Reactive Black-5 Removal by Ozonation as Post Treatment

NI Wantoputri¹, S Notodarmojo¹,², Q Helmy¹,²,³*
¹Environmental Engineering Department, Faculty of Civil and Environmental Engineering, Institut Teknologi Bandung, Indonesia
²Water and Wastewater Engineering Research Group, Environmental Engineering Department, Institut Teknologi Bandung, Indonesia
³Bioscience and Biotechnology Research Center, Institut Teknologi Bandung, Bandung, Indonesia

*corresponding author: helmy@tl.itb.ac.id

Abstract. The textile industry is one of industries that growing rapidly in Bandung, Indonesia. It discharges enormous quantity of highly colored wastewater due to the use of water in large quantity and the use of dyes in the production process. One of the problems in processing textile wastewater with conventional biological treatment method is the ineffectiveness of color removal. A further treatment as post treatment is needed for treated wastewater discharge to remove the color. One of the method that known has high efficiency for textile color removal is by using ozonation method. In this ongoing study, the decolorization of artificial textile wastewater containing azo dye reactive-black 5 (RB5) from secondary treatment was investigated in a continuous system. Artificial treated textile wastewater from secondary biological treatment is made using 5 mg/L azo dye RB5 in 16 L volume batch reactor. The experiments show that the efficiency of color removal achieved is 100% within 10 minutes of reaction time with 24.66 mg/minutes of ozone dosage. In continuous system operation, ozonation process also conducted in 16 L volume reactor with up flow and down flow of influent feeding and HRT 10 minutes, 30 minutes and 50 minutes. The experiments show that the color removal was fluctuated and for median oscillation in certain interval contact time for each HRT, but higher color removal efficiency achieved in HRT 50 minutes.

Keywords: azo dye, COD, continue system, decolorization, ozonation, post treatment, RB 5

1. Introduction
The processes in textile industry are mainly consist of desizing, dyeing, bleaching, printing and finishing which consume large number of water, and consequently generate enormous quantity of wastewater [1]. The textile wastewater contains high color, high concentration of organic and inorganic compounds and heavy metal with its high color become the main concern in textile wastewater treatment [2]. High color in textile wastewater caused by the using of various dyes in textile processes. In Indonesia, dyeing process in textile industries generally use the synthetic dyes. Azo dyes isone of commercial reactive synthetic dyes that most widely used in textile process, about 70% of the world dye production and characterized by nitrogen double bonds (-N=N-), linked to aromatic groups [3]. During the dyeing process, about 40%-90% of dyestuff are fixed to the fabric and the rest is going to the treatment system.
[3]. This highly colored wastewater can cause water pollution, aesthetic problem and affect human health, therefore it should be treated before discharge to the environment.

Textile wastewater contains BOD with concentration about 80-6,000 mg/L, COD concentration is about 150-12,000 mg/L and ratio COD and BOD is about 1.5: 1 to 3:1 [4,5]. Biological treatment is one of the treatment system which is usually applied to treat textile wastewater. Because of the polyromantic structure with high molecular weight containing nitrogen, sulfur and metal in most of dye molecules, biological treatment is still ineffective to remove the textile wastewater color [1]. Therefore, needed other method as an alternative and advanced treatment system to enhance the biodegradability of organic and to remove the color contain in wastewater, such as Ozonation [2]. Ozone (O₃) is a strong oxidizing agent because of its instability and has high oxidation potential (2.08 eV) [6]. Ozone molecule has selective characteristic and prefer to attack the unsaturated chromophore bonds which are often associated with color [7].

In recent study, a lab scale ozonation process as pre-treatment conducted to remove RB5 dye in 2 L volume reactor using batch system and the results showed that the color and COD removal efficiency was 75% and 46,4% respectively by initial concentration 100 mg/L RB5+1 gram/L starch [8]. Another study, Reactive Black 5 (RB-5) dye was treated using ozonation as pre-treatment and then using biological treatment by moving bed biofilm reactor (MBBR) in 5 L volume reactor. The results showed that by using ozone as pre-treatment, the removal efficiency of color and COD was 81,2% and 83,63% respectively in 24 h hydraulic retention time, higher than without using ozonation [5].

Some textile industries still use the ground water in their process. The large quantity of the ground water taken can make the ground water surface decrease and make the scarcity of groundwater supply. Therefore, the large quantity of textile wastewater has potency to be reused using ozonation as advanced treatment. In this study, ozonation process will be applied in treating RB-5 dye solution as post treatment, simulating advanced treatment of textile treated wastewater from secondary biological treatment to remove the rest of color contain in it.

2. Research Method

2.1. Materials

Synthetic textile wastewater was prepared simulating treated textile wastewater from secondary biological treatment using azo reactive black-5 (RB5) dye with concentration 5 mg/L. Ozone was generated from dry air using aerator as feed gas by a corona discharge with quartz tube type ozone generator (model number: BO-1030QY) from Shenzhen Blueocean Industry Co., Ltd. Ozonation process of the dye solution was carried out in a acrylic reactor (diameter x height of 12 x 200 cm, respectively) with working volume 16 L (Figure 1) at room temperature with continuous system. This reactor was a scale up reactor from the previous study that used 2 L working volume in batch system. The Ozone generated from ozone generator was fed into reactor using flowmeter and introduced into the reactor through round flat air stone located at the bottom of reactor which produce fine bubbles.

2.2. Experimental procedure and analysis

2.2.1 Ozone dosage. Ozone produced from ozone generator which fed into the reactor was controlled using flowmeter. Ozone dosage was measured using iodometry method [9].

2.2.2 Ozonation process in batch operation system. Firstly, ozonation was conducted in a batch system reactor with working volume 16 L. The ozone gas flows into the reactor with flowrate 2 LPM and 3 LPM and generate ozone dosage 16, 44 mg/minute and 24,66 mg/minute respectively. Ozonation in this batch reactor stopped when the color removal has achieved steady state condition. The ozone dosage which showed the higher color removal efficiency in this process will be used as optimum dosage in the continuous operation system.
2.2.3 Ozonation in continuous operation system. The optimum ozone dosage obtained from batch experiment is used for ozonation process in continue system using three variation hydraulic retention time (HRT). The HRT was determined based on the batch system result. In this ozonation process, there are two kinds of influent flow feeding applied, they are up flow (Influent enter to the reactor from the bottom) and down flow (influent enter to the reactor from the upper).

2.2.4 Analytical method
The main parameters measured in this study is color and dissolved ozone ($O_3$). The color absorbance of RB5 was measured using Genesis 10S UV-VIS type spectrophotometer at wavelength 595 nm (maximum wavelength of RB5). The dissolved ozone $O_3$ also measured using a checker disk HI38054 Ozone Test Kit from Hanna Instrument with colometric method adapted from EPA recommended DPD method 330.5.

![Diagram of ozonation process in the study](image)

**Figure 1.** Diagram of ozonation process in the study (a) continuous operation with up flow influent feeding system (b) continuous operation with down flow influent feeding system

3. Results and Discussion

3.1. Ozonation process in batch operation system
In the batch operation system, 16 L of 5 mg/L RB-5 solution was ozonated with ozone dosage 16.44 mg/minute and 24.66 mg/minute. The removal efficiency of RB-5 using two variation of ozone dosage shown in Figure 2. In two minutes contact time, the color removal efficiency was about 49% for 16.44 mg/minute ozone dosage and 74% for 24.66 mg/minute ozone dosage. The decolorization rate of 5 mg/L RB5 solution rate was almost complete in 8 minutes with color removal efficiency achieved 97.5% for
16.44 mg/minute ozone dosage and 99.6% for 24.66 ozone dosage. The color disappears completely in 10 minutes contact time with efficiency 100% for each ozone dosage. The results showed that increasing the ozone dosage from 16.44 to 24.66 mg/minute increases the rate of decolorization because the ozone consumption per volume of dye solution also increase [10]

![Figure 2](image)

**Figure 2.** Color removal efficiency of 5 mg/L RB5 as the function of ozonation time

### 3.2. Ozonation Process in Continuous System Operation

In the batch system operation process, color removal achieved completely 100% in 10 minutes contact time for both ozone dosage. For continuous system operation, 24.66 mg/minute ozone dosage was used to prevent the shock loading and the HRT used were 10 minutes, 30 minutes and 50 minutes with 120 minutes of ozonation process for each HRT. The color removal efficiency of 5 mg/L RB-5 dye solution in ozonation process for each HRT with upflow and downflow influent feeding continuous system operation shown in Figure 3 and Figure 4, respectively.

![Figure 3](image)

**Figure 3.** Color removal efficiency of 5 mg/L RB5 as the function of ozonation time in each HRT for up flow continuous system operation
The color removal efficiency of 5 mg/L RB-5 dye solution in two kind influent feeding system (up flow and downflow) in figure 3 and figure 4 showed the similar pattern which is fluctuative, formed an oscillation in certain time interval for each HRT and did not achieved steady state condition yet for 120 minutes ozonation time. But from both figures, the longer HRT tends to have higher color removal efficiency with short distance between peak level and bottom level of the oscillation. The longer HRT, the longer time influent filled the reactor and contact with ozone in the reactor. Therefore, to achieve steady state condition, the HRT of influent feeding might be longer. The dissolved ozone ($O_3$) concentration, might affect the color removal efficiency in this continuous influent feeding system. In HRT 50 minutes with downflow influent feeding system (Figure 5), when the RB-5 dye concentration decrease, the dissolved ozone measured tend to increase and when the RB-5 dye concentration increase, the dissolved ozone measured tend to decrease which means by the increasing dissolved ozone concentration, the RB-5 dye concentration tend to decrease and increase the color removal efficiency.

The other important aspect that should be considered in affecting color removal efficiency in continuous reactor system was hydrodynamic reactor aspect like non optimal mixing of ozone bubbles that could make the ozone bubbles not well distributed along the reactor (completely mixing only happened in some part of reactor, like in the bottom). The non-optimal mixing of ozone bubbles along the reactor
can also make dead zone where some parts of RB-5 dye solution in reactor did not contact with ozone molecule. The other hydrodynamic aspects are type and size of ozone bubbles and also the effect of hydraulic retention time of influent feeding. The visual color degradation of 5 mg/L RB-5 synthetic treated textile wastewater in upflow continuous system operation with HRT 50 minutes shown in Figure 6.

![Figure 6](image)

**Figure 6.** Visual color degradation of 5 mg/L RB-5 dye in upflow continuous system operation with HRT 50 minutes

Ozonation process, also called selective oxidation can decolorize azo dye contain in wastewater effectively by breaking the conjugated azo bonds associated with the dye [11]. The first stage of dyes decolorization probably involves reaction between ozone molecule with the single chromophore group such as azo group dyes (like RB-5) or carbon-carbon double bond connecting aromatic rings [1]. In the batch operation system, the decolorization of 5 mg/L RB-5 dye solution in relatively short ozonation times, 10 minutes, showed the degradation of the aromatic fragments of the dyes molecules through the -N=N- chromophore double bond breaking and oxidation of their intermediates with evidence the absorbance decay in the UV region [1,12]. For the continuous system operation, the decolorization of 5 mg/L RB-5 dye solution also happened because of the -N=N- double bond breaking by ozone molecule. The absorbance decay in the UV region for 5mg/L RB 5 dye solution in continuous influent feeding system with HRT 50 minutes shown in Figure 7. The change of the peak position in the UV region from 595 nm (maximum wavelength of RB-5) to around 255 nm indicate the new smaller organic by product with aromatic structure [10].

![Figure 7](image)

**Figure 7.** The absorbance decay in UV region spectra during ozonation process in continuous influent feeding system with HRT 50 minutes in 120 minutes ozonation time
4. Conclusion
The ozonation process, in a scale up 16 L batch reactor, treating 5 mg/L RB-5 dye solution simulating the treated textile wastewater from secondary biological treatment shows high efficiency of color removal in short time ozonation, 10 minutes. The result gives promising efficiency in removing dye color as post treatment and the effluent of ozonation process have high potency to be reused. In continuous system operation, the color removal efficiency for 120 minutes ozonation time still did not achieved steady state condition yet and formed oscillation pattern, similar for both, up flow and downflow influent feeding system. The longer HRT, gave the higher color removal efficiency.

Acknowledgment
The study was performed within the ITB-P3MI research scheme; a research programs on community service, and innovation on ITB research group which is co-funded by the Indonesian Ministry of Research, Technology and Higher Education (Ristek-Dikti) Research Grant Fiscal Year 2018.

References
[1] Colindres P, Yee-Madeira, Reguera R. 2010. Removal of Reactive Black 5 from aqueous solution by ozone for water reuse in textile dyeing processes. Desalination. 258: 154-158
[2] Basak Serden, Ozgun Dilek, Ozdemir Sebnem, Cinar Ozer. 2015. The Inhibition Effect of Ozonation in Textile Wastewater. World of Journal Environmental Research. 5 : 122-129
[3] Zheng Qing, Dai Yong and Han Xiangyun. 2016. Decolorization of azo dye C.I. Reactive Black 5 by ozonation in aqueous solution: influencing factors, degradation products, reaction pathway and toxicity assessment. Water Science & Technology. 73.7
[4] Azbar N, Yonar T, and Kestioglu K. 2004. Comparison of various advanced oxidation processes and chemical treatment methods for COD and colour removal from polyester and acetate fiber dying effluent. Chemosphere. 55:81-6.
[5] Pratiwi R, Notodarmojo S, and Helmy Q. 2018. Decolourization of removal black-5 textile dyes using moving bed bio-film reactor. IOP Conf. Series : Earth and Environmental Science 106 012089
[6] Billinska Lucyna, Zylla Renata, Smolka Krzysztof, Gmurek Marta and Ledakowicz. 2017. 25, 5 (125): 54-60
[7] Soares Olivia Salome G P, Faria Patricia C.C, Orfao Jose J M, and Pereira Manuel Fernando R. 2007. Ozonation of Textile Effluents and Dye Solutions in the Presence of Activated Carbon under Continuous Operation. Separation Science and Technology. 42:7, 1477-1492
[8] Suryawan IWK, Helmy Q, Notodarmojo S. 2018. Textile wastewater treatment : Color and COD removal of reactive black 5 by ozonation. IOP Conf. Series : Earth and Environmental Science 106.012102
[9] APHA, Standard method for the examination of water and wastewater, 17th eds. APHA, AWWA and WPCF Washington DC, 1989, 3646 p
[10] Tehrani-Bagha A.R, Mahmoodi N.M, Menger F.M.2010. Degradation of a persistent organic dye from colored textile wastewater. Desalination 260 : 54-58
[11] Abidin Che Zulzikrami Azner, Fahmi Muhammad Ridwan, Soon-An Ong, Makhtar Siti Nurfatin Nadhirah, and Rahmat Nazzery Rosmady. 2015. Decolourization of an azo dye in aqueous solution by ozonation in a semi-batch bubble column reactor. ScienceAsia. 41: 49-54
[12] Faria P.C.C., Orfao J.J.M, Pereira M.F.R. 2009. Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents, Applied Catalysis B:Environmental 88: 341.