Degradation of batik dye wastewater in basic condition by ozonation technique in bubble column reactor

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Abstract. Naturally, textile waste and its complexity will grow significantly in tandem with the increasingly diverse production of the textile industry. In Indonesia, one of the leading textile industry is batik industry. These textile dye compounds as well as their corresponding phenolic compounds in batik waste are considered and treated as well as can cause acute toxicity and mutagenic effects for aquatic ecosystems. Ozone is an effective wastewater treatment technique by using ozone formation which can optimize the degradation process of batik wastewater. This study aims to test the ability of ozonation techniques in the process of removal remazol blue (RB-19) batik dyes or phenolic compounds (phenol and 4-chlorophenol) in bubble column reactor under basic condition (pH about 10). From experiment result, it was found that in 60-minutes degradation process with ozonation technique for RB-19 dye reached 99.70% and 4-chlorophenol reached 62.79%. The optimum condition of the treatment process was obtained by using air flow rate 10 L/min for RB-19 dye and 12 L/min for 4-chlorophenol, using a multi ozone injection system, and flow rate of wastewater 250 mL/min.

1 Introduction

Nowadays, the growth of batik industry in Indonesia has brought the issues of complex wastewater that significantly grew. Synthetic dye and phenolic compounds are the content of batik wastewater that needs to be treated thoroughly. Remazol blue (RB-19) is one of the most commonly used and easily accessible dyes in the batik industry, but it is also difficult to degrade [1]. Phenolic compounds in textile industry wastewater were derived from the process of scouring, dyeing, and printing [2]. Parachlorophenol (4-chlorophenol) is a phenolic compounds that used as an intermediate in organic synthesis of dyes [3]. United States Environmental Protection Agency (USEPA) incorporates phenol into the priority list of wastewater substances to be eliminated because phenolic compounds have high toxicity and carcinogens [4].

According to PERMEN LH Number 5 Year 2014 regarding wastewater quality standards for the textile industry, the limit of phenolic compounds is 0.5 mg/L. Several previous studies have shown that the phenolic content in the textile finishing wastewater is about 4.1 - 241.53 mg/L [5]. It is still considered too high, therefore an effective technique is needed to achieve quality standards.

Several conventional methods have been undertaken to overcome wastewater containing dyes and phenolic compounds, but those methods are ineffective because dyes and phenolic compounds are resistant to degradation, take a long time of degradation time, and toxic byproducts can be formed [6]. One of effective technique that can be developed is the ozonation technique, this technique can degrade toxic compounds and dyes that are very difficult to degrade by conventional methods [7].

The use of ozone in wastewater treatment is growing rapidly due to its dual function as strong oxidizing agent and disinfectant. The unique characteristic of ozone is its decomposition in water into a hydroxyl radical which is the strongest oxidant in water [8].

In this study, ozonation technique is applied in bubble column reactor in basic condition for batik wastewater treatment that containing dyes and phenolic compounds. In bubble column reactor with multiple injection system, oxidation process occurs rapidly and intensively. This system also produces a more homogeneous system with larger mass transfer and mass contact area [9]. The highest percentage of batik wastewater degradation is determined by ozonation technique was obtain in basic condition [10]. It is expected that the results of this research can be an effective technique of wastewater treatment.

2 Materials and method

The experimental set-up used in this degradation study is the bubble column reactor with the semi-batch system. The reactor was equipped with multi injection system to stream the ozone/air into the wastewater. The ozone stream was produced by ozonator. The volume, height, and diameter of the reactor are 12 L, 190 cm and 9 cm, respectively. The ozonator used in this research is tubular DBD (dielectric barrier discharge) reactor. Fig. 1 shows the schematic diagram of experimental setup for ozonation technique.

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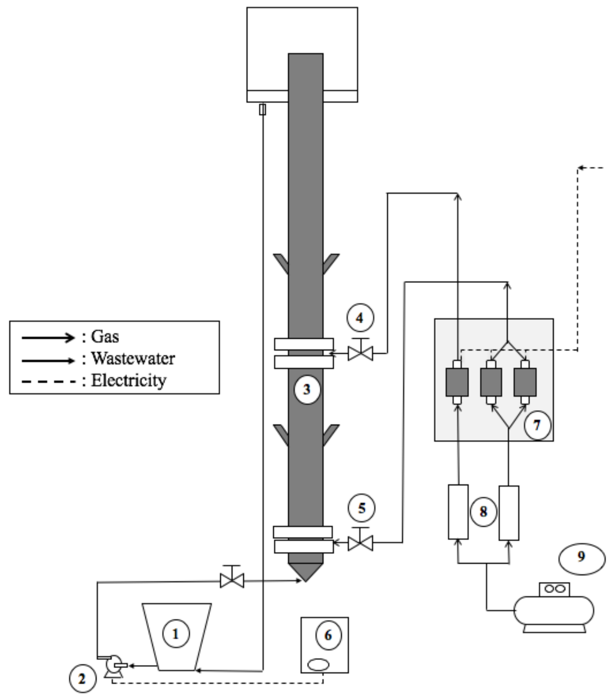


Fig. 1. The schematic diagram of experimental setup for ozonation technique

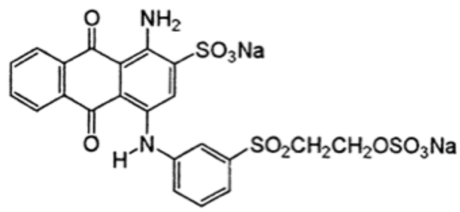
Table 1. Description of schematic diagram

1	Reservoir
2	Pump
3	Bubble Column Reactor
4	Gas Injection 1 (I_1)
5	Gas Injection 2 (I_2)
6	Power Supply
7	Ozonator Circuit
8	Flowmeter
9	Compressor

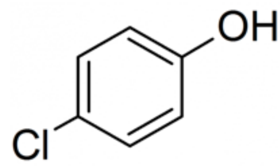
This study was started by hydrodynamics test and ozonator productivity test. Water and air were used in hydrodynamic test to prevent the possible future reaction. The gaseous ozone dosage from ozonator productivity test was determined with KI solution. Several experimental parameters such as air flow rate, ozone injection system, and wastewater flow rate were evaluated in this study. Air flow rates were 8 L/min, 10 L/min, and 12 L/min. The effects of ozone injection system were investigated with single injection and multi injection. Wastewater flow rates were 250 mL/min, 330 mL/min, and 390 mL/min.

The operating conditions in this study were initial concentration of remazol blue (RB-19) or 4-chlorophenol ± 50 mg/L, initial pH of wastewater 10, and conducted for 60 minutes with sampling at minute 0, 15, 30, 45, and 60. The molecular structures of remazol blue (RB-19) and 4-chlorophenol are shown in Fig.2.

The best operating conditions were obtained from concentration of RB-19 and 4-chlorophenol that obtained the highest percentage of degradation. The concentration of RB-19 and 4-chlorophenol were determined by using a spectrophotometer. Sample of 4-chlorophenol must be reacted with 4-aminoantipyrine before measured by spectrophotometer.



Remazol Blue (RB-19)



4-chlorophenol

Fig. 2. Molecular structures of RB-19 and 4-chlorophenol

3 Results and discussion

The results obtained during the study were discussed and analyzed which can be explained as below.

3.1 Hydrodynamic test

The hydrodynamic test in this bubble column was carried out using water as a liquid fluid and air as a gas fluid [11]. This test was performed to find out the phase contact profile between the liquid phase and the gas phase. The results of the hydrodynamic test on the bubble column reactor were obtained as follows.

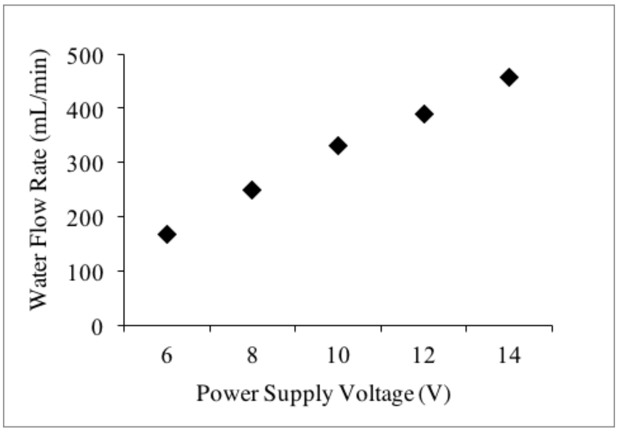


Fig. 3. The water flow rate curve with variation of power supply voltage

Fig. 3 shows the profile of the water flow rate with varying power supply voltage. It can be seen that the higher power supply voltage was given, the more water will be flow. The selected power supply voltages for the degradation process were 8 V, 10 V, and 12 V where the water flow rates were 250 mL/min, 330 mL/min and 390 mL/min, respectively.

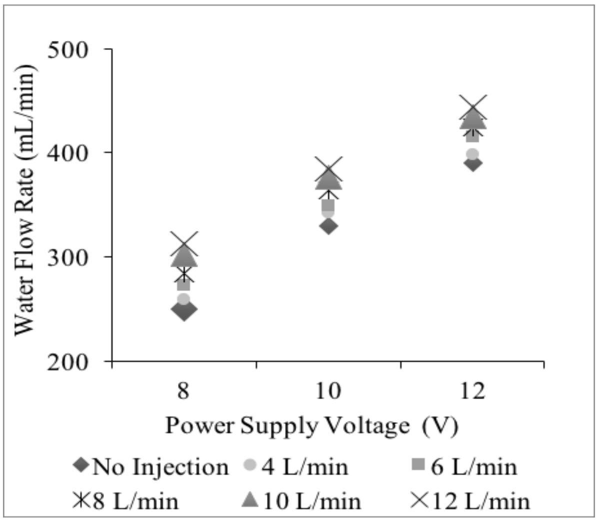


Fig. 4. The water flow rate curve with variation of air flow rate

Fig. 4 shows the profile of the resulting water flow rate curve with varying airflow injection rate. It can be seen that water flow rate was influenced by the presence of air injection. The value of water flow rate in the presence of air injection is higher than without the presence of air injection. Variations of air flow injection rate also affect the value of water flow rate as seen in Fig. 4, it can be concluded that the higher air injection flow rate, the water flow rate will be smaller.

The presence of air injection was increased the water flow rate because air injection in bubble column reactor produced bubble gas to lift up the water. The higher air flow rate that injected to reactor, the bigger bubble gas was produced [12].

3.2 Ozonator productivity test

The air containing oxygen was used to generate ozon. Variations of air flow rate at 8 L/min, 10 L/min, and 12 L/min produced the dosage of ozone as follows.

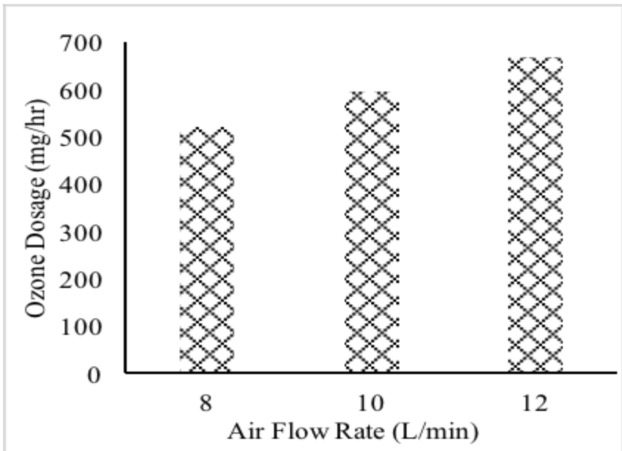


Fig. 5. Variation of air flow rate on ozone dosage

Fig. 5 shows the ozone dosage which produce by ozonator was affected by air flow rate. The higher flow rate of air enters ozonator, the higher ozone dosage to be generated. The highest ozone dosage was obtained at 12 L/min air flow rate with a dosage of ozone is 667 mg/hr.

3.3 The effect of airflow rate on degradation percentage

Air was entered the ozonator to produce ozone which will be injected to reactor. The variations of air flow rate in this study were 8 L/min, 10 L/min, and 12 L/min. The observations were done with single ozone injection system in I_2 and wastewater flow rate was 330 mL/min for 60 minutes.

Table 2. The effect of airflow rate on degradation percentage

Air Flow Rate	Remazol Blue Degradation	4-Chlorophenol Degradation
8 L/min	99.05%	53.21%
10 L/min	99.06%	54.78%
12 L/min	98.33%	56.05%

Based on Table 2, the highest degradation of remazol blue by varying the air flow rate was obtained at 10 L/min, however the highest degradation of 4-chlorophenol was obtained at 12 L/min. As seen on Table 2, the air flow rate was not significantly affect the percentage of remazol blue degradation. Results show that the degradation effect of remazol blue was not evident with high ozone dosage, but it was evident in degradation of 4-chlorophenol. The higher air flow rate was increased the percentage of 4-chlorophenol degradation. The increasing percentage of 4-chlorophenol degradation was occur because the higher flow rate of air produces the higher ozone dosage to degrade 4-chlorophenol, this theory was supported by hydrodynamic test results.

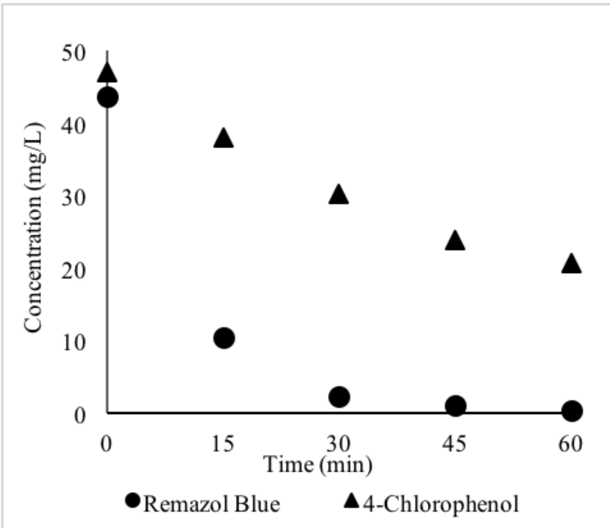


Fig. 6. Decreased concentration of remazol blue and 4-chlorophenol in air flow rate optimum condition

The decrease of remazol blue concentration with air flow rate of 10 L/min and 4-chlorophenol with air flow rate of 12 L/min can be seen in Fig. 6. The concentration of remazol blue and 4-chlorophenol was decreased with time. This decreased concentrations indicate there were degradation process by ozonation in bubble colum reactor from time to time.

3.4 The effect of ozone injection system on degradation percentage

Ozone injection system centered on the bottom of the column (I_2) was proved to degrade remazol blue and 4-Chlorophenol by 99.06% and 56.05% for 60 minutes of degradation with wastewater flow rate 330 mL/min. Bubble column reactor used in this research has multi injection, variation of injection system has been done to know its influence on percentage of degradation.

Table 3. The effect of ozone injection system on percentage of remazol blue degradation

Degradation of Remazol Blue			
Injection System	Air Flow Rate		Degradation
	I_1	I_2	
I_2	-	10 L/min	99.06%
$I_1 < I_2$	4 L/min	6 L/min	99.68%
$I_1 = I_2$	5 L/min	5 L/min	98.82%
$I_1 > I_2$	6 L/min	4 L/min	99.40%

Table 4. The effect of ozone injection system on percentage of 4-chlorophenol degradation

Degradation of 4-Chlorophenol			
Injection System	Air Flow Rate		Degradation
	I_1	I_2	
I_2	-	12 L/min	56.05%
$I_1 < I_2$	5 L/min	7 L/min	58.51%
$I_1 = I_2$	6 L/min	6 L/min	57.00%
$I_1 > I_2$	7 L/min	5 L/min	55.08%

Based on Table 2 and Table 3, the multi ozone injection system was produced a better degradation than single ozone injection system. The best degradation results for both wastewaters were occur during multiple injection system when ozone injection in I_1 is less than I_2 ($I_1 < I_2$). The highest degradation of remazol blue was obtained when the air injection of ozonator input for I_1 was 4 L/min and I_2 was 6 L/min with the result of degradation 99.68%. The highest degradation for 4-chlorophenol by 58.51% was achieved when the air injection of ozonator input for I_1 was 5 L/min and I_2 was 7 L/min. The multi ozone injection systems were proved to increase degradation process because the presence of ozone in bubble column reactor with the multiple injection system was evenly distributed to obtain more homogeneous degradation processes [11].

3.5 The effect of wastewater flow rate on degradation percentage

After obtaining the optimum conditions for air flow rate and ozone injection system, the ozonation were performed with variations of wastewater flow rate (250 mL/min, 330 mL/min, and 390 mL/min) to obtain the optimum conditions of the ozonation technique in degrading the concentration of remazol blue and 4-chlorophenol wastewater.

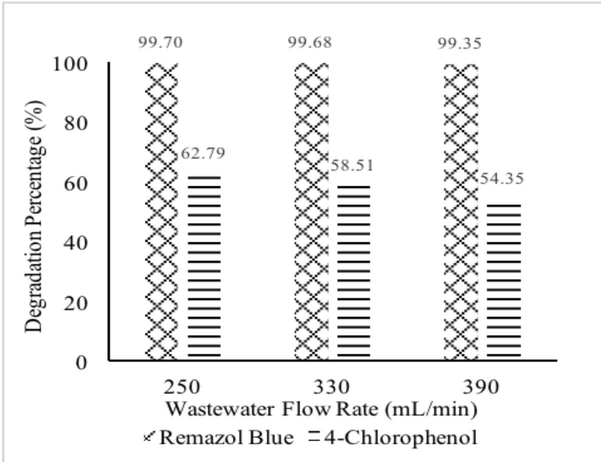


Fig 7. Variation of wastewater flow rate on the degradation percentage

Results of degradation of remazol blue and 4-chlorophenol with different wastewater flow rate are shown in Fig.7. The highest degradation for remazol blue and 4-chlorophenol were obtained when the wastewater flowrate was 250 m/L. The decreasing of wastewater flow rate will be increased the percentage of degradation wastewater, its because the residence time of wastewater in bubble column was longer. The contact time between wastewater and gas bubble (ozone) will be increased due to the longer wastewater stayed in reactor. The degradation of wastewater will be increased along with increasing contact time.

3.6 Comparison of remazol blue and 4-cholophenol degradation under optimum condition

The optimum condition was obtained by air flow rate for RB-19 dye and 4-chlorophenol were 10 L/min and 12 L/min, using ozone multi injection system, and wastewater flow rate was 250 mL/min. After 60-min ozonation under optimum condition, degradation of remazol blue and 4-chlorophenol were reached 99.70% and 62.79%, respectively. From previous studies reported in the literature, degradation reached 70.16% by ozonation in 60-min for 100 mg/L remazol blue [10] and the percentage of degradation 4-chlorophenol was 99.4% after the total of 24 h ozonation [13].

Based on Fig. 8, concentration of remazol blue and 4-chlorophenol were decreased along with the increasing degradation time. During 60 minute of degradation, remazol blue concentration was reduced from 47.10 mg/L to 0.19 mg/L, and 4-chlorophenol concentration was reduced from 48.10 mg/L to 17.90 mg/L.

During the first 30 minutes of degradation, the concentration of remazol blue dye was reduced significantly to 1.33 mg/L. It indicates that ozonation in bubble column was effective in degrading remazol blue dye within 60 minutes and reached 99.70%. However, to degrade 4-chlorophenol within 60 minutes only reached 62.79% because the phenolic compounds were more resistant to degrade than dyes, and also chlorine atoms in 4-chlorophenol was ozone-resistant. From Fig. 2, it appears that remazol blue has a larger molecular structure than 4-chlorophenol. Ozone reacts quicker with a larger molecular structures that contains double bonds, activated aromatic groups or amines [14]. Degradation of 4-chlorophenol as a simple phenolic compounds needs some longer time than degradation of remazol blue [15].

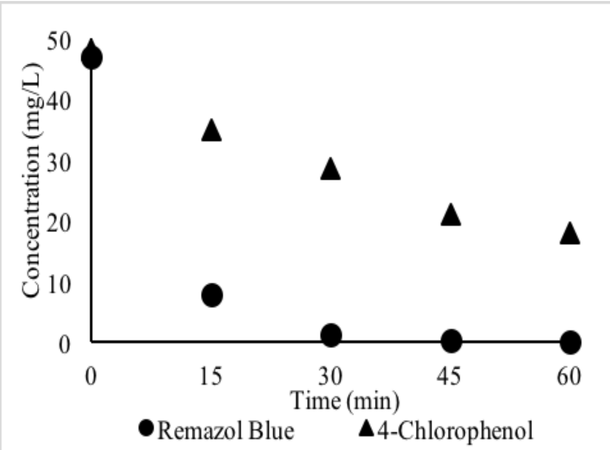


Fig. 8. Decreased concentration of remazol blue and 4-chlorophenol in optimum condition

4. Conclusion

Several experiments were conducted to degrade remazol blue and 4-chlorophenol compounds using ozonation technique. The results reveal that the ozonation technique in bubble column reactor with ozone multi injection system for 60 minutes at basic pH (pH = 10) was degrade 99.70% of remazol blue, however the 4-chlorophenol was 62.79%. Remazol blue were easier to degrade than 4-chlorophenol because of remazol blue has a larger molecular structure than 4-chlorophenol and ozone reacts faster with a larger molecular structure. Results show that the degradation processes were affected by air flow rate, ozone injection system, and wastewater flow rate. The optimum condition of the treatment process was obtained when air flow rate for RB-19 dye was 10 L/min and 4-chlorophenol was 12 L/min, using ozone multi injection system, and flow rate of wastewater 250 mL/min.

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