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Degradation of Congo Red Dye in Wastewater using Ozonation Method with H_2O_2 Catalyst

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ABSTRAK

Perkembangan sektor industri di Indonesia mengalami peningkatan yang sangat pesat khususnya pada industri tekstil. Meningkatnya jumlah industri berdampak pada jumlah limbah industri. Pewarna *congo red* merupakan salah satu zat warna yang sering digunakan dalam industri tekstil. Limbah pewarna industri perlu diolah agar tidak merusak lingkungan karena zat-zat yang terkandung berbahaya bagi lingkungan. Salah satu cara yang dapat digunakan untuk menetralisir limbah zat warna adalah dengan ozon. Ozon dapat digunakan di berbagai bidang seperti oksidasi senyawa anorganik/organik dan desinfeksi (atau pengendalian patogen). Katalis H_2O_2 digunakan untuk mempercepat proses ozonasi. Dalam penelitian ini variabel yang digunakan adalah waktu ozonasi (0,15,30,45,60 menit), kondisi pH (5,7,9) dan konsentrasi H_2O_2 (0,2.5,5,7,5,10) % massa. Berdasarkan penelitian diperoleh hasil bahwa semakin lama waktu ozonasi, semakin tinggi nilai pH, dan semakin banyak H_2O_2 yang digunakan maka semakin baik hasil proses ozonasi yaitu semakin rendah konsentrasi zat warna, COD, dan BOD_5 yang terdapat pada limbah cair.

Kata kunci**:** *Congo red*, Ozonasi, COD, BOD_5, Katalis H_2O_2.

ABSTRACT

The development of the industrial sector in Indonesia has increased very rapidly, especially in the textile industry. The increasing number of industries has an impact on the amount of industrial waste. Congo red dye is one of the dyes that are often used in the textile industry. Industrial dye waste needs to be processed so as not to damage the environment because the substances contained are harmful to the environment. One way that can be used to neutralize dye waste is ozone. Ozone can be used in many fields such as oxidation of inorganic/organic compounds and disinfection (or control of pathogens). H_2O_2 catalyst is used to accelerate the ozonation process. In this research the variables used were ozonation time (0.15,30,45,60 minutes), pH conditions (5,7,9) and the concentration of H_2O_2 (0,2.5,5,7.5,10) % mass. Based on the research, it was found that the longer the ozonation time, the higher the pH value, and the more H_2O_2 used, the better the ozonation process results, namely the lower the concentration of dyes, COD, and BOD_5 contained in the wastewater.

Keywords**:** *Congo red*, Ozonasi, COD, BOD_5, Katalis H_2O_2.

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1. Introduction

Environmental pollution in Indonesia is increasing from year to year. This is due to the development of industry in Indonesia. The increasing number of industries and becoming a magnet for population movement has an impact on increasing the amount of industrial waste and liquid waste. The increase in industrial liquid waste emissions since 2016 is more in composition than solid waste which is 61 percent (Badan Pusat Statistik, 2018). In addition to the increasing amount of waste, various consumption patterns that affect the material composition of the waste content are becoming increasingly difficult to decompose naturally, pollute the environment and endanger human health. Waste as the rest of a business or activity according to Law no. 32 of 2009 is divided into hazardous and toxic waste (B3) and non-B3 waste. B3 waste is sourced from the main activities of industrial processing, while non-B3 waste comes from domestic waste, agricultural waste, and some industrial waste.

Water pollution in Indonesia is usually found in rivers, this is because industrial waste is directly channeled into rivers without prior treatment. This situation will affect the quality of river water in Indonesia. The quality of river water in Indonesia is generally in a heavily polluted status, of the 82 rivers monitored in 2016 and 2017 there are 50 rivers

whose condition is relatively unchanged and there are 18 rivers whose quality is improving, but 14 rivers have deteriorated (Badan Pusat Statistik, 2018). Meanwhile, according to Podes, around 64 thousand villages in Indonesia (76.5 percent) which are traversed by rivers, as many as 25.1 percent of villages experience water pollution.

Sources of waste caused by the mining, energy and mineral industries are a fairly large contributor to liquid waste, namely 167.7 trillion in 2000 increasing to 1,028.8 trillion in 2017 (Statistik Lingkungan Hidup dan Kehutanan, 2017). In addition, the textile industry also contributes quite a lot of dye liquid waste. Dyes are organic compounds that represent a group of pollutants (D.L. Postai et al., 2016). The dyes commonly used in the textile industry are synthetic dyes. Synthetic dyes have 2 types of key groups in a dye molecule, namely chromophores and auxochromes. The chromophore group has a role in producing color, while the ausochrome group gives the color molecule its ability to dissolve in water and increases the affinity of the dye to the fabric fiber (Haryono, et al 2018). After dyes are exposed to water, they are difficult to remove, because they are resistant to photodegradation, biodegradation, and oxidation. In addition, dyes are of synthetic origin and have a very complex molecular structure, with stability designed to resist degradation by light, chemical, biological and other factors (DL Postai et al, 2016).

Textile dyes have various types, one of the textile dyes is congo red. Congo red is a dye that has a strong affinity for cellulose fibers so that it is easily bonded well, thus Congo red dye is widely used in the textile industry (Alya et al., 2018). Congo red is an anionic benzidine derivative that metabolizes to benzidine, which is a carcinogenic compound (Shafqat et al., 2020). In addition to being carcinogenic, congo red is toxic and has mutagenic effects (Wekoye et al., 2020).

Textile wastewater is often highly alkaline (pH 9.0-13.0, because fixation of dyes to fabrics requires a high pH) and highly saline (salinity 3.5-20%, containing Na^+, Ca^{2+}, Mg^{2+}, etc.) (Guo et al., 2020).

From a health point of view, dyes are toxic, carcinogenic and have mutagenic effects. In addition, they have detrimental effects on humans such as diseases of the eyes, skin, respiratory system, and irritation of the digestive tract. To treat colored waste there are several methods such as: coagulation, flocculation, reverse osmosis, precipitation, oxidation, reduction, membrane filtration, ultrasonic processes, anaerobic and aerobic processes, biochemical degradation, adsorption, microbiological decomposition and ozonation (Tenev et al, 2019).

One of the dye waste treatment is the ozonation method. Ozonation is a chemical oxidation process for removing the color of organic dyes (Aziz et al., 2018). The advantage of the ozonation process is that due to its strong oxidative properties, O_3 can be used in various fields, such as the oxidation of inorganic/organic compounds and disinfection (or pathogen control). However, this process also has drawbacks, including limited use of oxidants due to the formation of side products that may be toxic and cannot be decomposed. In addition, the low solubility of ozone in water will also lead to low ozone utilization efficiency resulting in high operating costs. The catalytic ozonation process can solve this problem, and it has received increasing attention in recent years.

In the catalytic ozonation process, the catalyst can increase the decomposition of O_3 and generate active free radicals, which can increase the degradation and mineralization of organic pollutants (Wang and Chen, 2020). In addition, in the presence of a catalyst, the efficiency of ozone utilization can also be increased to a certain extent. Wang and Chen (2020) conducted research on the ozonation process and ozonation with H_2O_2. The results showed that the degradation was significantly increased (55%) in the ozonation process with H_2O_2, compared to ozonation alone (30%). Direct oxidation by ozone molecules can cause degradation in both ozonation and peroxon processes, whereas the presence of H_2O_2 as a very important initiator can significantly affect the ozonation process and HO_2^- ions separated from H_2O_2 have a much higher ability than OH^- ions to initiate and accelerate the decomposition of O_3.

Based on these results, the research objectives was ozonation congo red with an H_2O_2 catalyst because H_2O_2 accelerates the OH^- yield in the ozone transformation process without causing secondary pollution, as well as being easy to operate (Fu et al., 2019). In addition, this study carried out variations in pH in order to obtain optimal results because pH is a key factor in the ozonation process (Jung et al., 2017).

2. Materials and Methods

The materials used in this research were synthetic wastewater containing congo red 50 ppm, H_2O_2 catalyst, NaOH 1 M, and HCL 1 M. The congo red used in this study was powder and the brand was Merck. The catalyst used in this study was H_2O_2 30% (liquid, brand: Merck). The equipments used in this research were ozonator, beaker glass (25 ml, 100 ml, 2000 ml), pH indicator, volumetric flask, UV-Vis Spectrophotometer, and digital scales. The ozone generator used in this reserch has an ozone gas output concentration of 400 mg/h, power consumption was 15W, and electrical requirement was AC220V±10%50Hz.

The variations of this ozonation condition were, pH= 5, 7, 9; catalyst concentrations were 2.5, 5.0, 7.5, 10.0 % mass; and ozonation times were 15, 30, 45, 60 minutes.

The wastewater treatment process containing congo red was conducted in batch condition. The research started with making wastewater synthetic sample. For making those wastewater sample, 50 mg of congo red was dissolved in 1000 ml of solution. The next step is to condition the sample according to pH

variations, namely acidic (pH=5), neutral (pH=7), and basic (pH=9). The first experiment was ozonation under acidic conditions. Waste conditioning under acidic conditions by adding HCl solution. The acidic pH used in this study was 5. Furthermore, ozonation of waste in neutral conditions, followed by ozonation in alkaline conditions (pH=9) by adding NaOH solution. Furthermore, at the best pH conditions, ozonation was carried out by adding an H_2O_2 catalyst. Variations in the concentration of the catalyst used were 0, 2.5, 5.0, 7.5, 10.0% mass. The waste from the processing was tested for dye content using a UV-Vis spectrophotometer, COD content using the SNI 6989.2:2019 method, and BOD_5 using the SNI 6989.72:2009 method.

3. Result and Discussion

3.1. Effect of Ozonation Time on Congo Red Wastewater Ozonation

The variables used to determine the effect of ozonation time were 0, 15, 30, 45, and 60 minutes. Tests were carried out to determine the concentration values, COD, and BOD_5 at each time with the initial concentration of 50 ppm Congo red dye with pH 7. The test results can be seen in Figure 1 and Figure 2.

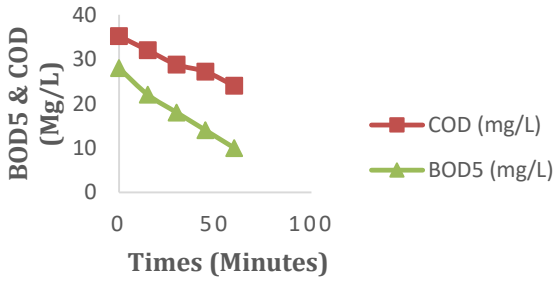

Figure 1. Effect of ozonation time on COD and BOD_5 content

Based on Figure 1, it can be seen that the longer the ozonation time, the lower of COD and BOD_5 content in wastewater. The effect of ozonation time on the congo red concentration can be seen in Figure 2, the longer the ozonation time, the lower of congo red concentration. Before ozonation, the concentration of congo red was 50 ppm, COD was 35.2 mg/L and BOD_5 was 28 mg/L. After ozonation process, the concentration of congo red decreased to 1 ppm, COD decreased to 24 mg/L, and BOD_5 decreased to 10 at ozonation times 60 minutes.

This is in accordance with the theory (Putri et al., 2016) which says that the longer the ozonation process, the more ozone is formed so that the ozonation becomes effective. In addition, the contact time of ozonation will increase the number of OH^- radicals so that the compounds in it will be oxidized (Fitri et al., 2016).

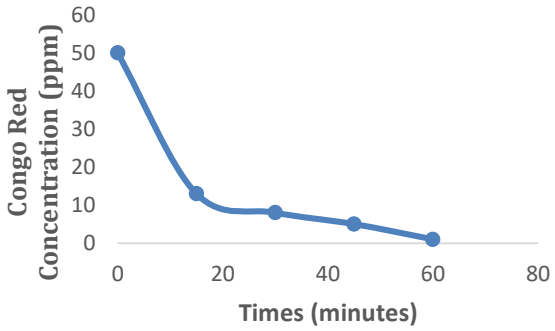

Figure 2. Effect of ozonation time on congo red concentration

3.2. Effect of wastewater pH on Congo Red Wastewater Ozonation

Subsequent research aims to determine the effect of pH during ozonation on the concentration of congo red, COD, and BOD_5. The research was carried out with variations in pH values of 5 (acidic), 7 (normal), and 9 (alkaline). Measurement of pH is a way to measure the concentration or activity of H ions (Sururi et.al., 2014). The research results can be seen in Figure 3, Figure 4, and Figure 5.

Based on Figure 3, Figure 4, and Figure 5, it can be seen that the ozonation process with pH 5 (acidic) decreased the concentration, COD, and BOD_5 (11 ppm, 32 mg/L, and 26 mg/L) which was less than the neutral pH (8 ppm, 28.8 mg/L, and 22 mg/L) and base (7 ppm, 25.8 mg/L, and 18 mg/L). This is in accordance with the theory (Estikarini, 2016) which states that the degradation of wastewater pollution mostly occurs better at neutral pH to alkaline pH, while in acidic conditions ozone does not work well. Based on research result, the ozonation process at alkaline pH is better because OH^- ions that exist can help free radicals HO_2 and OH to oxidize organic compounds.

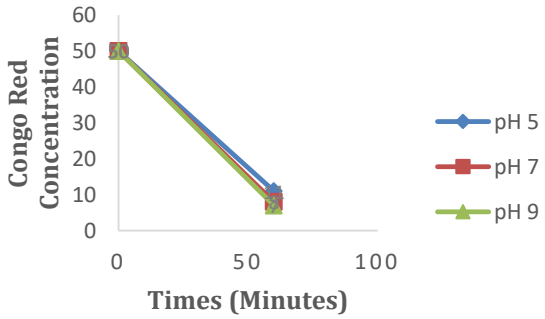

Figure 3. Effect of pH wastewater pH on Congo Red Cocentration

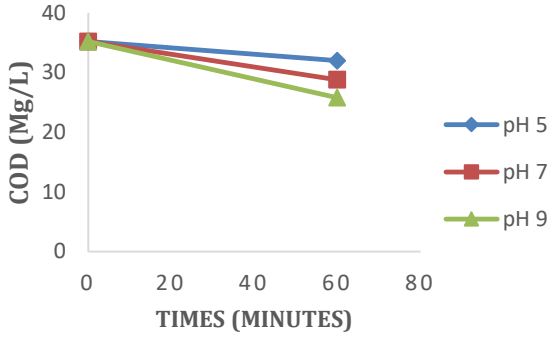

Figure 4. Effect of pH wastewater pH on COD of wastewater

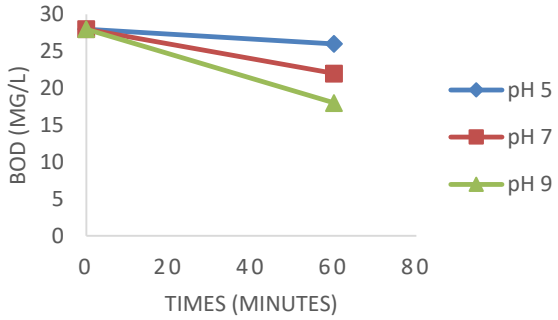

Figure 5. Effect of pH wastewater pH on BOD_5

3.3. Effect of Variation of H_2O_2 Catalyst on Congo Red Wastewater Ozonation

A catalyst is a component that can increase the rate of a reaction, but does not react. Catalyst is one of the important substances in the occurrence of a chemical reaction. This study aims to determine the effect of variations in the H_2O_2 catalyst on the concentration of dye, COD and BOD_5 in congo red wastewater before and after ozonation. The results can be seen in Figure 6, Figure 7, and Figure 8.

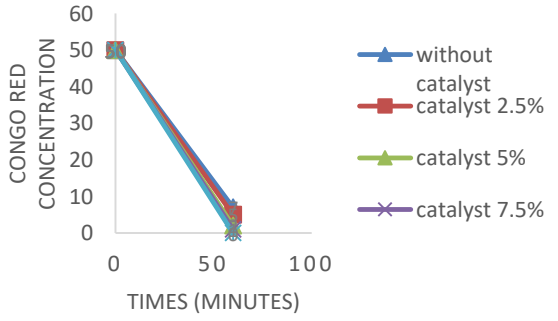

Figure 6. Effect of H_2O_2 Catalyst Concentration on Congo Red Concentration

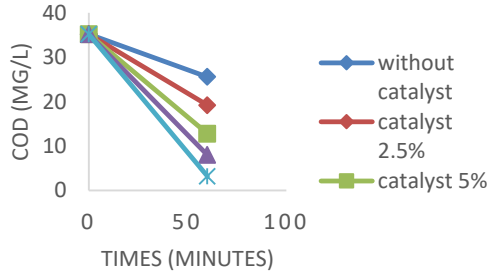

Figure 7. Effect of H_2O_2 Catalyst Concentration on COD

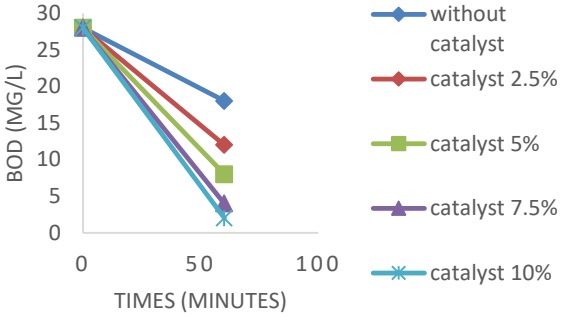

Figure 8. Effect of H_2O_2 Catalyst Concentration on BOD_5

Based on Figure 6, Figure 7, and Figure 8., it can be seen that the more H_2O_2 content, the lower the total concentration, COD and BOD_5. The best conditions were found in the amount of H_2O_2 10% mass with a concentration of 0 ppm, COD 3.2 mg/L, and BOD_5 2 mg/L. This is because the presence of H_2O_2 will produce many hydroxyl radicals which function to degrade dyes wastewater. Figure 6, Figure 7, and Figure 8. show that the more H_2O_2 added, the lower the concentration of dye, COD and BOD_5 in the wastewater. This results has met the threshold levels of COD and BOD_5 in the wastewater according to the regulations of the Ministry of Environment and Forestry. The reaction for the formation of hydroxyl radicals according to (Rini et al., 2019) in the addition of H_2O_2 is as follows.

$$O^{2-} + 2H^+ \rightarrow H_2O_2 \quad (1)$$
$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \quad (2)$$
$$h^+ + OH^- \rightarrow \cdot OH \quad (3)$$

Hydroxyl radicals can degrade color well because they have a high oxidation potential value of up to 2.8 eV. With a high oxidation potential value so that it can oxidize dyes into H_2O, CO_2 and other mineral acids.

4. Conclusion

Based on the results of the research, the conclusion of this research was: the effect of ozonation time on the concentration of dyes, COD and BOD_5 can be concluded that, the longer the ozonation time, the lower the value of solution concentration, COD and BOD_5 levels. The pH value affects the concentration of the solution, the levels of COD and BOD_5 where the more alkaline a solution is, the faster the ozonation

process occurs. The amount of catalyst H_2O_2 10% mass is the best for reducing dye concentration, COD and BOD_5 levels in the ozonation process of congo red dyes.

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