Treatment of tapioca starch wastewater with ozonation and adsorption

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Abstract. In this research, removal of cyanide and COD in tapioca starch wastewater by ozonation and adsorption using GAC examined. The method effectiveness evaluated from percentage of cyanide and COD degradation and ozone mass balance. Effect of degradation method, pH and ozone dose was determined using synthetic wastewater with initial cyanide concentration of 30 ppm and COD concentration of 1000 ppm. Using ozonation adsorption with pH 10 and ozone generation rate of 303 mg O$_3$/h, 91.75% cyanide and 68.94% COD from synthetic wastewater was removed in 1 hour. Tapioca starch wastewater with cyanide concentration of 8.5 ppm and COD concentration of 4625 ppm treated using the same operating condition. Using this method, 87.06% cyanide and 43.23% COD was removed.

1. Introduction
Indonesia is considered as one of the biggest cassava producer in the world with annual production of 2018 reached 24 million tons [1]. Most cassavas produced are used in industrial field especially tapioca starch industry. Indonesia provides 17% of tapioca starch universal production [2]. Tapioca starch industry requires huge amount of water for washing and extraction processes, up to 40-60 m$^3$ wastewater used for processing 1 ton of cassava [3]. Tapioca starch wastewater contains cyanide around 5.8-22 mg/L and COD (Chemical Oxygen Demand) around 11800-14000 mg/L [4-5]. According to Minister of Environment Decree No. 51/1995 about effluent quality standard for industrial wastewater, maximum concentration for cyanide is 0.5 mg/L and for COD is 300 mg/L. Tapioca starch wastewater contains compound above its maximum level. Cyanide in wastewater interacts with water forming weak acid and bonds with cations forming dangerous cyanide complex compounds [6]. Organic compounds such as glucose and other carbohydrate derivate generates high concentration of COD in wastewater.

One of removal methods that can be developed to process tapioca starch wastewater is advanced oxidation process (AOPs), which is a solution phase oxidation process which based on the generation and utilization of highly reactive radical hydroxil to remove organic compounds. Radical hydroxil can be generated from various ways such as ozonation, hydrogen peroxide and ultraviolet [7]. Organic compounds in wastewater is removed until 96% using ozonation method for 10 minutes and ozone dose of 100 mg ozone/108 mg COD at pH 8 [8]. Cyanide degradation using ozone obtains 95.1% removal with initial concentration of 30 mg/L while degradation using •OH obtains 99% cyanide removal with initial concentration of 100 mg/L [9-11].
Addition of GAC (Granular Activated Carbon) can be used to increase the effectivity of ozonation according to its role in •OH formation reaction from ozone decomposition [12]. Karamah et al. used combination of ozonation and adsorption method to remove phenol and the result shows 88.94% phenol removal with initial concentration of 100 mg/L [13]. Based on the work of Sánchez Castillo et al., this combination method also can be used to reduce contacting time needed for cyanide degradation compared to single ozonation method [14]. Dash et al. also found that GAC also has a role as adsorbent for cyanide and COD. Cyanide with initial concentration of 100 mg/L is adsorbed up to 84.9% by GAC [15]. The study of Aluyor and Badmus also proves that 96.34% COD can be adsorbed by GAC during 180 minutes contact [16].

In this study, removal of cyanide and COD from tapioca starch wastewater using combination of ozonation and adsorption in bubble column reactor was examined. The analysis of cyanide and COD degradation percentage, amount of •OHs, and also GAC surface area were evaluated to investigate the method effectiveness. Effect of degradation method, pH and ozone dose was determined using synthetic wastewater to get the condition for processing tapioca starch wastewater.

### 2. Experimental Details

The experiment begins with GAC pretreatment by washing with distilled water and dried for 6 hours at 120°C. Synthetic wastewater contains 20 mg/L cyanide and 1000 mg/L COD using sodium cyanide and glucose as reagent.

Research scheme is shown in Figure 1.

![Figure 1. Experimental set up of ozonation adsorption](image)

Ozone gas sprayed to the reactor through a venturi injector. Two kinds of ozonators with different capacity production used in this experiment. Ozonator A with ozone dose of 125 mg/hour and ozonator B with ozone dose of 303 mg/hour. They operated alternately to vary the ozone dosage. The bubble column reactor was made of acrylic material with internal diameter of 8 cm, thickness of 0.5 cm, height of 35 cm and total volume of 1.5 L. Independent variables used in this experiment are degradation method, initial pH and ozone dose. Controlled variables used are GAC dose of 50 gram, COD concentration of 1000 mg/L, cyanide concentration of 20 mg/L, wastewater flow rate of 90 L/hour, contacting time of 60 minutes and ozonator current of 220 V. Experimental variables used are cyanide and COD concentration, residual and off gas ozone concentration, •OH amount and GAC surface area. All of chemicals used are p.a. grade from Merck.

Removal process done within 60 minutes, with taking the sample every 15 minutes. Residual and off gas ozone concentrations examined every 30 minutes. Cyanide and residual ozone concentration measured using colorimetric method with HACH DR 890 instrumentation. COD concentration is measured using closed reflux and titrimetric. Off gas ozone concentration is measured using iodometric and GAC characterization is done by BET instrumentation.
3. Result and Discussion
After doing the preparation step, the experiment can be done with the process that has already explained before. Below are the result of the experiment, which are divided into nine subsections.

3.1. Hydroxyl Radical Quantification
Hydroxyl radical quantification aims to determine the effect of configuration and operating condition on •OH generated. Radical hydroxyl is analysed using permanganometric titration with reaction as shown in the following:

\[ 3\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 4\text{O}_2 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} \] (1)

\[ \text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{OH} \] (2)

The effect of GAC on •OH generation is examined from the quantity changes between single ozonation and ozonation adsorption method. •OH quantity for every configurations shows in Table 1.

| Variation         | Accumulated •OH (mg/L) |
|-------------------|------------------------|
| Single ozonation  | 4.998                  |
| Ozonation          |                        |
| pH = 7            | 6.783                  |
| pH = 10           | 7.701                  |
| pH = 13           | 8.568                  |
| Ozone dose        |                        |
| Ozonator A        | 7.701                  |
| Ozonator B        | 14.382                 |

Table 1 shows the difference of •OH generated from GAC addition. GAC can increase •OH produced from ozone decomposition because pyrol function group in the basal plane that interact with ozone producing hydro peroxide radical (HO\(_2^•\)) which needed in •OH generation. Beside this chemical reaction, GAC also trap ozone inside the pore thus ozone retention time in water increasing. GAC provides active sites that adsorb ozone physically and trigger ozone decomposition forming •OH [18].

In Table 1 shows the increment of •OH generated according to pH variations. Ozone decomposition rate increased in higher pH. In alkali solution with pH 10, ozone decomposition is done in less than 1 minute [19]. At pH 7, ozone tends to not decompose to •OH, meanwhile in alkali solution such as pH 10 and pH 13, ozone tends to decompose and the oxidation process is done with •OH as oxidation agent. In acid solution, ozone has reduction potential of 2.07 Volt and in alkali solution the reduction potential is only 1.24 Volt. The potential reduction difference is caused by •OH generation from ozone in basic solution therefore the amount of ozone molecules that work as oxidant decreases. According to ozone decomposition reaction mechanism, hydroxide anion is the initiator for •OH generation. In alkali solution, hydroxide anion is provided by KOH addition as pH regulator. KOH dissociates in water producing hydroxide anion and K\(^+\). Not only by degradation method and pH, •OH generation also affected by ozone dose. In Table 1 shows the •OH increased in higher ozone dose generated by ozonator B.

3.2. Single Compound Wastewater Removal Process
Removal process for single compound wastewater aims to determine the effectivity of ozonation adsorption method in degrading the compound without effected by other compound.
Result for cyanide removal process using ozonation adsorption is shown in Figure 2. In Figure 2 shows ozonation adsorption method removed cyanide up to 90.25% with final concentration of 1.95 ppm. Cyanide oxidation has first reaction order so cyanide concentration in the solution affects removal process. Cyanide oxidation by ozone has couple reactions as shown in the following:

\[
\text{CN}^- + \text{O}_3 \rightarrow \text{CNO}^- + \text{O}_2 \quad (3)
\]
\[
\text{CNO}^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + \text{NH}_3 \quad (4)
\]
\[
\text{CNO}^- + \text{O}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{HCO}_3^- + 1.5 \text{O}_2 \quad (5)
\]
\[
\text{NH}_3 + 4\text{O}_3 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 4\text{O}_2 + \text{H}^+ \quad (6)
\]

Cyanide oxidation has cyanate ion as intermediate compound according to reactions shown above. Accumulation of cyanate ion produced by cyanide oxidation causes available ozone or •OH tend to react with cyanate ion and not only with cyanide therefore cyanide oxidation is harder to be done since cyanate acts as competitor. The study by Kumar and Bose [11] shows that cyanide oxidation rate is higher than cyanate oxidation rate therefore in cyanide ozonation, accumulation of cyanate ion can affect removal of cyanide. Cyanide oxidation is also affected by shielding effect from water as main solvent. Cyanide contains nitrogen atom and cyanate ion as the intermediate product contains nitrogen and oxygen atom. Both atoms is highly electronegative and tend to bond with hydrogen atom forming hydrogen bonding [20]. Hydrogen bonding between the cyanide and cyanate with water induces shielding effect that complicates oxidation process.

High removal percentage in the first 15 minutes caused by oxidation process and adsorption by GAC. Cyanide ion adsorbs physically in GAC surface and oxidizes by ozone molecule that has been adsorbed before. Not only physically, chemisorption also happens between cyanide and GAC including other oxidator such as oxygen [21-22]. Cyanide oxidation by oxygen in GAC surface produces cyanate ion, which is more difficult to be adsorbed and oxidized in GAC surface therefore, it will accumulate in the solution [23]. Accumulation of cyanate ion is caused by both of cyanide oxidation, also chemisorption by GAC.

Result of COD removal process using ozonation adsorption method shown in Figure 3. Figure 4 shows that ozonation adsorption method removes COD up to 74.58% with final concentration of 254.24 ppm. There is no significant increment of degradation percentage for every 15 minutes sample taken because oxidation process dominated by direct oxidation than indirect oxidation. During the whole process, ozone is injected continuously therefore degradation process keeps happening. Glucose ozonation produced gluconic acid as the main intermediate product. The other dangerous byproducts such as formic acid or glycol derivatives are not produced much from the ozonation. Gluconic acid oxidation produces arabinose or tartric acid as main end products which can be found naturally and not toxic [24].
3.3. Effect of Degradation Method

Result of cyanide and COD removal with various degradation method shown in Figure 4.

Figure 4 shows that single adsorption method can remove up to 66.75% cyanide and proves that GAC can be used as adsorbent for cyanide, either physically or chemically. Single ozonation method removes 71.75% cyanide with solution's pH 7, oxidation process is dominated by direct oxidation with ozone molecule than indirect oxidation with •OH. The highest degradation percentage is 76% obtained by ozonation adsorption with GAC, makes removal of cyanide from ozonation adsorption higher because the removal of cyanide increased not only by oxidation, but also by adsorption. The degradation percentages obtained by three methods are slightly different because the synthetic wastewater’s pH used is 7. According to •OH quantification result, •OH produced in single ozonation is lower than ozonation adsorption. However, at pH 7, oxidation is dominated by ozone therefore the removal is not affected significantly by •OH generated. In addition, GAC as adsorbent saturates because of ozone decomposition in the surface and adsorption of other compound. The ability to adsorb decreases along with GAC saturation because micro pores surface covered and acid sites formed, making adsorption process is harder to be done [18].

Figure 4 also shows COD removal for every degradation methods. Single adsorption method obtains 19.36% COD removal, proving that GAC can be used as adsorbent for COD but the result is not promising. Using single ozonation method, 44.79% COD was successfully removed and better compared to single adsorption because ozone works in both electrophilic and nucleophilic reaction thus ozone often used in organic compound reaction [24,25]. The ozonation process happens for the whole 60 minutes because ozone injected continuously during the process. The highest degradation percentage obtained by using ozonation adsorption method with final percentage of 56.42%. The difference between COD degradation percentage of ozonation adsorption compared to single method is higher than cyanide percentage difference. This indicates that GAC addition in ozonation process affects ozone ability to remove COD better than remove cyanide.
3.4. Effect of pH
From •OH quantification, pH difference affects •OH generated in ozonation adsorption method. The difference of •OH quantity influences ozonation adsorption effectiveness in removing cyanide and COD. Effect of pH on cyanide and COD removal shown in Figure 5.

As shown in Figure 5, the highest degradation percentage for cyanide and COD obtained using solution at pH 10 with cyanide removal of 87.5% and COD removal of 63.68%. Alkali solution provides more hydroxide ion that initiates •OH generation. Hydroxide ion also removes cyanate ion according to reaction shown in Equation 4, therefore cyanide removal in alkali solution is higher. In basic pH, oxidation is dominated by •OH reaction than ozone. Based on its reduction potential, •OH with E° of 2.80 Volt oxidizes more than ozone with E° of 2.07 Volt [26,27,28]. Cyanide and COD oxidation has higher rate constant for indirect oxidation compared to direct oxidation. According to Kumar and Bose (2005), cyanide direct oxidation by ozone has rate constant of 2.6 x 10³ M⁻¹ s⁻¹ while indirect oxidation has rate constant of 8 x 10⁹ M⁻¹ s⁻¹ [11]. For glucose oxidation, direct oxidation has rate constant of - 0.17 M⁻¹ s⁻¹ while indirect oxidation has rate constant of 10⁹ M⁻¹ s⁻¹ [29]. Higher rate constant leads to faster reaction therefore during the same time, indirect oxidation removes more compound than direct oxidation.

Degradation percentage at pH 13 is lower than pH 10 because of adsorption ability of GAC decreases at pH 13 compared to pH 10. Adsorption by GAC optimized when the solution has pH lower than compounds pKa and is decreased when the pH is higher than pKa. Cyanide has pKa of 9.2 and glucose has pKa of 12.28 therefore adsorption at pH 10 is more effective than pH 13. At pH 13, which is higher than pKa, the adsorption is no longer optimized, and the removal is dominated by oxidation process using •OH. Meanwhile at pH 10, the adsorption is still effective thus the removal is caused by both adsorption and oxidation. Even though pH 7 is lower than cyanide pKa, but at pH lower than 8, cyanide involves in hydrolysis reaction and decreases adsorption process [30]. The COD degradation percentage at pH 7 and basic pH is slightly different, only about 6-7% although the rate constant difference between •OH and ozone for glucose is big. This result is caused by oxidation reaction selectivity between glucose and •OH at basic pH. At pH 7, glucose oxidation leads to gluconic acid as the main intermediate product forming in a high yield. On the other hand, the reaction selectivity at pH 10 explained by the difference in neighbouring around glucose molecules and the partial ionization of hydroxyl function at C1 position promotes the electrophilic attack at this position [31]. Therefore even though •OH tends to attack other atom randomly, the glucose oxidation only occurs at C1 position.

3.5. Effect of ozone dose
Effect of ozone dose on COD and cyanide removal using ozonation adsorption is shown in Figure 6.
Figure 6 shows that higher cyanide and COD degradation percentage is obtained using ozonator B with higher ozone dose compared to ozonator A. This results proves higher ozone concentration oxidizes more compound within the same time. As well as the explanation before, cyanide oxidation occurs harder in lower cyanide concentration because of cyanate ion accumulation and cyanide reaction order [32]. Both cyanide and COD oxidation affected by compound concentration in the solution therefore lower concentration making oxidation slower.

3.6. Analysis of ozone mass balance

Activation Ozone mass balance analysis aims to determine effectiveness and efficiency of ozonation adsorption method. During the removal process, ozone is injected in gas phase into the wastewater in liquid phase. Ozone used is amount of ozone from initial ozone dose minus off gas and residual ozone. Table 2 shows mean ozone used for removing cyanide and COD from analyzing sample every 30 minutes.

| Variation | Off gas ozone (mg) | Residual ozone (mg) | Ozone use (mg) |
|-----------|--------------------|---------------------|---------------|
| Single ozonation | 14.26 | 1.16 | 109.86 |
| Ozonation adsorption | 11.24 | 0.78 | 113.28 |
| pH 7 | 11.24 | 0.78 | 113.28 |
| pH 10 | 3.84 | 0.52 | 120.93 |
| pH 13 | 5.96 | 0.68 | 118.65 |
| Ozonator A | 384 | 0.52 | 120.93 |
| Ozonator B | 48.36 | 0.13 | 255.35 |

Table 2 shows residual ozone in ozonation adsorption method is lower than single ozonation proves there is ozone adsorption by GAC resulting lower ozone dissolved in wastewater, ozone decomposition and ozone reaction with available compound. Increment of residual ozone at pH 13 compared to pH 10 shows that ozone adsorbed amount by GAC at pH 13 is lower than pH 10. Removal process using ozonator B shows lower residual ozone because the amount of ozone adsorbed and ozone decomposition is higher than ozonator A. Off gas ozone from ozonator B is significantly higher than ozonator A because of difference ozone flow rate used in both ozonator. Ozonator B has higher flow rate compared to ozonator A therefore ozone from ozonator B diffuses harder than ozonator A because of shorter contacting time.

3.7. Analysis of GAC characterization after process

GAC characterization such as surface area and pore volume aims to determine the effect of ozonation to GAC surface. GAC surface area before and after ozonation adsorption process shown in Figure 7.
This result shows there is either cyanide, glucose or ozone adsorption by GAC making available active sites on the surface is less than before. According to the result, adsorption loading occurs up to 72% from the whole GAC available surface. This shows that there is still potential for further adsorption with optimized operating condition [33]. The changes of GAC surface area shows that after ozonation adsorption process, the regeneration for GAC is needed before it used again in another process because the sites are already filled by other compound.

### 3.8. Tapioca Starch Wastewater Removal Process

Before removal process done, tapioca starch wastewater characterized according to experimental parameters such as pH, cyanide, COD and TSS. To avoid the suspended solid interference, wastewater is filtrated. Characterization result for tapioca starch wastewater shown in Table 3. It shows that tapioca starch wastewater contains dangerous compound above the maximum level. The same wastewater measured after 7 days placed without treatment to find out the effect of natural degradation. From the result shown, tapioca starch wastewater still contains compound above the maximum level after 7 days without treatment. This indicates that tapioca starch wastewater cannot be stored without being treated first. Cyanide, COD and TSS removal result from tapioca starch wastewater using ozonation adsorption is shown in Figure 8.

| Parameter | Concentration | Maximum Level |
|-----------|---------------|---------------|
| pH        | 4.8           | 4.7           | 4.8           | 6-9          |
| CN        | 8.7           | 8.5           | 9.45          | 0.5 ppm      |
| COD       | 5311.87       | 4625          | 5128.7        | 300 ppm      |
| TSS       | 980           | 588           | 154           | 60 ppm       |

Figure 8 shows that ozonation adsorption method successfully removes 87.06% cyanide, 43.23% and 82.99% TSS. Using the same operating condition, the cyanide and COD degradation percentage of synthetic wastewater is higher than tapioca starch wastewater. This result is caused by higher COD concentration of tapioca and complex form of cyanide and COD in the tapioca starch wastewater compared to the synthetic one. Cyanide ion in tapioca starch wastewater bonds with glucosides compound and decompose to free cyanide ion and glucose with natural enzymatic reaction [34].
Cyanide in its free form can be oxidized and adsorbed as well as in synthetic wastewater but in tapioca starch wastewater, cyanide occurs in complex form therefore the oxidation is harder to be done. COD in tapioca starch is caused by organic compounds such as carbohydrates, protein and fat with complex molecular structure compared to glucose making the oxidation process is harder. Oxidation of organic compounds in wastewater forms smaller and less complex compounds, making TSS concentration by the end of process decreases.

4. Conclusion

- Ozonation adsorption method using GAC is more effective in cyanide and COD removal process than single ozonation and single adsorption method, because GAC can adsorb cyanide and COD, also increase \( \cdot \text{OH} \) generated in ozonation process.
- Cyanide and COD removal using ozonation adsorption influenced by initial pH and ozone dose. Highest degradation percentage obtained using ozonation adsorption method in synthetic wastewater at pH 10 and ozone dose of 303 mg/hour with cyanide degradation percentage of 91.25\% and COD degradation percentage of 68.94\% in 60 minutes.
- Tapioca starch wastewater removal process using ozonation adsorption obtains cyanide degradation percentage of 87.06\%, COD degradation percentage of 43.23\% and TSS degradation percentage of 82.99\%.

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