The effects of Ozonation and ultrasonic cavitation on batik wastewater treatment with coagulation-flocculation as pre-treatment

I N J Siahaan¹, A E Saputra¹, and E F Karamah*¹

¹Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia

*Email: eva.fathul@ui.ac.id

Abstract. The batik industry produces large volumes of wastewater with high organic content. Dyes in batik wastewater are difficult to degrade by biological processes. Therefore, further processing is needed to reduce pollutants before being released into the environment. This study aims to observe the performance of the ultrasonic cavitation, ozonation, and combination of ozonation/ultrasonic cavitation to treat batik wastewater, which was first given a coagulation-flocculation pre-treatment with Polyaluminium Chloride (PAC) coagulants. The variations applied were ultrasonic intensity (20%, 30%, and 60%) and pH of wastewater (4, 7, and 10). In this study, it was found that the combination of the ozonation/ultrasonic cavitation method with a pH of 4 and ultrasonic intensity of 20% produced the best performance, namely COD, TSS, and color (Pt-Co) removal of 77.02%, 95.15%, and 94.88%. The ultrasonic intensity and initial pH of wastewater played an important role in the performance of the treatment process. In the ultrasonic cavitation method with an ultrasonic intensity of 20%, the highest percentage of COD, TSS, and color (Pt-Co) removal was 65.59%, 91.51%, and 93.41%. The ozonation method in acidic conditions (pH 4) produced a better performance with COD, TSS, and color (Pt-Co) removal of 70.51%, 94.35%, and 96.10% for 60 minutes.

Keywords: Batik wastewater, coagulation, flocculation, ozonation, ultrasonic cavitation

1. Introduction

The process of producing batik requires large amounts of water, which causes large amounts of wastewater production. In Indonesia, the volume of water needed for batik processing is around 25 million m³ per year [1]. Nearly 85% of the water used ends up being wastewater that has the characteristic of cloudy and thick color, along with high temperature, pH, and organic content. The major contaminant in the batik industry wastewater comes from synthetic dyes. Synthetic dyes have a stable composition, are difficult to decompose, and prevent sunlight from entering the water, which can disrupt the balance of the aquatic ecosystem.

The coagulation process aims to destabilize colloidal particles by adding a coagulant and stirring at high speed. The addition of coagulants intends to bind colloidal particles in wastewater so that it can...
form the flocs. Meanwhile, flocculation is a process of forming flocs on slow stirring to increase the fusion of particles or agglomeration so it can easily deposit. Coagulation-flocculation is a cost-effective and efficient process of removing color, so it is prospective to apply in batik wastewater treatment. However, the coagulation-flocculation produces wastewater that does not meet the quality standards of wastewater disposed to the environment. Therefore, further processing is required.

Ultrasonic cavitation and ozonation are advanced oxidation processes that can increase wastewater biodegradability. Ozonation can increase biodegradability by oxidizing organic compounds directly and changing the organic chemical structure of wastewater. Meanwhile, ultrasonic cavitation is a technology that uses high-frequency ultrasonic waves to break down complex organic compounds into simpler compounds. The combination of ozonation and ultrasonic cavitation methods can reduce the concentration of organic pollutants and increase biodegradability in batik wastewater by producing a total organic carbon (TOC) removal of 85% [2] and decolorization of dyes up to 99.2% [3].

In this study, a pretreatment of batik wastewater using coagulation-flocculation was intended to remove the suspended or colloidal contaminants contained in the batik wastewater. The coagulant used is Polyaluminium Chloride (PAC) with the chemical formula of \( \text{Al}_{12}\text{Cl}_{12}(\text{OH})_{24} \). The reason for choosing PAC is because it is commonly used in wastewater treatment processes, works over a wide pH range, and has low corrosivity. Further, the methods of ultrasonic cavitation (U.C), ozonation (O), and a combination of ozonation and ultrasonic cavitation (O/U.C) were carried out to treat batik wastewater.

### 2. Materials and Methods

The duration of the batik wastewater treatment process in each method was 60 minutes. The independent variables used in this study were the ultrasonic wave intensity (20%, 30%, and 60%) for the ultrasonic cavitation and the initial pH of batik wastewater (4, 7, and 10) for the ozonation and combined method of ozonation/ultrasonic cavitation. The evaluation carried out on the performance of batik wastewater treatment was based on several parameters, namely COD, TSS, color (Pt-Co), and TOC.

The main equipment used in this study were Ultrasonic Processor E-Chrom Tech UP-800, Ozonator Aquasuper AS-002 with an average ozone production of 398.25 mg/hour at a flow rate of 6 L/minute, Nocchi centrifugal pump, and 5 Litres reservoir tank. The scheme of the research equipment is shown in Figure 1.

**Figure 1. Research Equipment Scheme.**

The materials used in this study were batik wastewater, 500 ppm PAC coagulant, 0.1 M potassium iodide (KI), 2 M sulfuric acid (\( \text{H}_2\text{SO}_4 \)), 0.05 M sodium thiosulfate (\( \text{Na}_2\text{S}_2\text{O}_3 \)), 2% starch indicator, 0.001
N potassium permanganate (KMnO$_4$), sodium hydroxide (NaOH), and water. All chemicals were supplied from Merck in the pro analysis class (p.a.), except sodium hydroxide (technical grade).

3. Results and Discussions

3.1 Characterization of Batik Wastewater

Initial characterization of batik wastewater aims to identify the amount of pollutant load on the wastewater so it can be used as a reference to measure the effectiveness of the wastewater treatment process. At first, batik wastewater went through a filtering process with a stainless-steel filter. The purpose of filtering was to reduce the contaminant on the wastewater. Furthermore, dilution was carried out with a ratio of one to four to minimize the formation of foam that interfere with the process. Table 1 shows the results of the initial characterization of batik wastewater.

Table 1. Comparison of the Results of Initial Characterization of Batik Wastewater.

| Parameter | Unit     | Raw Wastewater | After Filtering and Dilution | Adjustment of pH 4 | Government Standard |
|-----------|----------|----------------|------------------------------|-------------------|-------------------|
| pH        | –        | 10.08          | 9.97                         | 4                 | 6-9               |
| COD       | mg/L     | 29,509         | 5,428                        | 4,282             | 150               |
| TSS       | mg/L     | 1,525          | 285                          | 1,990             | 50                |
| Pt-Co     | mg/L     | 26,756         | 4,270                        | 28,280            | -                 |

In Table 1, it can be seen that the filtering and dilution treatments provided significant results for reducing levels of COD, TSS, and color (Pt-Co). The filtering process removed large particles by the filter media, while dilution caused the particles contained in the wastewater to be more dissolved. Before entering the next process, the pH adjustment was given to the wastewater. Adjusting pH to 4 caused a decrease in COD and an increase in TSS and color. This was due to the formation of flocs which came from the formation of salt due to the addition of acidic compounds to the alkaline wastewater. The formation of flocs triggers an increase in suspended solids and makes the color cloudy. Previous studies had shown that pH adjustment in batik wastewater with the addition of acid could reduce COD with a removal percentage of up to 79% [4].

3.2 Performance of Coagulation-Flocculation Method with Jar Test

In this study, the coagulation-flocculation method aims to reduce the pollutant load on the wastewater, especially colloidal particles in batik wastewater. The coagulation-flocculation process was carried out using a jar test with the addition of PAC coagulant. The comparison between the parameters of batik wastewater before and after the coagulation-flocculation process is shown in Table 2.

Table 2. Results of Parameter Testing on Batik Wastewater on Before and After Coagulation-Flocculation.

| Parameter | Unit     | Before Coagulation-Flocculation | After Coagulation-Flocculation |
|-----------|----------|---------------------------------|-------------------------------|
| pH        | –        | 4                               | 4.12                          |
| COD       | mg/L     | 4,282                           | 1,019                         |
| TSS       | mg/L     | 1,990                           | 145                           |
| Pt-Co     | mg/L     | 28,280                          | 1,078                         |

Table 2 shows that there was a significant reduction in COD, TSS, and Pt-Co. COD reduction occurred because of the high concentration of colloids after the adjustment of pH 4 in the batik wastewater. It increased the suspended solids content and turbidity. The increase in colloid concentration in the wastewater caused the collision frequency of the destabilized particles to increases so that the formation of flocs more easily occurred. Moreover, the addition of a coagulant that is a cation to
wastewater that has negative electric charges causes the formation of micro flocs and eventually forms particles of larger size (macro flocs).

The PAC coagulant underwent a hydrolysis reaction that results in insoluble aluminum polyhydroxide that settled and formed a large volume of flocs. The flocs formed are then removed the color and colloidal particles by adsorption onto/within the formed metal hydroxide [5]. Thus, there was a reduction in TSS and color (Pt-Co) in batik wastewater.

3.3 Hydroxyl Radical Quantification
Hydroxyl radical quantification test was carried out by circulating water for 60 minutes. The sample obtained was then tested by the permanganometric titration method. The use of water as a substitute for batik industrial wastewater was intended to prevent the formation of complex molecules that could interfere with the hydroxyl radical quantification. The results of the quantification of hydroxyl radicals can be seen in Figure 2.

Based on Figure 2, the highest number of hydroxyl radicals was produced by the combination of ozonation/ultrasonic cavitation with a pH of 10, which was 53 mg/L in the 60 minutes. Meanwhile, the least amount of hydroxyl radicals was produced by the ultrasonic cavitation with an ultrasonic wave intensity of 20%, which was 35 mg/L.

The combination of ozonation/ultrasonic cavitation with a pH of 10 produced the highest number of hydroxyl radicals because the formation of the largest oxidizing compounds occurred in alkaline conditions. In alkaline solutions, hydroxide ions (OH\(^{-}\)) were more abundant. The hydroxide ion acted as an initiator in the decomposition reaction of ozone to hydroxyl radicals [6]. Radical compounds formed between ozone and hydroxyl ions would react over with ozone to produce more hydroxyl radicals. Equations 1 and 2 show the decomposition reaction of ozone to hydroxyl radicals.

\[
O_3 + OH^- \rightarrow HO_2^- + O_2 \]  \hspace{1cm} (1)
\[
O_3 + HO_2^- \rightarrow \cdot OH + O_2^- + O_2 \]  \hspace{1cm} (2)

3.4 Ultrasonic Cavitation on Batik Wastewater Treatment
In the ultrasonic cavitation, the circulated wastewater had been given a pH adjustment so that it became pH 4. The application of acidic pH to azo dye treatment by the ultrasonic cavitation resulted in a higher degradation rate than alkaline conditions [7]. Figure 3 shows the percentage of parameter removal at 60 minutes for each of the independent variables.
The results presented on Fig. 3 shows that the ultrasonic cavitation with an ultrasonic intensity of 20% produced the highest percentage removal of TSS, COD, and Pt-Co. The high intensity of ultrasonic waves triggered a condition in which the solution is saturated with oxygen and peroxyl so that it formed hydrogen peroxide, as shown in equations 3 and 4 [8].

\[
\begin{align*}
O_2 + \cdot H & \rightarrow \cdot HO_2 \quad (3) \\
\cdot HO_2 + \cdot HO_2 & \rightarrow H_2O_2 \quad (4)
\end{align*}
\]

Hydrogen peroxide has a lower oxidation potential than ozone (2.07 V) and hydroxyl radical (2.8 V), which is 1.78 V. The lower oxidation potential can reduce the efficiency of the ultrasonic cavitation.

Based on Figure 4, the concentration fractions of COD, TSS, and Pt-Co tended to decrease with the length of processing time. The highest removal rate occurred in the ultrasonic cavitation with 20% ultrasonic intensity, with the removal of COD from 887 mg/L to 305 mg/L, removal of TSS from 165 mg/L to 14 mg/L, and removal of Pt-Co from 2,172 mg/L to 143 mg/L.

Then, followed by removal using the ultrasonic wave intensities of 30% and 60%. In the ultrasonic cavitation, hydroxyl radicals, hydrogen, and other radicals \((H_2O_2, \cdot HO_2^-, \cdot O_2)\) are produced by pyrolysis. These radical compounds, especially hydroxyl radicals, attack organic compounds in the bulk liquid and break down suspended solids in batik wastewater into soluble particles so that the concentration of TSS and Pt-Co decreases. Color removal can also occur due to processing carried out at pH 4. Acidic conditions accelerate the decolorization rate and this acceleration is caused by hydrogenation of negative charges, such as \(SO_3^-\), in an acidic environment \((SO_3^- \rightarrow HSO_3^-)\) [7].

### 3.5 Ozonation on Batik Wastewater Treatment

The process of wastewater treatment using the ozonation method was carried out with various pH (4, 7, and 10) to evaluate the performance of the ozonation in acidic, neutral, and alkaline conditions. Figure 5 shows the comparison of parameter removal produced by each variation.
Figure 5 shows that the largest percentage of parameter removal occurred in ozonation with a pH of 4. This was due to the use of auxiliary substances of soda ash (sodium carbonate) in the wax removal process in batik production [9]. The presence of carbonate ions in wastewater could be a hydroxyl radical scavenger or an inhibitor of OH. Carbonate is the largest OH scavenger that inhibited ozone decomposition [10]. Furthermore, the carbonate ion concentration increases with increasing pH [11]. At alkaline pH, carbonate consumed OH and inhibited the formation of $HO_2^-$, $O_2^-$, $O_3^-$, or other intermediates that can accelerate the decomposition of $O_3$ [12]. Thus, the presence of carbonate slowed down the decomposition process of ozone into hydroxyl radicals, thereby increasing ozone stability.

Based on Figure 6, the concentration of COD, TSS, and Pt-Co tends to decrease with the length of processing time. The highest removal of COD occurred during ozonation with pH 4, which reduced COD levels from 916 mg/L to 270 mg/L, TSS levels from 177 mg/L to 10 mg/L, and Pt-Co levels from 1,060 mg/L to 41 mg/L. Then followed by the ozonation method with pH 7 and pH 10. Under acidic conditions, $O_3$ molecules tend to react directly by breaking unsaturated bonds in azo compounds contained in the wastewater, such as cleavage of $\text{–N=}=\text{N–}$ and $\text{–C–N–}$ bonds [13]. Therefore, ozone can decompose organic compounds in batik wastewater and reduce COD levels.

$O_3$ reacts with the suspended solids in the wastewater by forming flocs that absorb colloids in the wastewater [14]. $O_3$ does not degrade suspended solids but acts as a coagulant agent which helps form flocs from suspended solids. Thus, the flocs formed will cause a decrease in TSS in the system [15]. In the ozonation, the color decreases due to the oxidative cleavage of chromophores (coloring compounds). Furthermore, the rate of dye decolorization in the ozonation was faster due to the electrophilic reaction between $O_3$ and the dye parent compound as well as the oxidation of the intermediate compound [7].

3.6. Combination of Ozonation/Ultrasound Cavitation on Batik Wastewater Treatment
The treatment of wastewater with a combination of ozonation/ultrasound cavitation used an ozone flow rate of 6 L/minute and an ultrasonic wave intensity of 20%. Figure 7 shows the results of the comparison of the largest TSS, COD, and Pt-Co removal percentages generated by each variation.
Based on Figure 7, the condition with pH 4 resulted in the highest percentage reduction in TSS, COD, and Pt-Co, then followed by pH 7 and pH 10. At higher pH, the degradation rate did not increase by radical reactions due to dissociation in •OH to an oxygen anion radical (O\(^-\)), which caused a reduction in •OH. The presence of inhibitors such as carbonates and bicarbonates play a role in inhibiting the decomposition of O\(_3\) to •OH.

The combination method of ozonation and ultrasonic cavitation at pH 4 resulted in the highest removal of COD, TSS, and Pt-Co, namely removal of COD levels from 1,328 mg/L to 305 mg/L, removal of TSS levels from 165 mg/L to 8 mg/L, and removal of Pt-Co levels from 1,862 mg/L to 95 mg/L. The application of ultrasonic cavitation was able to increase the mass transfer of O\(_3\) to the liquid phase thereby displacing the consumed O\(_3\) and leading to a higher percentage of COD removal [16]. Besides, the O\(_3\) molecule acts as an oxidizing agent for compounds that are more dominant than other active compounds under acidic conditions.

Therefore, the content of aromatic compounds in batik wastewater can be directly attacked by O\(_3\) resulting in a higher COD removal. On the other hand, the low removal of COD at neutral and alkaline pH conditions can be caused by an increase in the foam produced during waste treatment. The foam causes O\(_3\) to be trapped in it so that the decomposition and utilization of O\(_3\) is reduced. O\(_3\) produced in the combination of the two methods will react with the suspended solid organic fraction to convert it into dissolved organic matter [16]. The reduction of suspended solids contained in the wastewater will result in reduced color in the wastewater.

3.7. Ozonation and Ultrasonic Cavitation Method on TOC Removal of Batik Wastewater
In this study, the TOC levels test was carried out at the beginning and the end of the process at optimum conditions. The optimum condition chosen was the highest COD removal percentage from each process variation. The optimum condition for all methods is shown by the processing of batik wastewater with a pH of 4. The intensity of the ultrasonic waves selected for the TOC test using the ultrasonic cavitation is an ultrasonic intensity of 20%.
Total Organic Carbon (TOC) removal shows the amount of organic carbon that is completely mineralized into simple inorganic compounds, such as CO$_2$ and H$_2$O. The percentage of TOC removal for each method is presented in Figure 9.

Based on the research conducted, the most effective method for TOC removal is the combination method of ultrasonic cavitation and ozonation which can reduce TOC levels by 44.7 mg/L. The combination of ozonation/ultrasonic cavitation increases the mineralization of organic compounds in batik wastewater into harmless inorganic compounds. This is because the mass transfer of ozone in solution increases in the presence of ultrasonic irradiation. The microbubbles produced by ultrasonic cavitation cause a large part of the O$_3$ to enter the liquid phase or react at the gas-liquid interface [2]. The occurrence increases the contact area between the ozone in the gas phase and the liquid phase so that the mass transfer of O$_3$ into the wastewater will be greater. Thus, more ozone reacts with organic compounds.

There is a correlation between COD and TOC values. By definition, COD is the amount of oxygen needed to oxidize organic compounds and TOC is the amount of organic carbon that is oxidized. Based on Figure 9, the TOC removal for each method is lower than the COD removal. This is following the theory where the value of TOC reduction will always be smaller than the value of COD reduction because the TOC value shows how much the mineralized product is CO$_2$ and H$_2$O.

4. Conclusion

Based on the research conducted, it was found that the combination of ozonation/ultrasonic cavitation resulted in better removal of COD, TSS, and TOC than the ozonation and ultrasonic cavitation processes applied separately. In the ultrasonic cavitation, the lower ultrasonic wave intensity caused higher oxidation of organic compounds. Furthermore, the lower initial pH of batik wastewater in the ozonation method and the combination of ozonation/ultrasonic cavitation caused higher oxidation of organic compounds. To identify organic compounds contained in the wastewater as well as compounds that were produced by advanced oxidation processes, further testing with LC/MS is required.

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