The Influence of pH to LMW Organic formation:Aldehydes, in desinfection Process by Ozonation

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ABSTRACT

Desinfection process using ozone in drinking water treatment can produce Low Molecular Wieght (LMW) organics, which can serve as substrate for a pathogenic bacterial growth and some were also carcinogenic in nature. Because ozone is unstable in water, part of ozone will react directly with dissolved solutes, while the other part may decompose before reaction. The pH of water is important because hydroxide ions initiate ozone decomposition. The aim of this research is to find out the influence of pH to ozone decomposition and also to LMW organic formation, that is, aldehydes as indicator, in desinfection process by using ozone. Due to the instability of ozone, it has to be produced on site, using an ozone generator. Ozone gas will be supplied continually into a batch system contactor with 7 liters of water. Measurements of ozone and aldehydes were done at contact time values of: 3,5 and 10 minutes at any pH condition using spectrophotometry, and GC-MS methods. Water samples were taken from a filtration unit in the Water Treatment Plan (PDAM) Dago, in the city of Bandung. The results showed that decomposition of ozone in acid pH occurred more slowly than in neutral and base pH. This research also showed that aldehyde composition (%), decreased gradually until contact time value of 10 minutes. These results were influenced by the quantity of hydrophobic natural organic matter existing in water samples. At contact time (CT) below 0,081 mg-minute/L, aldehyde can not be detected at base pH, but it can be detected at neutral and acid conditions at any range of contact time. Aldehyde formation was also influenced by the quantity and kind of existing precursors, its concentration, and the duration of contact time or ozonation. In addition, it was found that pH asserted a significant influence only for first three minutes of contact time.

Key words: LMW organic, pH, ozone desinfection, aldehyde.

I. INTRODUCTION

The most important use of desinfectans in water treatment is to inactivate pathogenic organisms in water. Desinfection can be performed physically and chemically. In general, chemical substances used as desinfectans are oxidators, which react with organic and non organic matters. In Indonesia, the most common desinfectan is chlor. However, the use of ozone as desinfectan is currently increasing, as the increase use of bottled water.

Ozone is a strong oxidator, stronger than widely used desinfectans such as chlorine. In water, ozone will decompose into OH radicals which are the strongest oxidants in water (von Gunten, 2003).

Stability of ozone in the water is affected by water quality such as pH, the type and content of natural organic matter (NOM) and alkalinity. The reactions of ozone in water are generally

rather complex. In the water, only part of the ozone reacts directly with dissolved solutes, the other part may decompose before reaction (Hoigne, at al., 1983).

Desinfections process with ozone has been reported to produce Low Molecular weight (LMW) organics matter. LMW are organic compounds with molecular weight less than 500 Dalton (Nowrocki, 2002). LMW organics are formed in water which has precursor such as NOM. Microorganism for their growth and metabolisms could use LMW organics, so that the microorganism can experience re-growth in disinfected water (Kruithof, CJ, 2002). Among the LMWs, aldehyde LMWs such as formaldehydes and acetaldehydes are of primary concern due to its potential to cause cancer (Paode *et al*, 1997).

In Indonesia research about LMW in drinking water due to ozonation is rare. This research is undertaken in Indonesia because LMW organic formation as disinfection by products (DBPs) is influence by the characteristic raw water, which might be different from one country to another.

The aim of this research is to find out the influence of pH and water characteristic on ozone decomposition and on LMW organic formation, that is, aldehydes as indicator, in desinfection process using ozone.

II. MATERIALS AND METHODS

2.1. Samples

Samples were taken from effluent of the filtration unit from Water Treatment Plant Dago-Pakar belonging to the Bandung City Water Supply Authority, Bandung, West Java, Indonesia.

Ozonation was done at; (1) pH neutral, equal to 7.22; (2) pH Acid, H_2SO_4 was added at this condition until pH equal to 4; (3) pH base, NaOH was added until pH equal to 10.

2.2. Experimental set up

The experimental set-up is presented in Figure 1. The equipment used in this set up are air pump equipped with air flow meter (rotameter), ozone generator, and batch reactor for ozone-water reaction. The excess ozone are released from the reactor, and decomposed by scrubbing in KI solution.

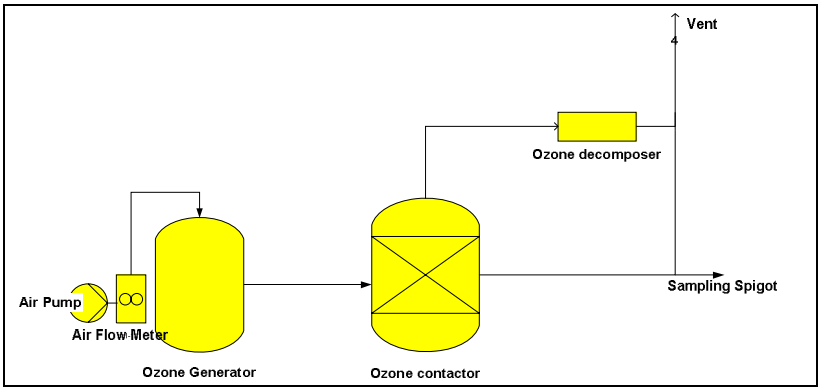

Figure 1. Experimental set-up

Air pump is applied to supply oxygen to ozone generator and then carry the mixture of air and ozone to the reactor. To distribute air to the reactor, a kind of a diffuser was applied. Air pump is provided with air flow meter, for measuring air supply to ozone generator. Air flow in this research was kept constant to a flow of around 2 L/minutes. Ozone generator is an appliance that alters air to become ozone. Ozone generator used at this laboratory study has a high voltage of more than 4000 Volt. Ozone, which was produced by ozone generator, will then be brought into a contactor where ozone in the form of gas phase will be transferred to become a liquid phase. The ozone containing air was then passed through a 7 liters batch contactor. The contactor was provided with a filter disc having pore diameter of 16-40μμ, and also a dispenser and a valve for water sampling. Contactor was also provided with air lift system for ascertaining homogeneity in this batch reactor.

2.3. Analytical methods

A. Aldehyde

Aldehyde was determined by GC-MS Shimadzhu QP 5000, extracted with hexane. Condition of measurement at this research are as follows: Column type DB 17 ; column length of 30 m and diameter of 0,25 mm; Temperature of injector 280 ^{0}C, and temperature of detector 280 ^{0}C; and linear velocity of 40,6; flow of 1,3 ml/minute; and sample injected to GC-MS equal to 1µ L.

B. Water Quality Measurement

Water quality parameters measured at this research are: pH, turbidity, temperature, alkalinity, concentration of Fe and Mn, Total Organic Compound (TOC) and also UV_{254}.

C. Measurement of Residual Ozone and Aldehyde

Concentration of residual ozone and LMW are measured at 3, 5 and 10 minute, graph yielded to show the relation of residence time and concentration residual of ozone and also the relation of residence time and concentration of LMW formed. Residual of ozone was determined according to standard method 4500-O3-B. Measurement Of LMW was done with gas chromatography with mass spectrometric (GC-MS). Aldehyde compounds were also measured by Gas Chromatographic Mass Spectrometry (GC-MS).

III. RESULT and DISCUSSION

3.1. Water Sample Quality

Table 1 shows water sample quality taken at filtration unit effluent. Here, only important parameters were examined.

Table 1. Important samples characteristics

No	Parameters	Value
1	pH	7,22
2	Temperature (^{o}C)	24
3	Alkalinity (mg/L CaCO3)	46,23
4	Total hardness (mg/L)	24,75
5	Manganese (Mn)	-
6	Fe(mg/L)	-
7	TOC (mg/L)	3,9
8	Turbidity (NTU)	1.5
9	UV 254 (abs)	0,012

Table 1, shows that pH sample from filtration unit is neutral (7,22), as the neutral range is 6-9. The alkalinity is 46.23 mg/L $CaCO_3$. Alkalinity as carbonate is known to inhibit the formation of LMW (von Gunten, 2003). TOC of the sample was 3,9 mg/L and UV_{254} (Abs) was 0,012. The value of TOC and UV 254 were used to indicate the existence of NOM as LMW organic precursors during ozonation.

3.2. LMW Content

The LMW concentrations of water samples taken before ozonation were measured by GC-MS. Due to existing difficulty in determining the concentration of each LMW compound or species, the results for each compound are presented in a normalized form, or in percentage against the total LMW detected.

Analytical results of water sample taken at filtration unit effluent showed the existence of isovaleraldehide, pentylpropiolate and hexanal. The relative concentration of isovaleraldehide compound was equal to 23,03%, pentylpropiolate compound 52,66%; and hexanal was equal to 24,31%.

3.3. Residual Ozone

Ozonation of water sample taken at filter effluent was done to find out the formation of DBPs in desinfection process. Figure 2 shows the measurement of residual ozone taken at various contact times and pH conditions.

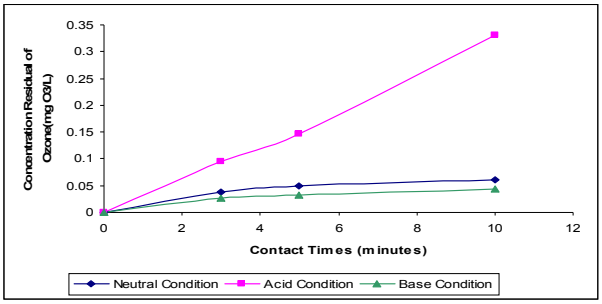

Figure 2. Ozone concentration for different pH condition

Figure 2 shows that concentrations of residual ozone in water samples are increasing until 10 minute of contact time at any pH conditions. The concentrations of residual ozone in water samples at acid condition are higher as compared to those in base and neutral conditions. This condition is likely to happen as the result of ions initiate ozone decomposition, which involves the following series of reactions (von Gunten, 2003):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (1)$$
$$O_3 + HO_2^- \rightarrow OH^* + O_2^* + O_2 \qquad (2)$$

According to reactions (1) and (2), the initiation of ozone decomposition can be artificially accelerated by increasing the pH or by the addition of hydrogen peroxide. As a result of the acid condition, ozone decomposition occurs more slowly than any higher pH conditions.

3.4. pH Influence to Aldhyde Formation

Figure 3 shows the compilation formation of aldehyde during desinfection process taken at different contact times (3,5, and 10 minutes) at any pH conditions.

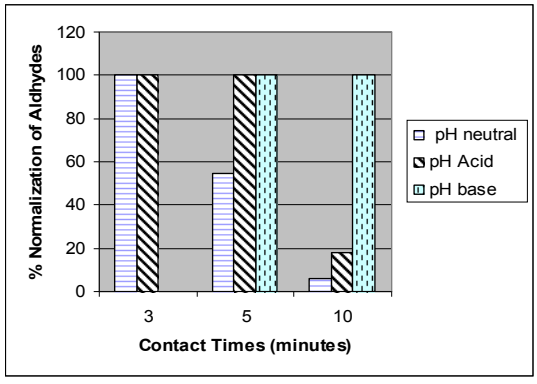

Figure 3. Formation of Aldhyde for different pH condition

Figure 3 shows that, pH influence significant only for first three minutes of contact time to aldhyde formation. In base condition, at 3 minutes of ozonation process, aldhyde was undetected. It happened because the addition of NaOH (strong base) in to the water sample. As a result, additional reactions happened. This result was also affected by residual of ozone value at this condition, which was at the lowest level as compared to residual ozone at the same contact time at any pH condition.

For extended contact times to 5 and 10 minutes, pH didn't give significant effect to aldhyde formation (Siddiqui (1997), and Hammes (2006)). The phenomenon of aldhyde formation in ozonation process was done by immediate polymer cleavage reactions.

Ozone decomposition attacks NOM polymers, producing hydroxyl and carbon radicals. The carbon radical reacts almost immediately with an oxygen molecule, giving a peroxy radical (Siddiqui et al.,1997):

$$\left[RH + O_3 \rightarrow ROO\bullet + OH\bullet\right]$$

A part of the peroxy radicals, thus produced, gives hydroperoxide. Another part of the peroxy radicals gives substances such as ketone and alcohol (Siddiqui et al.,1997):

$$\left[ROO\bullet + RH \rightarrow ROOH + R\bullet\right] \rightarrow$$
$$\left[R\bullet + O2 \rightarrow ROO\bullet \rightarrow \left[2ROO\bullet \rightarrow RO + ROH + O_2\right]\right]$$

The alcohols are further readily oxidized by ozone to aldehydes, and the type of aldehydes formed depends upon the class of alcohol involved (Siddiqui et al.,1997):

$$\left[RCH_2OH + O_3 \rightarrow RCHO + H_2O + O_2\right]$$

3.5. Precursor Influence to Aldhyde Formation

Concentration of ozon / TOC will give us information about precursor influence to aldhyde formation during desinfection with ozone.

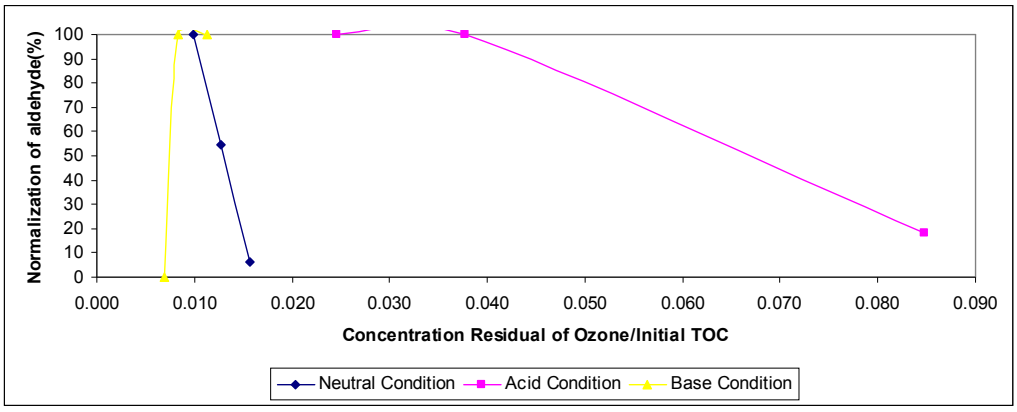

Figure 4. Comparison of Ozon/TOC at The Beginning of Aldhyde Formation

The value of organic compound measured by TOC was 3.9 mg/L and UV_{254} was 0.012 mg/L. TOC and UV 254 was used to indicate the existence of NOM and the type of NOM in the water. Figure 4 shows, in acid and neutral condition, aldehyde decreases gradually as ozone concentration per TOC increase. Removal of aldhyde at this process may result from the removal of hydrophobic organic material such as humic substances (which was aldehyde-former organic material, according to Schechter and Singer, 1994) by the preceding coagulation-flocculation process and followed by sedimentation process. It is known that hydrophobic macromolecule organics can be removed by coagulation process (Fair et al, 1966 and Bose,2007).

In base condition at ozone concentration per TOC less than 0.007 aldehyde was not detected, and increased up to 100 % at ozone concentration per TOC 0.008 and 0.011. This result must have linked with pH influence to ozone decomposition in the water.

3.6. CT Influence to Aldhyde Formation

CT value indicates the affectivity of desinfection process. Figure 5 shows, CT influence to aldhyde formation.

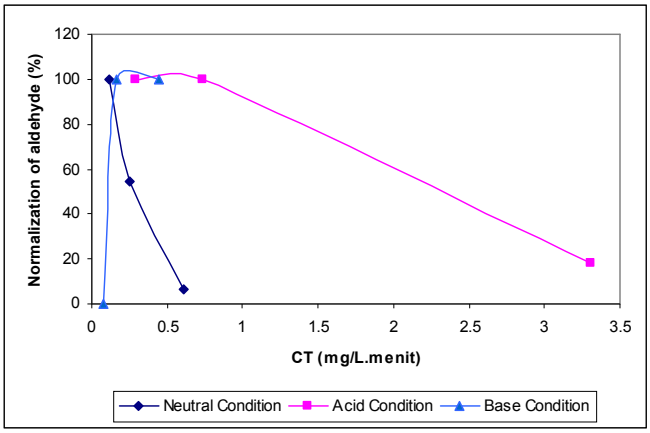

Figure 5. Relationship of CT and The formation of aldhyde composition

Figure 5 shows, in acid and neutral condition, aldehyde decreases gradually as CT increased. This result must have linked with precursor influence that it has been discussed before.

In base condition at CT below 0.081 mg. minute /L which happened at a base condition, aldhyde was not detected, but at higer CT value aldhyde was formed. This phenomenon occured because at CT below 0.081 mg.minute /L concentration residual of ozone is not strong enough to decompose NOM, at the same time OH radical will decompose aromatic compound to produce alkene (Yunzheng et al.,2004). Alkene was believed as aldhyde former raw material, thus at further oxidation process aldhyde was detected until 100%.

IV. CONCLUSION

Formation of LMW after desinfection process can be detected in an aldhyde form. Formation of aldhyde are affected by concentration of residual ozone, contact time and precursor types. Pre treatment process such coagulation-flocculation should be done before desinfection by ozone to reduce DBPs . The result showed that pH did not significantly effect aldhydes formation.

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