradasi pewarna di bawah paparan sinar matahari dan sinar UV, sekaligus menyelidiki efek dari berbagai faktor seperti massa, waktu, konsentrasi, dan pH untuk mencapai degradasi pewarna MB setinggi mungkin. Temuan menunjukkan bahwa pengurangan konsentrasi pewarna MB yang paling efektif terjadi ketika menggunakan komposit ZnO/SiO_2 dengan rasio 1:3, menggunakan 100 mg adsorben, disinari sinar UV selama 60 menit, dan bekerja dengan konsentrasi pewarna 10 g/l pada pH yang relatif netral, yaitu 6. Efisiensi degradasi pewarna yang diperoleh dalam kondisi ini adalah 97,63%.
Kata Kunci: *metilen biru, fotodegradasi, abu vulkanik, komposit ZnO/SiO_2*

1. Introduction

Methylene blue is one of the non-biodegradable organic pollutants because there is a benzene group that is difficult to degrade. Even if it is possible to degrade, it will take a long time. Compounds with benzene groups are carcinogenic. Waste treatment using the photodegradation process usually does not produce secondary waste as other methods such as adsorption, coagulation, and electrocoagulation. Photodegradation is the process of decomposing a compound with the help of photon energy using a photocatalyst material [1]. Examples of photocatalyst materials are Titanium Oxide (TiO_2) and Zinc Oxide (ZnO) are considered better because they can remove organic dye contaminants due to their environmentally friendly properties and chemistry ([2], [3]). To increase the effectiveness of waste degradation, the distribution of photocatalyst materials is expanded by depositing them on porous materials as host materials such as silica or zeolite[4].

Some terminology says it is a nanocomposite. Research for waste degradation using photodegradation for methylene blue degradation using TiO_2/natural zeolite photocatalyst with UV light irradiation. The results reported were the best methylene blue degradation efficiency of 12.56% [1]. The use of other semiconductors to degrade methyl orange is semi-conductor ZnO/Zeolite with UV black light irradiation has an efficiency of 65.67% [5]. Research on the synthesis of ZnO-Bentonite composites and their use in the methyl orange degradation process with UV light irradiation, which has the greatest efficiency in methyl orange degradation of 56.71 ± 0.65% [6], [7].

Methylene blue degradation with ZnO photocatalyst with sunlight with the highest methylene blue degradation efficiency at pH 7 of 87.7% [8], [9]. In addition, ZnO photocatalyst for methylene orange dye degradation with UV irradiation with λ_{max} 365 nm with the highest dye degradation efficiency of 64.9% [10], with methylene blue degradation of 70% [8], [9], [11]. In addition to using ZnO, dye degradation can also use TiO_2, congo red degradation with TiO_2 photocatalyst with the highest congo red degradation efficiency of approximately 70% [12]. Other studies also use TiO_2 photocatalysts for the degradation of methylene blue and congo red which respectively provide degradation efficiency of 91% and 90% [13].

Treatment of phenol waste with ZnO/SiO_2 photocatalyst with degradation efficiency ranging from 85% to 99.9% [14]. ZnO/SiO_2 photocatalyst for the degradation of methylene blue dye and the maximum result obtained is a degradation of 93% [15], [16]. Therefore, with a high enough efficiency in the use of ZnO semiconductor material and SiO_2 host material compared to using other semiconductor materials and host materials, it is better to use ZnO semiconductor material and SiO_2 host material for methylene blue dye degradation. In addition to the high efficiency, the reason for using silica is that the raw materials are very abundant. One of the raw materials for making silica is volcanic ash, volcanic ash is material released by volcanoes during eruptions.

Judging from the geological history, volcanic ash contains the main components of silica and alumina. The Yogyakarta Environmental Health Engineering Center in 1994 examined the content of Merapi volcanic ash, which contained 54.56% silicon dioxide (SiO_2), 18.37% aluminum oxide (Al_2O_3), 18.59% ferric oxide (Fe_2O_3), and 8.33% calcium oxide (CaO) [4], [17]. Volcanic ash is said to be pozzolanic, which is a material with a high main content of silica and alumina that can react with lime at low temperatures (room temperature) and in the presence of water to produce a hydrate that has binding or cementation properties [18]. With a large enough silica content in the volcanic ash of Mount Merapi, the silica content can be extracted to take its SiO_2 content to be applied as a host material in the photocatalyst process using ZnO semiconductor material for methylene blue dye degradation. Analyzing the ratio of ZnO and SiO_2 which gives the best results in the synthesis of ZnO/SiO_2 nanocomposites for the degradation of methylene blue dye waste. 2. Analyze the conditions that give maximum results on the degradation of methylene blue dye waste. 3. Determine the reaction order of methylene blue degradation with ZnO-SiO_2 composite.

2. Material and Methods

The equipment used in this research is laboratory glassware, analytical balance (Mettler PE300), Oven (HERAEUS KR 170E), Sonicator (Elmasonic S 30 H), Magnetic Stirrer, Furnace, UV-Vis, SEM (Hitachi SU-70), XRD (Philip Analytical X-Ray B. V), crucible and other supporting laboratory tools. The materials used were Mount Merapi volcanic ash, methylene blue dye waste, CH_3COOH p.a., KOH p.a., $Zn(CH_3COO)_2$, and distilled water.

Preparation and pretreatment of raw materials

The raw material in this research is volcanic ash from Mount Merapi which is taken directly from Cangkringan village which borders Klaten Regency. The next process is the pretreatment of raw materials. The volcanic ash raw material was washed and separated from other materials such as sand, soil, and stones. After drying and cleaning, the volcanic ash was sieved with a 100-mesh sieve.Sintesis Kalium Silikat (K_2SiO_3)

The next process is the synthesis of potassium silicate, this process is carried out by weighing 50 grams of volcanic ash to extract the silica content in it using a KOH base with a mass ratio of 1: 1 extractor and volcanic ash. Reflux was carried out for 4-5 hours. After refluxing for 4-5 hours, the mixture was cooled

and filtered. After filtering, the filtrate was allowed to stand to form a potassium silicate solution, (K_2SiO_3)[19], [20], [21].

Synthesis of ZnO/SiO_2 composites

The synthesis of ZnO/SiO_2 composites was carried out by a titration process, the filtered potassium silicate filtrate was taken with a certain volume and then titrated using 0.1 N zinc acetate with a volume ratio between potassium silicate filtrate and zinc acetate. The volume ratio used was 1:1; 1:2; 1:3. In addition to titrating with zinc acetate, potassium acetate is also titrated with acetic acid to neutralize the solution, the process of adding acetic acid and zinc acetate solution is carried out simultaneously and must reach the same mixing point between the volume of zinc acetate and pH. After that, the next process is agitation to form nanocomposite deposits. After the agitation process is complete, the next step is to check the pH of the solution again. If it is neutral then proceed to the next process, if not then neutralize first. After the solution is confirmed to be neutral, then filtered in the furnace at 600 °C for approximately 2 hours.[19], [22].

Photocatalysis application on methylene blue waste

This application process was carried out by weighing 25; 50; 75; 100; and 125 mg of ZnO/SiO_2 respectively and put into 25 ml of methylene blue solution with a concentration of 20 ppm. This photocatalyst application was carried out in UV and solar irradiation. UV irradiation was carried out at a wavelength of 350 nm within 60 minutes, irradiation with the sun was also carried out at intervals of 60 minutes. Then the best results of the process were irradiated with other variations, namely, variations in time, concentration, and pH. The time variations used were 30; 45; 60; 75; 90; 105; and 120 minutes, the concentration variations used were 10; 25; 35; 50; 75; 85; and 100 mg/l (ppm). While pH variations were carried out from pH 3 to pH 13[23], [24].

3. Results and Discussion

Synthesis of ZnO/SiO_2 composite

Several techniques or methods are used for the synthesis of nanocomposite photocatalyst materials, including the sol-gel method, grafting, and co-precipitation methods. In this study, the method used is the sol-gel method, the process uses a medium in the form of a solution, which will change phase to sol, and then will form a gel. Nanocomposite synthesis via sol-gell is widely chosen because of its ease and effectiveness, especially in the field of composite synthesis and organic-inorganic synthesis [25], [26], [27]. In this synthesis process, pH will greatly affect the shape and properties of silica gel, if the hydrolysis reaction occurs, the silica formed is SiOH, while if the condensation process occurs, the silica formed is SiO-Si [28]. Therefore, in this research, the synthesis was carried out at neutral pH which aims to maximize silica gel as an adsorbent capable of adsorbing with polar and nonpolar properties of silica gel.

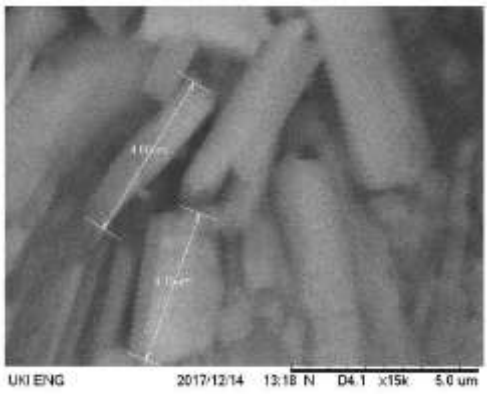


Fig. 1. SEM test results (size range 4-5 µm)

The surface morphology of a material can be seen through characterization using a Scanning Electron Microscope (SEM). Images generated from SEM can show the uniformity and shape of the crystals that make up a material. From the SEM analysis test results, it can be seen that the morphology of the synthesis results has a fairly good shape uniformity. In the sol-gel method, the synthesis results will provide a fairly uniform size uniformity (Sulistyono et al., 2018). In this study, the particle size was found to be around 4 µm, this is likely due to insufficient heating in the process, because the process of synthesizing nanoparticles

to produce a nano size of approximately 20 nm is around 1200 °C [29], [30], [31].

Methylene blue adsorption

The adsorption process was carried out with two variations, namely irradiation in sunlight and UV light. The results of the decrease in dye concentration after adsorption using ZnO/SiO_2 nanocomposites with a volume ratio of 1:1, 1:2, and 1:3 for 60 minutes with the help of sunlight are presented in Table 1. For additional information, the concentration of methylene blue dye before adsorption was 20 ppm.

Table 1. The efficiency of MB concentration reduction with ZnO/SiO_2 nanocomposite 1:1, 1:2, 1:3

Adsorbent Mass (mg)	UV light			Sunlight		
	1:1	1:2	1:3	1:1	1:2	1:3
25	95.6993	96.1655	94.3007	95.0000	95.4665	95.8159
50	93.9510	94.3007	92.2008	94.6504	95.3496	95.2331
75	93.8345	93.6014	95.9324	93.1352	94.5338	95.6993
100	95.3496	91.9697	96.9814	93.3683	91.9697	94.8834
125	92.6690	92.4359	95.9324	87.7739	93.3683	94.1841

From Table 1, a graph is made of the decrease in methylene blue dye concentration with ZnO/SiO_2 nanocomposite adsorbent under sunlight and UV light.

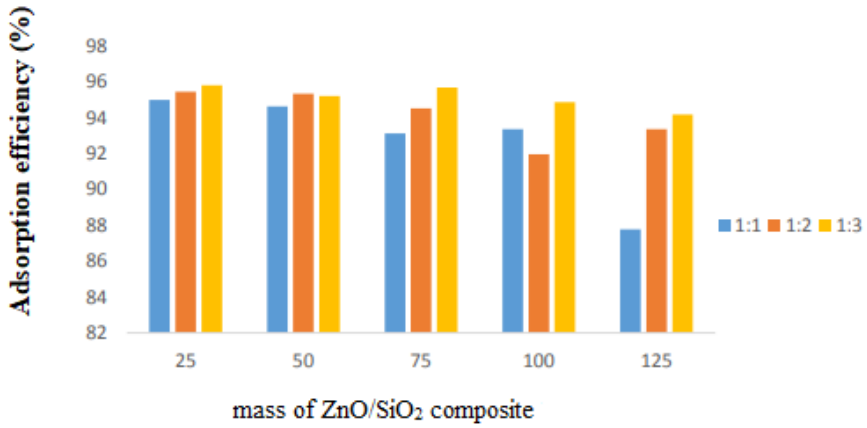


Fig. 2. Graph of the decrease in MB concentration with solar irradiation

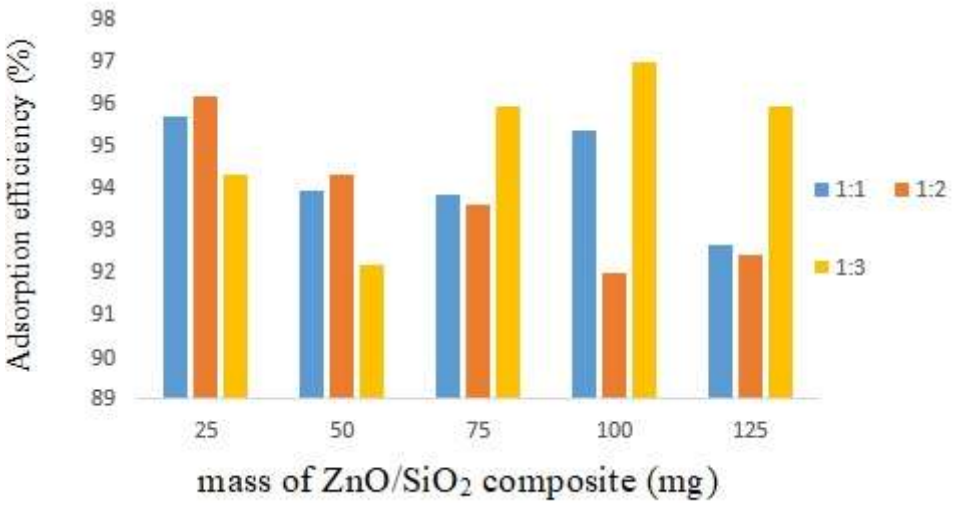


Fig. 3. Graph of the decrease in MB concentration with UV light

The highest concentration reduction of methylene blue dye with mass of ZnO/SiO_2 composite (mg) adsorbent occurred in UV irradiation with 100 mg adsorbent mass with a value of 96.9814%. This is

because the adsorbent used is a metal that is ZnO impregnated into SiO_2. Metals such as ZnO are more likely to work effectively with maximum absorption in the UV wavelength region. Meanwhile, sunlight only contains about 5% of UV light [32], [33], [34]. In the photocatalyst process using UV light irradiation has a higher efficiency value of reducing the concentration of methylene blue dye when compared to irradiation in sunlight. The efficiency in sunlight irradiation has a fairly high value, this is because in the adsorbent used, there are natural contaminants, namely dopants commonly called doping. Doping is a way to change the electrical properties and optical properties of semiconductors. When a semiconductor is doped with impurities, the semiconductor becomes extrinsic [32], [35]. One of the purposes of doping is to increase semiconductor conduction. An increase in electron concentration can also increase the width of the semiconductor energy band gap. So with the presence of natural dopants from volcanic ash, the adsorbent also works quite well in the photocatalyst process using sunlight [36].

The ZnO semiconductor photocatalyst process is not effective enough in visible light exposure, ZnO has an energy gap of 3.3 eV. In UV irradiation, the amount of ZnO for the adsorption process is greater so that the adsorption process is more effective. However, in this study, the adsorption results of sunlight irradiation are not much different from UV light. This is possible because of the presence of natural dopants from the SiO_2 synthesis raw material, namely volcanic ash. Merapi volcanic ash contains other metals such as aluminum oxide (Al_2O_3) 17.03%, calcium oxide (CaO) 8.91%, and ferric oxide (Fe_2O_3) 8.6%, as well as many other metals whose percentages are quite small [37]. Fe-TiO_2-SiO_2 synthesis with sol-gel method using $TiCl_4$ precursor. The resulting photoactivity is greater than with TiO_2-SiO_2. This is because Fe doping encourages TiO_2 to absorb light at higher wavelengths. The increase in TiO_2 photocatalyst activity is indicated by an increase in surface area and a decrease in the average particle size of the band gap energy as the amount of Fe increases. Therefore, in this study, the results of photocatalyst adsorption with visible light have quite good results because there are natural dopants in the adsorbent. The best results obtained are in the condition of irradiation with UV light with a mass of 100 mg adsorbent.

Adsorption kinetics

From the best results obtained, namely in conditions of a ratio of 1: 3 and with a mass of 100 mg adsorbent in UV irradiation, then in these conditions the time that produces the highest adsorption value is sought. The following are adsorption data on methylene blue with time variations under UV irradiation conditions with a mass of ZnO/SiO2 nanocomposite ratio of 1:3 as much as 100 mg.

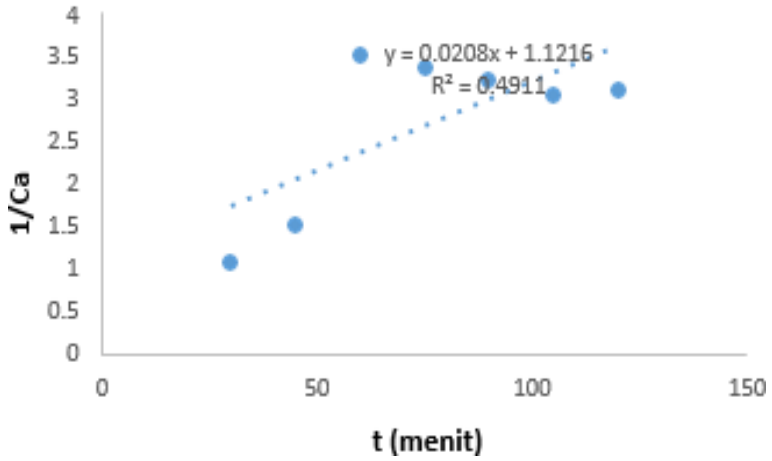
Table 2. Adsorption results with time variation with UV light irradiation

Time (Minutes)	Absorbance	C* (ppm)	Efficiency (%)
30	0.134	3.4242	82.8787
45	0.093	2.4685	87.6573
60	0.033	1.0699	94.6503
75	0.035	1.1165	94.4172
90	0.037	1.1631	94.1841
105	0.040	1.2331	93.8345
120	0.039	1.2097	93.9510

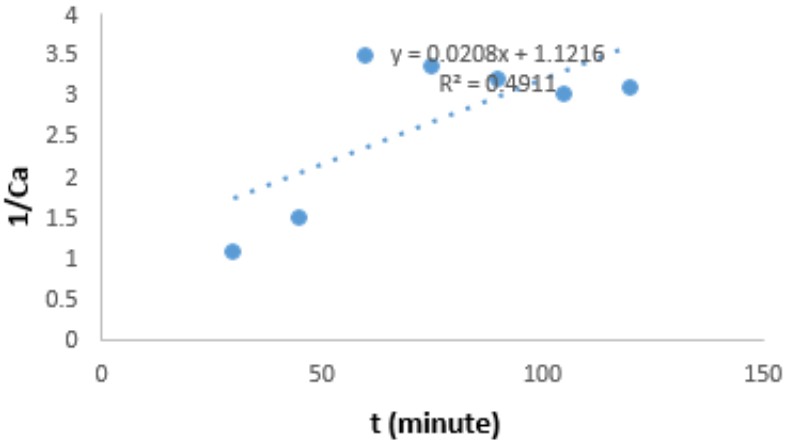
The results of adsorption on methylene blue, are then approximated by first-order kinetics, second-order kinetics, first-order Sanntosa, and pseudo-second-order Ho & Mc Kay in Table 3.

The relationship between first and second-order kinetics is shown in Figures 8 and 9, respectively. The resulting relationship between t/Ca vs ln(Co/Ca)/Ca is shown in Figure 10, while the relationship between t vs t/qt is shown in Figure 11. A graph of the relationship between t vs ln Ca is shown in Figure 3a, a graph of the relationship t/Ca vs ln (Co/Ca)/Ca is shown in Figure 3b, a graph of the relationship t vs 1/Ca is shown in Figure 3c, and a graph of the relationship t vs t/qt is shown in Figure 3d.

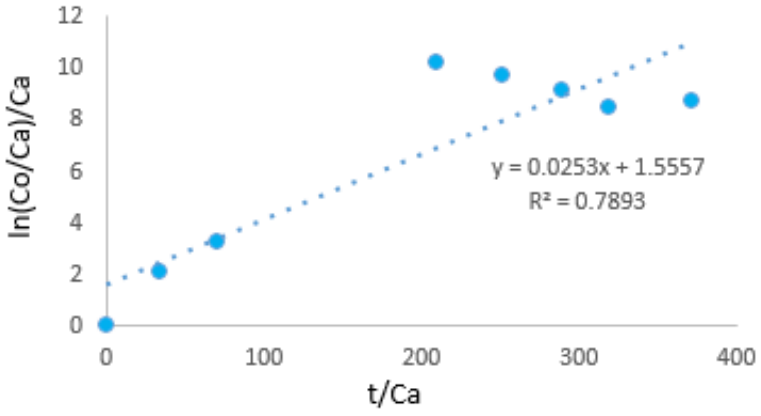
3a


y = 0.0208x + 1.1216
R² = 0.4911
1/Ca
t (menit)

3b


y = 0.0208x + 1.1216
R² = 0.4911
1/Ca
t (minute)

3c


y = 0.0253x + 1.5557
R² = 0.7893
ln(Co/Ca)/Ca
t/Ca

3d

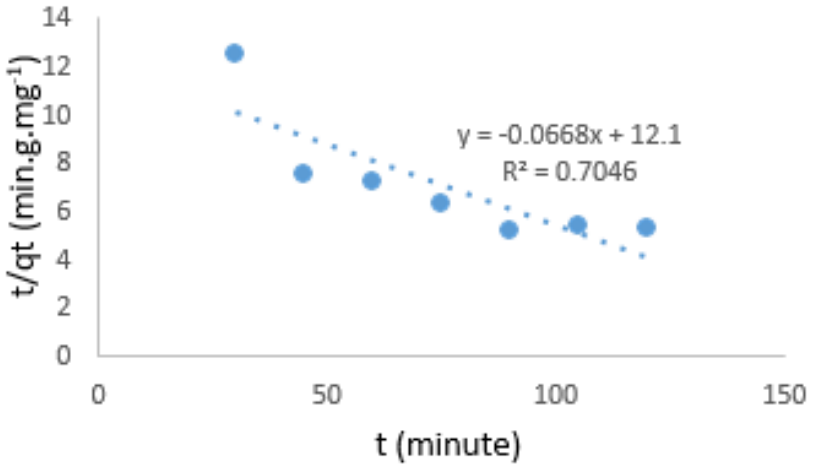


Fig. 3. First-order kinetic adsorption graph (3a), second-order kinetic adsorption graph, first-order pseudo kinetic adsorption graph (3c), and second-order pseudo kinetic adsorption graph (3d).

The reaction that occurs in the methylene blue photodegradation process is a radical reaction where there is a release and capture of electrons caused by the oxidizer formed during the photocatalyst process. The analysis using a UV-Vis spectrophotometer at a wavelength of 650 nm shows that there has been a decrease in the concentration of methylene blue after adding a photocatalyst with UV light irradiation. It has been reported that most of the degradation of organic compounds follows a pseudo-first-order reaction.

Table 3. Results of time variation adsorption data processing

Kinetics Model	Equation	Velocity Constant, k x 10^{-3} ($minute^{-1}$)	R^2
First-order kinetics	ln Ca = ln Co + 0.0105t	10.5	0.5465
2nd-order kinetics	$\frac{1}{Ca} = 0.0208t + \frac{1}{Co}$	20.8	0.4911
First Orde santosa	$\ln\frac{(\frac{Co}{ca})}{Ca} = 0.0253\,\frac{t}{Ca} + 1{,}5557$	25.3	0.7893
Pseudo orde II Ho & Mc Kay	$\frac{t}{qt} = \frac{1}{0.00036qe^2} + \frac{t}{qe}$	0.3688	0.7046

From Table 3, it can be concluded that the adsorption kinetics in this study are closer to the Santosa equation, namely the first-order pseudo equation with a velocity constant value of 25.3 min-1) and an R2 value of 0.7893. From Table 4, it can be seen that the R2 value does not get the maximum result, this is possible because the adsorption kinetics process is not only influenced by time but also by the stirring process and temperature. In different stirring conditions, the oxidation process is also different so the value tends to be difficult to get linear results. In addition, temperature can also affect the results obtained. The more exposure to UV light, the higher the temperature, whereas the value of k is always different in each different temperature condition, so it is quite difficult to get linear results.

Adsorption capacity

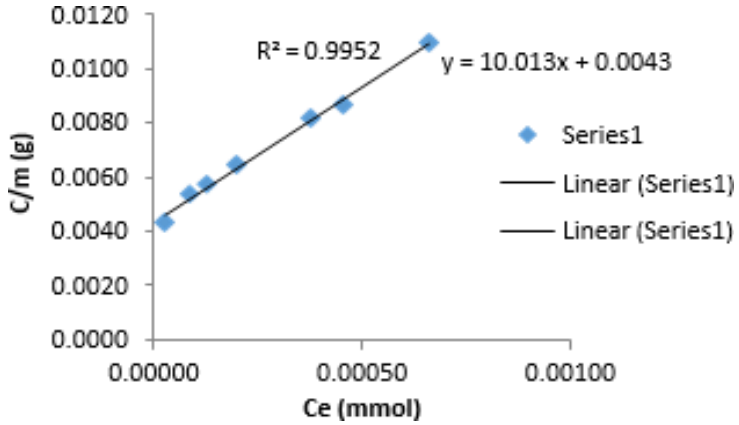
In addition to the Santosa and Ho Mc Kay equations obtained from the best results for time variations, Langmuir and Freundlich equations were also obtained from the concentration variations obtained. Based on the best results obtained, in these conditions, the concentration that produces the highest adsorption value is sought. The following are adsorption data on methylene blue with variations in time under UV irradiation conditions with a ZnO/SiO_2 nanocomposite mass ratio of 1:3 as much as 100 mg.

Table 4. Adsorption results with varying concentrations

Concentration (ppm)	Absorbance	C* (ppm)	Efficiency (%)
10	0.005	0.4149	95.8508
25	0.041	1.2634	94.9463
35	0.068	1.8881	94.6053
50	0.117	3.0209	93.9580
75	0.230	5.6713	92.4382
85	0.279	6.8041	91.9950
100	0.411	9.8811	90.1180

From the adsorption data table, a graph of the relationship between C/m Vs Ce was made to obtain the Langmuir equation shown in Figure 4a, and to obtain the Freundlich equation, a graph of the relationship between ln m Vs ln Ce was made, shown in Figure 4b.

4a



4b

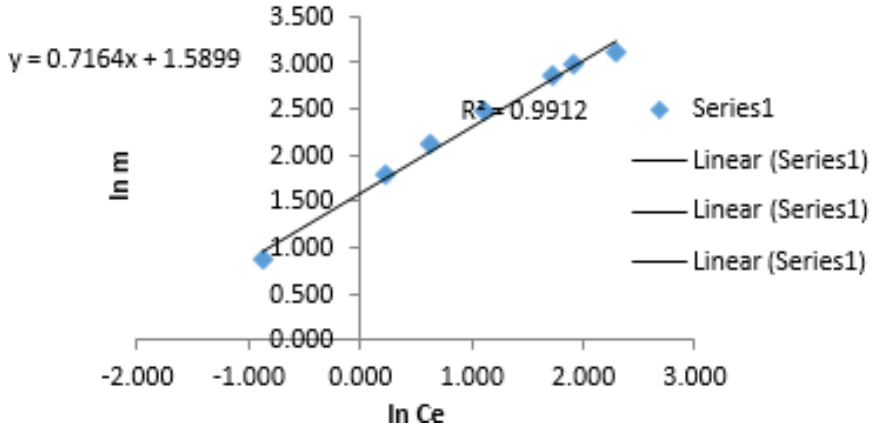


Fig. 4. Langmuir Equation Graph (4a) and Freundlich Equation Graph (4b)

Table 5. Adsorption data calculation results

Initial Concentration (mg/L)	Final Concentration (Ce) (mg/L)	Langmuir	Freundlich
0	0	b = 37.3514 mg/g	Kf = 4.9030
10	0.4149	K = 2328.6046	n = 1.3959
25	1.2634	E = 19.3376 kJ/mol	
35	1.8881		
50	3.0210		

Initial Concentration (mg/L)	Final Concentration (Ce) (mg/L)	Langmuir	Freundlich
75	5.6713		
85	6.8042		
100	9.8811		

The results of the calculation and based on the graph, this adsorption follows the equation of Langmuir, this is very realistic because the approach in the Langmuir equation is solution adsorption while in the Freunlich equation is gas adsorption. The adsorption capacity of Langmuir and Freundlich calculations is almost the same, this is possible because the Freundlich equation approach is a multi-layer adsorption approach, while this adsorption process is photocatalytic adsorption which means that the adsorption process is followed by an oxidation process obtained by irradiation from sunlight or UV. Therefore, this adsorption process can also be considered as a multi-layer adsorption process. The equation obtained from the graph is C/m = 10.013 Ce + 0.0043.

Variation of pH

To find out the pH that gives maximum results, pH variations were carried out on methylene blue dye adsorption, and the results were obtained as in Table 6 below.

Table 6. Variation of pH in dye adsorption with UV light irradiation

pH	Absorbance	C* (ppm)	Efficiency (%)
3	0.193	4.799534	92.00078
4	0.158	3.983683	93.36053
6	0.048	1.41958	97.63403
8	0.173	4.333333	92.77778
10	0.182	4.543124	92.42813
12	0.106	2.771562	95.38073
13	0.058	1.652681	97.24553

On the surface of the photocatalyst as well as organic pollutants. The efficiency of ZnO/SiO_2 photocatalyst for the degradation of methylene blue dye solution, with an initial dye concentration of 20mg/l and adsorbent mass of 100 mg over the pH range of 3-13. The maximum degradation efficiency of 97.63% was obtained at pH 6. It can be observed from the plot in Figure 5 that as the solution becomes more basic, the photocatalytic degradation efficiency of the catalyst tends to decrease due to the development of a negative charge on the catalyst surface, which induces repulsion on the negatively charged dye molecules (Tedla et al., 2015). Changes in pH cause differences in the number of active sites of ZnO/SiO_2. So that the methylene blue species changes with a change in pH, it is possible that at high pH there is a change in the color of methylene blue so that it is no longer specific to the light given.

4. Conclusion

The conclusions of the research that has been done are:

1. Comparison of ZnO and SiO_2 which gives the best results from the synthesis of ZnO/SiO_2 composites is at the condition of the ratio of the volume of potassium silicate filtrate and Zn Acetate 1: 3.
2. Conditions that provide maximum results for reducing the concentration of methylene blue dye using ZnO/SiO_2 composite adsorbents are under UV irradiation conditions with a mass of 100 mg adsorbent at pH 6 with a time of 60 minutes and a concentration of 10 ppm, with a resulting adsorption efficiency of 97.63%.

5. Acknowledgment

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