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

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ABSTRACT

Ozone is applied to the recirculation aquaculture system to reduce bacteria and parasites. Besides the sterilization effects, it is known that ozone has oxidizing effects on some water quality parameters. Therefore, oxidizing effects of ozone on ammonia (NH_4-N), nitrite (NO_2-N), nitrate (NO_3-N), and dissolved organic carbon were tested in this study. During the test, ozone effects on pH, dissolved oxygen (DO) and bromination were also monitored. Ozone concentrations were originally set 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 NH_4-N was oxidized within 12 h in all concentrations of ozone treatments, with the average oxidizing rate of 0.65 ± 0.28 mg NH_4-N/L per h. The 5 ppm of NO_2-N was oxidized within 1.5 h in all concentrations of ozone treatments at a rate of 4.5 mg NO_2-N/L per h. One of 5 ppm NO_3-N was oxidized by all concentration of ozone treatment after 24 h. In addition, ozone also oxidized dissolved organic carbon and maintained the concentration at about 2.9 ± 0.77 ppm from the 15 ppm of initial concentration by 12 h. DO was increased from 5.9 to 9.4 ppm within 30 min in all ozone treatment and stabilized thereafter. Bromate concentrations increased sharply within the first 6 h of ozonation at the rate of 7.3 ± 2.4 mg/L per h in almost all ozone treatments; the rate decreased to 2.5 ± 0.15 mg/L per h thereafter. However, bromate concentration was not increased in the ammonia experiment until all ammonia was oxidized. Therefore, further studies are needed to determine the relationship between NH_4-N concentration and bromate formation in seawater.

Keywords: Ozone; Organic carbon; Bromate; Ammonia; Nitrite; Nitrate

1. Introduction

Water quality is one of the most important factors in managing intensive aquaculture systems. Currently, researchers are attempting to find the simplest and cheapest way to maintain better water quality. Ozone has been widely used to sterilize pathogens from the supply and effluent water in aquaculture systems [1]. However, ozone treatment has been found to be effective on the removal of organic and inorganic metabolites in the aquaculture system [2].

Ozone can be applied in aquaculture because it is a powerful oxidative agent that has very unstable bonds in 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

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its oxidative potential increases. In aquaculture, ozone has been used for water disinfectant and water quality improvement [1]. Ozone also improves water quality by deactivating bacterial, fungal, and viral pathogens in aquaculture system [2,4–6]. Application of ozone in Recirculation Aquaculture System (RAS) has the purpose of using available water more efficiently. By applying ozone, it is able to increase water quality conditions because ozone removes dissolved organic compounds, ammonia and nitrite in addition to being a good disinfecting agent [7]. However, the use of ozone also brings some disadvantages to aquaculture systems such as the risk of bromate forming, ozone residual, and the high consumption of power to produce ozone [3].

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 [8]. Ozone oxidizes bromide to form hypobromite ion (OBr^-). Hypobromite continues to be oxidized to form bromate, or to form an unidentified species, possibly Bromine dioxide (BrO_2^-), which regenerates bromide ion [9]. 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 [10]. 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 [11].

Ozone is able to 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. It is only transferring ammonia from water to the atmosphere as the following reaction [12].

$$Br + O_3 + H \rightarrow HBrO + O_2 \tag{1}$$

$$NH_3 + HBrO \rightarrow NH_2Br + H_2O \tag{2}$$

$$NH_2Br + HBrO \rightarrow NHBr_2 + H_2O \tag{3}$$

$$NH_2Br + NHBr_2 \rightarrow N_2 + 3Br + 3H \tag{4}$$

Ammonia will oxidize to nitrite and continues to oxidize into nitrate by ozone via;

$$NH_4^+ + 3O_3 \rightarrow NO_2^- + 3O_2 + 2H + H_2O \tag{5}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{6}$$

Furthermore, ammonia could also oxidize directly into nitrate by the following reaction [13];

$$NH_4^+ + 4O_3 \rightarrow NO_3^- + 2H^+ + H_2O + 4O_2 \tag{7}$$

As mentioned above, ammonia will oxidized into nitrite and the final product will be nitrate.

In addition to ammonia, ozonation also decreased 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 [14]. Ozonation of NOM may create organic polymers that either enhances coagulation of are more easily coagulated; Ozone can breakdown complexes Fe and Mn which might be tied up with NOM; the release of the oxidized metals creates a source of coagulant [32]. Ozone could oxidize nitrite, nitrate, and ammonia along with total organic carbon (TOC) in the water. In another side, ozonation can also produce the brominated by-products. However, to our best knowledge, there is no report considering the effect of several levels of ozone concentrations water quality parameters such as ammonia, nitrite, nitrate, and TOC. Therefore, a series of experiments to determine the oxidation effects of ozone concentrations on ammonia, nitrite, nitrate, and TOC were conducted. During the ozone treatments, changes of dissolved oxygen (DO), pH, and bromate were monitored.

2. Materials and methods

2.1. System design

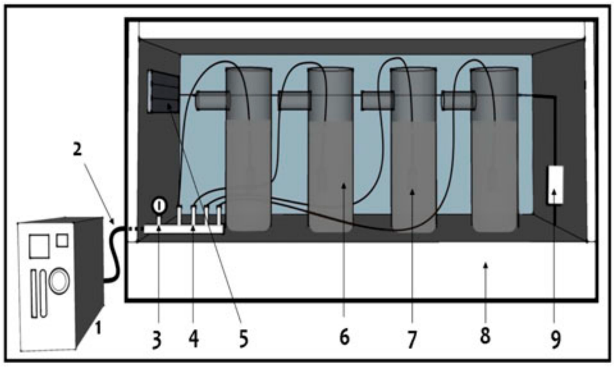

Fig. 1. Schematic representation of experimental system for testing oxidation effects of ozone on ammonia, nitrite, nitrate, and organic carbon. (1) Ozone generator; (2) Connector hose; (3) Pressure gauge; (4) Air flow meter; (5) Air conditioner; (6) Acrylic cylinder; (7) Aeration stone; (8) Work bench; (9) Thermo switch.

All the treatments were done within a fume hood (Fig. 1). Ten liters of acrylic cylinders were filled with

7 L each of sea water. Four tubes were installed in each with an ozone spreader (air stone) and bar thermometer. Ozone was introduced into each cylinder through a plastic hose and air stone. An airflow meter was installed for each cylinder to measure and adjust the amount of ozone added to the water. An ozone generator (Ozonetech, PC57L-10) with the capacity of 13 L/min of ozone gas was used. The fume hood was equipped with a ventilation system to remove excess ozone from the cylinders. An air temperature controller was installed in the fume hood to adjust the experimental temperature to 25˚C (Fig. 1).

2.2. Experimental procedure

After the system was setup, each acrylic cylinder was filled with 7 L of filtered seawater. The temperature was set at 25˚C and the initial DO, pH, and ozone concentrations were measured before ozone was injected. When the system was stabilized (about 20 min) and initial water quality parameters had been measured, ozone was continuously injected into the water at the rate of 1, 2, 3, 4, and 5 L/min. When ozone reached equilibrium concentration, initial source of each measurement was added to the water and samples were taken periodically. Water samples were periodically collected for the analysis of ozone and other water quality parameters. Periodical sampling intervals were established, dependent on the speed of changes of water quality parameters monitored.

Experiments were held in four different treatments, and all the treatments were used the identical system as explained previously. The only differentiation in each treatment is the chemical used for water parameter (ammonia, nitrite, nitrate, and TOC). Anhydrous ammonium chloride (NH_4Cl) was used as the ammonia source with a concentration of 5 ppm while the sodium nitrite ($NaNO_2$) with the initial concentration of 5 ppm was used as the nitrite source. In case of nitrate, sodium nitrate ($NaNO_3$) with the initial concentration of 5 ppm was used as the nitrate source. And then glucose (dextrose) was used as the carbon source in the equal concentration of TOC reached 15 ppm [15].

Ozonation of seawater resulted in side effects in addition to the main parameter measured. Therefore, while maintaining ozone equilibrium concentration, bromate, DO, and pH changes were also measured.

2.3. Water quality measurement procedure

2.3.1. Ozone measurement

Measurement of ozone residual (ozone equilibrium concentration) in the water was taken using Spectrophotometer Hach DR-2800. Samples were taken as much as the volume of the ampoules. Reagent (indigo reagent) was prepared and sealed inside of the commercial ampoule. The ampoules were immersed into the water treatments, and water samples were collected. After ampoules were fully filled with the water sample, ampoules were raised, reversed, and shakes gently. After few seconds, samples were measured under the spectrophotometer in wave length of 600 nm. Since the instability of ozone, the indigo reagent was used to calibrate and determine the ozone concentration in the water [33,34].

2.3.2. Ammonia measurement

Anhydrous ammonium chloride (NH_4Cl) was used as ammoniac source (APHA, AWWA, WEF. 1995). To observe the ammoniac degradation "Manual Phenate Method" was used by combined it with spectrophotometer OPRON 3000. The measurement was taken based on the standard method book for the examination of water and wastewater by APHA, AWWA, and WEF 1995. In this method, six reagents were made, standardized and used to determined ammoniac concentration.

2.3.3. Nitrate and nitrite measurement

The nitrate source was used is sodium nitrate ($NaNO_3$), while the nitrite source was used is sodium nitrite ($NaNO_2$) (APHA, AWWA, WEF. 1995). Samples were filtered first with the Whatman paper to remove suspended solid contain. After filtered, samples were enriched with color development reagent. The samples were then measured its absorbance level using spectrophotometer. For nitrate, the spectrophotometer at 543 nm of wave length was used, while measurement of nitrate was taken under the wave length of 220 and 275 nm.

2.3.4. TOC measurement

Glucose (dextrose) was used as the carbon source and TOC concentrations were conditioned to reach the level of 15 ppm. TOC measurement was taken under the HiPerTOC analyzer. For TOC 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 radiation to enhance the oxidation. The concentration of TOC was measured as the difference between "total carbons" and "inorganic carbon" results (Thermo Electron Corporation, 2009).

2.3.5. Bromate measurement

Bromate concentrations in this experiment were measured using spectrophotometer under the wave length of 590 nm. The reagents used were acetate buffer, phenol red indicator solution, chloramines-T solution, sodium thiosulfate, and bromide stock solution. Determination of bromate concentration could be carried out by comparing the data to the calibration curve of bromate [15].

3. Results and discussion

3.1. Ozone equilibrium concentration

Each loading rate of ozone treatment was resulting in different level of ozone equilibrium concentration in the seawater. One L/min treatment resulting 0.04 ppm, while 2, 3, 4, and 5 L/min of ozone-loading treatment resulting the equilibrium concentration of 0.11, 0.15, 0.19, and 0.23 ppm of ozone, respectively. The loading rate of ozone and its equilibrium level in the water were never the same level; as some parts were diluted in the water and the other parts were evaporate to the air as its buffer.

3.2. Ammonia oxidation

Five ppm of ammonia in seawater has entirely oxidized no longer than 12 h by ozone (Fig. 2). In this experiment, ammonia removal by ozone was relatively very fast in the first 3 h, and it is continues slowly within next 9 h until all ammonia concentration was oxidized. Ammonia removals by ozone were classified into two groups, which are the lower and higher ones. The lower ozone treatment (1, 2, and 3 L/min of ozone) has the removal rate of 0.55 ± 0.21 ppm/h with the removal acceleration of $y = 1.2873 \ln (x) + 1.141$ in average. The other is higher ozone treatment (4 and 5 L/min of ozone) with the removal rate of 0.75 ± 0.20 ppm/h by the removal acceleration of $y = 1.2108 \ln (x) + 1.3005$ in average. As distinct from ozone treatment, ammonia concentrations in the water treated by common aeration were only remained in the initial concentration by air loading rate of 1, 2, and 3 L/min, while for air loading rate of 4 and 5 L/min, it could reduce ammonia in about 5% from initial concentration.

Based on the reaction number 5 and 6, we know that ammonia could oxidize into nitrate accumulation either by direct or indirect reaction with ozone. In an identical culture system, different levels of ozone concentration were reported to have no effect on the oxidizing ability of ammonia [12]. The differentiation of ammonia removal rate in this experiment was suggested caused by foam fractionation. Because more air introduced into higher ozone treatment groups, more foam to accumulate on the surface of water treated. Tanaka and Matsumura have reported that the foam fractionation is able to remove ammonia from the water [16].

Although ammonia was removed from the water, nitrate accumulations were found increased rapidly in the first 12 h, and then, the increment was decreased into final experiment (Fig. 3). Ammonia was oxidized by ozone into nitrite and continuous to oxidize into nitrate. Here, by this experiment, the ammonia loading rate of 5 ppm/d was oxidized to be nitrate as much as 15.4 ± 0.29 mg/L in 24 h.

Based on the formulas of reaction number 5 and 6 and also mass balance, each molecule, ideally, 5 mg/L of initial ammonia should be oxidized into 17.23 mg/L of nitrate. The concentration of nitrate in this experiment was recorded at a level of 15.4 ± 0.29 mg/L. The difference between nitrate accumulated in this experiment and that in the calculation method is caused by the natural reaction involves ammonia ion. During the ozonation of ammonia, there are many possibilities for the formation of the other ions, such as brominated product, nitrogen ions, and other by-products [13]. In this experiment, ammonia was transformed into nitrate and some other by-products by ozone oxidation.

3.3. Nitrite oxidation

Ozone also reacted with nitrite and oxidized it into nitrates and other excess gas from the water. Five ppm of nitrite in seawater was oxidized completely within 90 min in all ozone treatment concentrations with an average removal rate of 4.45 ± 0.21 mg/L per h ($y = 1.3022 \ln (x) - 0.993$). After the first 30 min, nitrite concentration decreased 80% from 5 to 1 ppm and then continuously decreased to near zero within 90 min (Fig. 4).

This experiment was used five ppm of initial concentration, because an initial nitrite concentration of less than 10 mg/L is near the maximum nitrite concentration that would be found in an untreated, high-density fish hatchery [17–21]. The rate of nitrite removal was very high in the first 30 min; this result was in agreement with Lin and Wu [31], who reported that nitrite removal using an electrochemical could remove the initial total nitrite level of 5 mg/L in more than 30 min. In the application of ozone in seawater, some ammonia will oxidized into nitrite, which is only a temporary phase because nitrite itself will then be oxidized by ozone into nitrate. Nitrite is the temporary phase of reaction, resulting the relatively

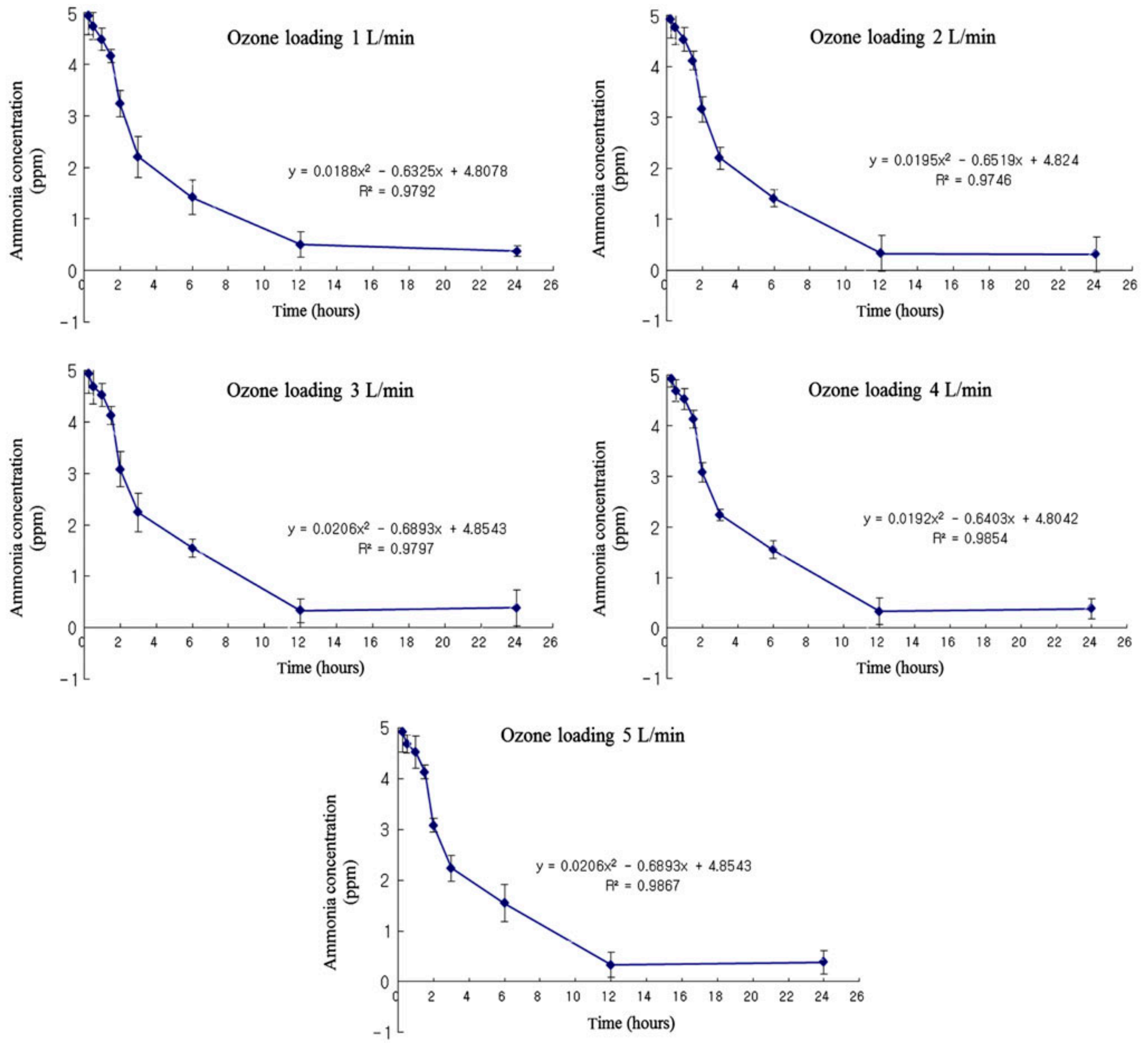

Fig. 2. Effect of five different concentration of ozonation on ammonia removal rates. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

short oxidation time of the nitrite concentration. The quick oxidation reaction of nitrite was also caused by the double reaction that could be happened by involving a nitrite ion, which are the direct reaction of nitrite with ozone [13], and reaction between nitrite and bromide acid which resulted from the reaction of bromide and ozone [12]. This result indicates that nitrifying bacteria, which decomposes ammonia and nitrite from the water, will no longer to be the limitation factor for aquaculture especially in RAS. In the conventional aquaculture especially in RAS, ammonia removal was by nitrification bacteria, and it is therefore even carried out though water supply and food has increased, the maximum density of carrying capacity still limited by the concentration of ammonia accumulated in the water since nitrobacteria population is limited to its space of growth. By the application of ozonation, ammonia removal will no longer depend on nitrobacteria population, as it is reduced by ozone [35].

3.4. Nitrate oxidation

Nitrate was oxidized from the initial concentration of 5–3.95 ppm after 12 h and remained at that level thereafter (Fig. 5). There were no significant differences

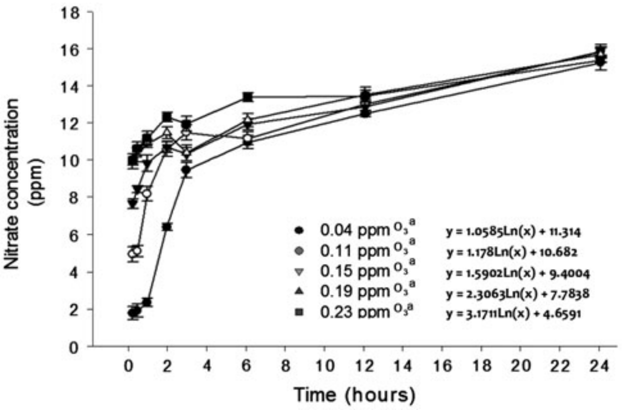

Fig. 3. Changes of nitrate concentrations during ammonia ozonation. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

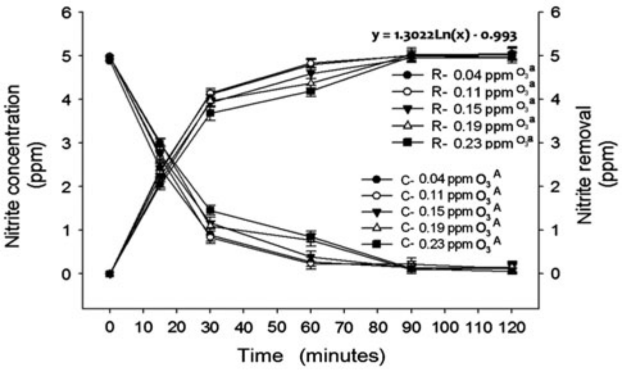

Fig. 4. Relationship between nitrite removal and nitrite concentration in seawater with five different ozone treatments. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

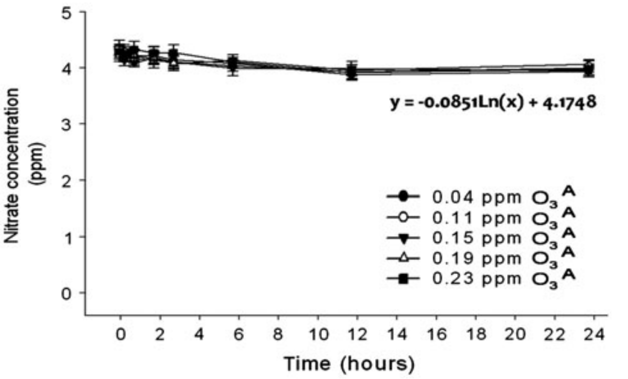

Fig. 5. Nitrate oxidation rate treated by five ozone concentrations. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

between the ozone treatments on nitrate oxidation. Nitrate removal rate averaged 0.36 ppm/h ($y = -0.0851 \ln(x) + 4.1748$). Oxidation of nitrate by ozone was complete within 12 h of treatment; after 12 h, there was no significant change ($p > 0.05$) in nitrate concentration. Similarly, in ozone treatment, ozone treatment, the nitrate concentrations were also remaining in the initial concentration, while the water was treated with the common aeration.

Nitrate is the final product of the nitrification process [22]. Therefore, it is accumulated in an intensive aquaculture system, especially in RAS. Ozone could not oxidize nitrate optimally because ozone and nitrate have the same number of active oxygen molecules. Nitrate already has three atoms of oxygen, so it cannot be oxidized by ozone, which also has the same electron valence from the oxygen molecule. Unlike in the biological process of denitrification in which nitrobacteria decompose the $NO_3^{-\bullet}$-N in the water into N_2 ion, which could then be easily released into the air, ozonation allows the nitrate remaining in treated water to accumulated easily. Therefore, denitrification may need to be part of the ozonation process when nitrate accumulation becomes toxic. So preventing $NO_3^{-\bullet}$-N formation becomes the key point, while the process of removing ammonia from the water by ozonation [12].

3.5. TOC oxidation

TOC concentration has consistently dropped during the ozonation process, leveling off when the concentration reached 2.98 ± 0.77 ppm in all treatments after 12 h except for the lowest ozone treatment which is leveling off in the concentration of 4.06 ± 0.46 ppm after 24 h (Fig. 6). This means that TOC reached an equilibrium concentration and remained there after. The TOC oxidation rate could be divided into three groups, the lowest, medium, and highest ozone treatments with the oxidation rate of 1.65, 2.22, and 2.25 ppm/h, respectively. This experiment indicated that the lowest ozone treatment (1 L/min) was removing significantly ($p < 0.05$) less TOC from the water, while the other concentrations were not significant different ($p > 0.05$) on the removal rate.

This experiment used glucose ($C_6H_{12}O_6$) as the organic carbon source. The TOC initial concentration was adjusted to 15 mg/L of organic carbon ion. The initial TOC was selected because it was reported as the average TOC concentration remained in intensive aquaculture systems [14,22]. Ozonation also reduced TOC levels by approximately 17% [23]. In this experiment, the lowest ozone treatment (1 L/min) was

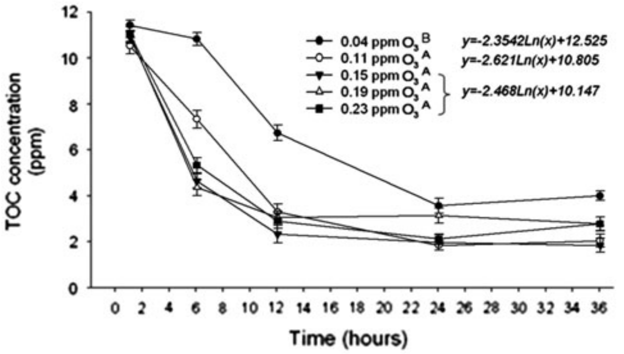

Fig. 6. Change of TOC concentration in the water treated with five different levels of ozone. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

significantly less in removing organic carbon contained in the water. This statement was also confirmed by Rosenthal [2], who explained that ozone at certain doses was not sufficient to oxidize organic compounds completely, but did break up large organic molecules into smaller, more easily biodegradable ones.

3.6. Ozonation by-products

3.6.1. Bromate formation

In this experiment, bromate concentration in the seawater was observed in three different treatments, and those treatments were bromate formation while ozonation of seawater without interferer, bromate formation while oxidation of ammonia, and the bromate formation while oxidation of TOC. Ozonation of seawater without any interferer was resulting in very high bromate formation. Bromate formation increased with ozone exposure time (Fig. 7). Bromate concentration was increased sharply into 79.28 ppm as long as 24 h of ozonation.

In the oxidation of ammonia, bromate formation was suppressed as long as ammonia still available in the water. Bromate concentration was remained at 0.33 ppm for the first 6 h and increased to 8.3 ppm for the next 6 h, then dramatically increased thereafter (Fig. 8).

In the oxidation of TOC, bromate formation also suppressed by the organic carbon contained in the water. During the first 12 h, all bromate concentration was found below of 10 ppm except for 5 L/min of ozone treatment (Fig. 9). After the 12 h, the TOC also exhausted, and bromate formations were sharply increased.

It is well known that ozonation of bromide-containing waters can oxidize the bromide ion (Br^-) to

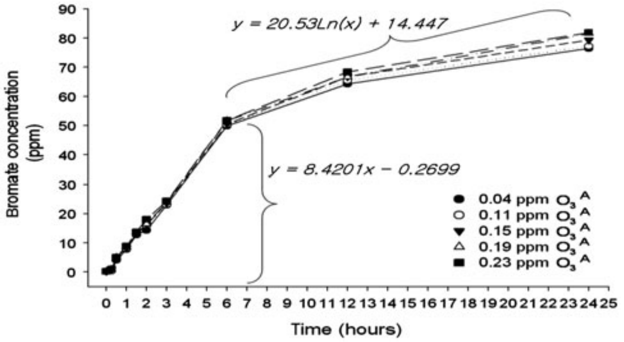

Fig. 7. Bromates formation for 24 h of ozonation process. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

bromate (BrO_3^-) ion within normal water quality ranges and treatment parameters [8,9,11,23–25]. The bromate ion (BrO_3^-) is the highest oxidation state of the bromide ion and ozone oxidizes bromide to hypobromite ion (OBr^-) [8]. Hypobromite continues to be oxidized to bromate or to an unidentified species, possibly Bromine dioxide (BrO_2^-), which regenerates bromide ion [9]. Formation of brominated by-product in ozonated waters is influenced by bromide ion concentration, the source and concentration of NOM, pH, dose of ozone, and reaction time [11].

The conversion of bromide ion into bromine and bromate are shown in the following two formulas:

$$O_3 + Br \rightarrow O_2 + OBr^- \tag{8}$$

$$2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^- \tag{9}$$

Bromide reacts with ozone to produce oxygen and hypobromite; hypobromite is then oxidized by ozone into bromate and oxygen. According to Bowen [26],

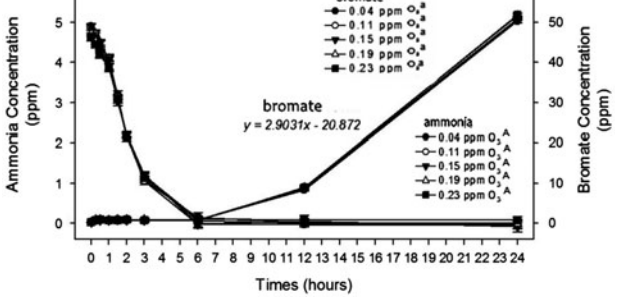

Fig. 8. Relationship between ammonia concentrations and bromate formation during the oxidation treatment of ammonia. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

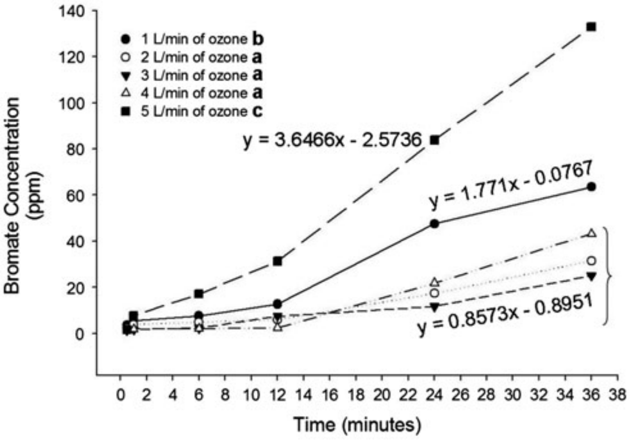

Fig. 9. Increment of bromate formation during oxidation of TOC treatment. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

common seawater has average bromide ion (Br^-) concentrations as high as 66 mg/L. Based on the above reactions, 66 mg/L of bromide ion could be converted into 105 mg/L bromate ion. In this experiment, the bromate reaches the level of 79.28 mg/L. This bromate concentration was relatively high compared with theoretical bromate production. The simplest method to decompose the oxidizing bromines is to use a reducing agent like an activated carbon column or by using Na_2SO_3 [12].

In this experiment, bromate concentration did not increase for 12 h, during the time that ammonia exists. Moreover, bromate will not be formed as long as ammonia is present in the water system. Bromide will be oxidized by ozone and react with ammonia into dibromamine ($NHBr_2$) or hypobromous acid (HOBr) and the other bromine ion [16]. In addition, ammonia has been suggested to be a potential quenching agent that may act to minimize bromate formation in water [27]. Ozone that was diluted to the water will react with existing TOC first before it can be reacting with bromide ion to form bromate. In addition, as a result of oxidation of TOC by ozone could produce compounds that can react with brominated ion such as BrO_3^-, Br^-, Cl^-, and SO_4^{2-} before it is oxidized by ozone into bromate [36,37]. Hofmann suggested that the formation of bromate may be highly coupled with the characterization and concentration of NOM [27].

3.6.2. DO changes

DO levels increased in all ozone treatments (Fig. 10). When ozone was introduced into the water, DO was increase from the level of 6.23 ppm in average into 9.2–9.6 ppm and stabilize thereafter. Even though ozone increasing DO into super saturation level, common aeration treatment only promote DO to reach saturation level at 7.2 ppm in average. No differences in DO levels were found among the aeration groups after 30 min and thereafter ($p > 0.05$).

In this experiment, DO was increased with ozonation. Ozone is a triatomic oxygen molecule (O_3), very reactive and ready to decay to oxygen (O_2) and enhance oxygen concentration in the water. DO is a critical parameter for aquatic organisms [28]. In fish culture, rather than temperature or other water quality parameters, DO is the most important. In highly intensive aquaculture systems like RAS, the ability to add DO to the water is the first priority to increase carrying capacity. Therefore, ozonation in high-density culture systems might be useful for increasing DO and carrying capacity.

3.6.3. pH changes

The pH levels increased significantly in all groups of ozone treatment. Additionally, pH levels increased with time from the initial pH of 8.1 in average to 8.5 ~ 8.7 (Fig. 11) by 20 min and stabilized thereafter.

Ozone decays in the water partly to 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 the dominant particles in the solution, it is called an advanced oxidation process. The decay of ozone to 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 is increased, the pH value will also increase [29,30]. These hydroxide ions act as an initiator for the decay of ozone [29]:

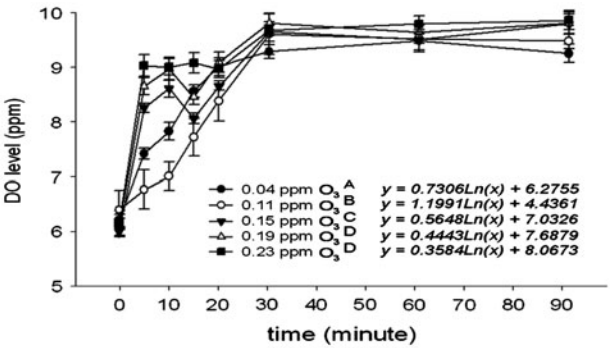

Fig. 10. Increment of DO concentration during five different levels of ozonation. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

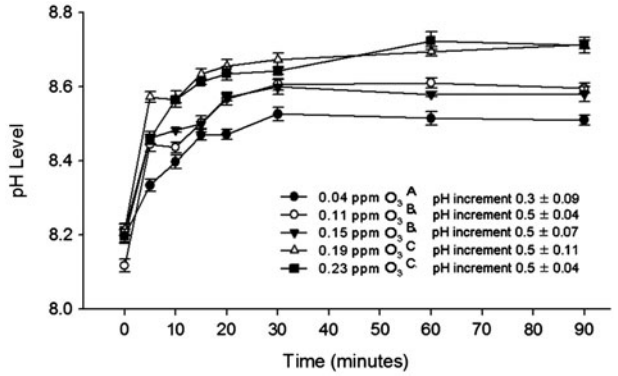

Fig. 11. Changes of pH level during ozonation process. Superscripts of the same letter at the end of each treatment concentration were not significantly different.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (10)$$

$$O_3 + HO_2^- \rightarrow {}^{\cdot}OH + O_2^{\cdot -} + O_2 \qquad (11)$$

$$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2 \qquad (12)$$

$$O_3^{\cdot -} + H_2O \rightarrow {}^{\cdot}OH + OH^- + O_2 \qquad (13)$$

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

4. Conclusion

The application of ozone to enhance water quality in aquaculture could remove ammonia and nitrite completely from the water. Although nitrate concentration potentially accumulated, nitrate is not really toxic for organism until the special condition. Ozonation of seawater have the compensation to form bromate ion, but with the existence of ammonia and organic carbon in the water, bromate forming could be suppressed depend on the ammonia and TOC concentration. However, in real application of ozonation in aquaculture, water is contains complexes chemicals and biological compound which may affect bromate formation. Nevertheless, in separated experiment, there was no one of factor could promote the bromate formation, and all those were functioned as inhibition agent of bromate formation. Based on the results of this study and also comparison with the chemical reaction in some references, ozonation can be applied safely into RAS. However, bromate formation level in the RAS with synergetic effect of existence of all component need to be studied and it should be the major consideration while application of ozone.

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