Retention time of ozone at various water condition

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Abstract. Ozone is a molecule composed of three atoms of O₂ (oxygen) formed by the merger of oxygen free radicals with molecular oxygen, ozone is unstable and reactive. Ozone serves as a disinfectant, decolorization, as well as to remove organic materials. Ozone can be formed by electrolysis, chemical radiation and corona discharge. The formation of ozone by corona discharge most widely used today. Ozone that is unstable and reactive has a retention time depending on the environment such as temperature, pH and mineral content. Ozone can be applied to foodstuffs solid or liquid food ingredients, including water, milk, vegetables and fruits that have variations in time, temperature, pH value and concentration of minerals. This study aimed to evaluate the influence of temperature, pH, type and concentration of mineral to the retention time of the ozone. In this research, we varied temperatures (5°C, 25°C and 40°C), type of water (distilled, aquabidest, and tap water), concentration of mineral Ca (0 ppm, 125 ppm and 250 ppm) and pH (5.5, 7 and 9.2). The result was analyzed descriptively using different t-test analysis to compare each treatment. The process of ozonation at low temperatures (5°C) has a longer retention time compared to high temperature, samples that contain low minerals have a longer retention time than samples containing high mineral, the addition of mineral (Ca) did not affect the retention time of ozone. Ozonation at acidic pH has a longer retention time compared to alkaline pH. The duration of ozonation 5 and 10 minutes have no different in retention time.

1. Introduction
Ozone is a molecule consisting of three oxygen atoms and has the chemical symbol of O₃ [1]. Ozone (O₃) is formed by the incorporation of an oxygen-free radical with molecular oxygen [2]. Ozone is an unstable gas and reactive, therefore the amount of ozone in the atmosphere tends to have low concentrations. Ozone has many uses, such as for disinfection of microorganisms because ozone is a strong oxidizing agent. Ozone is commonly used in the drinking water industry to kill microorganisms contained in drinking water. Currently ozone is used to kill algae and oxidize organic matter, thus eliminating unwanted taste, odor, and color caused by the reaction of organic matter.

Ozone has different stability depending on environmental conditions, such as temperature [3]. At low temperatures, ozone has a longer retention time compared to high temperatures. The retention time of ozone define as the time when ozone can dissolve in water. The stability of ozone is influenced by the retention time in water under certain conditions. Ozone has a strong oxidizing properties that can reduce microorganisms, therefore suitable for sterilization purposes [4]. Ozone utilization has been widely applied in areas such as in America and Japan ozone used for sterilizing raw foodstuffs as well as preservation of foodstuffs [5]. Foods that can be treated by ozone include solid foods such as...
vegetables and fruits, wheat, as well as hydrocolloid foods such as milk and fruit juices [2]. Foodstuffs that can be treated by using ozone are complex foodstuffs with different pH, mineral and temperature.

The stability of ozone is affected by its environment, such as pH, temperature, type water and mineral content. Therefore, it affects the retention time of ozone in water. At high temperatures, resistance and the presence of ozone in the water will decrease, whereas at low temperatures the presence of ozone in the water will be longer [6]. Another parameter that may affect the presence of ozone in water is pH. Water with acidic pH can inhibit ozone decomposition, because low pH indicates high alkalinity. Alkalinity is the presence of carbonate ions and bicarbonate in the water [7]. Water has a different amount of mineral content depending on the source and water treatment. The level of mineral contained in water can affect the stability of ozone. Research on how the mineral in the water affect the rate of ozone decomposition has not been much explored, therefore the current study will discuss the stability of ozone in water at different temperature, pH, water type and several variations of mineral content. Water with different mineral concentrations was achieved by using different types of water e.g. aquabidest, aquadest and tap water. Aquabidest is processed by double stage distillation, so it does not contain minerals. Meanwhile, aquadest are only once passed through the distillation process, so it contains less mineral. In contrast, tap water contains higher minerals compared to the other. In addition, to evaluate the effect of ozone stability as affected by mineral, variation of minerals content was added to aquadest [8]. The present study was evaluated the ozone stability in water at different pH, temperature, water type and variations in the amount of mineral content. The results of this study can be used as parameter for ozonation of other liquid-based food.

2. Materials and Methods

The raw materials used in this research were aquadest, aquabidest, tap water. Other materials used are pure oxygen (90-95%), chlorine as the reagent of ozone, CaCl₂, NaOH and HCl. Ozonizer TIP-01 was used to produce ozone, ozone test kit, digital camera, CM 400 chromameter.

The research method used was descriptive analysis conducted with two replicates for each sample namely: the dependent variable (X) is the concentration of ozone obtained, while the independent variable (Y) is temperature, pH, water type and mineral concentration.

| Different temperature | Different type of water | Different mineral concentrations | Different pH |
|-----------------------|-------------------------|---------------------------------|--------------|
| Y₁ = 5°C              | Y₄ = Aquadest           | Y₅ = 0 ppm CaCl₂                | Y₁₀ = pH 5,5 |
| Y₂ = 25°C             | Y₅ = Aquabidest         | Y₆ = 125 ppm CaCl₂              | Y₁₁ = pH 7,2 |
| Y₃ = 40°C             | Y₆ = Tap water          | Y₇ = 250 ppm CaCl₂              | Y₁₂ = pH 9,2 |

The parameter observed in this study (X) were the concentration of ozone in water after 5 and 10 minutes of ozonization at various condition as explained in table 1.

3. Result and Discussion

3.1. Ozonation at different temperature

Temperature is one factor that can affect the retention time and ozone solubility in the ozonation process [9]. The results of ozone retention time at various temperature is presented in figure 1. From figure 1, it can be seen that at the first 20 min after ozonation process (zone I), ozone concentration was fluctuating and unstable at all-time of ozonation and types of water tested. Ozonation for 5 and 10 minutes resulting almost the same ozone concentration, this is probably due to a slow diffusivity of the ozone gas phase to the liquid phase in the water [10]. The diffusivity of ozone was also influenced by the size of the bubbles produced. The diffusion rate between the ozone and the water depend on the surface area of the ozone bubbles [11]. High number of ozone diffused in water cause the ozone to easily decomposed so that the ozone concentration was easily decreased in a short time, whereas at low ozone concentrations, the decrease in concentration was slower because ozone has room to bind with other.
Figure 1. Ozone retention time at various temperatures: -- Aquadest 5°C (5 min), --- Aquadest 5°C (10 min), - - - Aquadest 25°C (5 min), --- Aquadest 25°C (10 min), ---- Aquadest 40°C (5 min), --- Aquadest 40°C (10 min).

Ozone is a reactive compound that readily binds to other compounds when ozone concentrations are high, nevertheless, at high concentrations ozone tend to be unstable. The ozonation process at 5°C has a longer retention time because ozone is hardly decomposed at low temperatures [12]. At high temperatures, the ozone tends to expand so that the solubility decreases. Solubility of ozone is influenced by temperature, the lower the temperature the higher ozone solubility will be, while at high temperature, ozone insoluble in water [9]. Furthermore, at high temperatures, ozone diffusivity was low because ozone in the gas phase has a lower density than water as compared in a liquid phase, so that ozone is easily released, whereas at low temperatures, ozone has a high diffusivity due to in the gas phase ozone tends not to expand so that ozone was easily to bind with water. Based on t-test (p <0.05) ozonation at 5°C was significantly different from ozonation at temperature of 25°C and at temperature 40°C, while temperature ozonation of 25°C was not significantly different at temperature of 40°C according to t-test (p <0.05).

3.2. Ozonation at different types of water

Mineral content in water is one of the factors that can affect the retention time and solubility of ozone in water. The ozonation process based on type of water uses, by mean of different mineral content, was performed by using aquadest, aquabidest and tap water at ozonation temperature of 5°C. Based on figure 2, in the first 20 min after ozonation for the aquadest samples, ozone concentration was fluctuatively decreased (zone I). The retention time of ozone in aquadest and aquabidest samples was 140 min, while for tap water samples was 20 min. Tap water ozonation process has a shortest retention time as compared to the other treatments, due to groundwater contains many minerals that can accelerate ozone decomposition during the ozonation process [8]. Aquadest and aquabidest do not contain minerals as they have undergone demineralization through distillation. Based on the results of Ca analysis performed by using AAS (Atomic Absorption Spectroscopy), the highest Ca content was presented in tap water (14.46 ppm). Thus, every 1 ppm of minerals contained reduces the ozone retention time for ± 10 minutes. Mineral content affects the diffusion of the ozone bubbles into water, the higher the mineral content, the easier the ozone to be decomposed and thus causes the retention time of ozone to be shorter [13]. According to Von Gunten [14]), ozone firstly decomposed inorganic compound then organic compounds will be decomposed afterwards. In the condition of water that contains many minerals such as tap water, ozone more easily decompose into O₂ (oxygen) and O* (free oxygen ions), while in condition of water with less minerals such as distilled water, ozone was decomposed longer.

According to the statement of Gottschalk et al. [13], mineral content affects ozone diffusivity into water. The retention time of ozone in tap water was the shortest due to the minerals containing in tap water so that ozone was easily decomposed by reacting with mineral. On the other hand, in aquadest and aquabidest which contained less minerals and organic compounds, ozone was decomposed at longer time thus it has a longer retention time. Furthermore, ozone did not react with inorganic
compounds such as minerals. Figure 2 shows that retention time of ozone at the temperature of 5°C in aquadest and aquabidest sample has a similar property, but it was significantly different from ozone in tap water.

**Figure 2.** Ozone retention time at various types of water: --- Ozonation *Tap water* (5 min), --- *Tap water* (10 min), --- *Aquabidest* (5 min), --- *Aquabidest* (10 min), --- *Aquadest* (5 min), --- *Aquadest* (10 min).

### 3.3. Ozonation at different mineral concentrations

The concentration of minerals or inorganic compounds in water may affect the ozone solubility. Inorganic or salt such as sodium, magnesium, bicarbonate, sulfate, chloride and silica contained at 1-1000 ppm in water [8] may affect diffusion from the ozone bubbles to the water. Oxidation by ozone was also be affected by the presence of mineral [13]. In this study, we added CaCl$_2$ mineral with Ca concentration of 0 ppm, 125 ppm and 250 ppm to aquadest. The results of ozone retention time at different Ca concentration at the temperature of 5°C is presented in figure 3.

**Figure 3.** Ozone retention time at various Ca concentrations; --- 0 ppm (5 min), --- 0 ppm (10 min), --- 125 ppm (5 min), --- 125 ppm (10 min), --- 250 ppm (5 min), --- 250 ppm (10 min).

From figure 3, at the first 20 min after ozonation process (zone I), ozone concentrations from all samples were high and fluctuates. The amount of Ca added affect the retention time of ozone, particularly it can be seen at concentrations of 125 ppm and 250 ppm (zone II). The addition of Ca into water confirmed that minerals can accelerate ozone decomposition. Based on the result above, mineral concentration influences the ozonation process. The increasing of mineral concentration decreased the ozone retention time. As the first compounds to be oxidized by ozone was inorganic compound then followed by organic compounds, the presence of inorganic minerals was mainly affected the ozonation process [14].
3.4. Ozonation at different pH

The pH value indicates the hydrogen ion activity and it affects the ozone retention time. The presence of hydrogen ions in water reduce the decomposition of ozone, thus results the longer ozone retention time. In this study, the ozonation process was carried out at different condition i.e. alkaline (pH 9.2), neutral (pH 7) and acidic (pH 5.5). The results of ozone retention time at different pH value and at the temperature of 5°C is presented in figure 4.

![Ozone retention time at various pH](image)

**Figure 4.** Ozone retention time at various pH: --- pH 5.5 (5 min), --- pH 5.5 (10 min), --- pH 7 (5 min), --- pH 7 (10 min), --- pH 9.2 (5 min), --- pH 9.2 (10 min).

From figure 4, at the first 20 min of ozonation process (zone I) the concentration of ozone was fluctuated especially at pH 5.5 and pH 7. This was occurred due to the unstable ozone properties so that the time of sampling (every 4 minutes after ozonation) was not proportional to the decrease in ozone concentration. The retention time of ozone after 5 min ozonation at acid pH was more than 200 minutes, neutral pH was more than 100 minutes while the alkaline pH has the shortest retention time of 60 minutes. The same results were also observed for 10 min of ozonation. This was in accordance with research conducted by Mandavgane et al. [15] the retention time of ozone in acid pH was longer than the alkaline pH. This was occurred due to water with acidic pH can inhibit ozone decomposition and low pH indicates high alkalinity. Alkalinity in water exhibits carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$) which cause the ozone half-life was increased and the reduced the reaction of a OH radical [7].

Reaction of carbonate and bicarbonate with OH radical is presented in equation (1, 2). The carbonate and bicarbonate ions will react with the OH radical compound so that the ozone will not quickly decompose, thus the ozone retention time will be longer, whereas at high pH, the OH radical was formed easily and it inhibit ozone decomposition, thus the ozone concentration was declined rapidly [15].

\[
\text{OH}^- + \text{CO}_3^{2-} \rightarrow \text{CO}_2^{2-} + \text{HO}^-
\] (1)

\[
\text{OH}^- + \text{HCO}_3^- \rightarrow \text{CO}_2^{2-} + \text{H}_2\text{O}
\] (2)

According to Tizaoui et al. [16], ozone decomposition at a high pH was occurred because the hydroxide ions contributing to ozone decomposition and may cause the reaction as presented in equation (3, 4).

\[
\text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2
\] (3)

\[
\text{O}_3 + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}_2 + \text{O}_2
\] (4)

The ozonation at pH 5.5 was significantly different from the ozonation at pH 7 as well as for the pH of 9.2. Based on chemical reaction at equation (3, 4), it can be seen that ozone decomposition...
converts the OH-group to water (HO$_2^-$) and more quickly breaks down because the ozone decomposed faster to O$_2$, thus causing the ozone retention time at higher pH was shorter.

4. Conclusion
The ozonation process was influenced by various factors such as temperature, water type, mineral concentration and pH value. Ozonation at low temperatures has a longer retention time compared to high temperatures. Water that contain high minerals has a shorter retention time compared to low minerals samples, in addition ozonation at low pH has a longer retention time compared to the sample at high pH. To maximize the ozonation process especially in liquid-based food, ozonation should be performed at low temperature (5°C), samples should not contain minerals and has acidic pH because these condition could reduce the time of ozone decomposition to increase retention time.

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