The Use of Zinc Oxide (ZnO) Photocatalyst for Photodegradation of Car Wash Wastewater

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Untreated motor vehicle waste has the potential to damage the environment. The photodegradation method can decompose pollutants with the help of UV-A light and photocatalysts. Zinc Oxide (ZnO) is a photocatalyst capable of degrading motor vehicle washing waste. This study aims to investigate the ability of ZnO as a photocatalyst in degrading pollutants in motor vehicle waste. The independent variables in the experiment were the mass of ZnO and the contact time. The variables used were mass 0.5, 0.75, and 1 gram with a contact time of 2, 3, and 4 hours. The experimental results showed that ZnO irradiated with UV-A lamp was able to degrade organic substances. The mass and contact time of ZnO affect the effectiveness of photodegradation. These results show that the use of ZnO photocatalyst for photodegradation of Carwash Wastewater may be future technology to treat car wash wastewater.

Keywords: Photodegradation; effectiveness; motorized vehicle washing; wastewater treatment; Photocatalyst.

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Article history: Received 7 August 2022, Accepted 26 September 2022, Published January 2023.
http://dx.doi.org/10.12962/j24604682.v19i1.14019
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I. INTRODUCTION

Disposal of car wash wastewater can directly cause a decrease in environmental quality [1]. A decrease in environmental quality can be in the form of increased levels of pollution in water bodies. The content of chemical oxygen demand (COD), total suspended solids (TSS), and detergents in water bodies can increase if large amounts of waste are disposed [2]. Wastewater discharged into water bodies must comply with the Regulation of the Minister of Environment and Forestry Number 68 of 2016 concerning domestic wastewater quality standards and regulation of the minister of the environment of the Republic of Indonesia number 5 of 2014 concerning Wastewater quality standards for business and/or industrial activities soaps, detergents, and vegetable oil products. Therefore, it is necessary to treat the waste resulting from motor vehicle washing.

One method of reducing organic compounds in wastewater is photocatalyst [3]. A photocatalyst is a chemical transformation process carried out by a catalyst and requires light. Ultraviolet light (UV) A is used so that the catalyst is active and then a reaction will occur with the nearest compound or with compounds that are on the surface of the catalyst. Materials used in photocatalysts are generally semiconductors consisting of sulfide and oxide types [4]. Photocatalyst technology is considered not to produce secondary pollution or waste [3].

Zinc Oxide (ZnO) is a unique material with semiconductor, and piezoelectric properties, and exhibits some pyroelectric properties. ZnO is an inorganic compound that usually appears as a white powder and has useful properties such as good transparency, relatively high electron movement, and a relatively wide band gap [4]. ZnO is a crystal that can be used in various needs, as a catalyst or catalyst support, as well as a semiconductor [5]. Photocatalysis using ZnO has been used to degrade phenol [6], a dye in textiles [7,8,9], but its use for the degradation of car wash waste has never been used. This study aimed to assess the effectiveness of photodegradation by ZnO photocatalyst to treat carwash waste. The results of this study are expected to be an alternative technology that can be applied to the car wash in the future.

II. METHOD

Motor vehicle washing wastewater is treated by the photodegradation method using a ZnO photocatalyst. The treated waste is irradiated using a UV-A lamp as a photon energy source which will initiate the photodegradation process in the waste. Stirring is done using a magnetic stirrer so that the photodegradation process can occur effectively. The experiment setup is shown in Fig. 1. The photodegradation experiment started with 1000 mL of motor vehicle washing wastewater added to a 1 L glass beaker. 0.5 grams of ZnO photocatalyst was added to a 1 L glass beaker. A 1 L beaker glass was added to the reactor. The sample was stirred using a magnetic stirrer. Samples were irradiated using 4 lamps of UV-A light for 2 hours. The beaker glass was removed from the reactor and then precipitated. The whole procedure was repeated with a contact time of 3 and 4 hours. The same procedure was also
Data analysis begins by looking for the percentage of photodegradation effectiveness based on the measurement results that have been carried out. The effectiveness of photodegradation can be determined by the equation:

\[
\text{Photodegradation effectiveness} = \frac{a - b}{a} \times 100\% \tag{1}
\]

where \(a\) is the initial concentration before the experiment and \(b\) is the pollutant concentration after processing \[10\]. The data will be processed by multiple linear regression analysis contained in the SPSS software. Multiple linear regression can see the effect of two or more dependent variables. This method will conclude the existence of a linear relationship or a straight line between the dependent variable and each predictor \[11\].

Furthermore, the photodegradation kinetics analysis was carried out using reaction rate kinetics of order 0 and order 1. The most effective reaction rate kinetics was obtained from a comparison of the analysis of order 0 and order 1. The reaction rate of order 0 was not affected by the increase in the concentration of the reagents. The equation for the reaction order 0 is obtained through the equation:

\[
C_A = C_{A_0} - kt \tag{2}
\]

where \(C_A\) is the concentration of \(A\) at \(t = t\), \(C_{A_0}\) is the concentration of \(A\) at \(t = 0\), \(k\) is the photodegradation rate constant, and \(t\) is time \[12\].

The rate of a first-order reaction depends on the concentration of the reactants raised to the power of one, the reaction rate is directly proportional to the concentration of the reactants \[13\]. The first order equation is obtained from the equation:

\[
\frac{\Delta C}{\Delta t} = k(C_0 - C_t) \tag{3}
\]

where \(t\) is time (hours), \(k\) is the coefficient of degradation reaction rate, \(C_0\) is the concentration degraded at a time (0), and \(C_t\) is the concentration degraded at time.

Based on the reaction rate of order 0 and order 1, the most effective degradation was obtained. After that, the modeling was carried out to determine the most suitable kinetic model between the literature and the data in the study. Can be plotted based on the removal of pollutants from pollutant uptake in the analyzed wastewater \[14\].

III. RESULTS AND DISCUSSION

A. Mass Effect of ZnO

The results showed that the mass affects changes in pH. The pH of the motor vehicle washing waste before the experiment was 8.23 which was close to alkaline. At a mass of 1 gram with a contact time of 4 hours the results of changes in pH reached 7.70. The results of multiple linear regression analysis show that the output significance value is 0.009 < 0.05. Changes in the pH value can be seen in Fig. 3. Photodegradation experiments showed that the mass of ZnO affected the degradation of COD parameters. This effect is also supported by the results of multiple linear regression analysis for COD parameters, namely 0.043 < 0.05. The effectiveness of photodegradation reached 95.20% with a mass of 1 gram of ZnO and a contact time of 4 hours.

The pH value plays a role in the formation of hydroxyl radicals. Alkaline pH conditions will affect the charge on the ZnO particles \[15\]. The carbon dioxide formed in the photodegradation process will increase the hydrogen content in the waste, resulting in a change in pH parameters. The surface of ZnO particles can have a positive, uncharged, or negative charge. When the pH of the solution is less than 7, the ZnO surface has a positive charge. The ZnO surface that has no charge...
occurs when the pH is around 7. pH of the solution greater than 7 will cause the ZnO surface to be negatively charged [16]. This is presumably because the longer the contact time, the more hydroxyl radicals are formed, following the results of previous studies, namely the more mass of ZnO added, the more ZnO particles that will react with wastewater. This is based on [16] COD decreased from 15,023 to 350 mg/L. The study used 1 gr/L ZnO and a contact time of 4 hours.

The results of the photodegradation experiment showed that the addition of ZnO mass affected the degradation of TSS. Based on the results of multiple linear regression analysis, the TSS parameter has a coefficient of 0.006 < 0.05. The TSS parameter has a degradation effectiveness of 37.42% at a mass of 1 gram and a contact time of 4 hours. The degradation of TSS parameters can be seen in Fig. 3(c). TSS levels have decreased in value but do not meet the quality standards that have been set. Physically, the treated water in the experiment looks clear. The suspended particles causing the high TSS particles have a maximum particle size of 2 m, larger than the colloid particle size. A high TSS value can hinder the penetration of light into wastewater [17]. Suspended material is a zone where a heterogeneous chemical reaction occurs. Suspended substances will form initial deposits which will reduce the production of organic substances in the water. Suspended substances consist of solid substances such as mud, sand, and clay as well as suspended particles consisting of biotic and abiotic [18].

Turbidity degradation in motor vehicle washing wastewater increases with increasing catalyst mass. This is supported by the results of multiple linear regression analysis for the turbidity parameter 0.013 < 0.05. Based on Fig. 3(d), the turbidity parameter degradation graph shows good results. The lowest effectiveness of photodegradation can be seen in the addition of a catalyst mass of 0.5 grams at a contact time of 2 hours, which is 93.25%. While the highest photodegradation effectiveness was obtained when the addition of 1 gram of catalyst with a contact time of 4 hours was 99.76%. There is no effect of adding too much mass to the turbidity of the wastewater.

For phosphate parameters, the addition of ZnO mass did not affect the degradation process. The results of multiple linear regression analysis are not influenced by the mass variation of ZnO, which is obtained with a value of 0.167 > 0.05. The highest photodegradation effectiveness for phosphate parameters was 68.30% with a mass of 1 gram and a contact time of 1 gram. It can be seen in Fig. 3(e) that the degradation of phosphate parameters is fluctuating. Phosphate value decreased but did not meet the quality standard of the Regulation of the Minister of the Environment of the Republic of Indonesia Number 5 of 2014 which is 3 mg/L. With the addition of 0.5 grams of ZnO mass, the decrease in phosphate value tends to decrease with increasing contact time, and the effectiveness of degradation at contact times of 2, 3, and 4 hours, namely 69.92, 41.93, and 47.23%. With the addition of 0.75 grams of ZnO mass, the effectiveness of the degradation also decreased at the contact times of 2, 3, and 4 hours, namely 51.50, 49.72, and 44.94%. While the effectiveness of the degradation at the addition of 1 gram of ZnO increased, at contact times of 2, 3 and 4 hours the percentages obtained were 54.05, 59.13, and 68.30%.

B. Effect of Contact Time

Contact time does not affect changes in pH values with the results of multiple linear regression analysis pH parameters are 0.178 which is greater than 0.005. At a contact time of 2 hours, the results of changes in pH values with masses of 0.5, 0.75, and 1 gram were 7.90, 7.87, and 7.73. At a contact time
The COD degradation process for a mass of 1 gram followed the order of 1. The value of the linear correlation coefficient on the curve of order 1 ($R^2 = 0.920$), the confidence level reached 92% at a mass of 1 gram. Kinetic modeling was carried out to determine the kinetic model following the results of the study. The modeling can be seen in Fig. 4. At a mass of 0.5 grams, order 0 is set for kinetic modeling. Meanwhile, the mass of 0.75 and 1 gram were assigned the order of 1 as the kinetic modeling. Based on the modeling, wastewater treated using ZnO with a mass of 0.5 grams can be modeled with an order of 0, and COD can be degraded to below the quality standard at a contact time of 4 hours. At a mass of 0.75 and 1 gram of COD the most optimally degraded at a contact time of 10 hours.

Photodegradation experiment results show that the TSS parameter is not affected by the contact time in the degradation of its value. The result of multiple linear regression analysis of the TSS parameter is 0.714, which means it is greater than 0.05. Based on Fig. 3(c), the decrease in TSS parameters at a contact time of 2 hours for masses of 0.5, 0.75, and 1 gram were 495.00, 485.00, and 512.00. At the contact time of 2 hours, the decrease in TSS parameters for masses of 0.5, 0.75, and 1 gram were 459.00, 485.00, and 483.00. The decrease in TSS parameters at a contact time of 2 hours for masses of 0.5, 0.75, and 1 gram were 438.00, 420.00, and 373.00. This shows that the more catalyst added can reduce the capture power by the catalyst to photon energy so that the oxidation process by $h^+$ and the reduction process by $e^-$ becomes inhibited [19].

The rate of photodegradation kinetics of TSS parameters for masses of 0.5 and 0.75 grams was assigned the order of 0 as kinetic modeling. The values of the linear correlation coefficient ($R^2$) on the order 0 curves at masses of 0.5 and 0.75 grams are 0.625 and 0.616, with confidence levels reaching 62.5 and 61.6%, respectively. While the mass of 1 gram is assigned the order of 1 as kinetic modeling. The value of the linear correlation coefficient ($R^2$) on the order 1 curve at a mass of 1 gram is 0.965 with a confidence level of 96.5%. The modeling graph can be seen in Fig. 4. Based on the kinetic

<table>
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<th>Experiment</th>
<th>Variation</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>TSS (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>Phosphate (mg/L)</th>
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<tr>
<td>Contact Time (hours)</td>
<td>Catalyst Mass (grams)</td>
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<td>HPSF</td>
<td>HPA</td>
<td>HPSF</td>
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of 3 hours, the results of changes with masses of 0.5, 0.75, and 1 gram were 7.90, 7.83, and 7.77. While the contact time of 4 hours resulted from changes with masses of 0.5, 0.75, and 1 gram, namely 7.80, 7.77, and 7.70. Changes are fluctuating, and the value of changes is not stable with increasing contact time.

COD parameters are influenced by variations in contact time in decreasing levels. Based on the results of multiple linear regression analysis the COD parameter is 0.020 $< R^2 < 0.05$. It can be seen in Fig. 3 that there is a decrease in COD parameters with increasing contact time. UV A contact time affects the waste by increasing the percentage of degradation. At the contact time of 1 hour with 0.5 gram ZnO mass, the percentage of photodegradation was 90.25%. As for the mass of 0.75 grams, the percentage of photodegradation is 93.02%. Then for a mass of 1 gram, the percentage of photodegradation is 95.20%. The longer the contact time, the longer the interaction time between UV A light, waste, and ZnO. It will increase the production of hydroxyl radicals [6]. The longer the contact time, the longer the interaction between wastewater and photocatalyst. So that the degradation process is more effective caused by the wastewater molecules hitting the ZnO surface evenly [7].

The degradation process parameters of COD, TSS, turbidity, and phosphate can be calculated as the rate of degradation or the rate of degradation of the photodegradation process. A comparison of order 0 with order 1 is needed to obtain a significant reaction rate. The kinetics of order 0 were obtained from plotting $t$ (time) with the measurement levels at each sampling time. First-order kinetics is obtained from the value of In COD which is plotted with $t$ (time).

The reaction order in the COD degradation process for a mass of 0.5 grams follows the order of 0. This is indicated by the value of the linear correlation coefficient on the curve of order 0 ($R^2 = 0.966$), the confidence level reaches 96.6% at a mass of 0.5 grams. The COD degradation process for a mass of 0.75 grams followed the order of 1. The value of the linear correlation coefficient on the curve of order 1 ($R^2 = 0.997$), the confidence level reached 99.7% at a mass of 0.75 grams.
FIG. 4: Graph of phosphate modeling (a) a mass of 0.5 grams with an order of 0, (b) a mass of 0.75 grams, and (c) a mass of 1 grams. TSS modeling graph (d) a mass of 0.5 grams of order 0, (e) a mass of 0.75 grams of order 0, and (f) a mass of 1 gram of order 1. Turbidity modeling (g) a mass of 0.5 grams of order 1, (h) a mass of 0.75 grams of order 1, and (i) a mass of 1 gram of order 1.

modeling, the most optimal contact times for TSS degradation for masses of 0.5, 0.75, and 1 gram of ZnO were 23, 20, and 21 hours.

Photodegradation experiments showed that the turbidity of the wastewater decreased with increasing contact time. The results of multiple linear regression analysis for the turbidity parameter $0.032 < 0.05$. In addition, in Fig. 3(d) it can also be seen that the turbidity degradation showed good results. Physically, it can be seen that the wastewater is getting clearer. The highest percentage of degradation occurred when the contact time was 4 hours and the addition of 1 gram of ZnO catalyst. Based on the photodegradation process of ZnO catalyst in wastewater, due to UV A lamp irradiation on water, electron pairs ($e^-$) and holes ($h^+$). The hole formed will react with water on the ZnO surface so that it will form OH$^-$. The electrons will reduce O$_2$ to form O$_2^-$ [8]. OH$^-$ will form a hydroxyl radical (OH) which will play a role in oxidizing the organic compound in question and then it will be converted into simple compounds such as carbon dioxide and water. The reaction has the following mechanism [19]:

$$\text{ZnO} + h\nu \rightarrow h^+ + e^- \quad (4)$$
$$e^- + O_2 \rightarrow O_2^- \quad (5)$$
$$h^+ + OH^- \rightarrow \text{OH} \quad (6)$$
$$\text{OH} + \text{organic compound} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (7)$$

Turbidity parameters were modeled using photodegradation kinetics based on order 0 and order 1. The mass modeling of 0.5, 0.75, and 1 gram was set to order 1. The value of the linear correlation coefficient ($R^2$) on the order 1 curve at a mass of 0.5, 0.75, and 1 gram were 0.941, 0.838, and 0.955 with confidence levels reaching 94.1, 83.8, and 95.5%, respectively. Order 1 modeling for masses of 0.5, 0.75, and 1 gram can be seen in Fig. 4. The graph in Fig. 4 shows that at a mass of 0.5, 0.75, and 1 gram the optimal contact time to degrade turbidity is at 10 hours.

Photodegradation experiments on phosphate parameters were not affected by contact time. Based on the results of multiple linear regression analysis, the significance value for the phosphate parameter is 0.774. The decrease in phosphate parameters tends to fluctuate. The decrease in levels is shown in Fig. 3. The highest percentage of degradation for phosphate parameters occurred when 1 gram of ZnO was added with a contact time of 4 hours. At a contact time of 2 hours, the largest percentage of degradation occurred when 0.5 grams of ZnO was added. However, at the contact time of 3 and 4 hours, the largest percentage of degradation occurred when 1 gram of ZnO was added with a percentage of 59.13 and 68.30%, respectively. This can happen because when electrons and holes are formed, both will experience recombination so that they will not react with water or oxygen which will reduce the levels of hydroxyl radicals that will be formed. Another thing that can happen is that when the contact time is longer, high photodegradation results can be formed so that the interaction between the ZnO surface and wastewater will be reduced. Then it causes the photodegradation process to be less effective [20].

The kinetic modeling of mass 0.5 and 0.75 gram was determined based on the order of 0. The value of the linear correlation coefficient ($R^2$) on the curve of order 0 at masses of 0.5 and 0.75 grams was 0.54 and 0.413, with a confidence level of 54 and 41.3%. As for the mass of 1 gram, the order of 1 is set as kinetic modeling. The value of the linear correlation coefficient ($R^2$) on the order 1 curve for a mass of 1 gram is 0.961 with a confidence level of 96.1%. The modeling graph can be seen in Fig. 4. Based on kinetic modeling, the most optimal contact times for TSS degradation for masses of 0.5, 0.75, and 1 gram of ZnO were at 9, 9, and 30 hours.
IV. CONCLUSION

These results indicate that ZnO photocatalyst may be used for photodegradation of car wash wastewater. The most effective mass of ZnO photocatalyst is 1 gram in to the treatment of motor vehicle washing waste, where the decrease in pH parameters reached 7.70, the degradation of COD parameters reached 95.20%, for TSS reached 37.42%, and for turbidity reached 93.25%. Meanwhile, the most effective of contact time is 4 hours, where the degradation of COD parameters reached 95.20%, and for the turbidity reached 99.76%.

Acknowledgment The author would like to thank the Head of the Multifunctional Laboratory, Ar-raniry State Islamic University Banda Aceh who has supported this research.