Study Photodegradation of Acid Orange 7 Using ZnO Waste Batteries

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Abstract. This research aims to determine the ability of ZnO waste batteries to degrade Acid Orange 7. The first, synthesized zinc acetate precursors from Zn waste batteries. Next, synthesized ZnO from the precursor of zinc acetate and impregnated with zeolite to form a ZnO-Zeolite composite used the sol-gel method. Photodegradation test for Acid Orange 7 dye used a time 30, 60, 120 , 240, 360 and 480 minute, concentration of 30, 50,75, 100, 150ppm with variations in pH 3, 5, 7, 9 and 11. Measurement of degradation resultsconcentration of Acid Orange 7 dye used a UV-Vis Spectrophotometer at a wavelength of 484.45 nm. The results showed that ZnO-Zeolite composites were able to degrade Acid Orange 7 dyes at pH 7, 480 minute, concentration 50 ppm with a degradation percentage of 94.15%.

1. Introduction
The textile industry has become one of the industries that have experienced rapid development in Indonesia and has a positive impact on the welfare of the community, including reducing the number of unemployed, increasing income, and the output of the industry. However, many textile industries dispose of staining waste into the environment without prior processing, which results in inhibiting the penetration of sunlight into the water, thus disrupting the photosynthetic activity of microalgae and threatening the sustainability of aquatic ecosystems. Based on the consequences, it is necessary to conduct an effort to overcome the problem of textile dye waste before being disposed into the environment. Some methods that can be done include the method of ultraviolet radiation, biodegradation and ozonolysis. [3]. This method requires relatively high operational costs. Other methods that can be used, such as coagulation, electrocoagulation and chlorination [5]. However, the method also has a disadvantage, such as the emergence of problems due to the production of new phases containing more concentrated pollutants. One method that is easy and relatively inexpensive to apply is the photodegradation method, this method can decompose dyes into components that are simpler and safer for the environment. The color of photodegradation can be conducted using photocatalyst materials and ultraviolet (UV) radiation. Photocatalyst materials such as ZnO are able to absorb the solar spectrum and quantum light more than TiO₂. The researcher tried to make a photocatalyst with a better size distribution by dispersing semiconductor particles on solid support materials such as zeolite. Zeolite can be as a supporting of solid material which is able to disperse semiconductor materials, thus preventing the sintering process in semiconductor materials, because zeolites have a porous structure, a large surface area, so that more catalysts can be developed [8]. pH has an important role during the photodegradation process to produce hydroxyl radicals. The more hydroxyl radicals formed, the greater the ability of photocatalysts to oxidize organic compounds [1]. Indigo Carmines dye degradation results in 44.24% using TiO₂-Zeolite catalysts occurring at pH 5 [2].
ZnO-Zeolite catalyst was able to degrade azo Acid Blue92 at pH 6 [6]. The results of the degradation of blueberry methylene using ZnO-activated carbon occur at pH 11 [9].

The use of ZnO catalyst impregnated with zeolite and activated carbon as mentioned above, generally uses ZnO which is synthesized from pure zinc acetate precursors. For this reason, the researcher was interested to analyze the effect of pH on the photodegradation of Acid Orange 7 azo dyes using ZnO, which was synthesized from battery waste and impregnated with zeolite.

2. Experimental

2.1. Material

The materials used are anode of zinc-carbon primary battery waste, natural zeolite, 96% ethanol, sodium carbonate solids (Na2CO3), glacial acetic acid (CH3COOH), concentrated hydrochloric acid (HCl), sodium hydroxide (NaOH) 2 M, zinc chloride (ZnCl2) 25%, silver nitrate solids (AgNO3), distilled water, aqua bides, Acid Orange 7 solids, filter paper, aluminum foil, and Whatman filter paper.

2.2. Preparation of Zeolite

Natural zeolite is crushed and sifted to a size of 150 mesh. Then washed, the washing results were filtered and dried in an oven at a temperature of 110°C for 2 hours. The result of washing zeolite was added 75 mL ZnCl2 25%, then shaker for 4 hours. Filtered zeolite, washed distilled water. Then oven at 110°C.

2.3. Preparation of Zinc Acetate

A total of 10 grams of Zinc-Carbon battery anode is dissolved in 10 ml of concentrated HCl. The solution is left until most of the anodes dissolve. The solution is filtered, the filtrate is added with a solution of 0.75 M sodium carbonate as much as 200 mL. The suspension formed is then filtered and dried at room temperature. The suspension formed is then added with 20 mL of glacial acetic acid until a clear solution is formed. The solution is then heated to form a gel and solidifies at room temperature. The solid is then mashed and stored in an airtight container.

2.4. ZnO-Zeolite Composite Synthesis

ZnO-Zeolite composites are made with a mass ratio of ZnO: Zeolite 5: 1. Zn (CH3COO)2 weighed 8.989 grams respectively and added zeolite as much as 0.664 grams, then dissolved into 16 mL ethanol. The mixture is reflux while stirring for 2 hours at 760°C. Then 45 mL of 2 M NaOH was added and stirred for 1 hour with a magnetic stirrer. The mixture was left overnight and then filtered [9]. The precipitate in the oven at 600°C and continued with calcination at 400°C. ZnO-Zeolite composites were characterized using Scanning Electron Microscopy (SEM-EDX).

2.5. Determination of optimum pH degradation of Acid Orange 7 dye

Acid Orange 7 dye solution was made with a concentration of 50 ppm, then 20 mL was taken and then put in 5 beakers. Acid Orange 7 solution is regulated by pH to pH 3, pH 5, pH 7, pH 9 and pH 11. Next, 50 mg of ZnO-Zeolite is added to the beaker. Then, stir it with a magnetic stirrer and irradiate it with UV light for 480 minutes. After being irradiated with UV light, then centrifuged at a speed of 7000 rpm for 15 minutes, then measured the absorbance using a UV-Vis spectrophotometer.

2.6. Determination optimum concentration of acid orange 7 dye degradation

A total of 20 ml of Acid Orange solution using the optimum pH with variations in concentrations of 30, 50, 75, 100, 150. Then, 50 mg of ZnO-Zeolite was added to the beaker. Then, stirred and irradiated with UV light for 480 minutes. Then centrifuged for 15 minutes, and measured the absorbance using a UV-Vis spectrophotometer.
2.7. Determination of optimum time interaction of acid orange 7 dye substance
A total of 20 mL of Acid Orange solution uses optimum pH and concentration with a variation of time 30, 60, 120, 240, 360, and 480 minutes. Then, 50 mg of ZnO-Zeolite is added to the beaker. After that, stirred and irradiated with UV light the sample was centrifuged for 15 minutes, and measured the absorbance using a UV-Vi spectrophotometer.

3. Results and Discussions
ZnO-Zeolite photocatalysts are synthesized using zeolite and zinc acetate precursors derived from battery waste. The synthesis of ZnO-Zeolite photocatalyst was carried out using the sol gel method, which is the process of phase change from sol to gel based on the hydrolysis process and precursor condensation. The growth of ZnO particles from the precursor of zinc acetate generally experiences 4 stages, namely solvation, hydrolysis, polymerization and transformation into ZnO [7]. The reaction mechanism is:

Solvation step:
\[ \text{Zn(CH}_3\text{COO)}_2 \xrightarrow{\text{ ethanol}} \text{Zn}^{2+} + 2\text{CH}_3\text{COO}^- \]

Hydrolysis step
\[ \text{Zn}^{2+} + 2\text{CH}_3\text{COO}^- + 2\text{NaOH} \xrightarrow{\text{stand + air}} \text{Zn(OH)}_2 + 2\text{CH}_3\text{COONa} \]

Polymerization step
\[ \text{Zn(OH)}_2 + 2\text{H}_2\text{O} \xrightarrow{} \text{Zn(OH)}_4^{2+} + 2\text{H}^+ \]

Transformation step
\[ \text{Zeolit} + \text{Zn(OH)}_2^{2+} \xrightarrow{} \text{ZnO-Zeolit} + \text{H}_2\text{O} + 2\text{OH} \]

![Figure 1. Results of ZnO-Zeolite Composite Synthesis](image)

The characterization results show a structure that clumps with the clump surface of the material are small-sized scattered randomly. The clump is thought to be a zeolite material while the small material scattered randomly on the surface of the clot is thought to be a Zinc Oxide (ZnO) material.
Figure 2. SEM analysis of the Results of ZnO – Zeolite magnification 10.000x

ZnO - Zeolite EDX analysis showed the mass percentage of O element = 22.67%, Al = 1.77%, Si = 6.19%, and Zn = 64.36%. The data prove that the ZnO-Zeolite composite was successfully synthesized.

3.1. Determination of optimum pH degradation of Acid Orange 7 dye

PH parameters are very influential in the process of degradation of dyes. Each dye has an optimum pH, depending on the type of dye and the conditions at that time. pH 7 is the optimum pH with a degradation percentage of 94.15%. (Figure 3). At pH 7 OH radicals formed in the photodegradation process better decomposite the Acid Orange 7 dyes than in acidic or basic conditions. The same thing was found in the Pertiwi study (2018) which obtained the results of dyestuff degradation at an optimum pH 7.

Under acidic conditions, the exclusive force between the photocatalyst and the dyestuff will cause a decrease in adsorption and a decrease in the dyestuff photodegradation. In addition, ZnO has a tendency to dissolve by decreasing the pH of the solution [4].

Figure 3. The percentage degradation of dye Acid Orange 7 at various pH.
Under acidic conditions, the surface of the catalyst is covered by the Acid Orange 7 dye molecule which causes absorption of UV radiation on the surface of the catalyst to decrease. As in alkaline conditions, the degradation of Acid Orange 7 less effective. This is because under alkaline conditions the dye will cause many OH- bound to the surface of the catalyst. The amount of OH- which is bound to the surface of the catalyst, will prevent the absorption of dyes to the surface of the catalyst. So, the process of photodegradation decreases. Increasing pH will reduce the presence of OH radicals obtained from the results of dye degradation by photocatalysts [2].

The best time to degrade Acid Orange 7 is for 380 minutes with a degradation percentage of 75.33%. The structure of Acid orange 7 is quite stable and has one azo group (N = N). So that the time needed by hydroxyl radicals is longer to break the unsaturated bonds found in Acid Orange 7.

Determination of optimum concentration to know the best concentration on the photodegradation of Acid Orange 7. At concentrations of 150 ppm and 300 ppm there was a decrease in the percentage of degradation of 73.56% and 34.95% respectively. This occurs because the higher concentrations of dyes, the number of molecules is more. Therefore, it requires a higher number of hydroxide radicals. The percentage of degradation decreases with the increasing of concentration. This is because the catalyst has reached the maximum limit in degrading dyes. the concentration needed to degrade Acid Orange 7 dyes is 50 ppm with a degradation percentage of 94.15%.

4. Conclusions
It was concluded that pH affected the degradation activity of Acid Orange 7 using ZnO impregnated zeolite (ZnO-Zeolite) with a degradation percentage 94.15% at optimum pH 7.

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