Batik wastewater treatment by the hydrodynamic cavitation and Ozonation with coagulation-flocculation pretreatment

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Abstract. Wastewater discharged by Batik’s industry still contains a high concentration of dyes and pollutants, thus can contaminate the water’s ecosystem. Because of that, in this study, Batik wastewater was treated by the hydrodynamic cavitation, ozonation, and combination of those two. By using PAC, a coagulation-flocculation-based pretreatment technic was conducted first to increase the effectiveness of the main wastewater treatment process. Then, variations in flow rate (2 L/min, 4 L/min, and 6 L/min) and initial pH of wastewater (4, 7, and 10) were evaluated to analyze its effect on the pH changing and the degradation of TSS, COD, color (Pt-Co), and TOC. The best result obtained from this research was by the application of the combination technic, which can eliminate 95.19%; 78.85%; 96.42%; and 60.56% of TSS, COD, color (Pt-Co), and TOC, respectively after 60 minutes treatment.

Keywords: Batik Wastewater, Coagulation, Hydrodynamic Cavitation, Ozonation

1. Introduction
Industrial Ministry of Indonesia highlights that in the past few years Batik industry has developed rapidly, based on the revenue generated from the export. It directly gives positive contributions to the betterment of the nation’s economy and the community’s life quality. Nonetheless, the negative impact in the increasing amount of wastewater generated from the production process should be taken into account. Batik wastewater mostly contains dyes that are rich in the content of unsaturated organic compounds like aromatic hydrocarbon, phenol, nitrous hydrocarbon, and their derivatives [1].

Prior to being discharged, those hazardous dyes must be treated first in order not to cause water pollution. To handle that, generally, Batik industry applies the coagulation-flocculation process combined with the filtration technic. The ease of operation and the use of a cheap-in-price and easy-to-find chemical have favored the application of this process. However, this process has some shortcomings like the insignificant decolorization percentage (only 50-80%) and also low COD degradation (30-70%) which further means the use of polishing technologies is mandatory in order to comply with the government regulation about the wastewater discharge standard [2].

Ozonation by using ozone can be a promising polishing technology. As a strong oxidant, ozone can react directly and decompose easily to form hydroxyl radical which further can degrade the organic pollutant and dissolved metal within the wastewater. Ozone is also a well-known chemical for decolorizing, and deodorizing the wastewater. Moreover, the major advantages of ozonation are an environmental-friendly technology, requiring the relatively small-sized area to operate, not a time-consuming process, not using the other chemicals to generate some oxidative compounds, and not...
producing hazardous byproducts for the environment [3]. By considering that ozone is a hardly dissolved chemical and reacted selectively with the other species in water, thus the combination with hydrodynamic cavitation was conducted in this research.

Hydrodynamic cavitation can in general be defined as the phenomena of the formation, growth, and subsequent collapse of microbubbles or cavities produced by pressure variations which are obtained using the geometry of the system creating velocity variation. These phenomena can be created by passing in the fluid through a constriction such as a venturi injector, cavities generator unit used in this research. The combination of hydrodynamic cavitation and ozonation aims for increasing the wastewater degradation effectivity due to the enhancement of ozone molecules mass transfer from the gas phase to the bulk solution [4].

The objective of the present work is to evaluate the effect of the combination of the hydrodynamic cavitation and ozonation as a polishing technology for Batik wastewater. Variations in flow rate and initial pH of wastewater were conducted. Furthermore, to evaluate the performance of the process, some parameters such as Total Suspended Solid (TSS), Chemical Oxygen Demand (COD), color (Pt-Co), and Total Organic Carbon (TOC) were tested.

2. Materials and Methods

2.1 Materials
Batik wastewater was obtained from a local Batik Plant in Tegal, Central Java.

2.2 Experimental Setup
The experimental setup was consisted of a venturi injector-based hydrodynamic cavitation reactor and an ozonator, illustrated in Figure 1. The venturi injector used was Venturi Mazzei type 384. This injector was equipped with a nozzle as an inlet for ozone gas generated by the ozonator which enabled direct contact between cavities and ozone. Ozonator used was a commercial-type Aquasuper AS-002 with the ozone production rate was 398.25 mg/h.

2.3 Methods
The initial step of wastewater treatment was conducted by the coagulation-flocculation pretreatment by utilizing the Poly Aluminium Chloride (PAC, molecular formula: \( \text{Al}_{12}\text{Cl}_{12}\text{(OH)}_{24} \)) coagulant as presented on Fig. 1.

![Figure 1. Experimental setup](image-url)
By understanding that the coagulant works optimum in the certain range of pH, thus before being added, the pH of Batik wastewater should be adjusted to 4 in accordance with the result obtained by other by adding the sulphuric acid (H2SO4 p.a.) from Merck [5]. Then, the PAC solution 500 ppm was added into 500 mL of Batik wastewater. By using the jar tester Velp Scientifica JLT6 unit, firstly the wastewater was stirred quickly with the velocity of 200 rpm for 4 minutes and then stirred slowly (40 rpm) for 10 minutes. To make the colloidal particles settled, let the wastewater rested for 30 minutes and after that filtered it by using the filter paper. Batik wastewater was further treated by the cavitation- and ozonation-based polishing technologies.

3. Results

3.1 Effect of Coagulation-Flocculation Pretreatment

The pH adjustment and coagulation-flocculation pretreatment processes have changed the characteristic of Batik wastewater whose changes are depicted as follow.

Table 1. The comparison of Batik wastewater characteristics after pH adjustment and coagulation-flocculation

| Parameter | Unit | Initial Characteristic | After pH Adjustment to 4 | After Coagulation-Flocculation | Standard Discharge Limit |
|-----------|------|------------------------|-------------------------|-------------------------------|-------------------------|
| pH        | –    | 10.08                  | 4                       | 4.12                          | 6 - 9                   |
| TSS       | mg/L | 1525                   | 1990                    | 145                           | 50                      |
| COD       | mg/L | 29509                  | 4282                    | 1019                          | 150                     |
| Pt-Co     | mg/L | 26756                  | 28280                   | 1078                          | –                       |

Based on Table 1, the pH adjustment process has increased the TSS and Pt-Co concentration. This result indicated that when sulphuric acid was added into the naturally-alkaline wastewater, flocs (which were salts) were produced as a product of the neutralization reaction. Those macroflocs could not dissolve perfectly in the wastewater, hence the concentration of the suspended solid was higher after the addition of acid. Furthermore, this increased the turbidity of wastewater, which made the percentage of light penetrate the water became lower (Pt-Co concentration was higher).

Meanwhile, the pollutant concentration has decreased when the coagulation-flocculation process was applied on wastewater. This was happening because PAC as a coagulant could destabilize colloidal particles in wastewater which initiated the formation of huge and heavy flocs, thus settled due to the effect of gravitational force. Filtration was then applied to separate those flocs from the wastewater, leaving the wastewater with a lower concentration of TSS, COD, and Pt-Co.

3.2 Batik Wastewater Polishing Technology

3.2.1 Hydrodynamic Cavitation-based Polishing Technology

For each circulation flow rate, the following is the result of Batik wastewater treatment with the hydrodynamic cavitation-based polishing technology at 60 minutes.

Figure 2. Effect of Wastewater Circulation Flow Rate on the Degradation Percentage of TSS, COD, and Pt-Co by the Hydrodynamic Cavitation Process (Initial pH = 4, Processing Time = 60 minutes)
Figure 2 shows that the optimum degradation of TSS, COD, and Pt-Co was by the application of circulation flow rate 6 L/min, followed by 4 L/min and 2 L/min. Higher flow rate meant higher fluid velocity passing through the constriction of a venturi injector than the inlet fluid velocity, which further indicated a higher pressure drop happening on that constriction area. The fluid pressure fell lower below its saturated vapor pressure indicating more gases would be formed. These gases were actually cavities. More fraction of cavities collapsed, thus more hydroxyl radicals would be produced. The higher concentration of hydroxyl radicals, consequently the degradation of organic pollutants in wastewater would be more massive which could be directed to the reduction of TSS, COD, and Pt-Co concentration. This finding was actually appropriate with the result obtained by Dhanke and Wagh [6] and Randhavane and Khambete [7].

3.2.2 Ozonation-based Polishing Technology

For each initial pH of wastewater, the following is the result of Batik wastewater treatment with the ozonation-based polishing technology at 60 minutes.

![Figure 3. Effect of Wastewater Initial pH on the Degradation Percentage of TSS, COD, and Pt-Co by the Ozonation Process (Wastewater Flow Rate = 6 L/min, Ozone Flow Rate = 6 L/min, Processing Time = 60 minutes)](image)

Figure 3 shows that the optimum degradation of TSS, COD, and Pt-Co was by the application of acidic conditions (initial pH of wastewater = 4) followed by the neutral and alkaline conditions, respectively. This result indicated that the degradation of the organic pollutant was favored by the direct and selective reaction between ozone molecules with the unsaturated hydrocarbon compounds (contained the bonds of C=C, C=N, N=N, etc) through the Criegee Mechanism to form peroxide hydrogen (H₂O₂) which later initiated the non-selective radical mechanism [8].

Naturally, Batik wastewater is alkaline in pH and contains carbonate ions in a huge number. These strong alkali ions come from the crystal or powder of sodium carbonate (Na₂CO₃) which in the Batik production process are the important chemical to accelerate the integration of dyes into the fiber of Batik, to adjust the pH, and to improve dyes’ purity. Within wastewater, these chemicals were dissociated to form carbonate ions which were the hydroxyl radical scavenger agent or the strong inhibitor for the hydroxyl radical, due to the fact that they could consume hydroxyl radical resulted by the ozone decomposition through the reaction mechanism as follow [8,9].

\[
\text{CO}_3^{2-} + \text{HO}^• \rightarrow \text{OH}^- + \text{CO}_3^{••}
\]  \hspace{1cm} (1)

Khuntia (2015) also stated that the carbonate ions could inhibit the formation of these ions including HO₂•, O₃, O₂, or the other intermediates which were the catalyst for the ozone decomposition reaction [10]. This inhibition would stabilize the ozone in its molecular form, which consequently initiated the selective reaction with the organic pollutant.

3.2.3 The Combination of Hydrodynamic Cavitation and Ozonation-based Polishing Technology

For each initial pH of wastewater, the following is the result of Batik wastewater treatment with the combination of hydrodynamic cavitation and ozonation-based polishing technology at 60 minutes.
Figure 4. Effect of Wastewater Initial pH on the Degradation Percentage of TSS, COD, and Pt-Co by the Combination Process (Wastewater Flow Rate = 6 L/min, Ozone Flow Rate = 6 L/min, Processing Time = 60 minutes)

Figure 4 shows that the optimum degradation of TSS, COD, and Pt-Co was by the application of acidic conditions (initial pH of wastewater = 4) followed by the neutral and alkaline conditions, respectively. This finding indicated that the direct oxidation of dyes by the ozone molecule would be dominant to happen than the indirect oxidation reaction initiated by the hydroxyl radicals. Saharan, et al. (2011) explained the reasons behind that finding.

In the acidic condition, a huge amount of SO\textsubscript{3}\textsuperscript{-} ions which could be found within dyes would be protonated. As a result, these dyes were present in a molecular state, became more hydrophobic, thus more likely to be located or preferred to be at the gas-water interface of the collapsing cavities. In that region, the dyes would be reacted directly with the hydroxyl radical, consequently increasing the decolorization percentage. Meanwhile, in the condition where pH > 7, dyes would be ionized, became more hydrophilic, thus more likely to be located at the bulk liquid.

Due to the hydroxyl radical recombination reaction in the cavities, hence the fraction of radicals that could diffuse into the bulk liquid region would be insignificant (generally around 10%), which further minimizing the dyes’ degradation reaction with the hydroxyl radical and reducing the decolorization percentage [11]. This result was actually supported by Barik an Gogate [12] and also Pradhan and Gogate [13].

3.3 The Performance Comparison among Several Polishing Technologies

Below is the comparison of the TSS, COD, and Pt-Co degradation percentages for each optimum condition in each process.

Figure 5. Performance Comparison among Several Polishing Technologies (Processing Time = 60 minutes).
Notes: KHD stands for Hydrodynamic Cavitation, O for Ozonation, and KHD-O for the Combination
Figure 5 shows that the treatment by using the combination-based polishing technology gave the best result in TSS, COD, and Pt-Co degradation compared with the single cavitation or ozonation. This occurred because of three factors. First, the mechanical action of the hydrodynamic cavitation enhanced the dissolution of ozone and the generation of additional hydroxyl radicals, leading to a faster reaction rate with the organic substrate. Second, the hydrodynamic cavitation improved the mass transfer of ozone, which resulted in more ozone entering the liquid phase or reacting on the gas-water interface. Third, aeration of ozone might increase the turbulence of the aqueous solution and enabled more related substances to migrate from the collapsing cavities into the bulk of the solution [14].

3.4 Effect of Polishing Technologies on TOC Degradation

Total Organic Carbon (TOC) is a parameter to measure the mineralization rate of an oxidation process. Chang, et al. (2006) supported by Saharan, et al. (2011) stated that the mineralization is a reaction phenomenon to convert the organic compounds into the simple and nontoxic inorganic compounds [11,15]. Higher TOC degradation level means the higher conversion of organic compounds into the inorganic compounds, such as CO$_2$ and H$_2$O. In this part, TOC degradation is measured only at the optimum condition of each polishing technology, and the results can be observed as follow.

Figure 6 shows that the combination-based polishing technology gave the best result for TOC degradation. This was caused by the fact that the oxidation of organic compounds initiated by more oxidative agents (ozone and hydroxyl radical) in number and the enhancement of ozone mass transfer occurred in the solution which further could accelerate the mineralization and make it right on target than the single cavitation or ozonation.

4. Conclusion

It can be summarized that to treat the Batik wastewater which has pre-treated first by the coagulation-flocculation process, the combination of hydrodynamic cavitation and ozonation-based polishing technology gave the best result in degradation of TSS, COD, Pt-Co, and TOC up to 95.19%; 78.85%; 96.42%; and 60.56% respectively. Also, in the application of the hydrodynamic cavitation-based technology, a higher wastewater circulation flow rate gives higher degradation percentages in the parameters of TSS, COD, Pt-Co, and TOC. The operation of ozonation- and combination-based technology to treat the Batik wastewater was favored under acidic conditions and was very much dependent on the pH of wastewater, state (whether molecular or ionic), and nature (hydrophobic or hydrophilic) of the pollutants.

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