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Thesis for the Degree of Master of Fisheries Science

Oxidation Effects of Different Levels of Ozone on Ammonia, Nitrite, Nitrate and Dissolved Organic Carbon in Seawater

PUKYONG NATIONAL UNIVERSITY
부경대학교

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August 2010

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해수의 암모니아, 아질산, 질산성질소 및 용존유기탄소 산화에 미치는 오존의 영향

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Oxidation Effects of Different Levels of Ozone on Ammonia, Nitrite, Nitrate and Dissolved Organic Concentration in Seawater

A Dissertation

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Effects of different levels of ozone on ammonia, nitrite, nitrate and dissolved organic carbon in seawater

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Abstract

Ozone is applying to the recirculation aquaculture system (RAS) by the purpose to reducing bacteria and parasites. In stead of sterilization effects, it is known that ozone has oxidizing effects on some water quality parameters such as nitrogen compounds and organic carbon. Therefore, oxidizing effects of ozone on the total ammonia nitrogen (TAN), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), and dissolved organic carbon were tested. During the test, ozone effects on the pH, dissolved oxygen (DO) and bromide concentration were also monitored. Ozone treatment concentrations were originally set up to 0.05, 0.1, 0.15, 0.2 and 0.25 ppm, but actual treatment concentrations were maintained at 0.04, 0.11, 0.15, 0.19 and 0.23 ppm. The 5 ppm of TAN was oxidized within 12 hours in all concentrations of ozone treatments with the average oxidizing rate of 0.65±0.28 mg NH_4-N/L per hour. The 5 ppm of NO_2-N was oxidized within 1.5 hour in all concentration of ozone treatments and the oxidizing rate was 4.5 mg NO_2-N/L per hour. One out of 5 ppm NO_3-N was oxidized by all concentration of ozone treatment after 24 hours. Ozone also oxidizes dissolved organics carbon and maintains the concentration about 2.9±0.77 ppm from the 15 ppm of initial concentration. Average value of pH was increased from 8.1 to 8.6 in all ozone treatments within 20 minutes and stabilized there after. The DO were also increased from 5.9 ppm to 9.4 ppm within 30 minutes in all ozone treatment and stabilized there after. Bromate concentrations were increased sharply within the first 6 hours of ozone treatments at the rate of 7.3±2.4 mg/L per hour in all ozone treatments and the rate was decreased up to 2.5±0.15 mg/L per hour there after. However, bromate concentration was not increased until all TAN was oxidized. Therefore, further studies are needed to find out the relationship between TAN concentration and bromate formation in seawater.

Keywords: ozone, organic carbon, bromate, ammonia, nitrite, nitrate.

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I. INTRODUCTION

It is commonly known as economic-principal of aquaculture that is increasing total production per unit volume of culture media to get more beneficiaries (Huet, 1994). Therefore, aquaculturist usually trying to increase the culture density to get more yields. In another side, once we increase the culture density, we need to pay more attention to the water quality. Because water quality is one of the important factors to manage intensive aquaculture system. Nowadays, people tried to find the simplest and cheapest way to maintain good water quality. The best way to maintain good water quality is increasing the daily water exchange rate in a high density aquaculture system, because it will remove accumulated colloidal solids, refractory organics and nitrogenous metabolic compounds. However, consideration of water, budgets and the cost of heating or cooling the system are major constrains of this method. One of the alternative methods of removing those metabolic wastes is mechanical filter. But this method also needs expensive filter and maintaining costs. Recently ozone treatment is effective on the removal of organic and inorganic metabolites in aquaculture system (Rosenthal, 1980). Ozone has been widely used to sterilize pathogens from the supply and effluent water in aquaculture systems (Ghomi et al., 2007).

Ozone or trioxygen (O_3) is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that much less stable than the diatomic O_2. Ozone is a clear, blue colored gas that produces an easily detected pungent odor at concentrations as low as 5 parts per million (ppm) in atmospheric air. At higher concentrations of ozone, the air becomes acrid and extremely hazardous to health. Ground-level ozone is an air pollutant with harmful effects on the respiratory systems of animals (Ghomi et al., 2007). Ozone is formed when an oxygen molecule forced to bond with a third atom of oxygen (O) (Rice and Netzer, 1985).

Ozone can be applied in aquaculture because ozone is a powerful oxidative agent that has very unstable bond in the chemical chains. At low pH (<7), molecular ozone (O_3) is the dominant form. When pH increases, O_3 turns into very short-lived hydroxyl radicals and its oxidative potential increases. In aquaculture, ozone was used as water disinfectant and water quality improvement (Ghomi et al., 2007). As we know that ozone also improve water quality in addition to the function of deactivating bacterial, fungal and viral pathogens in culturing water (Rosenthal, 1980; Owsley, 1991; Liltved et al., 1995; Wedemeyer, 1996).

Ozone has been used in recirculation aquaculture systems (RAS) to reduce fish disease (Owsley, 1991; Bullock et al., 1997), but ozone is more frequently added to water-recirculation systems to clarify the water and to oxidize nitrite, dissolved non-biodegradable organic material, or organic particulate matter (Otte et al., 1977; Otte and Rosenthal, 1979; Rosenthal and Otte, 1980; Rosenthal, 1981; Williams et al., 1982; Sutterlin et al., 1984; Rosenthal and Kruner, 1985; Paller and Lewis, 1988; Poston and Williams, 1988; Reid and Arnold, 1992).

The use of ozone in the RAS has the meaning of using available water more efficiently. Applying ozone are able to increase water quality conditions because ozone is able to remove dissolved organic compounds, ammonia and nitrite along with such a good disinfectant agent (Magara et al., 1995). However, the use of ozone also brings some disadvantages to the aquaculture systems. Such of the risk followed the application of ozone are bromate forming, ozone residual, and high consumption of power to produce ozone. (Rice and Netzer, 1985).

Ozone is dangerous to the fish and can cause mortality depends on ozone concentration and fish species. Generally, danger limit of ozone concentration in the aquaculture is above 0.25 ppm (Coman et al., 2005). According to the report from The State of New South Wales (2005), residual concentrations of 0.01-0.1 ppm ozone can be effective to reducing the bacterial load and that of 0.1-0.2 ppm can be effective to disinfection. Also 0.2-0.4 ppm of residual ozone showed significant disinfection effect after oxidation of organics in aquaculture effluent.

The other parameter we have to concern while ozonation is bromate forming. Bromide ion (Br^-) is defined as an inorganic ion found in surface water and ground water, where sea water is intruding or the impact of connate, also industrial and oil-field brine discharge (Symons, 1999). Bromate ion (BrO_3^-) is the highest oxidation state of the bromide ion. The bromate ion can be formed during the ozonation of bromide-containing waters (Symons, 1999). Ozone oxidizes bromide to form hypobromite ion (OBr^-). Hypobromite continues to be oxidized to form bromate or to form an unidentified species, possibly BrO_2^- that regenerates bromide ion (Glaze and Weinberg, 1999). Brominated by-product formation in ozonated water is influenced by bromide ion concentration, the source and concentration of natural organic matter (NOM), pH, ozone dose, and reaction time (Bonacquisti, 2006). It is important to note that ozonation under higher pH conditions produces higher bromate concentrations, such that with sufficient bromide and ozone applied to meet an ozone residual for disinfection, tens of micrograms per liter of bromate can be formed (Faust and Aly, 1998).

The simplified reactions of bromide ion and ozone has described by Bonacquisti (2006) as follows:

$$O_3 + Br \rightarrow O_2 + OBr^- \ \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$O_3 + OBr^- \rightarrow O_2 + BrO_2^- \ \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$O_3 + BrO_2^- \rightarrow O_2 + BrO_3^- \ \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Wilde and Soracco (1983) reported that Total Residual of Bromide (TRB) could be lethal for some fish either by high concentration or because the acute doses. Further more, they reported that TRB of 0.81 mg/L for 96-h or by the 164 mg/L in accumulation doses could kill juvenile while on adult fatheads minnow

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would be lethal in the doses of 1.17 mg/L for 96-h or 248 mg/L in accumulation doses. In case of blue gills, lethal concentration of TRB would be 0.63 mg/L for 96-h or 301 mg/L in accumulation concentration.

Ozone also could oxidize ammonia to some other relevant molecule. Ammonia may decompose to N_2 by several chain reactions but ozone does not decompose ammonia into the innocuous N_2. Its only transfer ammonia from water to the atmosphere as following reaction (Yang et al., 1999).

$Br + O_3 + H \rightarrow HBrO + O_2$ ....(4)
$NH_3 + HBrO \rightarrow NH_2Br + H_2O$......................................(5)
$NH_2Br + HBrO \rightarrow NHBr_2 + H_2O$..................................(6)
$NH_2Br + NHBr_2 \rightarrow N_2 + 3Br + 3H$ ....(7)

It has been known that ammonia will oxidize to nitrite and continues to oxidize into nitrate by ozone via;

$NH_4^+ + 3O_3 \rightarrow NO_2^- + 3O_2 + 2H + H_2O$ ....(8)
$NO_2 + O_3 \rightarrow NO_3 + O_2$..(9)

In the other way, ammonia could also oxidize directly into nitrate by following reaction (Haag et al., 1984);

$NH_4^+ + 4O_3 \rightarrow NO_3^- + 2H^+ + H_2O + 4O_2$.......................(10)

From the mentioned above, it was giving understanding that ammonia will oxidized into nitrite and the final product will be nitrate.

The other parameter we should consider before applying ozone into aquaculture system is Total Organic Carbon (TOC) because TOC is also oxidized by ozone. Interaction of ozone with organics in aquaculture system is complex.

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However, it is known that ozonation decreases organic carbon concentrations by: direct oxidation of organic compounds; coagulation of small organic particle into larger ones and more easily removed by mechanical filtration; and breaking down large “refractory” organic molecules into more biodegradable ones (Krumins et al., 2000).

Summerfelt et al. (1997) reported that ozonation improving particle filtration and, therefore, lowered suspended solids loads in the culture water. Rosenthal (1981) reported that ozone could improve the BOD_5 of the water. According to above information, the ozone at certain dose was not sufficient to oxidize the organic compounds completely, but did break up large organic molecules into smaller, more easily biodegradable ones. The ozone demand created by the NOM and nitrite in the RAS affecting disinfection capacity in the water because the ozone concentration applied in RAS are relatively low and the dissolved ozone reacts quickly with NOM, so that the residual ozone cannot be maintained to provide sufficient ozone concentration and contact time for disinfection (Bullock et al., 1997). The NOM is a parameter that including all forms of organic carbon and can be quantified using a number of analytical techniques (e.g. TOC, chemical oxygen demand).

According to all information mentioned above, ozone oxidizes nitrite, nitrate, and ammonia along with TOC in the water. It also well known that ozonation can produce brominate by-product. However, practical data of the effect of several levels of ozone concentrations on water quality parameter such as ammonia, nitrite, nitrate and TOC are not available. Therefore, a series of experiments about the oxidation effects of ozone concentrations on ammonia, nitrite, nitrate, and TOC were tested. During the ozone treatments, changes of dissolved oxygen, pH, and bromate were monitored.

II. MATERIAL AND METHOD

2.1. System Design

All the treatments were done in inside of the fume hood (Figure 1). Ten liters of acrylic cylinders were used and filled with 7 Liter of sea water in the fume hood. Each of four tubes was installed with ozone spreader (air stone) and bar thermometer. Air stone was connected to the air flow meter and then headed out from the ozone generator. Ozone was introduced into each cylinder through plastic hose and air stone. Airflow meter was installed for each cylinder to measure and adjusting the amount of ozone added into to the water. Ozone generator (*Ozonetech*, PC57L-10) with the capacity of 13 L/min of ozone gas was used. The fume hood was equipped with ventilation system to blow out the excess ozone from the cylinders. An air temperature controller was installed in the fume hood to adjust the experimental temperature at 25^{o}C.

Ozone reaction perform was significantly effected by temperature (Rice, Rip G. & Netzer, Aharon. 1985), so in this experiment air controller and thermo switch were used to stabilize the temperature at 25^{o}C.

Salinity was checked and monitored by hand refractometer (*ATAGO hand-held refractometer*) to maintain constant salinity.

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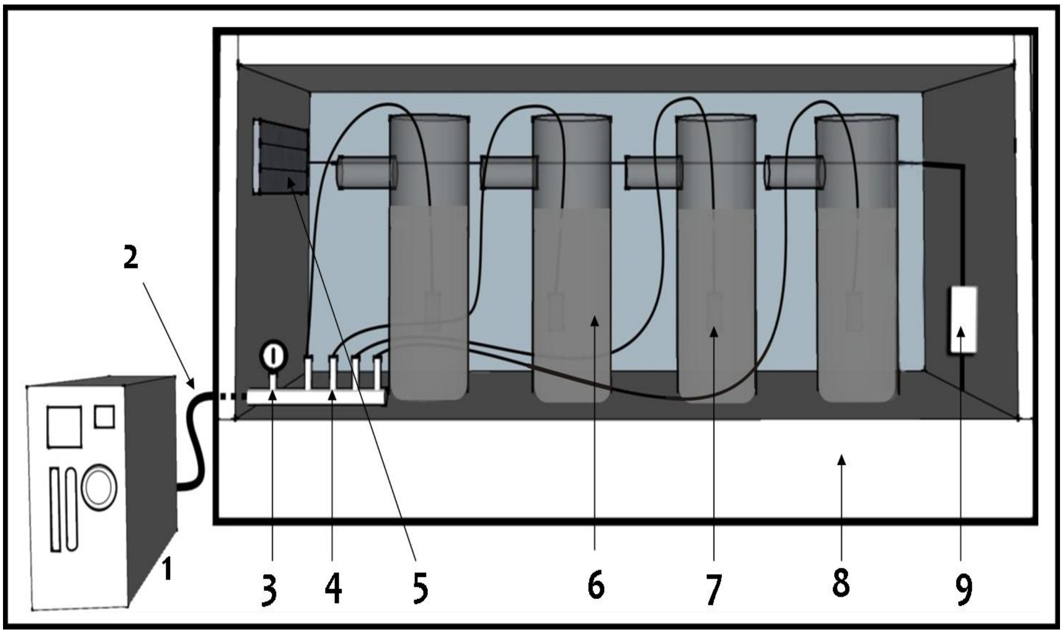

Figure 1. Ozonation of seawater inside of fume hood while testing some of the water parameter.

1. Ozone generator
2. Connector hose
3. Pressure gauge
4. Air flow meter
5. Air conditioner
6. Acrylic cylinder
7. Aeration stone
8. Work bench
9. Thermo switch

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2.2. Experimental Procedure

After set up the system, each acrylic cylinder was filled with 7 L of filtered seawater. The temperature was set at 25^{o}C and the initial DO, pH, and ozone concentration were measured before ozone was injected. When the system was stabilized and the initial water quality parameters were measured ozone was continuously injected in the water at the rate of 1 L/min, 2 L/min, 3 L/min, 4 L/min and 5 L/min. Water samples were periodically collected for the analysis of ozone and other water quality parameters. Periodical sampling intervals were depending on the speed of change of water quality parameters monitored.

2.3. Ozone Concentration for Treatment

This section of experiment was set to manage the composition or portion of ozone to introduce to the water so the certain level of ozone equilibrium concentrations can be maintain by adjusting the amount of ozone introduced. Determination of ozone concentration was calibrated and corrected by the formula of ozone constant loss of absorbance (Bader and Hoigné, 1981).

Ozone treatment concentrations were designed to maintain at 0.05 ppm, 0.1 ppm, 0.15 ppm, 0.2 ppm, and 0.25 ppm according to effective concentration to sterilization of microorganism and toxic levels to the fish in aquaculture water. However, actual concentrations were maintained at 0.04 ppm, 0.11 ppm, 0.15 ppm, 0.19 ppm and 0.23 ppm. For these levels of ozone equilibrium concentrations, amount of ozone injected to the water were 1 L/min, 2 L/min, 3 L/min, 4 L/min, and 5 L/min respectively.

Ten minutes after ozone was injected to the water at rate of 1 L/min, 0.04 ppm of ozone concentration was reached and stabilized. After 20 minutes ozone injected to the water at the rates of 2, 3, 4, and 5 L/min ozone concentration were reached are 0.11, 0.15, 0.19 and 0.23 ppm respectively and stabilized (fig.2).

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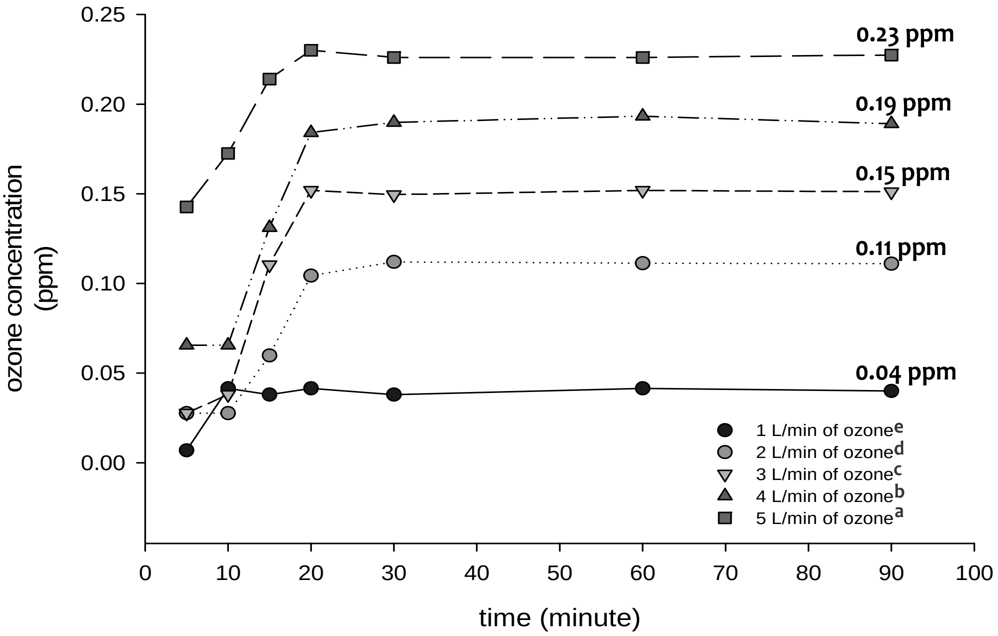

Figure 2. Relationship between ozone loading rate and equilibrium concentration

Ozone equilibrium concentration resulted in this part than was used to treat another water quality parameter to check the effects of ozone concentration to the water quality. Water quality parameter were treated are ammonia, nitrate, nitrite, TOC and ozonation by-product (Bromate forming, DO, and pH).

2.4. Ammonia Oxidation

Anhydrous ammonium chloride (NH_4Cl) was used as the ammonia source (APHA, AWWA, WEF., 1995) with the concentration of 5 ppm. Water media were ozonated until the equilibrium concentration before the ammonia source had added. When the ozonation still running, samples to monitor the ammonia concentrations were taken periodically by 15, 30, 60, 90, 120 minutes, 3, 6, 12, and 24 hours from the beginning of treatment.

To observe the ammonia oxidation "*Manual Phenate Method*" was used by combined it with spectrophotometer OPRON 3000. The treatment was triplicates to reduce the experimental error.

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To remove the possible oxidation effects of common aeration on ammonia concentration, same treatment without ozone were done. Nitrite and nitrate are monitored because these two are by-products of ammonia oxidation. Bromates one of by-products of ozonation in seawater was also monitored in this process.

2.5. Nitrite Oxidation

Sodium nitrite ($NaNO_2$) with the initial concentration of 5 ppm was used as the nitrite source. The samples were collected periodically by 15, 30 minutes, 1, 2, 3, 6, 12, and 24 hours from the beginning of treatment. Nitrite oxidation was measured by Spectrophotometer (Hach DR-2000) (APHA, AWWA, and WEF., 1995).

2.6. Nitrate Oxidation

Sodium nitrate ($NaNO_3$) with the initial concentration of 5 ppm was used as the nitrate source. The sample was collect periodically by 15, 30 minutes, 1, 2, 3, 6, 12, and 24 hours from the beginning of treatment. Fluctuation of nitrate concentration was measured with “ultraviolet spectrophotometric screening method” based on the standard method by APHA, AWWA, and WEF (1995). In this method measurement of nitrate was done under the wave length of 220 nm and 275 nm. 220 nm of wave length was used to obtain NO_3^- reading and a wave length of 275 nm was used to determine interference due to organic matter. (APHA, AWWA, WEF., 1995).

2.7. TOC Oxidation

Glucose (dextrose) was used as the carbon source. The TOC concentration was conditioned to reach the level of 15 ppm. This concentration has reported as an average TOC levels in recirculation aquaculture systems. Water sample to analyze TOC was taken in the interval of 1 hour after the adding of

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glucose and then periodically at 6, 12, 24 and 36 hours after the treatment.

TOC measurement was done under the *HiPerTOC* analyzer. For total organic carbon measurement, sample was injected into a gas-sparged reactor containing acidified potassium persulfate ($K_2S_2O_8$) solution; continued by exposures the solution using elevated ultraviolet (UV) radiation to enhance the oxidation. The concentration of (TOC) was measured as the difference between "total carbons (TC)" and "inorganic carbon (IC)" results (Thermo Electron Corporation, 2009).

2.8. Ozonation by-product

Ozonation of seawater is always brought the side effect instead of the main parameter measured. Therefore, while the maintaining of ozone equilibrium concentration, ozonation by-product (bromate, DO and pH) were also measured.

2.8.1. Bromate formation

Water samples were collected periodically at 5 min, 30 min, 1h, 1h 30min, 2, 3, 6, 12, and 24 hours. Bromate concentrations were measured using spectrophotometer (*Opron 3000*) under the wave length of 590 nm.

2.8.2. DO Increment

DO level were measured by *insitu* method to get a more accurate measurement and reducing bias. In this experiment, Oxyguard oxygen meter “*handy MK III*” were used. The DO measurement was done each time while the other water parameters were sampled.

2.8.3. pH Increment

In this experiment, pH level around 5 to 9 were expected, other wise sample have to be treated before another parameter such us ammonia, nitrate, nitrite also bromate could measured, because those parameters were interfered much by the pH level out of mentioned range (APHA, AWWA, WEF., 1995).

2.9. Statistical Analysis

Data were analyzed by analysis of variance (ANOVA) and means of treatment were compared by Duncan Post-Hoc test using SPSS 16.0 and Sigma Plot 10.0 statistical software version.

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III. RESULT

3.1. Ammonia Oxidation (NH_4-N)

In this experiment, ozone could oxidize ammonia at the rate of 0.65 ± 0.28 mg NH_4-N/L/hour in average. This oxidation was quickly started when 5 ppm of initial ammonia source was added into the water. Almost all ammonia was oxidized within 12 hours and there were no significant differences among the treatments on the oxidation rates of ammonia. Two hours after the ozone treatments started ammonia dropped from 5 ppm up to 3.15 ppm. After 3, 6, 10 and 12 hours, the ammonia was dropped further to 2.21, 1.18, 0.52 and 0.1 respectively.

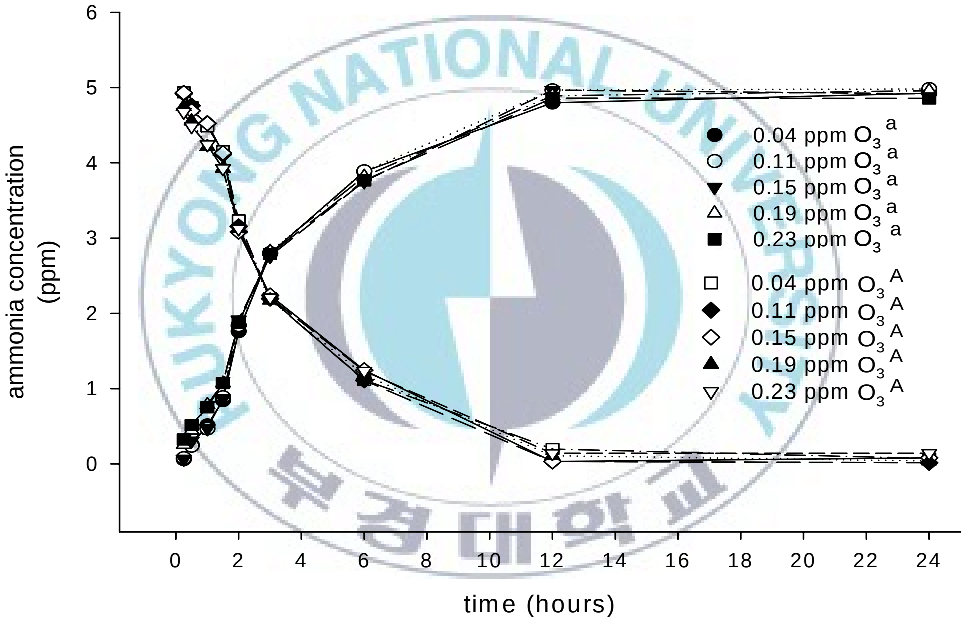

Figure 3. Effect of 5 different concentration of ozonation on ammonia removal rates.

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At the ozone treatment, concentration of 0.04 ppm, 0.11 ppm, and 0.15 ppm, 5 ppm of ammonia were oxidized with the rate of 0.55±0.21 ppm/hour (*y=1.2873Ln(x) +1.14*). At the higher ozone concentrations of 0.19 and 0.23 ppm, ammonia oxidized with the rate of 0.75±0.20 ppm/hour (*y=1.2108Ln(x) +1.3005*).

3.1.1. Nitrite Changes

While the ozonation of ammonia, nitrite change in the water was also monitored as the reaction of ammonia oxidation by ozone. Here the result was shown that by 5 ppm of ammonia in the water, ozone could maintain nitrite concentration to be below of 2 ppm NO_2-N as long as 24 hours. Data was showing that after 12 hour nitrite concentration seems to be almost zero. It was because after the 12 hour, ammonia as a nitrite source has exhausted or oxidized fully, so the nitrite input was also stopped. While the nitrite input was stopped, the nitrite oxidation by ozone still continued, after the certain time the nitrite concentration has been also oxidized fully and almost disappeared from the water. The fluctuations of nitrite concentration in the water as long as ozonation of ammonia are shown in the following table. O_3

Table 1. Nitrite concentration while the ozonation of ammonia treatment

Time	**Ozone Concentration (ppm)**				
(hours)	**0.04**	**0.11**	**0.15**	**0.19**	**0.23**
0.5	1.82	1.95	1.89	1.89	1.99
1	1.70	1.89	1.89	1.80	1.93
2	1.70	1.89	1.70	1.76	1.89
3	1.51	1.51	1.70	1.78	1.51
6	0.94	0.75	1.51	1.32	0.75
12	0.17	0.36	0.36	0.55	0.17
24	0.00	0.17	0.02	0.04	0.17

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3.1.2. Nitrate formation

Monitoring the ammonia oxidation process still continued by measuring nitrate formation while the ozonation of ammonia. It was known that ammonia could oxidize into nitrite and continuous oxidized into nitrate. The previous study has shown that ammonia was oxidized into nitrite by ozone. Here by this experiment, we can know that ammonia was oxidized to the final residual is nitrate. This result was shown by 5 ppm of ammonia in the water, ozone could oxidize it into nitrate as much as 15.4 ± 0.29 mg/L in 24 hours.

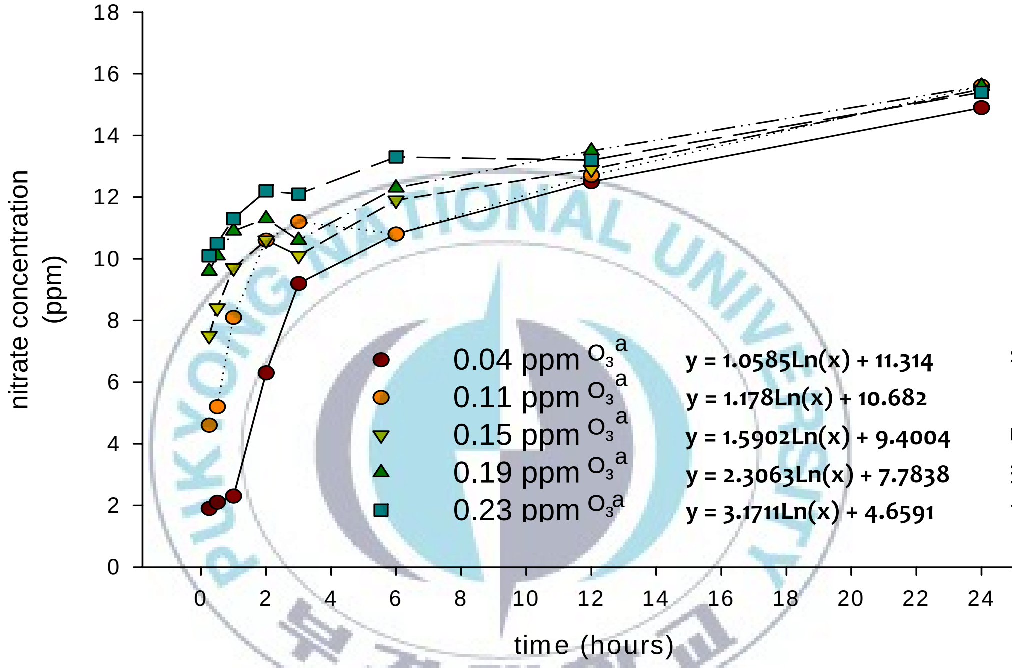

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Figure 4. Changes of nitrate concentration while the ozonation of ammonia.

Nitrate formation process was different in each ozone concentration treatment, even so, the nitrate formation rate was resulted with no significantly different ($p>0.05$) after 12 hours of ozonation of ammonia. Nitrate concentration was formed quickly in the first 3 hours and get decrement there after. The nitrate concentrations resulted in the ozonation of 5 ppm of ammonia were showing in the following table;

Table 2. Nitrate formations while the ozonation of ammonia

Time	**Ozone Concentration (ppm)**				
(hours)	**0.04**	**0.11**	**0.15**	**0.19**	**0.23**
0.25	1.9	4.6	7.5	9.6	10.1
0.5	2.1	5.2	8.4	10.1	10.5
1	2.3	8.1	9.7	10.9	11.3
2	6.3	10.6	10.6	11.3	12.2
3	9.2	11.2	10.1	10.6	12.1
6	10.8	10.8	11.9	12.3	13.3
12	12.5	12.7	12.9	13.5	13.2
24	14.9	15.6	15.5	15.6	15.4

3.1.3. Bromate Formation

The last parameter was measured in the ammonia treatment is the bromate fluctuation. The bromate fluctuation was measured along with the ozonation of ammonia in the water. The result was showing that bromate concentrations are suppressed in the levels of 0.33 ppm before 6 hours, and increased up to 8.3 ppm from the 6 hours until 12 hours, than bromate concentrations were dramatically increase after 12 hours from the starting treatment. After 24 hours of ozonation, bromate concentration were reach the number of 50.7 ppm with the formation rate is $y = 2.9031x - 20.872$.

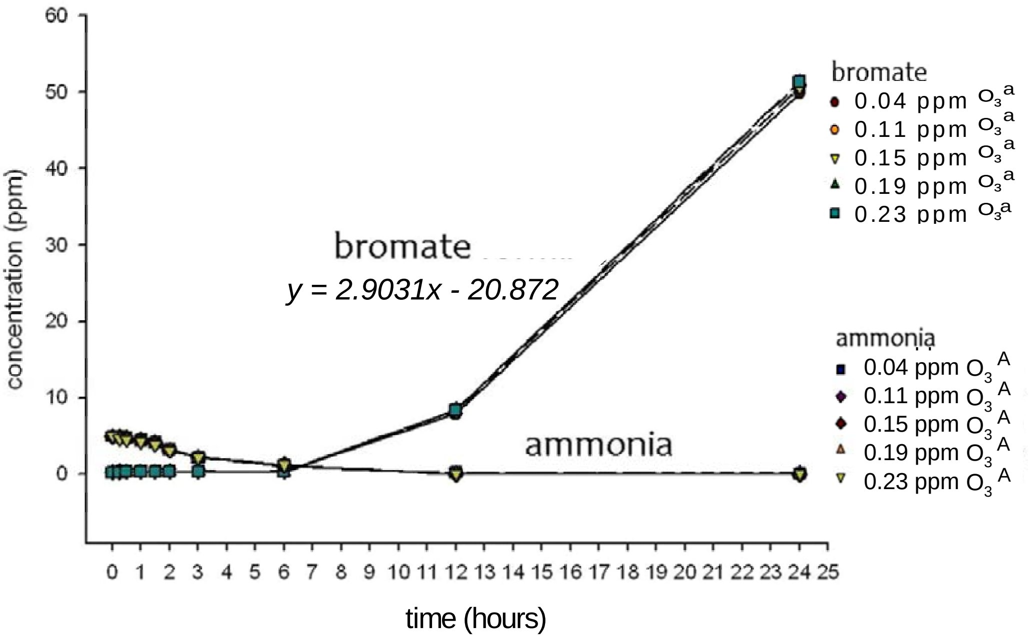

Figure 5. Bromate forming in the ammonia-contain water

3.1.4. Effect of common aeration on the ammonia oxidation

Effects of common aeration on oxidation of ammonia were tested for 24 hours. Five ppm of initial ammonia concentration was not changed in the treatment groups of 1, 2, 3, and 4 L/min air. However, 5 L/min air treatment group showed significant oxidation effects on ammonia. The concentration dropped 1 ppm immediately after the aeration and remained for 24 hours.

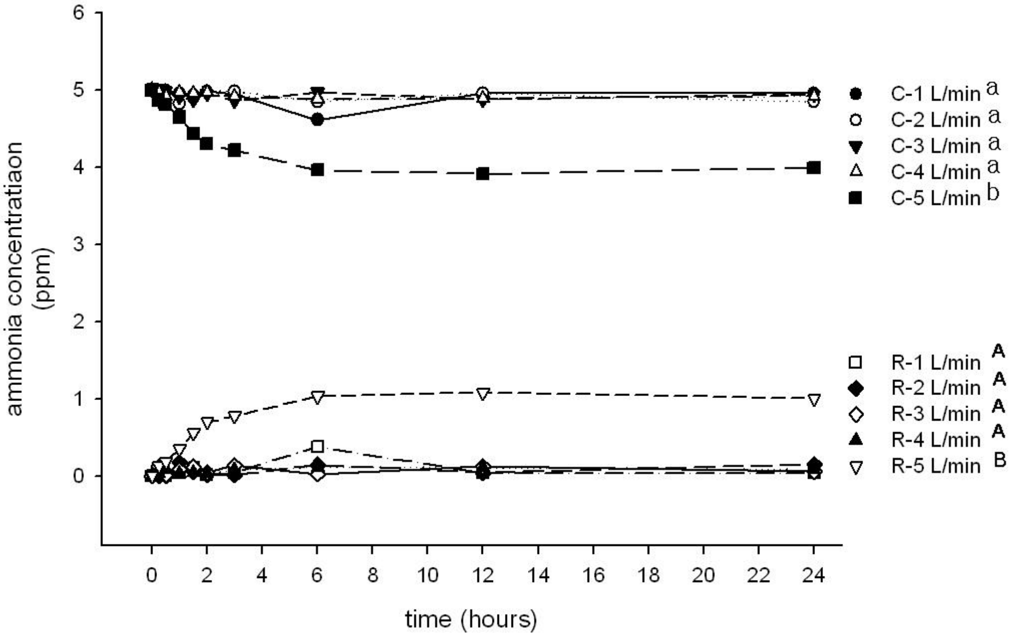

Figure 6. Relationship of ammonia concentration with the common aeration

3.2. Nitrite (NO_2^-) Oxidation

Ozone could also react with nitrite and oxidizes it into nitrates and some other excess gas from the water. In this experiment, initial of nitrite concentration was completely oxidized by ozone into the nitrite concentration in the water almost zero.

Nitrite with the loading rate of 5 ppm in 7 L of seawater was oxidized completely by 90 minutes in all ozone concentration with the nitrite removal rate was 4.45 ± 0.21 mg/L per hour in average (*y= 1.3022Ln(x)-0.993*), were the "*y*" is the removal amount in relation with "*x*" is the time exposure of ozone.

At the first 30 minutes, nitrite concentration had been decreased ±80% from the initial concentration of 5 ppm up to 1ppm, than continuous to decrease until almost zero at 90 minutes.

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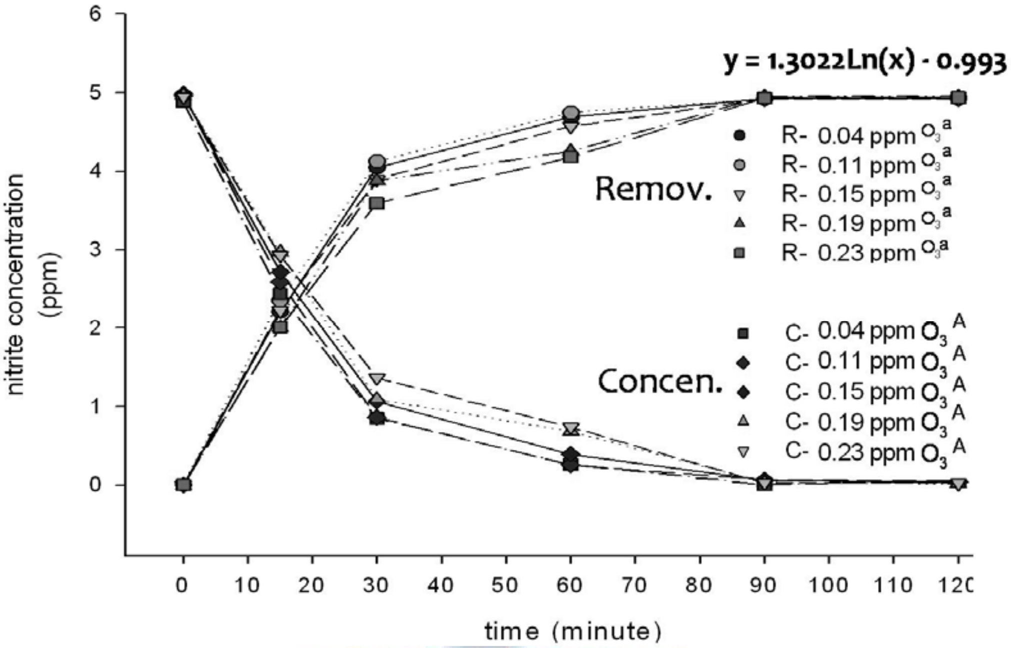

Figure 7. Relationship of nitrite removal and nitrite concentration in the seawater while ozonated by 5 different of ozone loading rate.

Each ozone concentration treatment were giving the significant different ($p \leq 0.05$) of oxidizing ability to the nitrite. Event so, the differentiation was only about the acceleration time to oxidize nitrite, because after 90 minutes nitrite concentration was oxidized entirely in every ozone concentration treatment..

After the 90 minutes and further ozonation, it was not giving significant different ($p > 0.05$) on the nitrite removal. It is not meaning that ozone oxidation able to be stopped, but because of the artificial nitrite source in the water was used up, or the nitrite in the water was oxidized completely by ozone.

In the ozone loading rate of 1 L/min, nitrite was oxidized by removal rate of $y=1.7312Ln(x)+2.5006$. Ozone loading rate of 2 L/min also bring the removal rate of $y=1.6377Ln(x)+2.6492$, while the loading rate of 3 L/min was oxidizing nitrite in the number of $y=1.7324Ln(x)+2.4463$. The last two of highest loading

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rate (4 and 5 L/min) were bring the removal rate of *y=1.861Ln(x)+2.2254* and *y=1.8884Ln(x)+2.1199* respectively.

3.3. Nitrate (NO_3^-) Oxidation

The experiment was showing that nitrate concentrations get the decrement in about 20% from the initial concentration of 5 ppm to the final concentration of 3.95 ppm by 12 hours and remaining there after. Differentiations in the ozone treatment were not affecting the oxidation of nitrate concentration. Nitrate removal rate is 0.36 ppm/h in average ($y = -0.0851Ln(x) + 4.1748$)

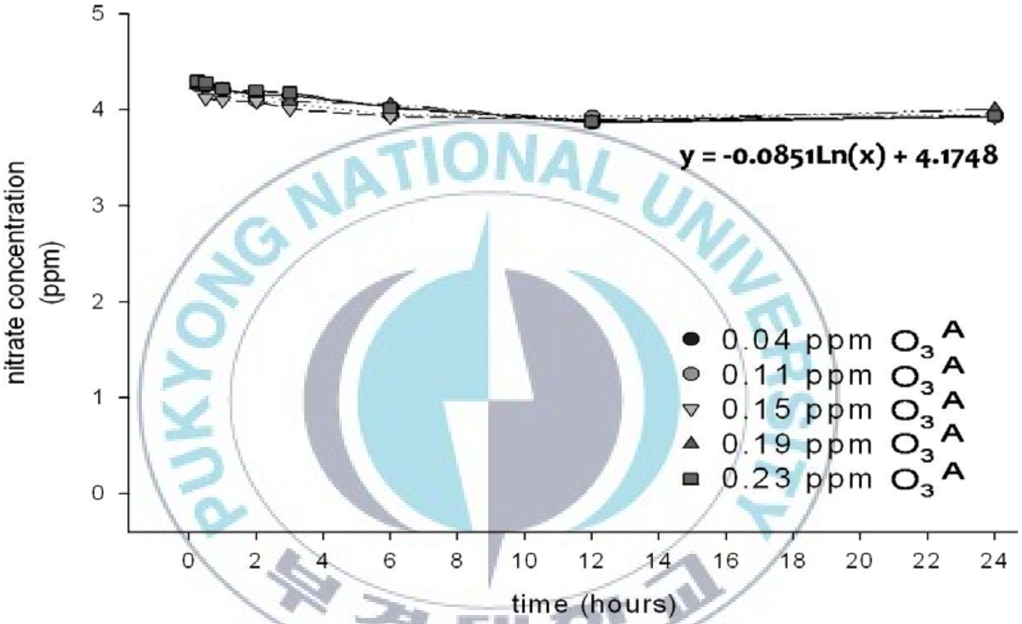

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Figure 8. Nitrate oxidation rate by ozone

The decrement of nitrate concentration by ozone was small in relatively, so that here the experiment was followed by monitoring the fluctuation of nitrate concentration in the common aeration. The result was showing that the nitrate concentration looked so stabile while aerated with common aeration in 24 hours.

Nitrate concentrations with the initial of 5 ppm were remaining at 4.95±0.03 ppm while ozonated as long as 24 hours. By the result of this experiment, it has proven that the 20% of nitrate decrement was caused by ozone.

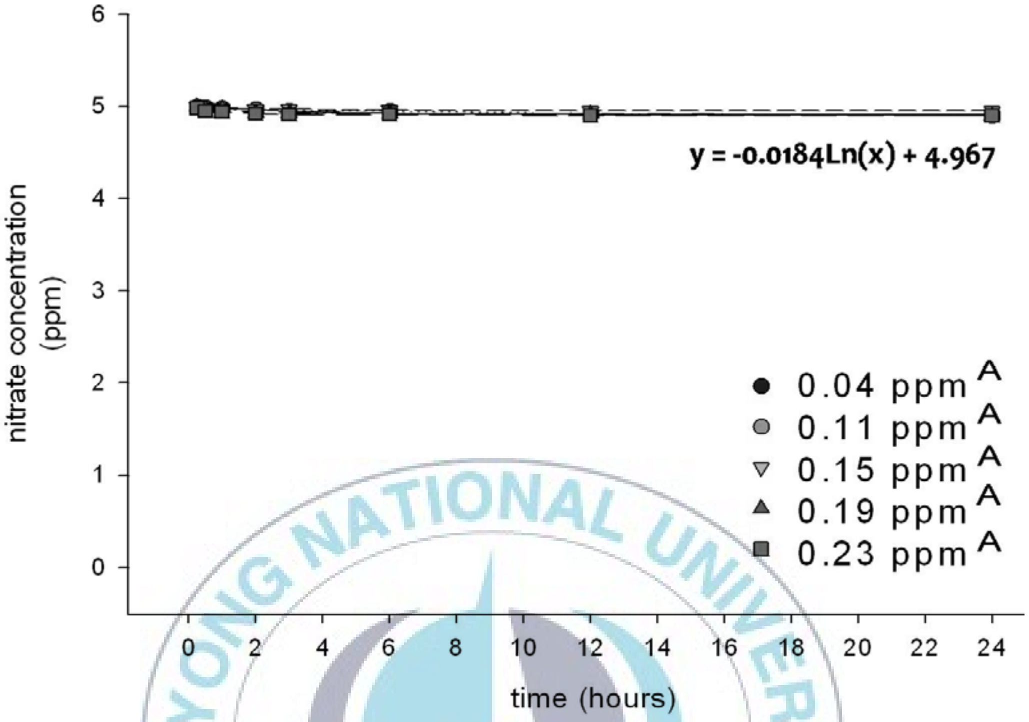

Figure 9. Nitrate oxidation level by common aeration.

3.4. TOC Oxidation

The result of this experiment was shown that the TOC concentration has consistently dropped during the ozonation process and getting constant in the concentration about 2.98 ± 0.77 ppm in all ozone treatment after 12 hours. The TOC oxidation rate by ozone treatment was differentiated into tree group, which are the lowest ozone concentration treatment, the second ozone concentration treatment and the highest ones. The lowest ozone loading rate was giving removal rate in the smallest number with the removal rate of 1.65 ppm/hours ($y=-2.3542Ln(x)+12.525$). The ozone loading rate of 2 L/min was also giving

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carbon removing rate significantly ($p \leq 0.05$) higher with the removal rate 2.22 ppm/hour ($y=-2.621Ln(x)+10.805$). Different with the two other, here in this tree of highest ozone loading rate (3, 4 and 5 L/min), the carbon removal rate was no different significantly ($p>0.05$) among the three, while the carbon removal rate was 2.25 ppm/hour ($y=-2.468Ln(x)+10.147$).

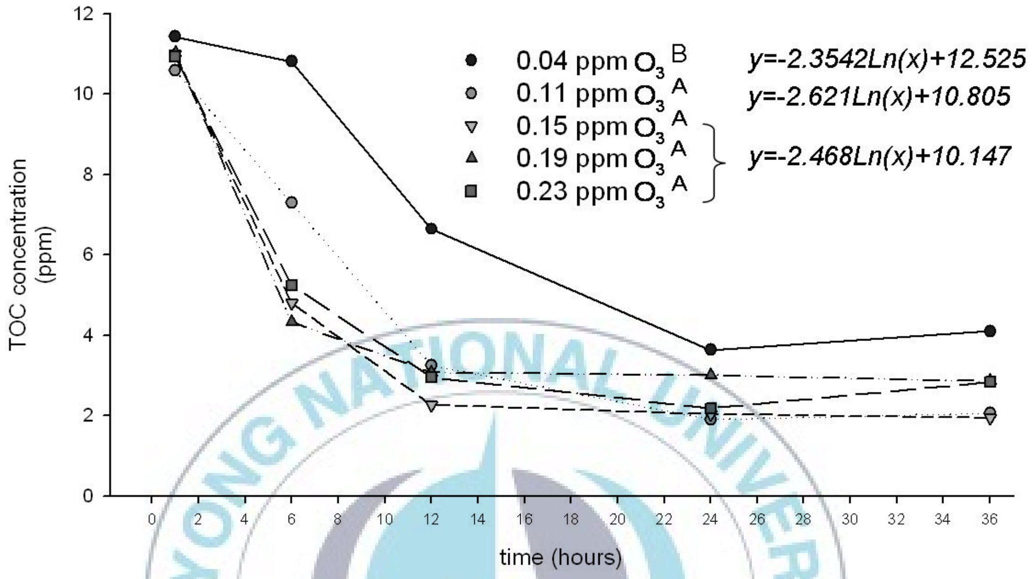

Figure 10. Concentration of TOC in the water in relation with the ozonation process.

Further analysis was done by statistical process using univariate-ANOVA, and the result was showing that the TOC concentration was not significant different ($p>0.05$) for each ozone treatment except for treatment of 1 L/min of ozone after 12 hour and there after. Based on the concentration of ozone treatment, the treatment of 0.04 ppm of ozone were significantly lower to remove TOC in the water, while the other ozone concentration treatment were no significant different ($p>0.05$) each other.

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Analysis based on the time, there were no significant different of the TOC concentration after 12 hours in each ozone concentration treatment. Its mean that the TOC were reach the equilibrium concentration and it is maintained at concentration below of 3 ppm for all treatment.

3.5. Ozonation by-product

3.5.1. Bromate (BrO_3^-)

The ozonation of seawater was spurring to the bromate formation. There is no significant different (p>0.05) from each concentration of ozone to the bromate forming acceleration, even though higher ozone concentration could produce the higher bromate concentration. In the 24 hours of an experiment, ozonation was produce bromate in the number of 79.28 ± 2.46 mg/L in average.

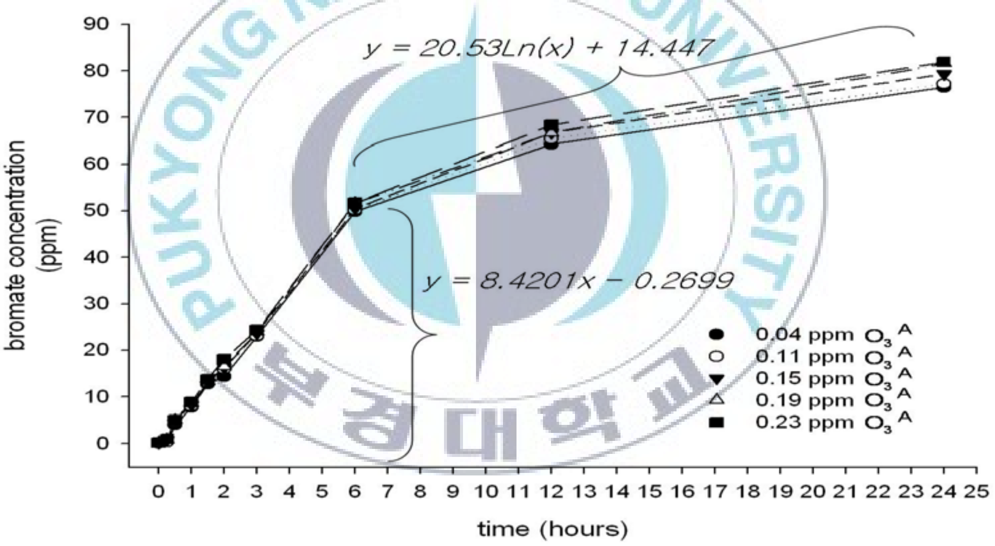

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Figure 11. Bromates formation as long as 24 hours of ozonation process.

Bromate formation was increase sharply in the first 6 hours, it was 7.29 ± 2.4 mg/L per hour ($y = 8.4201x - 0.2699$). While the second step (after the 6 hours) the increment was slower, it was having the increment of 2.48 ± 0.15 mg/L per hour ($y = 20.53Ln(x) + 14.447$).

3.5.2. Dissolved Oxygen (O_2)

Every level of ozone concentration are giving increment for the DO level, the further analysis was showing that each concentration bring the different increment except the last two highest loading rates (Duncan Post Hoc). The fluctuations of DO level in the ozonation treatment were shown in figure 12.

When the 7 L of seawater was enriched by 1 L/minute of ozone loading rate (0.04 ppm), the DO level in the water was increased much from 6.0 ± 0.06-ppm to be 9.2 ± 0.26 ppm in the average with the increment rate is $y = 0.7306Ln(x) + 6.2755$. In case of 2 L/mint ozonation treatment, there was also showing the significant increment ($p \leq 0.05$) of DO level. The initial DO was 6.1 ± 0.11 ppm and then increased into 9.4 ± 0.09 ppm in average of super saturation level with the increment rate is $y = 1.1991Ln(x) + 4.4361$.

The next treatment is ozone with the loading rate of 3 L/min. Here also in this treatment was giving DO increment, by the initial DO of 5.9 ± 0.14 ppm it was increased into 9.4 ± 0.07 ppm in the average of super saturation level with the increment rate is $y = 0.5648Ln(x) + 7.0326$.

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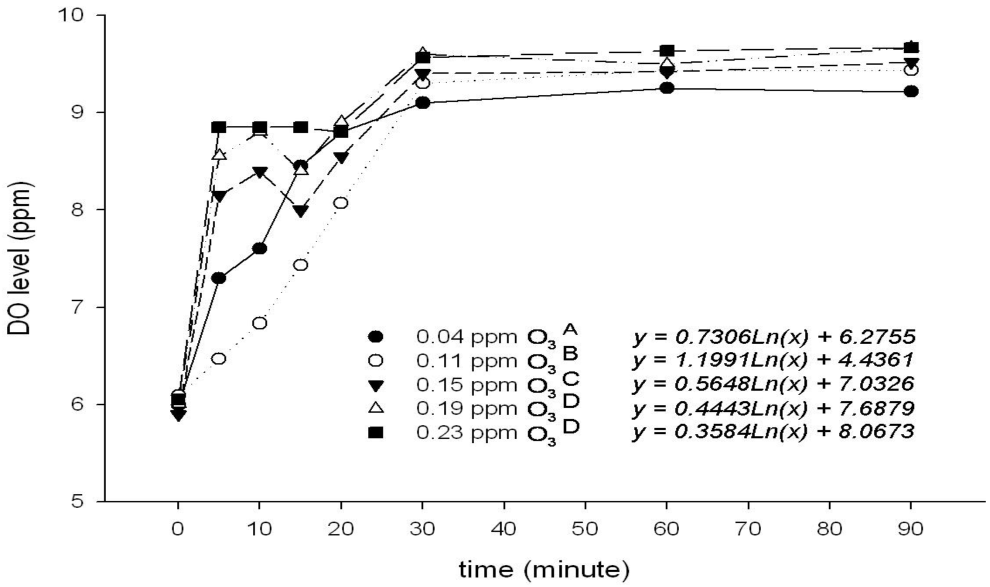

Figure. 12. Increment of DO level as long as ozonation process.

For the ozone loading rate of 4 L/min the initial DO was 6.0 ± 0.29 ppm and increased up to 9.6 ± 0.14 ppm with the increment rate is $y = 0.4443Ln(x) + 7.6879$. While in the ozone loading rate of 5 L/mint the initial DO was 6.1 ± 0.41 ppm and then increased into 9.6 ± 0.07 ppm in the super saturation concentration with the increment rate is $y = 0.3584Ln(x) + 8.0673$.

To monitor the effect of ozone to the DO, here in this experiment was also followed by measurement of DO level while aerated with the common aeration. The result was showing that the DO saturation level only about 7.18 ± 0.08 ppm in the average. The statistical analysis of DO level with ozonation compare by the DO level without ozonation (only common aeration) was different significantly ($p \leq 0.05$) in the equilibrium state. The fluctuation of DO level while aerated by common aeration was figured out in the following table.

Table 3. Effect of 5 different levels of common aeration on dissolved oxygen levels of 7L seawater in 10L size acrylic cylinder.

Time	Aeration Loading Rate (L/min)				
(minute)	1	2	3	4	5
0	6.1 ± 0.06	5.9 ± 0.11	6.0 ± 0.14	5.9 ± 0.29	6.0 ± 0.41
5	6.4 ± 0.00	6.4 ± 0.06	6.4 ± 0.05	6.5 ± 0.45	6.5 ± 0.05
10	6.6 ± 0.90	6.4 ± 0.06	6.5 ± 0.00	6.7 ± 0.40	6.5 ± 0.05
15	7.0 ± 0.35	6.8 ± 0.06	6.9 ± 0.00	7.0 ± 0.50	6.8 ± 0.05
20	7.1 ± 0.20	6.9 ± 0.06	7.0 ± 0.05	7.1 ± 0.10	6.9 ± 0.00
30	7.1 ± 0.30	7.1 ±0.10	7.2 ± 0.00	7.2 ± 0.20	7.3 ± 0.06
60	7.1 ± 0.25	7.2 ± 0.06	7.0 ± 0.08	7.3 ± 0.10	7.4 ± 0.06
90	7.2 ± 0.30	7.1 ± 0.06	7.1 ± 0.03	7.2 ± 0.06	7.3 ± 0.06

On the treatment of common aeration, DO levels were getting to the saturation levels after 30 minute of aeration. Differentiations of aeration loading rate were not resulting in the different concentration of oxygen saturation levels ($p>0.05$).

3.5. 3. pH

The pH level in all concentrations was increased to get to the point around 8.5 – 8.7 and then starting to be stabile there after. By statistical the ozone treatment was significantly ($p \leq 0.05$) affecting the pH level in the water.

It was also showing that each concentration giving the significant different in the final pH level, except for 4L/min and 5L/min of ozone treatment (Duncan Post Hoc). Analysis by the time, it was shown that after 20 minutes of ozonation

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the pH level got into the stability, because further ozonation was not giving any significant different ($p>0.05$) on pH level.

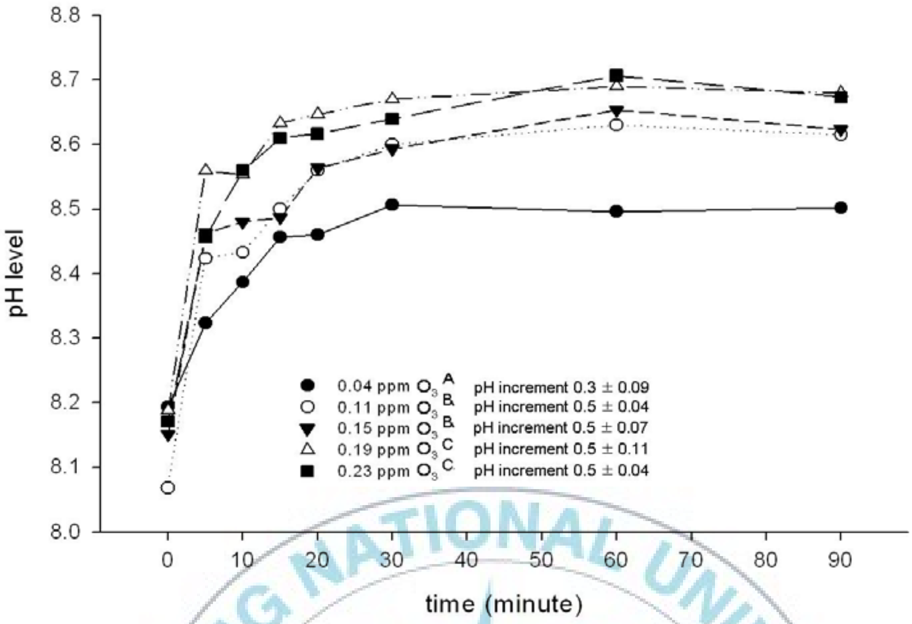

Figure 13. The changes of pH level while ozonation process.

In the first ozone concentration treatment (1 L/min of ozone), the pH level was increased in the number of 0.3 ± 0.09 by the initial pH of 8.2 ± 0.05 to be final pH of 8.5 ± 0.16. While in the second treatment (2 L/min of ozone) pH level was increased from 8.1 ± 0.07 to the final pH level of 8.6 ± 0.12. The next ozone concentration (3 L/min of ozone) was also giving an increment as much as 0.5 ± 0.07, from the initial pH of 8.1 ± 0.05 to the final pH level of 8.6 ± 0.16. The other last two ozone concentrations (4 L/min and 5L/min of ozone) were also increasing pH level with the ozone loading rate are 8.2 ± 0.05 increase to 8.7 ± 0.16 and 8.2 ± 0.04 increase to 8.7 ± 0.08 respectively.

In order to have control and to check the fluctuation of pH level, whether causing by the ozone or because the water splashing by aeration only, the experiment was also completed with the measurement of pH fluctuation on the

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treatment of common aeration. The result was shown that the pH levels are almost constant in every loading rate. The condition of pH level in the treatment of aeration by common air was shown in the table following.

Tabel 4. The average of pH level in the treatment of aeration by common air.

time (minute)	1 L/mnt	2 L/mnt	3 L/mnt	4 L/mnt	5 L/mnt
0	8.1 ± 0.00	8.1 ± 0.02	8.2 ± 0.02	8.1 ± 0.00	8.2 ± 0.00
5	8.2 ± 0.01	8.2 ± 0.01	8.1 ± 0.03	8.2 ± 0.01	8.2 ± 0.01
10	8.1 ± 0.01	8.1 ± 0.02	8.1 ± 0.04	8.1 ± 0.05	8.1 ± 0.03
15	8.1 ± 0.01	8.1 ± 0.00	8.2 ± 0.02	8.1 ± 0.07	8.1 ± 0.00
20	8.1 ± 0.00	8.1 ± 0.01	8.2 ± 0.01	8.1 ± 0.05	8.1 ± 0.02
30	8.2 ± 0.01	8.2 ± 0.01	8.1 ± 0.01	8.2 ± 0.11	8.2 ± 0.06
60	8.1 ± 0.03	8.2 ± 0.00	8.1 ± 0.07	8.2 ± 0.04	8.2 ± 0.01
90	8.2 ± 0.15	8.2 ± 0.02	8.1 ± 0.01	8.1 ± 0.00	8.2 ± 0.00

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IV. DISCUSSION

4.1. Ozone equilibrium concentration

Ozone is generally dissolved in the water to disinfect bacteria, virus and other microorganisms, the other hand is to be oxidizing agent while removing solids of dissolved minerals, and to neutralize undesirable chemicals. (Forneris et al., 2003) Ozone is generated in the air and is forced into the water by some instrument, which would make the ozone concentration in the water very vary. The differentiation of those concentrations were caused by many factors, such as ozone loading rate, ozone solubility, partial pressure of ozone, oxygen saturation level and some other parameters (Townshend, 1979). Moreover it has been recognized that the occurrence of rapid chemical reactions may enhance the mass transfer from gas phase into liquid phase (Danckwerts, 1970). To better understanding of ozone mass transfer mechanisms, and to provide the theoretical basis for the development of efficient ozone contactors, it is necessary to measure individual mass transfer parameters and elucidate their effects on ozone absorption. The applicability of these empirical correlations was experimentally supported by Zhou and Smith (2000); Le-Sauze et al. (1993); Roustan et al. (1987); Rakness et al. (1988) and Zhou et al. (1994). The overall, amount of ozone mass that could transferred to the different phase will be affected by different operating conditions, water quality and facility setup.

Even though the ozone concentration is difficult to maintain, estimation can be done to determine how much the ozone could dissolved into the water. Determination of ozone concentration in the water could be calculated by the ozone solubility which is very interfered by temperature. Ozone solubility was reported by Orcutt and Seevers (1936) that it could be calculated using "Bunsen absorption coefficient"

$$Cs = \beta * M * P \tag{11}$$

Cs = Concentration dissolved gas (kg/m^3)
M = Density of the gas
β = Bunsen adsorption coefficient
P = Partial pressure

By the formula above, it could recognize that the solubility will be increased in line with the partial pressure of the subjected gas in the water. Partial pressure is the pressure which the gas would have if it alone occupied the volume, and partial pressure was given by neither gas loading nor the pressure of the gas itself. Based on the previous consideration, the treatment in this experiment was set out to use the various ozone loading rate to get the differentiation on the ozone equilibrium concentration. By using the different ozone loading rate it was assumed that ozone amount and the partial pressure of ozone in the water will be different, and finally it could make the gradation of ozone equilibrium concentration in the water.

In the other hand, especially for estimating/measuring the dissolve ozone, the following formula was also applicable (Van Slyke and Sendroy, 1924);

$$H = pO_3/S \times Cg \quad \rightarrow \quad (S = 1/Hc)$$

$$H = pO_3/(1/Hc) \times Cg \tag{12}$$

$$Cg = pO_3/H \times (1/Hc) \tag{13}$$

$$Cg = (pO_3 \times Hc)/H \tag{14}$$

Where,

H = Henry (atm/L/mol)
S = solubility factor (-)
pO_3 = partitial pressure ozone (Pa)
Hc = Henry's constant (-)
Cg = concentration ozone gas to dissolve to the water (kg/m^3)

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Ozone is unstable material so it is needed to applying the known measurement of constant loss of absorbance of indigo reagent to calibrate the measurement. The known measurement is “Swiss Standard Method for the Determination of Ozone (Indigo Method)”. The principle of this measurement is Ozone rapidly and stoichiometrically (1:1) decolorizes indigo trisulfonate in acidic solution. The decrease in absorbance is linear with increasing concentration over a wide range. The proportionality constant at 600 nm is $0.42 \underline{+} 0.1\ cm^{-1}$ per mg/L ($A\varepsilon = 20{,}000\ L\ Mol^{-1}.cm^{-1}$). It is therefore recommended that the measurements be based on the known and constant loss of absorbance of the Indigo Reagent, namely a factor $f = 0.42 \pm 0.01$/cm per 1 mg/L ozone dosed. (Bader and Hoigné, 1981)

$$mg\ O_3/L = \frac{100\ x\ \Delta A}{f\ x\ b\ x\ V} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

Where:

ΔA = different in absorbance between sample and blank

b = path length of cell, cm.

f = 0.42

V = volume of sample

The factor *f is* based on a sensitivity factor of 20.000/cm for the change of absorbance (600 nm) per mol of added ozone per liter. It was calibrated by iodometric titration method. The factor f = 0.42 corresponds to an absorption coefficient for aqueous ozone, € = 2950/M.cm at 258 nm. (Bader and Hoigné, 1981)

By the formula given above, it will possible to calculate the ability of water to be capable to hold the ozone amount in the water column. Even so, in the reality of reaction between ozone and water it was not always consistent in the

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role. In this experiment, five level of ozone loading rate was used and the given fluctuation of ozone concentration was monitored. The result of this experiment was shown that the ozone equilibrium concentration was not really exact by what the design made. The experiments were set up to maintain the ozone concentrations in the number of 0.05, 0.1, 0.15, 0.2 and 0.25 ppm in the seawater. Even so the real equilibrium concentrations were maintained were 0.04, 0.11, 0.15, 0.19 and 0.23 ppm of ozone in the water. The present bias was causing by the differentiation of ozone solubility. The degree of solubility of ozone gas is dependant on the concentration in gas and thus dependant on the partial pressure. Another important factor influencing the solubility is the temperature. Besides temperature, pH and ion concentration in the solution are also the main factors which could influencing the solubility of ozone. The discussion above could be summarized if the solubility will be increased if:

- Ozone concentration in the air has increase (oxygen);
- Aeration pressure has increase (oxygen);
- The water temperature are decrease;
- The amount of solutes are decrease;
- pH are decrease;
- Excess of UV-light.

While the experiment of ozonation and observing the equilibrium concentration of ozone in the camber, the experiment was also monitoring the fluctuation of dissolved oxygen (DO) and pH level in the water as long as ozonation process. The Result of the experiment was shown that the DO has much increased by the ozonation process.

4.2. Ammonia Oxidation

The ozonation of ammonia was proven to forming nitrite and nitrate, also affecting the bromate forming. This was explained in the reaction no. 8 and 9 in the chapter 1. It was indicated that nitrite has possibly formed by the direct reaction of ammonia with ozone (reaction no. 8 chapter 1). And the other way, nitrite will also continue to oxidize into nitrate by the reaction no. 9 chapter 1. It is been known that ammonia can be also oxidized directly into nitrate via reaction no. 10 chapter 1. In the other case, ammonia was also able to react with bromide by ozone to produce bromamide (NH_2Br), bromimide ($NHBr_2$), and tribromide (NBr_3) by the following formula, (Tanaka and Matsumura, 2002).

$$HOBr + NH3 \rightarrow NH2Br + H2O \text{.....................................} (16)$$

$$HOBr + NH2Br \rightarrow NHBr2 + H2O \text{.................................} (17)$$

$$HOBr + NHBr2 \rightarrow NBr3 + H2O \text{...................................} (18)$$

On the result of this experiment, it was showing that there are two kind of difference ozone ability in order to oxidize ammonia. The two differentiations are lower concentration (0.04, 0.11 and 0.15 ppm of ozone), which could remove ammoniac by the number of 0.554 ± 0.25 mg NH_4-N/L/hour and the other was the higher concentration (0.19 and 0.23 ppm of ozone) which could remove ammonia in the number of 0.747 ± 0.30 mg NH_4-N/L/hour. Those two kinds of ozone oxidation ability was considered as the differentiation which has been given not from the gradation level of ozone concentration, but rather than causing by foam fractionation. In the same and identical culture system, the gradation level of ozone concentration was reported to not giving any significant effect on the oxidizing ability to ammonia (Yang, et al., 1999) (Tanaka and Matsumura, 2002). In case of foam fractionation effect, here the experiment was also followed by measuring the fluctuation of ammonia concentration in the identical system but the ozone fed was substitute by common aeration. The result was also showing that the lower concentration of a gas feed system cannot give the significant oxidation ability to the ammonia concentration. In the other hand, system which was feed by the higher of common gas could decrease the ammonia concentration by the relatively small number which is 1 ppm during an experiment conducted. The foam fractionation was reported to be able to remove ammonia from the water (Tanaka and Matsumura, 2002). Based on this result so that it could be concluded that the differentiation of oxidizing ability of the ozone was causing by the foam fractionation from the higher ozone feed system.

Ammonia will oxidize into nitrite and then continues to be nitrate, so that in this experiment, monitoring the nitrite and nitrate concentration fluctuation during the ozonation process was also done. The measurement of nitrite fluctuation showing that nitrite concentration could be maintained below 2 ppm as long as ozonation process. Actually it was the dynamic concentration, not the real state of concentration; because that concentration was build up from the oxidized ammonia before continue to oxidize into nitrate. It was also known that after 12 hours nitrite concentration has recorded nearly by zero. That was because the nitrite source is stopped, the nitrite source here is the ammonia which oxidized by ozone. After the 12 hours of ozonation ammonia was oxidized completely, so that the nitrite source was stopped, even not longer from that the nitrite concentration also used up and converted into nitrate.

Oxidation process from ammonia will accumulated into nitrate, so that here in this experiment the state of nitrate concentration was also monitored. The result was showing that nitrate concentration has increasing rapidly into the first 12 hours, after the 12 hours nitrate increment was much slower than previous. The deceleration was happen because the ammonia as the main source is almost used up by reaction and oxidized well. By the function of reaction no.8, 9 and 10 in the chapter 1, we can do comparison from each mass molecule to determine the possible nitrate which would be formed by the initial ammonia of 5 ppm. So that by the ratio of mass molecule, the 5 ppm (mg/L) of initial ammonia ideally by the reaction no. 8 it should be able to oxidized into 12,78 mg/L of nitrite. Than by the mentioned amount of nitrite it would be able to oxidize into 17, 23 mg/L of nitrate in the seawater based on the reaction no. 9. In the other way, ammonia also could be converted directly into nitrate by reaction no. 10. According to that reaction, the 5 ppm (mg/L) of initial ammonia ideally could be converted into 17, 23 mg/L also. So that by mathematically 5 mg/L of ammonia could be oxidized into 17, 23 mg/L of nitrate. This was proven by the result of monitoring nitrate concentration in the ozonation of seawater enriched by artificial ammonia source. There was shown that by 24 hours of ozonation, concentration of nitrate was recorded in the level of 15.4 ± 0.29 mg/L.

4.3. Nitrite Oxidation

An initial nitrite concentration of less than 10mg/L is about the maximum nitrite concentration level that could be found in an untreated, high density fish hatchery (Liao and Mayo, 1972; Otte and Rosenthal, 1979; Poxton and Allhouse, 1982; Kruner and Rosenthal, 1983; Bovendeur et al., 1987). This experiment was showing that by 5 ppm (mg/L) of initial nitrite it has completely removed from the water in about 90 minutes. The acceleration of nitrite removal was very high in the first 30 minutes; this was also relatively same in comparison with the result that reported by Lin and Wu (1995), they were reporting that nitrite removal using electrochemical could remove the initial total nitrite of 5 mg/L by more than 30 min.

In the real application of ozone in seawater, the existence of ammonia will oxidized to be nitrite, and it was only temporary phase because nitrite itself will also oxidized by ozone into nitrate. Because nitrite is the temporary phase of reaction, so that the state of nitrite concentration could oxidize in the sort time relatively. Other than that, the quick oxidation reaction of nitrite also caused by the double reaction that could happen by involving nitrite ion, that are the direct reaction of nitrite with ozone (Haag et al., 1984), and the other is the reaction between nitrite with bromide acid which was resulted from the reaction of bromide and ozone (Yang et al., 1999). Based on the previous study, so that the nitrification bacteria which has decompose ammonia and nitrite from the water will no longer to be the limitation factor for aquaculture to remove it from the water.

4.4. Nitrate Oxidation

Nitrate is the ion that we can say as the residual or final result of nitrogen removal from the water by ozone. So that the higher ammonia and nitrite content in the water will resulting the higher nitrate accumulation in the end of reaction. Because In the ozonation process nitrate forming could be happen by some reaction such as from oxidation of ammonia and the other is from oxidation of nitrite. Nitrate is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identical oxygen atoms in a trigonal planar arrangement (Black, 1985). Nitrate have already tree atom of oxygen ion, so that it could not be oxidized by ozone which also have the same electron valence. The reaction process was described as mentioned before (reaction no. 8 and 9 chapters 1). It was also possible that ammonia directly oxidized into nitrate via reaction no. 10 chapter 1 (Haag et al., 1984).

Unlike in the biological process of denitrification which nitrobacteria could decompose the NO_3^- –N in the water into N_2 ion and than could easily spelled out from the water to the air. In the ozonation the NO_3^-–N formed in this process remains in the treated water and could accumulated easily. So, restraining NO_3^- –N formation becomes the key point of this process from while removing ammonia from the water by ozonation (Yang et al., 1999).

Here in this experiment, nitrate was increasing much by the existence of ammonia and nitrite. After the nitrogen ion source is unavailable so the nitrate forming are stopped. Even so in the experiment of ozonation of artificial nitrate, the result was shown that nitrate concentration could reduce in the number of 20% by the initial concentration. It was considering caused whether by direct or indirect reaction of ozone.

4.5. TOC Oxidation

Here in this experiment ozone was oxidizing TOC source and maintaining it in the concentration of 2.98 ± 0.77 ppm. The experiment was using glucose ($C_6H_{12}O_6$) as the organic carbon source. Glucose which was used is derived from the "right-handed form" of glucose, denoted D-glucose. D-glucose is often referred to as dextrose, especially in the food industry. Ozonation improved particle removal for doses of less than about 0.7 mg ozone per mg TOC (Rosenthal, 1980). They further reported that ozone doses of approximately 7~10 mg/L (approximately 0.1~0.2 mg ozone per mg TOC, this author's calculation) in a RAS could increased the BOD_5 of the water.

Dextrose-glucose was used as the initial TOC and by the mass molecule ratio, certain amount of glucose could calculate to support TOC in certain concentration in the water.

$$C_6H_{12}O_6 \rightarrow 6C^{2+} + 6H_2O + 3O_2 \quad \dots\dots\dots\dots\dots\dots (19)$$

Based on the reaction above, it was showing that mass molecule of dextrose ion comparison with carbon ion are having proportion of $C_6H_{12}O_6 : C = 180 : 72$. According to this ratio, so that TOC initial concentration was adjusted in the number of 15 mg/L of carbon ion. The initial TOC was selected because the mentioned number was reported as the average TOC concentration remained in the intensive aquaculture system (Krumins et al., 2000) (Tango et al., 2003).

During the experiment, TOC concentration was suppressed from the initial concentration of 15 mg/L up to below 3 mg/L and maintained in the mentioned concentration, while each treatment are not giving any significant effect ($p>0.05$)

except for the lowest ozone concentration. This result was also confirmed by the experiment reported by Summerfelt et al (1997). They found that ozonation reduced TOC levels by approximately 17%, although the reductions for two different ozone dosage rates were 'similar.' This report presents the progress of an experiment to quantify the decrement in organic carbon as a function of the ozone dose.

In the other hand, the ozone treatment with the lowest concentration (0.04 ppm of ozone) was removing TOC in significantly ($p \leq 0.05$) lower than the other treatment. This subject had considered was caused from the ozone treatment which is to low to oxidizing more of organic carbon. Ozonation appears to affect colloidal stability by transforming NOM and altering its interactions with the colloidal particles, dissolved metal ions, or coagulant. This statement was also confirmed with the experiment reported by Rosenthal (1981), he was explained that ozone at certain dose was not sufficient to oxidize the organic compounds completely, but did break up large organic molecules into smaller, more easily biodegradable ones.

4.6. Ozonation by-product

4.6.1. Bromate Formation

It is well known that ozonation of bromide-containing waters can oxidize the bromide ion (Br^-) to be bromate (BrO_3^-) ion within normal water quality treatment parameters (Gillogly et al., 2001; Symons, 1999; Singer, 1999; Glaze and Weinberg, 1999; Jacangelo, 1997; Faust and Aly, 1998). When the bromide ion in the water was oxidized by ozone it can result in the formation of organic or inorganic bromine by-product. The bromate ion (BrO_3^-) is the highest oxidation state of the bromide ion (Symons, 1999). Ozone oxidizes bromide to form hypobromite ion (OBr^-). Hypobromite continues to be oxidized to form bromate or to form an unidentified species, possibly BrO_2^-, which regenerates bromide ion

(Glaze and Weinberg, 1999). Brominated by-product formation in ozonated waters is influenced by bromide ion concentration, the source and concentration of natural organic matter (NOM), pH, ozone dose, and reaction time (Faust and Aly, 1998).

Ozone reacts with bromide ions, and to a lesser extends with chloride ions, to form oxidants toxic to fish and shellfish. The most important are hypobromous acid (HOBr) and hypobromite ion (OBr^-), both have strong biocidal effects. By prolonged ozonation hypobromite ion can be further oxidized to bromate (BrO_3^-), which is a persistent compound. During the experiment, BrO_3^--Br increased until the final concentration in the end of experiment is 79.28 ± 2.46 mg/L. The relatively high yield of BrO_3^--Br during bromide decomposition was perhaps due to the relatively high bromide contain in the water. Common seawater has reported to have bromide ion (Br^-) as much as 66 mg/L in average and by standard condition (Bowen, 1966). Based on that, so the result of this experiment was showing that bromate concentration almost reach the maximal concentration depend on the bromide supply. The estimation of conversion of bromide ion into bromate could be done by the following formula;

$$O_3 + Br \rightarrow O_2 + OBr^- \quad \text{...} (20)$$

Based on the above reaction we can calculate the ratio of mass molecule to determine the bromine. So that by 66 mg/L of bromide ion it could converted into 79.2 gr/L of hypobromite ion and further by the reaction of;

$$2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^- \quad \text{...} (21)$$

The hypobromite ion could convert to be bromate as much as 105.6 gr/L. The bromate concentration which was resulted here is very high relatively compared to the maximal possibility of bromate forming. While it is possible to

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remove BrO_3^--Br by an activated carbon column, the strength of activated carbon would possibly be weakened due to the considerably high BrO_3^--Br concentration. The simplest method to decompose the oxidizing bromines is to use a reducing agent like Na_2SO_3 (Yang et al., 1999).

The concentration of bromines (HBrO and BrO^-), which are the intermediary compounds of the process, was represented of bromide in the water. Since the reaction of HBrO with NH_3 is extremely fast (Haaget al., 1984), the measured BrO^- Br was the summation of bromines and various bromo derivatives of ammonia when ammonia existed. Moreover, bromate will not be formed as long as ammonia is still present in the water system. The bromide will oxidized by ozone and react with ammoniac into dibromamine ($NHBr_2$) or hypobromous acid (HOBr) and the other bromine ion (Tanaka and Matsumura, 2002). Recent research has suggested that the formation of bromate may be highly coupled to the characterization and concentration of NOM (Hofmann, 2000). NOM is a parameter that encompasses all forms of organic carbon and can be quantified using a number of analytical techniques (e.g. total organic carbon (TOC), chemical oxygen demand). In addition, ammonia has been suggested to be a potential quenching agent that may act to minimize bromate formation in water (Hofmann and Andrews, 2000). The statement above was also proven by the result of this experiment. Here by the ammonia experiment, bromate concentration was also monitored. The result was also showing that bromide concentration increased much after the 12 hours, the same period that the ammonia was oxidized almost all.

4.6.2. DO increment

Ozone is the triplet of an oxygen molecule (O_3) which was very reactive with the other molecule because it was unstable unlike O_2 molecule. Based on the chemical bond, ozone will always turn converted into oxygen (O_2) before react with the other molecule, the existing of the heave atoms will be effecting about how much oxygen will produce. For a heavier atom, the effect will be more drastic. As increasing the heave molecule contains in the water the oxygen production will be fewer (Naumov and Von sonntag, 2008) (Munoz et al., 2001). By the above study, so that we can understand well if the water exposure by ozone, the ozone amount and the heave molecule inside of the water will be the promotes factor of DO increment (Liu et al., 2001).

Dissolved oxygen (DO) is the critical important parameter for the aquatic organism (Wheaton, 1977). While in the fish culture, instead of temperature and other water parameter, DO is the most important, based on it so the DO fluctuation is needed to be monitored. In the aquaculture, RAS specially, the ability to add up dissolved oxygen to the water is the first limiting factor in a fish carrying capacity. To maintain the adequate DO levels in culture tank, oxygen must be added to the tank at a rate what the system needed. The consumption rate of DO in a RAS is difficult to calculate so that the monitoring and maintaining DO as what the system needed should prepare well. The amount of oxygen required by the system is mostly depending on the length of time waste solids remain within the system and the bio-filter configuration.

In case of application of ozone to the RAS, DO parameter still could not predict by the basic experiment. Here by the result of this experiment we have to do a further experiment about applying ozone to the real RAS while checking the DO fluctuation, before we could apply the ozone to the RAS with the mass scale. This experiment was shown that ozone could increase DO level reach to the super saturation level, but it should be comparing with the DO require by RAS system before it could be applying to the RAS.

This experiment was showing that by the water temperature of 25 ^{0}C, ozonation was able to spurring DO into 9.4 ± 0.07 ppm. In the common seawater, DO saturation level is around 7.4 ppm (La Don Swann, http://aquanic.org), this was also shown by the followed experiment about dissolved oxygen in the common aeration. There were also recorded that common aeration could only promote the DO level into the saturation level at the number of 7.18 ± 0.08 mg/L from the initial DO of 6.0 ± 0.07 mg/L. This increment will be neither the advantages nor the disadvantages according to the system condition and also species culture.

4.6.3. pH changes

When the ozone is produced it will decay rapidly, because ozone is an unstable ion with a relatively short half-life. The half-life of ozone in the water is a lot shorter than in air. Ozone half life in the water with the temperature of 20 ^0C is 20 minutes while the ozone half life in the air is 3 days by the same temperature (Lenntech. Co. Ltd, 1998). Ozone will decays in the water partly in reactive of OH-radicals. Therefore, the assessment of an ozone process always involves the reactions of two species: ozone and OH-radicals. When these OH-radicals are in the dominant particles in the solution, it is called an advanced oxidation process (AOP). The decay of ozone in OH-radicals in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases by first order kinetics. When the formation of OH-radicals was increased the pH value will also increases (Ershov and Morozov, 2008) (Lenntech. Co. Ltd, 1998). In a solution with a high pH value, there are more hydroxide ions present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone (Ershov and Morozov, 2008):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad \ldots\ldots\ldots\ldots (22)$$

$$O_3 + HO_2- \rightarrow {}^{\bullet}OH + O_2^{\bullet-} + O_2 \quad \ldots\ldots\ldots\ldots (23)$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \quad \ldots\ldots\ldots\ldots (24)$$

$$O_3^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad \ldots\ldots\ldots\ldots (25)$$

The radicals that are produced during reaction above can introduce other reactions with ozone, causing more OH-radicals to be formed. In addition the pH influences acid/base equilibriums of some compounds and also the reaction speed of ozone.

The acceptable number of pH level for fish culture is usually ranged at 6.5 to 9.0 of pH level. When the water is very alkaline (> pH 9), ammonium in water is converted to toxic ammonia, which can kill fish. On the other hand, acidic water (< pH 5) could strip out the metals from rocks and sediments. These metals have an adverse effect on the fish metabolism rates and ability to take in water through their gills, and can be fatal as well (Howerton, 2001). Pond waters with pH of 3.6-5.4 have been reported to exert toxic effects on a range of fishes including mortality, reduced growth and poor reproduction. Waters with a pH of less than 6.0 have also been associated with poor productivity (Swingle, 1957). In relation with the pH level, the result of ozone experiments were shown that ozone treatment will not produce the harm pH condition for fish culture, even so this still depend on the system and fish cultured condition.

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V. CONCLUSION

Ozone equilibrium concentrations were maintained in the levels of 0.04, 0.11, 0.15, 0.19, and 0.23 ppm when amount of ozone were introduced into 7 litters of water with rate of 1, 2, 3, 4, and 5 L/min, respectively. Five mg/L of ammonia was oxidized by all ozone concentrations and average removal rate was $y=1.2567Ln(x)+1.2048$ and 0.65±0.28 ppm/h. All ozone treatment concentration also oxidize 5 ppm of nitrite with the average rate of $y = 1.3022Ln(x)-0.993$ and 4.45±0.21 ppm/h. The oxidation rates of ammonia and nitrite by ozone were not significant different ($p>0.05$) among the treatment ozone concentrations. Based on the result above, 0.04 ppm of ozone was enough for oxidizing ammonia and nitrite, but further study of ozone concentration lower than 0.04 ppm is needed.

Ozone treatment was not much effective to reduce nitrate concentration in this experiment.

Ozone treatment was also effective to oxidize TOC. Fifteen mg/L of TOC was reduced up to 3 mg/L for 12 hours with the ozone treatment concentration of 0.11, 0.15, 0.19 and 0.23 ppm and average removal rates of them were $y=-2.3542Ln(x)+12.525$ and 1.65±0.90 ppm/h for 0.04 ppm of ozone treatment, $y=-2.621Ln(x)+10.805$ and 2.22±1.35 ppm/h for 0.11 ppm of ozone treatment and $y=-2.468Ln(x)+10.147$ with 2.25±0.23 ppm/h for the average of 0.15, 0.19 and 0.23 ppm of ozone treatment.

During the ozonation treatment, bromate was formed up to 78 mg/L for 24h without ammonia existence. The average bromate formation rate was $y = 8.4201x-0.2699$ with 7.29±2.4 ppm/h for the first 6 hours and $y = 20.53Ln(x) + 14.447$ with 2.48±0.15 ppm/h for next 18 hours. While ammonia concentration was remained, bromate concentration was remaining under 0.33 mg/L, but after all ammonia exhausted, bromate formation was sharply increase.

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