Research article

Textile Wastewater Post Treatment Using Ozonation

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Abstract

The textile industry is one of the industries that discharge an enormous quantity of highly colored wastewater because of the large amount of water used in the process. Textile wastewater is the potential to polluting the environment due to the high color contained in it. One of the problems in processing textile wastewater with conventional treatment methods is the ineffectiveness of color removal. A post-treatment is needed for treated wastewater to remove the color. One of the methods is by using the ozonation method. In this preliminary study, the decolorization of artificial textile wastewater containing azo dye reactive-black 5 (RB5) from secondary treatment was investigated in a batch system. Artificial treated textile wastewater from secondary biological treatment was made using 5.26 mg/L azo dye RB5 in 16 L volume of the reactor. The preliminary batch study showed that the optimum color removal achieved in 24.66 mg/minute ozone dose in a batch system with 20.89 mg/minute ozone consumption. Within 5 minutes of ozonation, color removal achieved was 100%, and COD removal achieved was 75%.

Keywords: color removal, ozonation, post-treatment, reactive black 5, textile wastewater

1. Introduction

The textile industry is an industry that is proliferating on a large scale and a home industry scale. In the textile industry’s production process, there are two types of processes, namely dry and wet processes. The dry process is in the weaving industry, while the wet process is in the textile finishing industry (Moertinah, 2008). The wet process is a stage in the textile production process that requires large amounts of water used for sizing and dyeing textiles using chemical substances. According to Colindres et al., 2010, in general, 200 - 500 L of water is needed to produce 1 kg of finished textile products. The waste produced from the wet process is textile liquid waste which contains high concentrations of dyes due to the use of textile dyes (Holkar et al., 2016).

There are two types of dyes used in the textile industry: natural dyes and artificial (synthetic) dyes. Most industries use synthetic dyes in their processes (Benkhaya et al., 2018). In the dyeing process, about 40% - 90% of the dye is bound to the textile fibers and the rest will be wasted in liquid waste so that in general, the textile waste has a high color concentration due to the use of dyes in the process (Zheng et al., 2016). The group of dyes that are most widely used in the textile industry globally, around 70%, are azo reactive dyes because they have good properties, simple dyeing procedures and are resistant to fading (Qiu et al., 2014). One type of reactive warno azo substance that is most widely used in the textile industry is Reaktive Black 5 (RB5), which is also most commonly found in aquatic environments (Zheng et al., 2016).
The large quantity of textile wastewater and the high amount of dye contained therein cause textile wastewater to be treated first before being disposed of into the environment. This is because textile waste contains toxic compounds, including synthetic azo dyes, which can cause pollution in water bodies (Sarkar et al., 2017). Textile dyes in textile waste are difficult to process because synthetic dyes have a complex molecular structure that makes them more stable and difficult to degrade (Mohamed and Walaa, 2016). Textile waste processing using biological methods is a widely used treatment. However, processing with this method still leaves dyes in the processed textile waste, so further processing is needed to remove the color in textile waste. This is because the color content that is still present in processed textile waste can cause pollution in water bodies and can disrupt the ecosystem of water bodies.

One technology that is widely applied as a solution in removing dyes contained in textile waste is ozone. Ozonation is the process of treating liquid waste by utilizing ozone molecules. Ozone is a molecule that has three negatively charged oxygen atoms (O3) which is unstable, has a short half-life so that it will return to its original form (O2) in a relatively short time, and acts as a strong oxidizer with a potential oxidation value of 2.07eV (Tabrizi, 2013). The reaction mechanism of ozone with inorganic substances and dissolved organic substances can be divided into two ways, namely direct mechanisms with ozone molecules and indirect mechanisms with hydroxyl radicals (von Gunten, 2003). The ozonation process can be carried out as further processing of textile waste after it is processed using biological processing that has not effectively removed color (Basak et al., 2015). Waste treatment using ozonation generally results in high pollutant removal effectiveness (Mohapatra et al., 2014).

Research related to the textile waste ozonation process that has been carried out includes research conducted by Suryawan et al., 2017, namely processing artificial textile waste using ozonation-based R.B. 5 dye batches as pretreatment. With an ozone rate of 40.88 mg/minute to treat artificial color waste RB-5 with a 100 mg/L concentration, the resulting color removal efficiency was 96.9% for 300 minutes of ozonation time and 70.1% for COD removal efficiency during 120 minutes of ozonation time. In pretreatment, the need for ozone and energy is relatively high because textile waste still contains various pollutants with high concentrations. Therefore, this study is a preliminary study that aims to remove the remaining dyes from previously treated or post-treatment textile waste so that ozone and energy requirements are not as large as those required in pretreatment.

2. Methodology

This ozonation research was carried out on a laboratory scale in batches using a cylindrical acrylic reactor. This reactor has a working volume of 16 liters with a diameter of 12 cm and a height of 200 cm. The scheme of the ozonation process can be seen in Figure 1. The aerator’s air will be converted into O3 using the ozone generator, whose flow rate is regulated through the airflow meter and enters the reactor’s bottom. To form a fine bubble, an air stone is added to the bottom of the reactor. At the top of the reactor is connected to potassium iodide (K.I.) absorbent, which functions to absorb free O3 coming out of the reactor.

Textile waste used is artificial waste that simulates processed textile waste from secondary processing. The manufacture of artificially treated textile waste is carried out by dissolving 5.26 mg/L of Reactive Black 5 dye into tap water. The ozonation process was carried out in batches for 30 minutes with three variations of the ozone rate, namely 8.22 mg/minute, 16.44 mg/minute, and 24.66 mg/minute. After the ozone process is complete, the optimum ozone rate is determined.

The parameters measured in this study were color parameters and chemical oxygen demand (COD). Measurement of the intensity of the color of the waste was carried out using a Jenway 6305 UV-VIS type spectrophotometer. The wavelength used in measuring the color removal intensity is the maximum wavelength of 595 nm. The calibration curve used is $y=0.0249x-0.012$, where the value is the absorbance, and the x value is the dye concentration RB5 in mg/L. This calibration curve’s function is to determine the concentration of the dye R.B. 5 measured in mg/L.
The ozone used comes from the ozone generator, and the determination of the ozone rate is carried out by the iodometric method based on the oxidation of potassium iodide (K.I.) by ozone and the production of iodine. The amount of ozone is determined indirectly through an iodometric titration which is based on the I2- reaction with O3. This study’s dissolved ozone concentration was measured in a specific period for each experiment’s variation using an ozone test kit visually according to the colorimetric method adapted from the EPA (Environmental Protection Agency), DPD method 330.5. The parameters analyzed in this study were the dye concentration R.B. 5 and COD value and the efficiency of removal of these parameters for each variation according to the following equation:

$$\eta(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%$$  \hspace{1cm} (1)

dengan $\eta$: Elimination efficiency (%)
$C_0$: Initial concentration (mg/L)
$C_t$: Time concentration (t) (mg/L).

3. Result and Discussion

In this preliminary study, artificial textile waste was used, which is made by dissolving the RB5 dye into as much as 5 mg per one liter of tap water. The initial color concentration of artificial waste was determined by entering the absorbance read on the spectrophotometer into the dye calibration curve RB5. This artificial waste simulates textile waste that has been treated by secondary treatment. The characteristics of this artificially treated textile waste are based on research conducted by Panswad et al., 2001, which carried out azo reactive textile dye removal using a combination biological processing anaerobic-aerobic sequencing batch reactor (SBR). The concentration of color and COD produced in the effluent were 3.1 mg / L and 24.11 mg / L, respectively, with an effluent pH of 8.5 (Panswad et al., 2001). In this study, 5 mg of RB5 dye per one liter of tap water was used, which produced a color concentration of 5.26 mg / L and COD of 25.6 mg / L with an average pH, which is in the range 6 - 9 according to industrial wastewater quality standards. Textiles. The characteristics of artificially treated textile waste used in the experiment can be seen in Table 1.
There are three variations of the ozone rate used in this study, namely 8.22 mg/minute, 16.44 mg/minute and 24.66 mg/minute. The reactor has a height of 1.5 meters to approach the bubble column reactor for the field's ozonation process. The column's high use also means that the ozone that enters the reactor has a longer time to stay in the reactor. Color removal in the ozonation process in batches at an ozone rate of 8.22 mg/minute, 16.44 mg/minute, and 24.66 mg/minute can be seen in Figure 2.

Based on Figure 2, in the second minute of the ozonation process, the resulting color concentration for an ozone rate of 8.22 mg/minute; 16, 44 mg/minute and 24,66 mg/minute, namely 4.26 mg/L; 1.81 mg/L and 1.19 mg/L respectively. The removal efficiency produced in the second minute of ozonation was 19.08% for an ozone rate of 8.22 mg/minute; 65.65% for an ozone rate of 16.44 mg/minute; and 77.75% for the ozone rate of 24.66 mg/minute. The concentration of color removal reached a steady condition, namely at the 15th minute of ozonation at the ozone rate of 8.22 mg/minute and the 5th minute for the ozone rate of 16.44 mg/minute and 24.66 mg/minute. In the 5th minute of ozonation, the color removal for the ozone rate of 16.44 mg/minute is 96.44% and for the ozone rate of 24.66 mg/minute is 100%. The fastest color removal occurred at an ozone rate of 24.66 mg/min as shown in Figure 2. With the same dye concentration of 5 mg/L; a higher ozone rate provides greater color removal efficiency at a faster time. As the ozone rate increases, the ozone consumption per volume of dye will also increase (Tehrani-Bagha et al., 2010).

There are two types of color removal mechanisms by ozone, namely direct and indirect. In the direct mechanism, ozone will directly oxidize the dye. In the indirect mechanism, ozone will be decomposed into O.H. radicals with an oxidation potential of 2.8 eV. The oxidation potential of O.H. radicals is higher than the oxidation potential of ozone (Tabrizi, 2013). Degradation of dyes during the ozonation process can occur because ozone oxidizes the dye molecules in its aromatic structure and the dye molecules' saturation side (Venkatesh et al., 2017). In the ozone process, the first stage of ozone will attack the chromophore group, which is the color group in azo dyes such as reactive black 5, by oxidizing it (Bilinska et al., 2017). Reactive dyes such as R.B. 5 dissolve quickly in water compared to dispersion dyes, so ozone can easily react with reactive dyes (Somensi et al., 2010).
Visual color changes due to batch ozonation process are artificially treated textile waste with an initial concentration of 5 mg / L can be seen in Figure 3, Figure 4, and Figure 5 for the ozone rate of 8.22 mg/minute; 16.44 mg/minute and 24.66 mg/minute, respectively.

Figure 3. Removal of dye RB5 with a concentration of 5 mg/L with an ozone rate of 8.22 mg/minute

Figure 4. Removal of dye RB5 with a concentration of 5 mg/L with an ozone rate of 16.44 mg/minute

Figure 5. Removal of dye RB5 with a concentration of 5 mg/L with an ozone rate of 24.66 mg/minute

The chemical oxygen demand (COD) parameter is a parameter that is also examined in this preliminary study. The removal of COD in the ozone process for the three ozone rates can be seen in Figure 6.

Figure 6. COD removal in the ozonation process with three variations of the ozone rate

COD removal in the batch ozonation process shown in Figure 6 shows that the COD concentration is steady from the 5th minute of ozonation for the three ozone rates. The concentration of COD contained in artificially treated textile waste was 25.6 mg / L. In the second minute of ozonation, COD removal for the ozone rate of 8.22 mg/minute and 16.44 mg/minute is 37.5%, and for the ozone rate of 24.66 mg / L is 50%. After 30 minutes of the ozonation process, the COD concentration was 10.67 mg / L; 6.4 mg / L and 6.4 mg / L for an ozone rate of 8.22 mg / minute; 16.44
mg/minute and 24.66 mg / minute, respectively. At a 24.66 mg/minute rate, the COD removal was obtained with a faster decrease in COD concentration from the available data. The effectiveness of decreasing COD concentrations through the ozonation process increases with increasing ozonation time (De Souza et al., 2010). The decrease in COD concentration in the ozonation process can be caused by breaking the azo N = N bonds contained in reactive black 5 and the decomposition of the chromophore groups (Shimizu et al., 2013). The breaking of the azo bond can be seen from the shift in the wavelength of the dye R.B. 5 which is explained by the absorbance of the dye RB5 which has shifted and decreased (Colindres et al., 2010). The shift in wavelength of dye R.B. 5 due to batch ozonation with an ozone rate of 24.66 mg/minute can be seen in Figure 7. In Figure 7, it can be seen that the maximum wavelength of dye R.B. 5 during the ozonation process has shifted. At minutes to zero ozonation, the wavelength shows a value of 595 nm as the maximum wavelength of the dye RB5, then after 30 minutes of ozonation, the wavelength shifts to 275 nm.

![Figure 7. Shifting of R.B. 5 wavelength during the ozonation process with an ozone rate of 24.66 mg/minute](image)

In the ozone process, not all of the reactor’s ozone will dissolve entirely and react with the dye RB5. Since ozone does not react completely, it will produce residual ozone. Following the mass balance concept, namely Input Reaction+Output, the ozone consumption in a solution or called a reaction can be calculated by the input minus the output. The ozone consumption in the ozone process for the three ozone rates can be seen in Table 2.

| Variation | Input Ozone Rate (Gases) (mg/minute) | Ozone Consumption (Liquid) (mg/minute) | Ozone Residue (Gases) (mg/minute) |
|-----------|-------------------------------------|---------------------------------------|----------------------------------|
| 1         | 8.22                                | 8.01                                  | 0.21                             |
| 2         | 16.44                               | 15.38                                 | 1.06                             |
| 3         | 24.66                               | 20.89                                 | 3.77                             |

Based on Table 2, it can be seen that the ozone consumption in solution (mg / minute) for the ozone rate is 8.22 mg / minute; 16.44 mg/minute and 24.66 mg/minute, namely 8.01 mg / minute; 15.38 mg/minute and 20.89 mg / minute, respectively. The greater the ozone rate, the greater the ozone consumption in solution (Tehrani-Bagha et al., 2010).
4. Conclusion

Textile waste that is processed using secondary processing has not been able to get rid of color maximally so that there are still residual colors in the processing effluent. The remaining color still needs to be processed further by using an ozonation process. In this preliminary study, a batch ozonation process was carried out to treat artificially treated textile waste, simulating the effluent from secondary processing. The ozonation process in batches was carried out with three variations of the ozone rate, namely 8.22 mg/minute, 16.44 mg/minute, and 24.66 mg/minute. The ozone rate that produced the most incredible color removal efficiency in the fastest time was the ozone rate of 24.66 mg/minute with an ozone consumption of 20.89 mg/minute. The efficiency of color removal with an initial color concentration of 5.26 mg/L at the 2nd and 5th minutes of ozonation was 77.35% and 100%, respectively. Meanwhile, the removal of COD for 30 minutes of ozonation is 75%, with steady conditions starting to reach the 5th minute of ozonation.

Acknowledgment

The author would like to thank the Bandung Institute of Technology's P3MI Research Grant for funding this research.

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