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Effects of Ammonia Concentrations on Bromate Formation in Seawater During Ozonation and Oxidation Effects of Ozone on Ammonia, Nitrite and Nitrate

by

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해수 오존 처리시 암모니아 농도가 브로메이트 생성에 미치는 영향 및 암모니아,아질산,질산염의 산화에 미치는 영향

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A dissertation

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Abstract

Effects of ammonia concentrations on bromate formation and oxidation effects of ozone on nitrogen compound were studied. During ozonation in seawater ammonia will react very quickly with free bromine to produce bromamines. Bromamines are then oxidized to bromide and nitrate. The presence of ammonia in this cycle prevents bromate formation until all ammonia react with bromamines.

Ammonia was significantly ($p < 0.05$) suppressed bromate formation in seawater during ozonation. The linear relationship was found between ammonia concentrations and the suppression time of bromate formation, bromate was not formed for 6 minutes when 0.5 mg/L ammonia was treated. When 1, 2, 3, 4 and 5 mg/L of ammonia were treated bromate formation was suppressed for 15, 30, 45, 60 and 75 minutes, respectively. No bromate was formed when 1, 2, 3, 4 and 5 mg/L of ammonia were added continuously with the intervals of 15, 30, 45, 60 and 75 minutes, respectively. Nitrite and nitrate were significantly ($p < 0.05$) oxidized by 0.1 mg/L of ozonation. Average reduction rate of nitrite and nitrate were measured. During ozonation DO was increased from 7.87 to 14.60 mg/L within 24 hours and pH level was decreased from 8.20 to 7.81 within 6 hours.

Keywords: ozone, bromate, ammonia, nitrite, nitrate

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I. INTRODUCTION

Recirculating aquaculture system (RAS) provide potential advantages in aquaculture. Those advantages include flexibility in site selection, reduced water usage, lower effluent volumes, better environmental control, and higher intensity of production. However, if stock densities and levels of water reusing rate increase, metabolic wastes accumulate rapidly, and water quality control becomes difficult. Accumulation of fine colloidal solids, dissolved organics and nitrite can impair biofilter function and increase BOD and stress level in the cultured stock. Increasing the daily water exchange rate in RAS will remove accumulated colloidal solids, refractory organics and nitrite, but this will also increase water budget and the cost of heating or cooling in the system. The alternative removal method of the organic wastes is use of an oxidizing agent, such as ozone (NSW Government).

Ozone (O_3) is a three-atom allotrope of oxygen in which the oxygen atoms are held together in an unstable bond. A loosely bound single oxygen atom is quickly break away and reacts with most of the organic and inorganic molecules, and it come down into contact with ozone. Hence, ozone is a powerful oxidizing agent (Lawson, 1995) and an effective disinfectant in aquaculture. It also destroys viruses, bacteria, fungi and protozoans, providing its broad application in the aquaculture industry (Buchan et al., 2005).

The effectiveness of ozone as a disinfecting agent is a function of dosage and contact time. Contact time is acquired by dispersing ozone throughout the culture water. Contact time and required ozone concentration vary with the target microorganisms and water quality (Lohr and Gratzek, 1986). At low dosages and short contact times, ozone reliably reduces waterborne microbes and maintains high water clarity in the systems (Summerfelt and Hochheimer, 1997). In addition to its disinfecting properties, ozone is reported to reduce nitrite, BOD and COD (Evans, 1972; Colberg and Lingg, 1978), and to precipitate certain heavy metals like iron and manganese (Wheaton, 1977). Ozone also breaks long-chain organic molecules into shorter chain molecules that can be more easily biodegraded (Lawson, 1995).

During ozone treatment in fresh water, ammonia is converted to nitrate, but the rate of this reaction is very slow and cannot be expected to remove ammonia effectively. Therefore, ozone treatment cannot be considered as a suitable method for nitrogen removal in freshwater. In seawater, however, oxidation of ammonia by ozone would be different from freshwater, due to the presence of chloride and bromide ions (Tanaka and Matsumura, 2002). According to them, during ozone treatment of water containing bromide, ammonia can be converted to nitrogen gas, either directly by ozone or by the oxidized bromide.

Bromide is a natural, albeit minor, constituent of in waters and its concentrations in water depend primarily on the geochemistry of the materials in which the water has come into contact (Kjensmo, 1997). Tango and Gagnon (2003) mentioned that ozone in sea water will react with bromide in sea water, produce hypobromous acid, and lead to bromate formation which has toxic effect to fish.

The attempts to reduce bromate in ozonated waters are particularly by pH depression or contact time control, but one option to explore is the addition of ammonia (Berne et al., 2004). Berne et al. (2004) reported ammonia will react very quickly with free bromine ($HOBr/BrO^-$) to produce bromamines ($NH_2Br/NHBr_2$). Bromamines are then oxidized to bromide and nitrate during ozonation in seawater. It is hypothesized the presence of ammonia in this cycle can prevent bromate formation until ammonia reacts with bromamines in seawater during ozonation.

The aim of the present study is to find effects of various concentrations of ammonia to bromate formation. Concentration of nitrite and nitrate are increasing when ammonia is oxidized, the effect of ozonation on nitrite and nitrate oxidation were also studied.

II. MATERIALS AND METHODS

2.1. System Design and Experimental Procedures

All experiments were done in a fume hood to remove excess ozone from the cylinders (Figure 1). Four 10 L acrylic cylinders were filled with 7 L of seawater each. Each acrylic cylinder was installed with an ozone distributor (air stone) that was connected to an ozone generator (*Ozonetech*, PC57L-10, Korea) with the capacity of 13 L/min of ozone. An airflow meter was installed for each cylinder to measure and adjust the amount of ozone added to the water. Air conditioner or heater was installed in the experimental room to adjust the experimental temperature to 20°C.

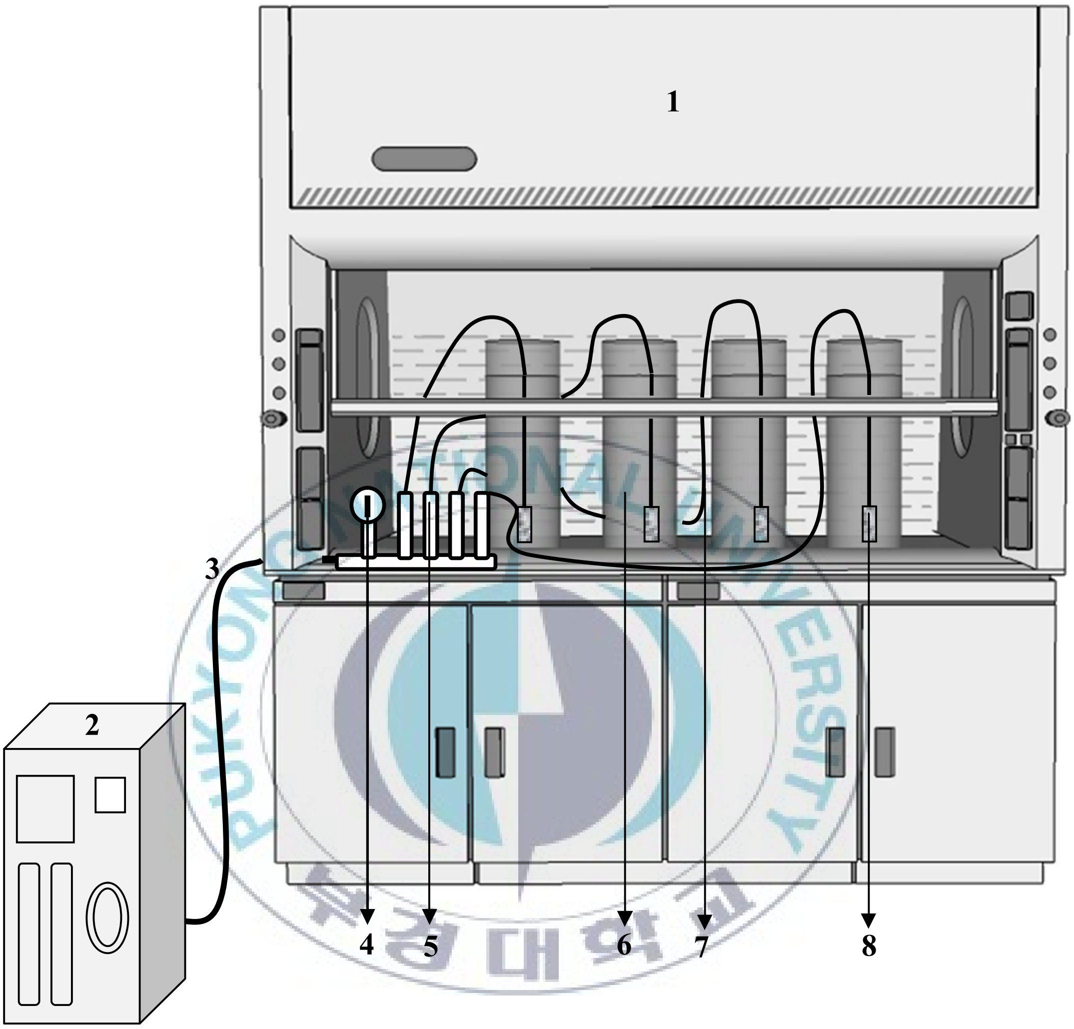

Figure 1. A schematic drawing of the experimental system. 1. Fume hood; 2. Ozone generator; 3. Connector hose; 4. Pressure gauge; 5. Air flow meter; 6. Acryl cylinder; 7. Aeration hose; 8. Air stone.

The initial DO and pH were measured before ozone was injected. When the ozone concentration in the system was stabilized at 0.1 mg/L, initial water quality parameters (NH_3, BrO_3, NO_2, NO_3) were measured. The reason to choose 0.1 mg/L ozone concentration was based on the effective concentrations for sterilization of microorganism (Timmons and Ebeling, 2007). Water samples were periodically collected for analyzing of water quality parameters.

2.2. Effects of Ammonia on Formation of Bromate

Anhydrous ammonium chloride (NH_4Cl) was used as the ammonia source. To observe the ammonia, "Manual Phenate Method" (APHA, 1995) was used with the spectrophotometer (OPRON 3000, Hanson Technology Co., Korea). Bromate concentrations were measured using this spectrophotometer at 590 nm (APHA, 1995). The treatment was run in triplicate with one control. Experiments were conducted in 3 different procedures.

The First experiment was conducted to observe the relationship between ammonia concentration and bromate formation by "single application" of ammonia. Ammonia concentrations in the first experiment were 1, 2, 3, 4 and 5 mg/L. After each concentration of ammonia applied to the ozone treated water, water samples were taken at 0, 15, 30, 45, 60, 75, 120 and 360 minutes after the ammonia application and the concentrations of ammonia and bromate were analyzed.

The second experiment with 0.5 mg/L of ammonia was conducted to find out the exact time when bromate concentration start to increase within the first 15 minutes. Water samples were taken at 0, 1, 2, 3 ,4, 5, 6, 7, 8, 9 and 10 minutes after the ammonia application.

The third experiment was conducted to observe the relationship between ammonia concentration and bromate formation by "multiple applications" of ammonia. The application time of each concentration of ammonia was according to the results of single application of ammonia. The application time intervals of the tested ammonia concentrations of 1, 2, 3, 4 and 5 mg/L were 15, 30, 45, 60 and 75 minutes, respectively. Water samples were taken at 0, 15, 30, 45, 60, 75, 90, 105 and 120 minutes for all ammonia concentration.

2.3. Nitrite Oxidation

Sodium nitrite ($NaNO_2$) with the initial concentrations of 0.5, 1 and 1.5 mg/L were used as the nitrite source. Samples were taken at 0, 10, 20, 30, 40, 50 and 60 minutes. Nitrite oxidation was measured by the spectrophotometer, HACH DR-2000, USA (APHA, 1995).

2.4. Nitrate Oxidation

Potassium nitrate (KNO_3) with the initial concentration 1, 2 and 3 mg/L were used as the nitrate source. Samples were taken at 0, 10, 20, 30, 40, 50 and 60 minutes. Oxidation of nitrate was measured by the spectrophotometer, HACH DR-2000, USA (APHA, 1995).

2.5. pH Changes During Ozonation

E-comet pH meter (P25, Istek Co., Korea) was used to measure the pH changes. Three buffer solutions were used to calibrate the pH meter. Those buffer solutions are buffer of 4, 7 and 10 pH buffer solution from the *Samchun* chemical company. pH level was measured at 0, 1, 2, 3, 4, 5 and 6 hours.

2.6. DO Changes During Ozonation

DO levels in the ozonating water were measured *insitu* every hour for 24 hours to get a more accurate measurement and reduce bias. The Oxyguard oxygen meter (*Handy Mk III*, Denmark) were used.

2.7. Statistical Analysis

Data were analyzed by analysis of variance (ANOVA) by the MINITAB 16 Statistical software.

III. RESULTS

3.1. Effects of Ammonia on Formation of Bromate

3.1.1. First experiment - single application of 1, 2, 3, 4 and 5 mg/L of ammonia

Bromate formations were delayed in the certain time by ammonia addition. When 1 mg/L of ammonia was treated, actual concentration of ammonia was 1.07 mg/L. After 15 minutes of ozonation, ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate in the control increased up to 21.1 mg/L. (Table 1; Figure 2). After 30 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 18.9 mg/L while that in the control was 24.4 mg/L. Bromate was increased up to 43.0 mg/L at 360 minutes in the treatment group, while in the control was increased up to 51.1 mg/L.

Table 1. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 1 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	1.07 ± 0.04	0	0
15	0	0	21.1
30	0	18. 9 ± 1.11	24.4
45	0	20.7 ± 1.28	31.1
60	0	33.0 ± 1.69	38.9
120	0	38.9 ± 1.11	46.7
360	0	43.0 ± 1.69	51.1

*Ozone concentration: 0.1 mg/L

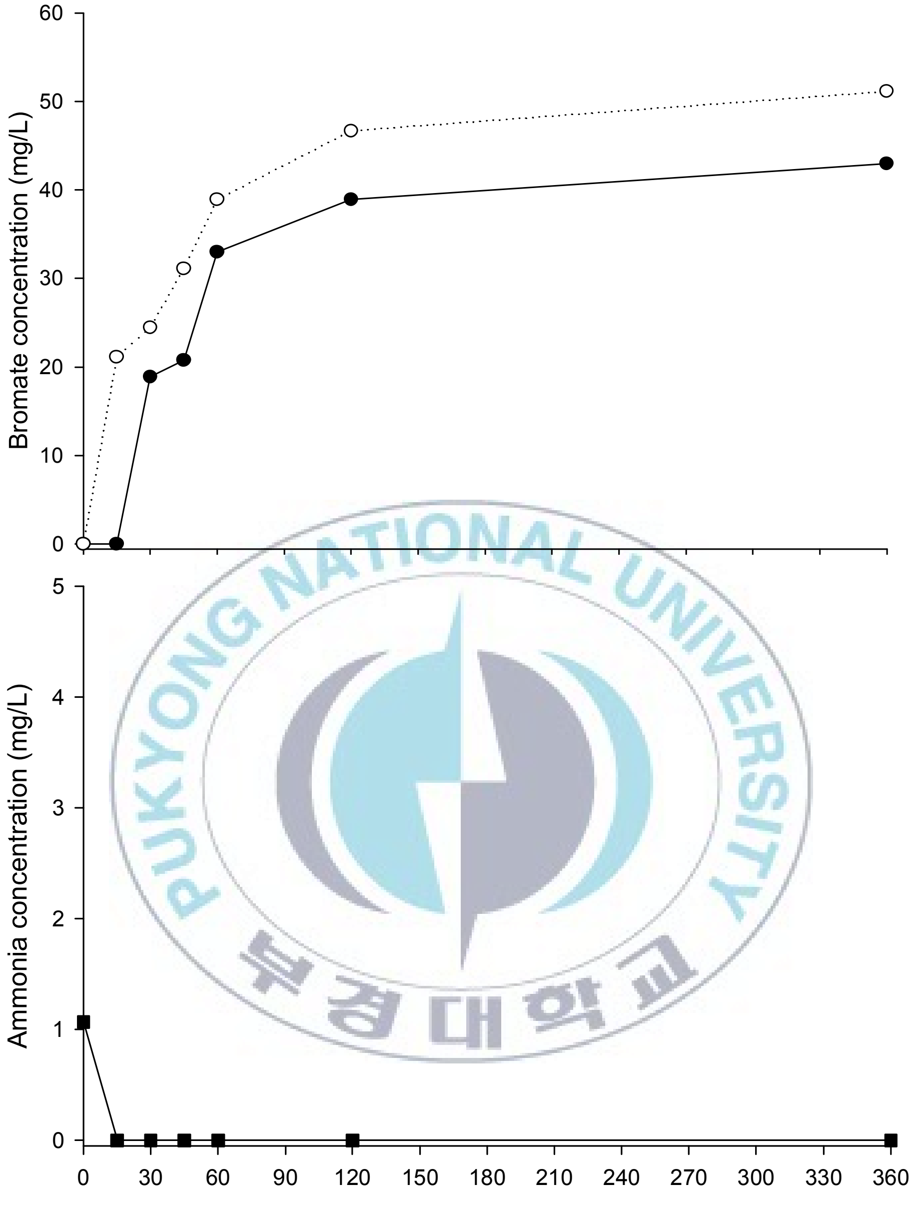

Figure 2. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 1 mg/L ammonia treated group and non-treated (control) (···○···).

When 2 mg/L of ammonia was treated, actual concentration of ammonia was 2.02 mg/L. After 30 minutes of ozonation, ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate in the control increased up to 22.2 mg/L (Table 2; Figure 3). After 45 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 18.2 mg/L while that in the control was 33.3 mg/L. Bromate was increased up to 45.6 mg/L at 360 minutes in the treatment group, while in the control was increased up to 50.0 mg/L.

Table 2. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 2 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	2.02 ± 0.01	0	0
15	1.10 ± 0.06	0	18.9
30	0	0	22.2
45	0	18.2 ± 2.79	33.3
60	0	30.7 ± 1.69	42.2
120	0	35.9 ± 0.64	44.4
360	0	45.6 ± 1.69	50.0

* Ozone concentration: 0.1 mg/L

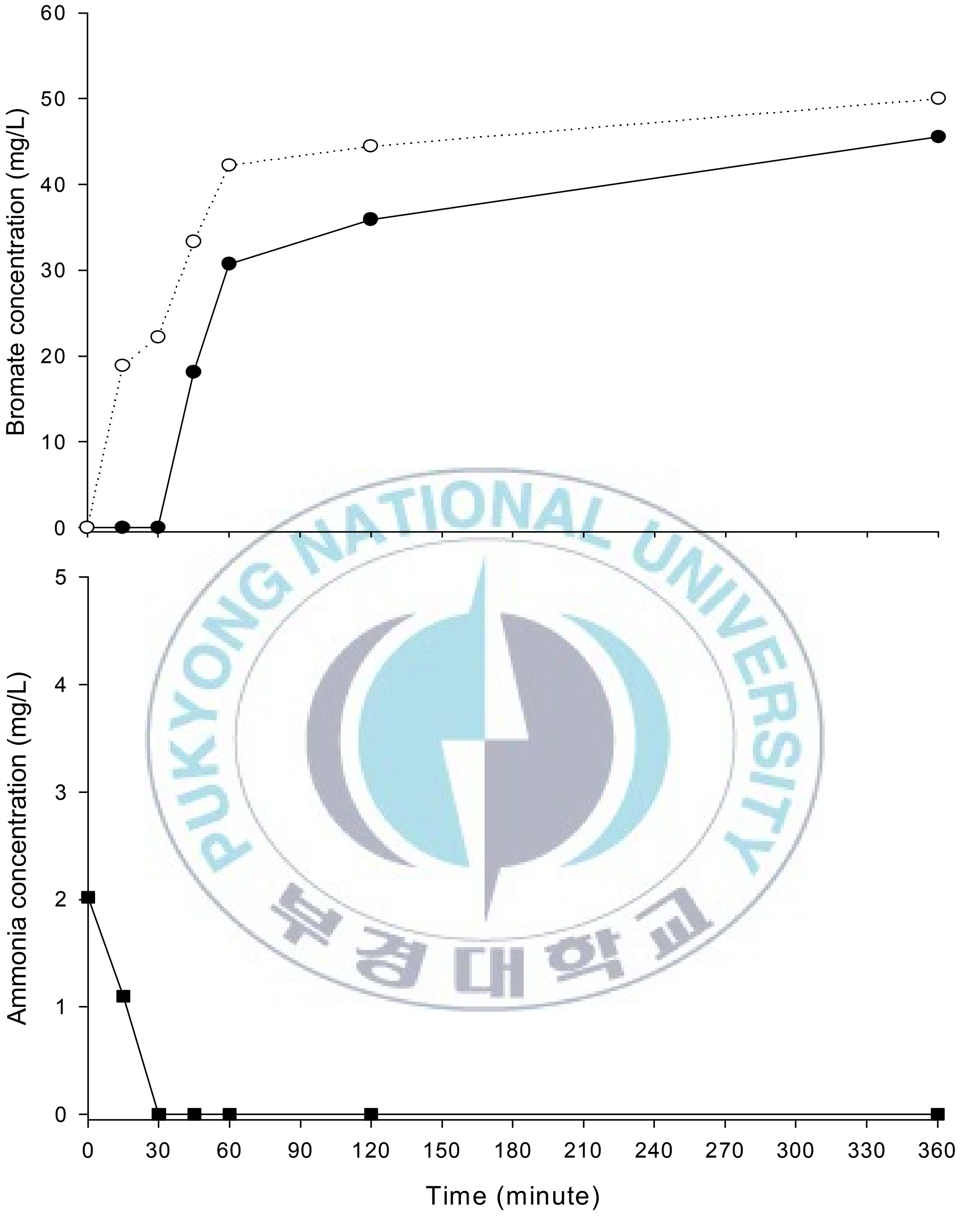

Figure 3. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 2 mg/L ammonia treated group and non-treated (control) (···○···).

When 3 mg/L of ammonia was treated, actual concentration of ammonia was 3.03 mg/L. After 45 minutes of ozonation, ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate in the control increased up to 23.3 mg/L (Table 3; Figure 4). After 60 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 17.4 mg/L while that in the control was 28.9 mg/L. Bromate was increased up to 33.3 mg/L at 360 minutes in the treatment group, while in the control was increased up to 48.9 mg/L.

Table 3. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 3 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	3.03 ± 0.04	0	0
15	1.91 ± 0.07	0	16.7
30	1.19 ± 0.15	0	17.8
45	0	0	23.3
60	0	17.4 ± 1.69	28.9
120	0	25.9 ± 1.70	35.0
360	0	33.3 ± 2.22	48.9

*Ozone concentration: 0.1 mg/L

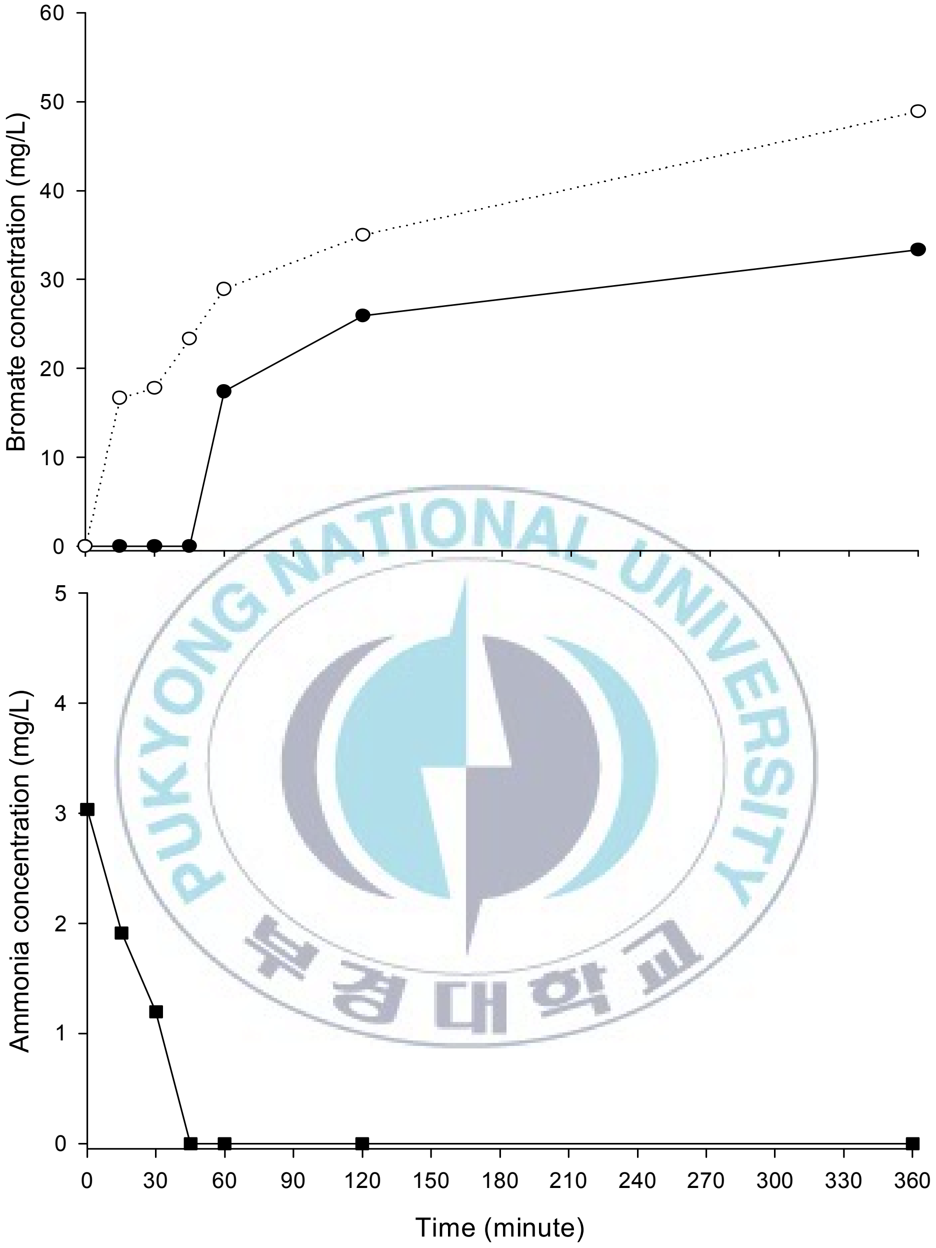

Figure 4. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 3 mg/L ammonia treated group and non-treated (control) (···○···).

When 4 mg/L of ammonia was treated, actual concentration of ammonia was 4.02 mg/L. After 60 minutes of ozonation, ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate in the control increased up to 37.8 mg/L (Table 4; Figure 5). After 120 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 19.6 mg/L while that in the control was 46.7 mg/L. Bromate was increased up to 26.7 mg/L at 360 minutes in the treatment group, while in the control was increased up to 52.2 mg/L.

Table 4. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 4 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	4.02 ± 0.006	0	0
15	3.22 ± 0.05	0	20.0
30	2.19 ± 0.22	0	22.2
45	1.32 ± 0.015	0	28.9
60	0	0	37.8
120	0	19.6 ± 2.31	46.7
360	0	26.7 ± 1.11	52.2

*Ozone concentration: 0.1 mg/L

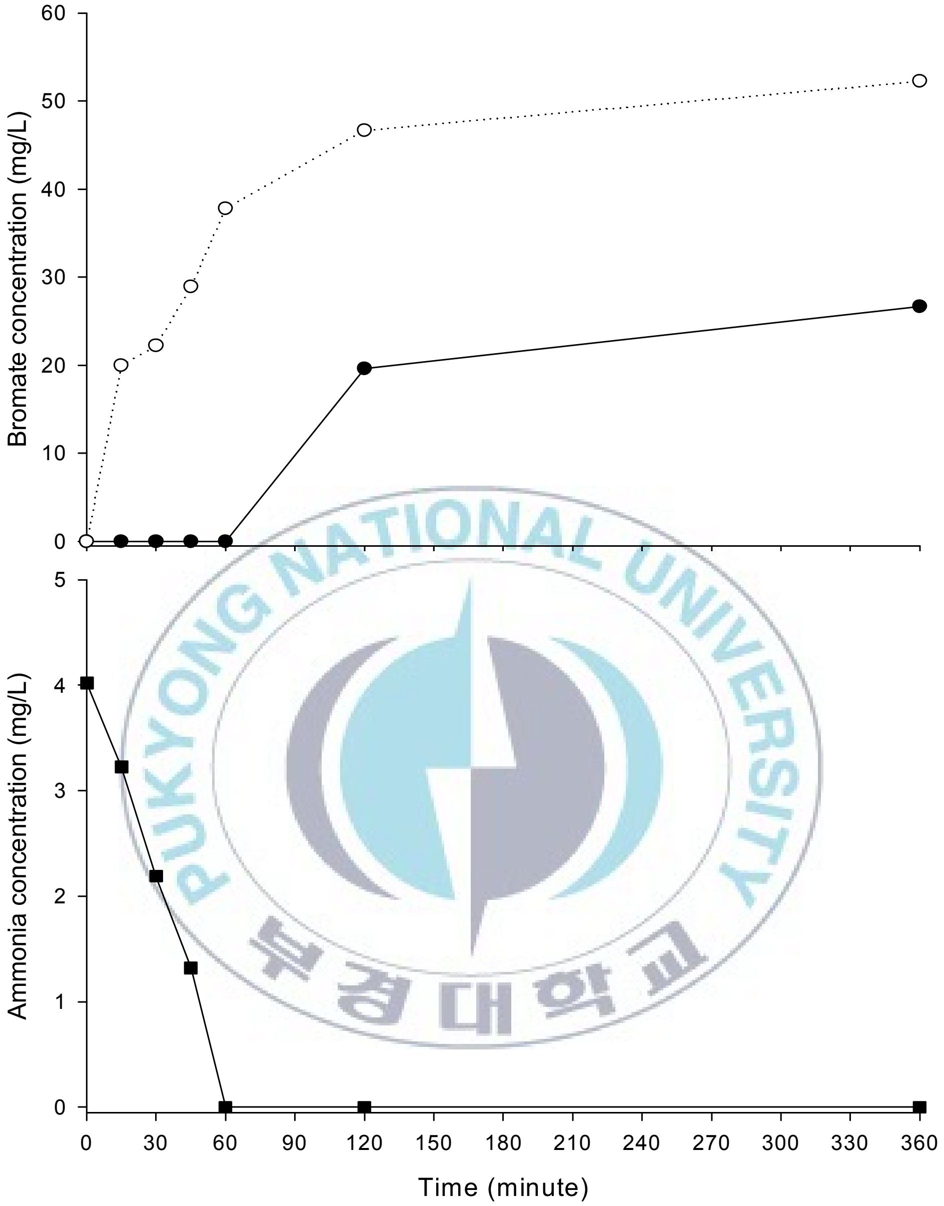

Figure 5. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 4 mg/L ammonia treated group and non-treated (control) (···○···).

When 5 mg/L of ammonia was treated, actual concentration of ammonia was 5.00 mg/L. After 75 minutes of ozonation, ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate in the control increased up to 37.8 mg/L (Table 5; Figure 6). After 120 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 12.6 mg/L while that in the control was 43.3 mg/L. Bromate was increased up to 20.7 mg/L at 360 minutes in the treatment group, while in the control was increased up to 50.0 mg/L.

Table 5. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 5 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	5.00 ± 0.02	0	0
15	4.08 ± 0.01	0	16.7
30	3.02 ± 0.04	0	20.0
45	2.03 ± 0.01	0	25.6
60	1.28 ± 0.01	0	32.2
75	0	0	37.8
120	0	12.6 ± 1.69	43.3
360	0	20.7 ± 1.69	50.0

*Ozone concentration: 0.1 mg/L

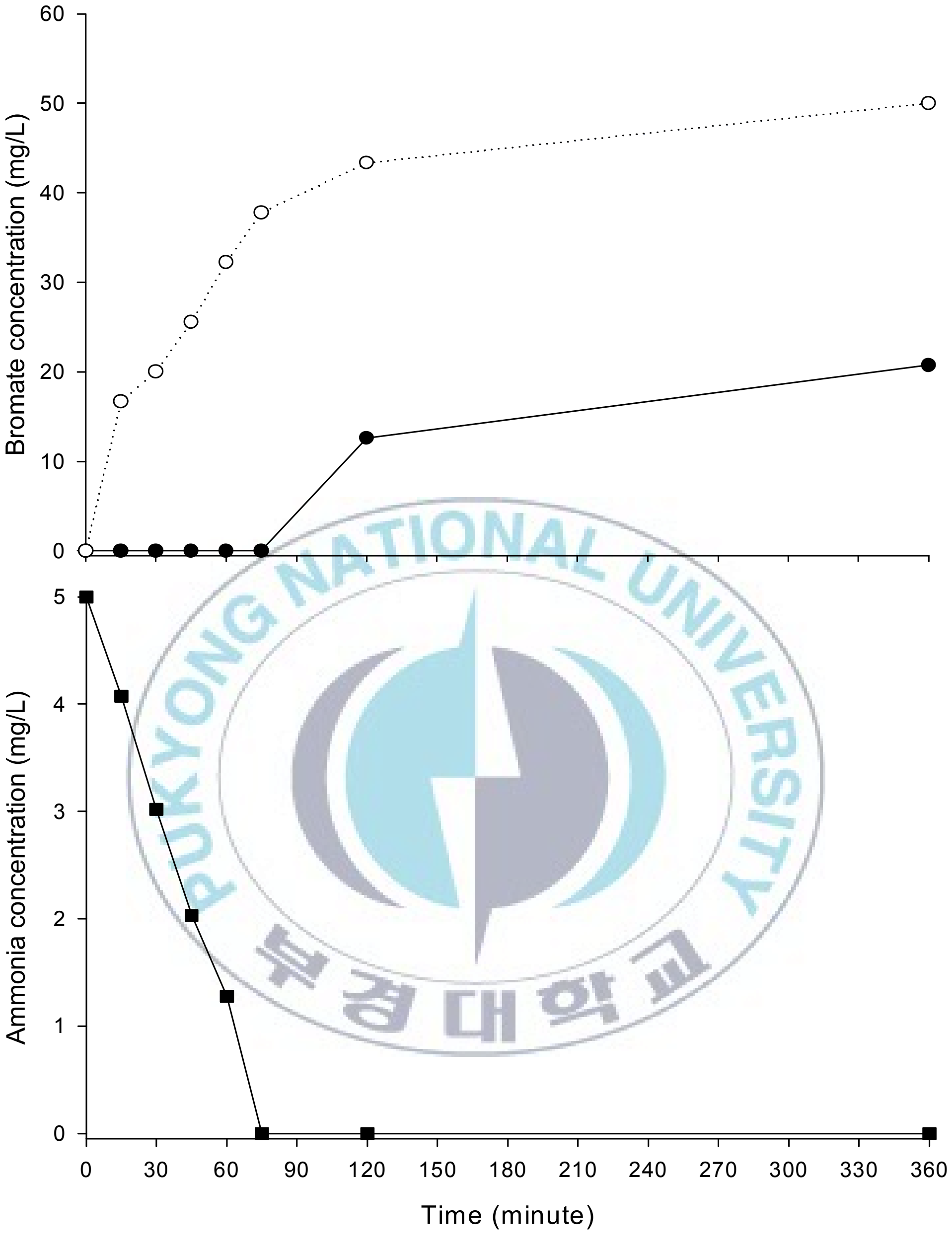

Figure 6. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 5 mg/L ammonia treated group and non-treated (control) (···○···).

Bromate formation in each control of 1, 2, 3, 4 and 5 mg/L was compared. The comparison of bromate formation in the control during ozonation is shown in Figure 7.

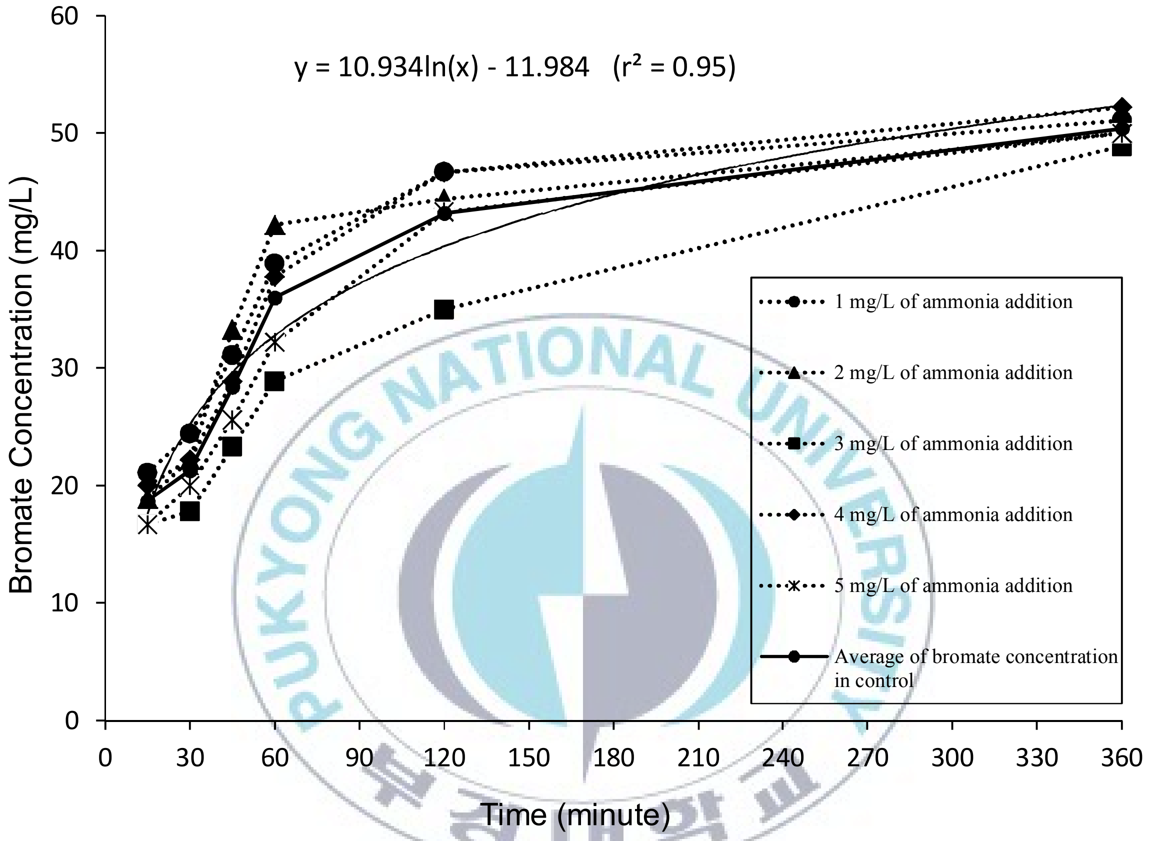

Figure 7. Comparison of bromate formation in the control during ozonation.

3.1.2. Second experiment - single application of 0.5 mg/L of ammonia

Ammonia with a concentration of 0.5 mg/L was added in this experiment. When 0.5 mg/L of ammonia was treated, actual concentration of ammonia was 0.50 mg/L. After 6 minutes of ozonation ammonia was not detected in the treatment group, and bromate was not formed yet, but bromate increased up to 6.67 mg/L in the control (Table 6; Figure 8). After 7 minutes of ozonation, bromate was formed in the treatment group, and average concentration was 0.85 mg/L while that in the control was 7.44 mg/L. Bromate was increased up to 2.56 mg/L at 10 minutes in the treatment group, while in the control was increased up to 11.11 mg/L.

Table 6. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 0.5 mg/L of ammonia and non treated (control) for 6 hours

Time (minute)	Treatment		Control
	Ammonia (mg/L)	Bromate (mg/L)	Bromate (mg/L)
0	0.50 ± 0.030	0	0
1	0.41 ± 0.006	0	1.11
2	0.31 ± 0.006	0	2.22
3	0.22 ± 0.015	0	3.89
4	0.15 ± 0.006	0	4.44
5	0.09 ± 0.006	0	5.56
6	0	0	6.67
7	0	0.85 ± 0.22	7.44
8	0	1.48 ± 0.64	8.89
9	0	1.85 ± 0.64	10.00
10	0	2.56 ± 0.22	11.11

*Ozone concentration: 0.1 mg/L

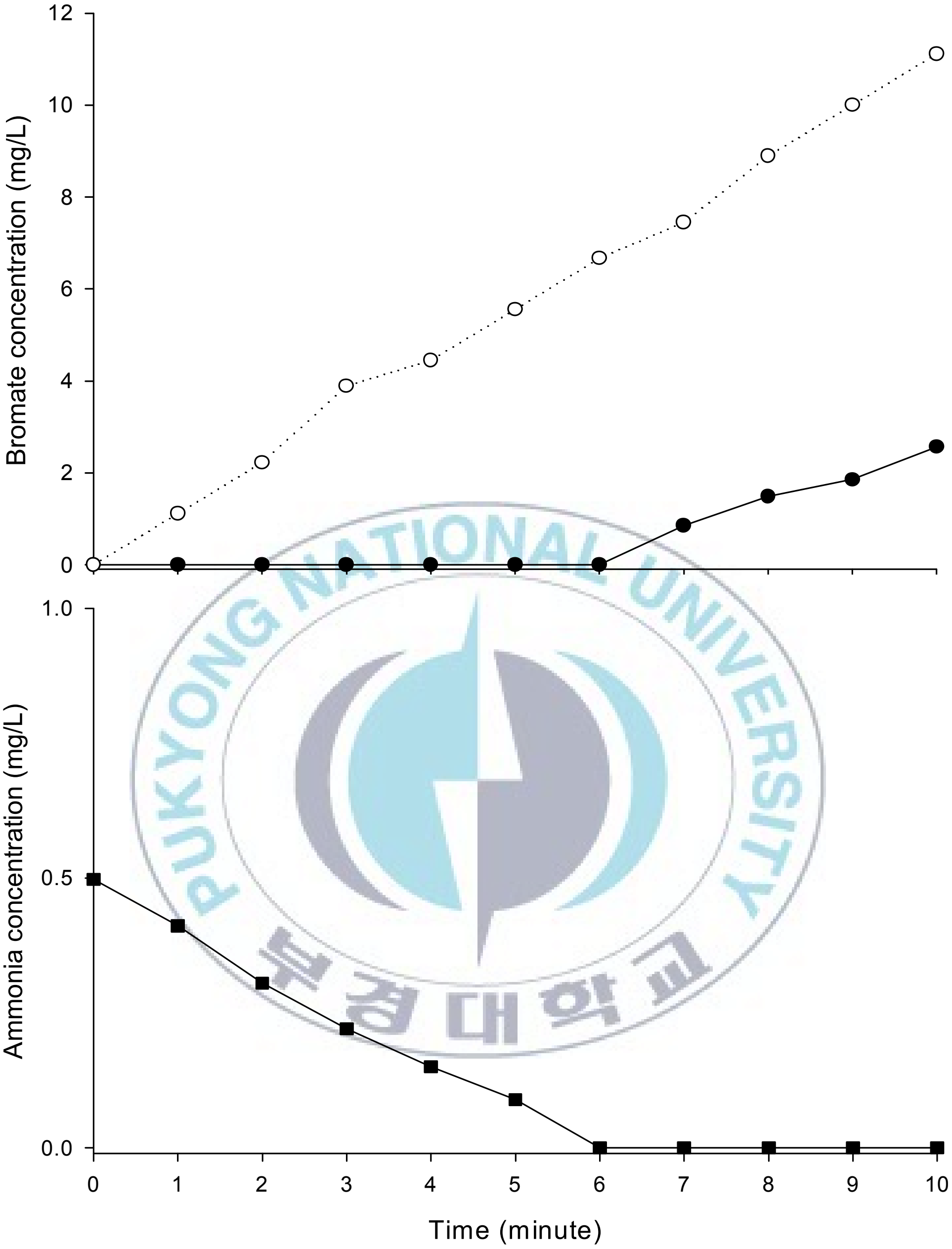

Figure 8. Changes of ammonia (···■···) and bromate concentrations (···●···) in the ozonated seawater with 0.5 mg/L ammonia treated group and non-treated (control) (···○···).

Regarding to the bromate suppression time in each experiment of single application, the linear relationship was found between ammonia concentration and bromate suppression time (Figure 9).

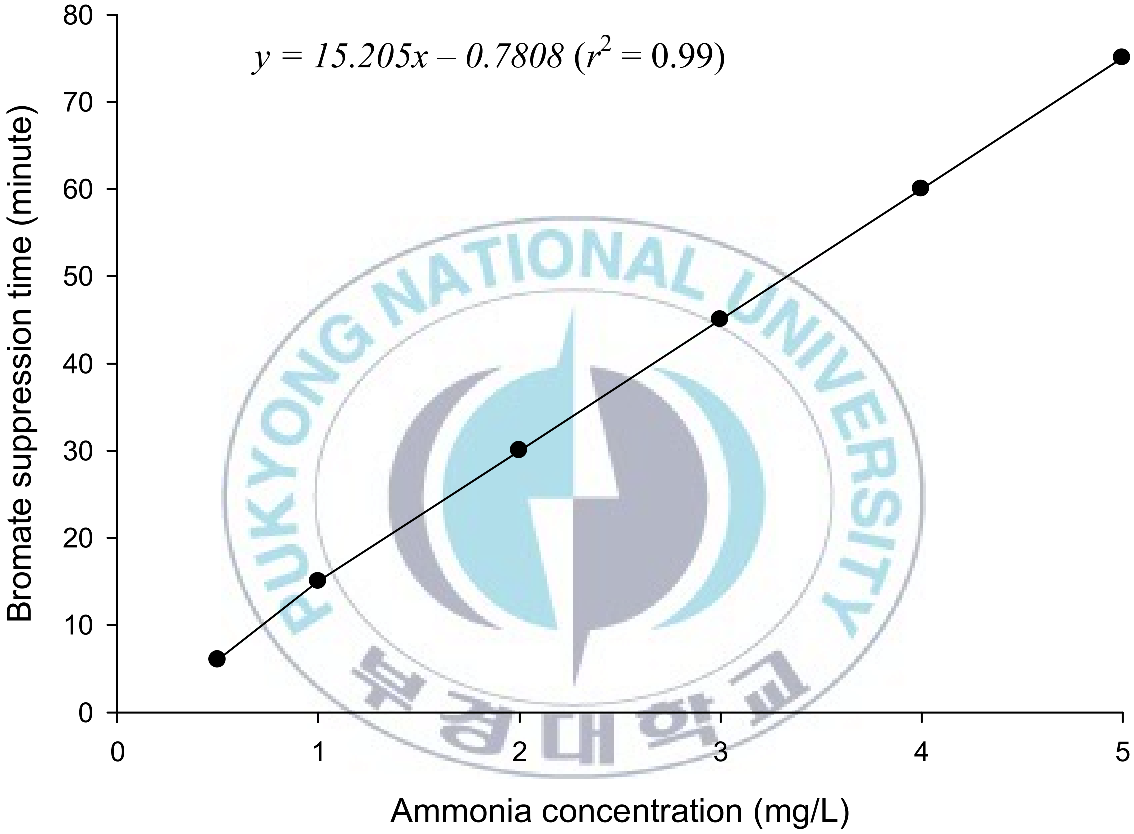

Figure 9. Relationship between ammonia concentrations and bromate suppression time.

3.1.3. Third experiment - multiple application of ammonia

Regarding to the first experiment in this experiment ammonia was added continuously every 15, 30, 45, 60 and 75 minutes for 1, 2, 3, 4 and 5 mg/L of ammonia, respectively. Ammonia concentrations were maintained from 0.93 to 1.04 mg/L when added 1 mg/L of ammonia every 15 minutes to the seawater with 0.1 mg/L of ozonation. Bromate was not detected for 120 minutes of ammonia treatment period. Changes of ammonia and bromate concentrations in the ozonated seawater treated with 1 mg/L of ammonia every 15 minutes is shown in Table 7 and Figure 10.

Table 7. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 1 mg/L of ammonia every 15 minutes for 120 minutes

Time (minute)	Ammonia (mg/L)	Bromate (mg/L)
0	1.04±0.06	0
15	1.00±0.10	0
30	0.98±0.17	0
45	1.00±0.10	0
60	1.00±0.03	0
75	0.93±0.09	0
90	1.07±0.09	0
105	0.96±0.14	0
120	1.00±0.07	0

*Ozone concentration: 0.1 mg/L

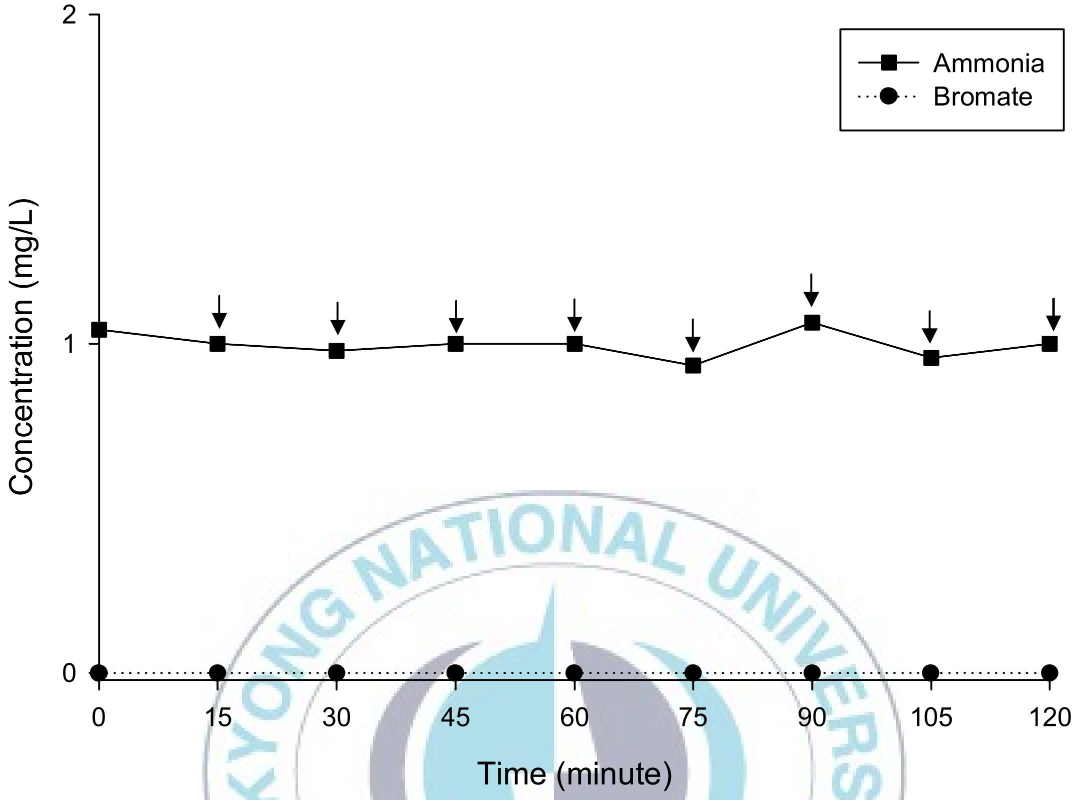

Figure 10. Changes of ammonia (–■–) and bromate (···●···) concentrations in the seawater ozonated with 0.1 mg/L of ozone and added 1 mg/L of ammonia every 15 minutes for 120 minutes. Arrows represent ammonia addition.

Ammonia concentrations were maintained from 1.99 to 2.01 mg/L just after 2 mg/L of ammonia was added every 30 minutes to the seawater with 0.1 mg/L of ozonation. Fifteen minutes after the ammonia treatments, the ammonia concentrations in the seawater were dropped around 1.13 mg/L. Bromate was not detected for 120 minutes of ammonia treatment period. Changes of ammonia and bromate concentrations in the ozonated seawater treated with 2 mg/L of ammonia every 30 minutes is shown in Table 8 and Figure 11.

Table 8. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 2 mg/L of ammonia every 30 minutes for 120 minutes

Time (minute)	Ammonia (mg/L)	Bromate (mg/L)
0	2.02±0.01	0
15	1.12±0.03	0
30	1.99±0.02	0
45	1.13±0.03	0
60	2.03±0.01	0
75	1.13±0.03	0
90	2.02±0.02	0
105	1.13±0.04	0
120	2.01±0.02	0

*Ozone concentration: 0.1 mg/L

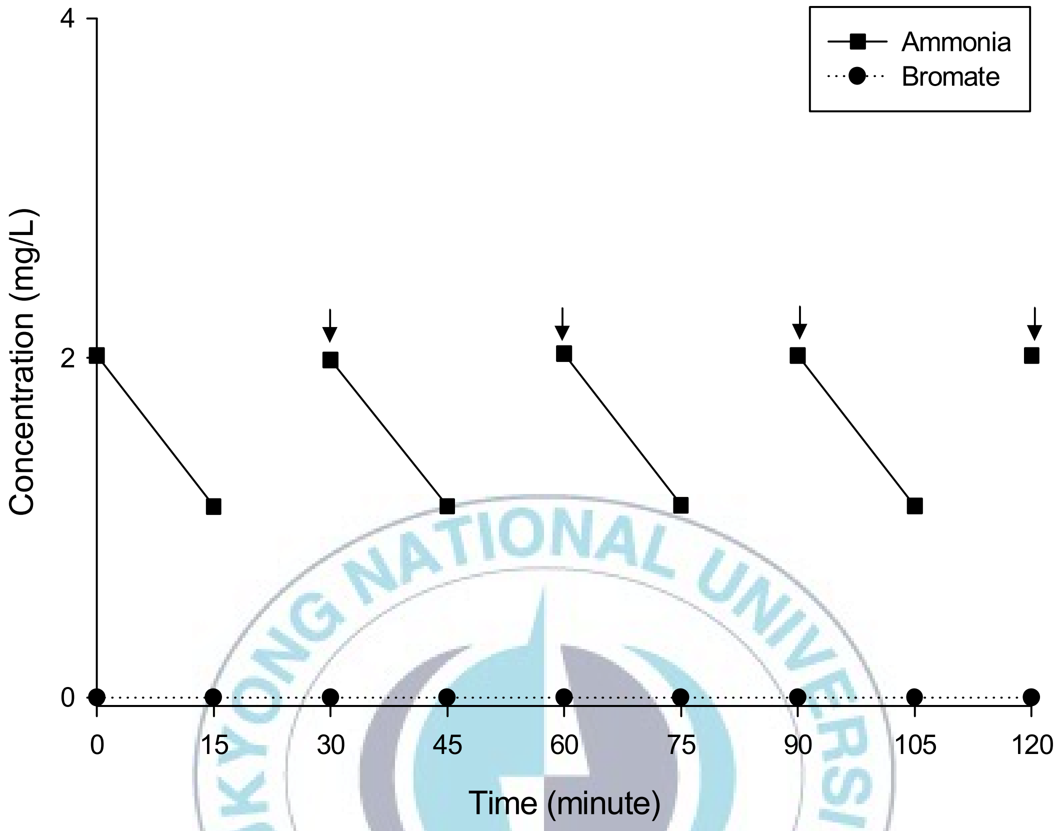

Figure 11. Changes of ammonia (–■–) and bromate (···●···) concentrations in the seawater ozonated with 0.1 mg/L of ozone and added 2 mg/L of ammonia every 30 minutes for 120 minutes. Arrows represent ammonia addition.

During the test period 3 mg/L of ammonia was added every 45 minutes in the seawater ozonated with 0.1 mg/L of ozone. Bromate was not detected during this period. Just after the ammonia added ammonia concentrations were remained from 2.98 to 3.01 mg/L. After 15 minutes, ammonia concentrations were decreased from 1.99 to 1.88 mg/L and those concentrations were further decreased up to 1.19 to 1.08 mg/L after 30 minutes. Changes of ammonia and bromate concentrations in the ozonated seawater treated with 3 mg/L of ammonia every 45 minutes is shown in Table 9 and Figure 12.

Table 9. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 3 mg/L of ammonia every 45 minutes for 120 minutes

Time (minute)	Ammonia (mg/L)	Bromate (mg/L)
0	3.05±0.01	0
15	1.99±0.03	0
30	1.19±0.14	0
45	2.98±0.02	0
60	1.88±0.08	0
75	1.08±0.05	0
90	3.01±0.04	0
105	1.91±0.04	0
120	1.14±0.04	0

*Ozone concentration: 0.1 mg/L

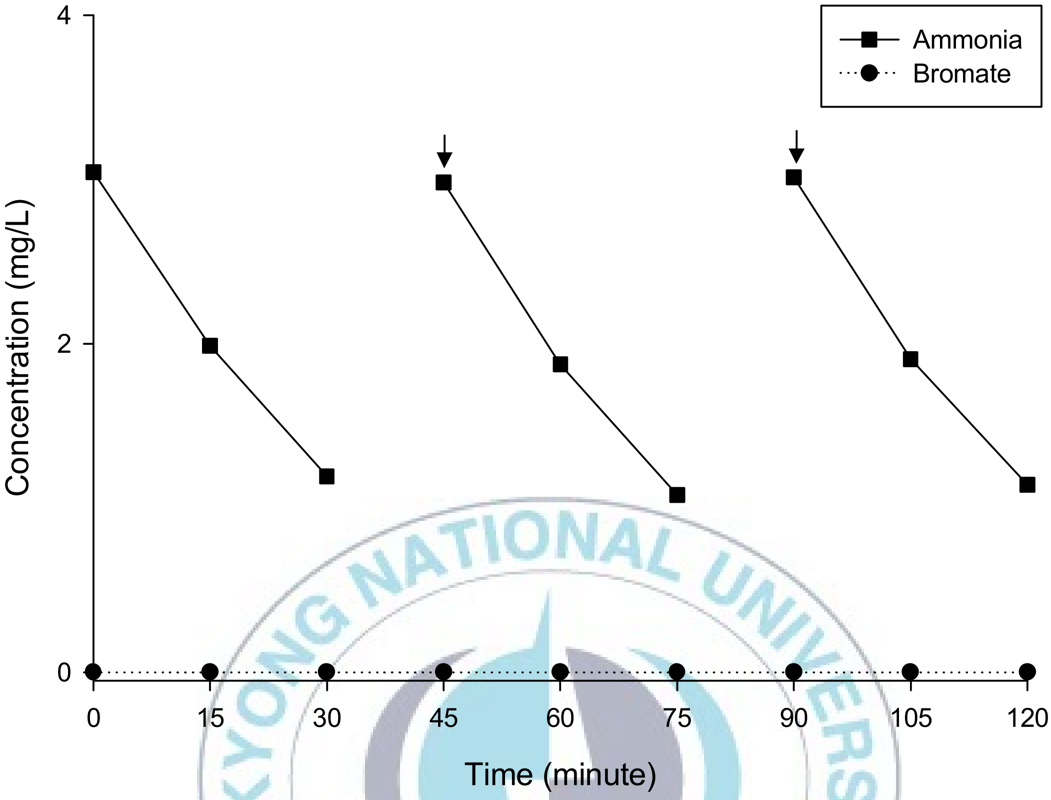

Figure 12. Changes of ammonia (–■–) and bromate (···●···) concentrations in the seawater ozonated with 0.1 mg/L of ozone and added 3 mg/L of ammonia every 45 minutes for 120 minutes. Arrows represent ammonia addition.

When 4 mg/L of ammonia was added every 60 minutes to seawater ozonated with 0.1 mg/L of ozone, the concentration decreased continuously. The concentration of ammonia dropped to 3.24 mg/L after 15 minutes and further dropped to 2.06 mg/L after 30 minutes. At 45 minutes after the first treatment, ammonia concentration was dropped until 1.22 mg/L. Bromate was not detected for 120 minutes. Changes of ammonia and bromate concentrations in the ozonated seawater treated with 4 mg/L of ammonia every 60 minutes is shown in Table 10 and Figure 13.

Table 10. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 4 mg/L of ammonia every 60 minutes for 120 minutes

Time (minute)	Ammonia (mg/L)	Bromate (mg/L)
0	4.05±0.01	0
15	3.24±0.01	0
30	2.17±0.18	0
45	1.29±0.02	0
60	4.00±0.01	0
75	3.23±0.01	0
90	2.06±0.04	0
105	1.22±0.02	0
120	4.01±0.01	0

*Ozone concentration: 0.1 mg/L

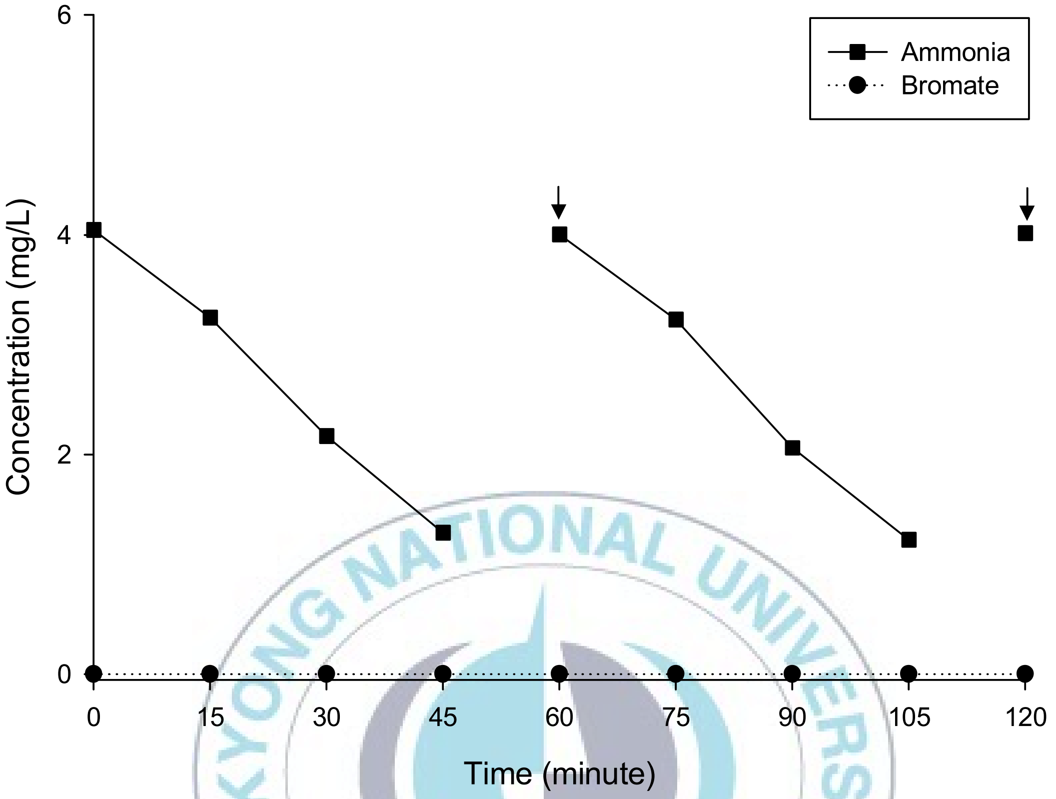

Figure 13. Changes of ammonia (–■–) and bromate (···●···) concentrations in the seawater ozonated with 0.1 mg/L of ozone and added 4 mg/L of ammonia every 60 minutes for 120 minutes. Arrows represent ammonia addition.

Bromate was not detected for 120 minutes when 5 mg/L of ammonia was added every 75 minutes. Ammonia concentration was dropped to 4.04 mg/L after 15 minutes and continuous decreased to 2.99 mg/L after 30 minutes. Ammonia concentration was further decreased to 2.02 after 120 minutes. Changes of ammonia and bromate concentrations in the ozonated seawater treated with 5 mg/L of ammonia every 75 minutes is shown in Table 11 and Figure 14.

Table 11. Changes of ammonia and bromate concentrations in the ozonated seawater* treated with 5 mg/L of ammonia every 75 minutes for 120 minutes

Time (minute)	Ammonia (mg/L)	Bromate (mg/L)
0	5.02±0.02	0
15	4.04±0.02	0
30	2.99±0.04	0
45	2.00±0.02	0
60	1.20±0.02	0
75	5.01±0.02	0
90	4.07±0.02	0
105	3.00±0.04	0
120	2.02±0.01	0

*Ozone concentration: 0.1 mg/L

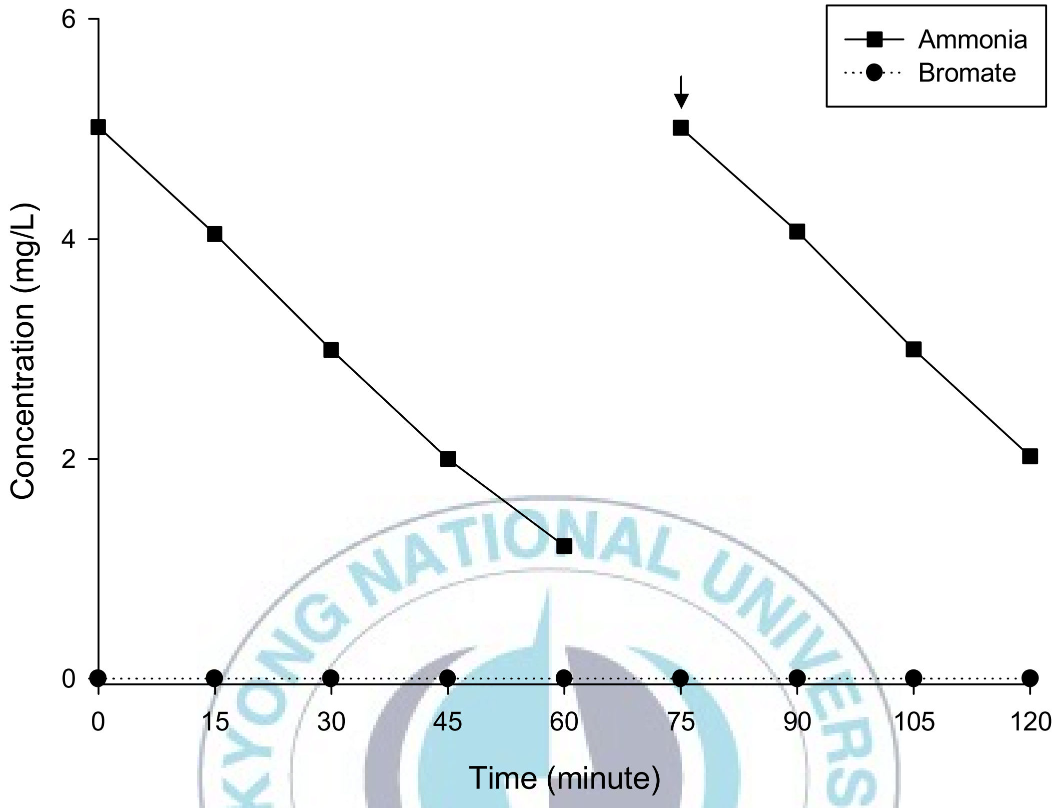

Figure 14. Changes of ammonia (–■–) and bromate (···●···) concentrations in the seawater ozonated with 0.1 mg/L of ozone and added 5 mg/L of ammonia every 75 minutes for 120 minutes. Arrow represent ammonia addition.

3.2. Nitrite oxidation by ozonation

Three concentrations of nitrite, 0.05, 0.10 and 0.15 mg/L in the seawater were treated with 0.1 mg/L of ozone for 60 minutes and the concentrations changes are shown in Table 12 and Figure 13. When 0.05 mg/L of nitrite was treated with ozone, concentration dropped continuously. The nitrite concentrations at 10, 20, 30, 40, 50 and 60 minutes were 0.045, 0.038, 0.034, 0.027, 0.015 and 0.003 mg/L, respectively. When 0.10 mg/L of nitrite was treated with ozone, the concentrations dropped until 0.049 mg/L after 60 minutes. When 0.15 mg/L of nitrite was treated with ozone, nitrite concentration was decreased to 0.107 mg/L after 60 minutes.

Table 12. Effect of 0.1 mg/L of ozonation on nitrite oxidation for 60 minutes

Time (minute)	Nitrite (mg/L)		
	0.05	0.10	0.15
0	0.050±0.002	0.107±0.015	0.151±0.003
10	0.045±0.002	0.080±0.001	0.144±0.002
20	0.038±0.001	0.073±0.002	0.139±0.001
30	0.034±0.001	0.069±0.001	0.127±0.001
40	0.027±0.001	0.061±0.001	0.118±0.001
50	0.015±0.001	0.054±0.001	0.111±0.002
60	0.003±0.001	0.049±0.001	0.107±0.004

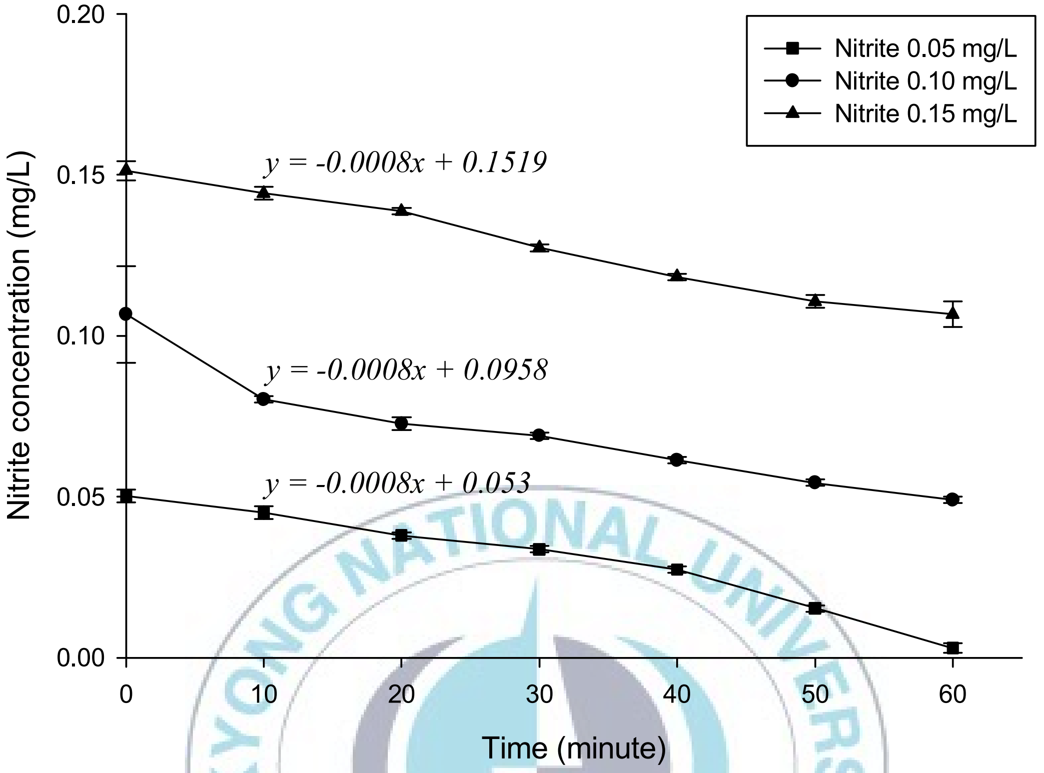

Figure 15. Trends of nitrite concentrations in the seawater treated with 0.1 mg/L of ozone.

3.3. Nitrate oxidation by ozonation

Three concentrations of nitrate, 1, 2 and 3 mg/L were treated with 0.1 mg/L of ozone in the seawater. Concentrations changes are shown in Table 13 and Figure 16. When 1 mg/L of nitrate was treated with ozone, concentration was decreased continuously and the concentrations were 1.00, 0.96, 0.88, 0.75, 0.70 and 0.63 mg/L for 10, 20, 30, 40, 50 and 60 minutes, respectively. When 2 mg/L of nitrite was treated with ozone, nitrite concentration was dropped until 1.64 mg/L after 60 minutes. When 3 mg/L of nitrite was treated with ozone, nitrite concentration was decreased to 2.65 mg/L after 30 minutes and continuously dropped to 2.57 mg/L after 60 minutes.

Table 13. Effect of 0.1 mg/L of ozonation on nitrate oxidation for 60 minutes

Time (minute)	Nitrate (mg/L)		
	1	2	3
0	1.10±0.005	2.03±0.06	3.00±0.01
10	1.00±0.01	1.83±0.06	2.85±0.015
20	0.96±0.005	1.78±0.01	2.72±0.01
30	0.88±0.01	1.71±0.005	2.65±0.005
40	0.75±0.005	1.69±0.01	2.62±0.01
50	0.70±0.005	1.66±0.005	2.59±0.01
60	0.63±0.01	1.64±0.005	2.57±0.01

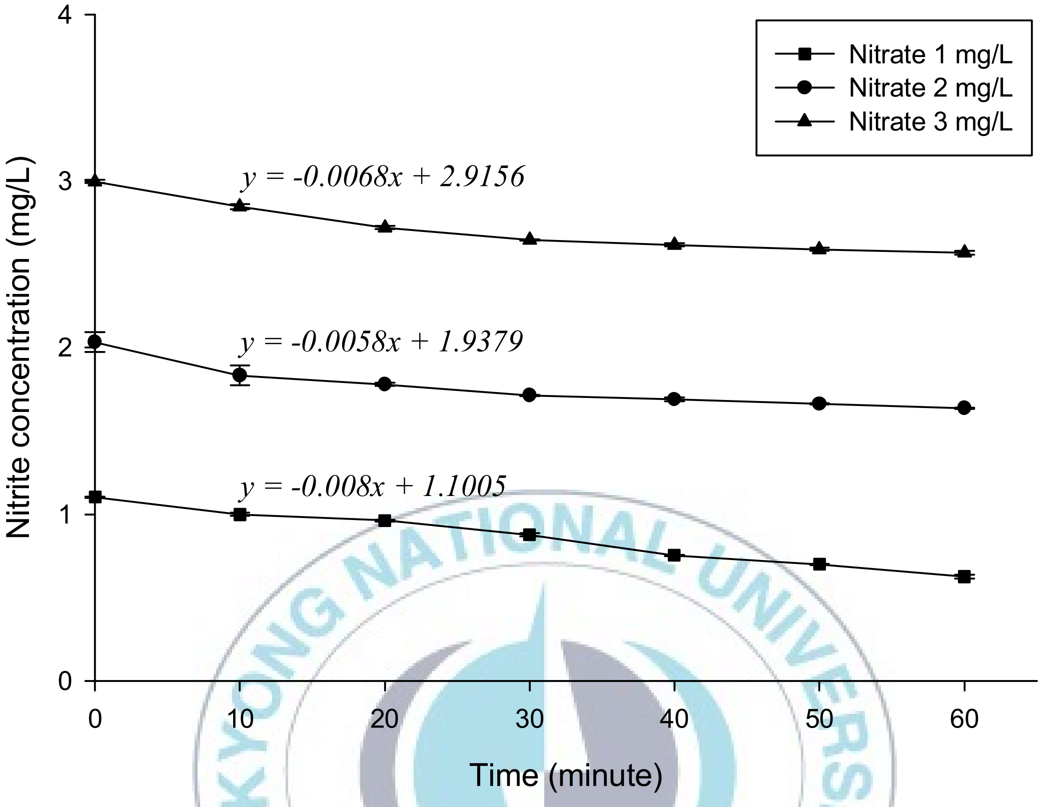

Figure 16. Trends of nitrate concentrations in the seawater treated with 0.1 mg/L of ozone.

3.4. Dissolved oxygen change during ozonation

Dissolved oxygen was increased during ozonation (Table 14 and Figure 17).

Table 14. Effect of 0.1 mg/L ozonation on dissolved oxygen for 24 hours

Time (hour)	Dissolved oxygen (mg/L)
0	7.87±0.05
1	9.40±0.10
2	12.50±0.10
3	13.17±0.11
4	13.60±0.10
5	14.17±0.06
6	14.37±0.11
7	14.47±0.06
8	14.53±0.06
9	14.60±0.00
10	14.57±0.06
11	14.60±0.00
12	14.60±0.00
13	14.60±0.00
14	14.60±0.00
15	14.60±0.10
16	14.57±0.06
17	14.60±0.00
18	14.60±0.00
19	14.57±0.06
20	14.60±0.00
21	14.60±0.00
22	14.60±0.00
23	14.60±0.00
24	14.60±0.00

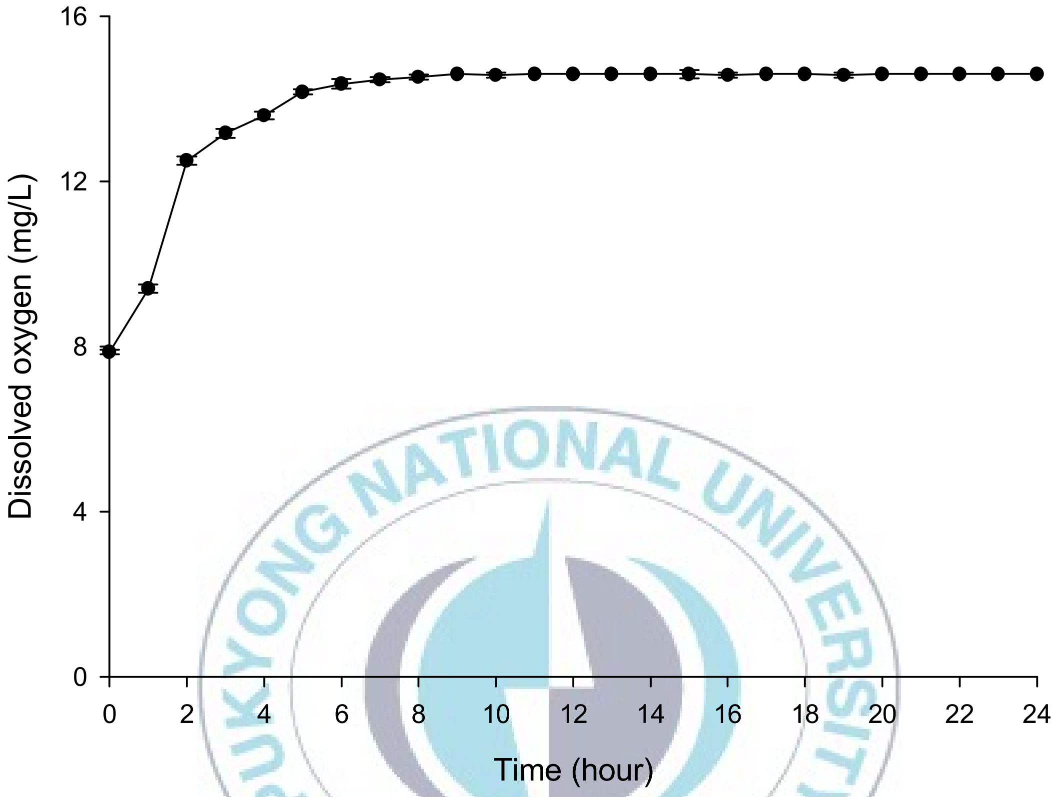

Figure 17. Increment of DO concentration during ozonation.

When 0.1 mg/L of ozone was treated in seawater, dissolved oxygen was increased from 7.87 to 9.40 mg/L within 1 hour and after 3 hours increased to 13.17 mg/L. Dissolved oxygen was continuously increased up to 14.53 mg/L after 8 hours. Started from 11 hours to 24 hours DO concentration was stabilized at 14.60 mg/L.

3.5. pH change during ozonation

During ozonation in seawater pH level was decreased (Table 15 and Figure 18). pH level was decreased from 8.20 to 8.06 within 2 hours, after 4 hours was decreased to 7.95 and continuous decreased to 7.81 after 6 hours.

Table 15. Effect of 0.1 mg/L of ozonation on pH changes for 6 hours

Time (minute)	Mean
0	8.20±0.01
60	8.18±0.02
120	8.06±0.01
180	7.98±0.01
240	7.95±0.01
300	7.86±0.01
360	7.81±0.01

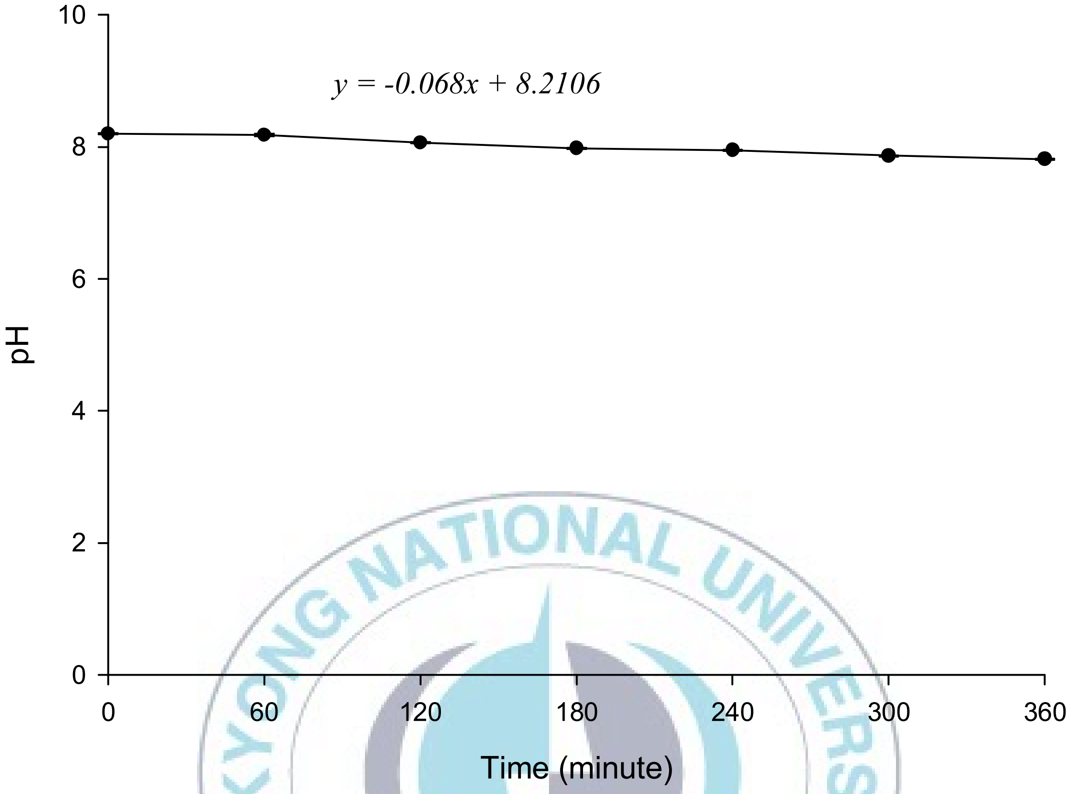

Figure 18. pH change during ozonation.

IV. DISCUSSION

4.1. Effects of Ammonia on Formation of Bromate

4.1.1. Single application of ammonia

Ammonia plays an important role in the suppression of bromate formation. Ammonia was significantly ($p < 0.05$) suppressed bromate formation in sea water ($y = 15.205x - 0.7808\ r^2=0.99$). Relationship between ammonia concentrations and bromate suppression time is shown in Figure 9.

In this experiment bromate was not detected during the presence of ammonia in seawater during ozonation (Table 1 ~ 6 and Figure 2 ~ 7), bromate formation was delayed for 6, 15, 30, 45, 60 and 75 minutes by 0.5 to 5 mg/L of ammonia addition, but once ammonia is gone in the treatment group, bromate concentration was continuously increased in seawater during ozonation. Bromate concentration in each control of 1, 2, 3, 4 and 5 mg/L ammonia addition was not significant different ($p > 0.05$) and was continuously formed from beginning at the rate of $y = 10.934\ln(x) - 11.984$ ($r^2=0.95$) on average. Comparison of bromate formation in the control during ozonation is shown in Figure 7.

Many researchers (Haag and Hoigne, 1983; Song et al., 1997; Von Gunten and Hoigne, 1994; Von Gunten and Oliveras, 1998) reported that bromate formation during ozonation of bromide-containing waters is due to three general pathways involving only molecular ozone (*direct pathway*) or both molecular ozone and hydroxyl radicals produced from ozone decomposition (*direct-indirect* and *indirect-direct pathways*). According to them, in *direct-indirect pathway*, bromide is oxidized first by ozone and form to hypobromite BrO^- (in equilibrium with hypobromous acid HOBr). BrO^- can then react with hydroxyl radicals to form BrO^o which disproportionates to bromite BrO_2^-. In the *indirect-direct pathway*, hydroxyl radicals first oxidize Br^- to form Br^o and further oxidized to BrO^o. In this process, the presence of ammonia will reacts very quickly with free bromine (HOBr/ BrO^-) to produce bromamines (monobromamine NH_2Br, dibromamine $NHBr_2$, and tribromamine NBr_3), but without the presence of ammonia it will be lead to bromate formation by *direct pathway*. It is important to note that the free bromine is required as an intermediate in bromate formation in two pathways (*direct* and *direct-indirect*) and so ammonia potentially can affect these pathways. Bromamines are then oxidized to bromide and nitrate which creates a secondary cycle for bromide regeneration (Berne et al., 2004).

Rahmadi (2010) reported that bromate concentration was increased up to 0.33 mg/L after 6 hours when 5 mg/L of ammonia was added during injection of various concentrations of ozone in seawater, while in this experiment 5 mg/L of ammonia was suppressed bromate formation up to 75 minutes, and after 6 hours bromate was formed up to 50 mg/L. Continuous ozonation experiments of bromide solution have been conducted in the presence of ammonia by Berne et al. (2004). In their experiment bromate formation was delayed by 60 to 160 minutes. The ratio between ozone and ammonia concentration was 1:56 when bromate formation delayed by 60 minutes, while in this experiment the ratio was 1:40.

4.1.2. Multiple application of ammonia

Bromate was not formed when 1, 2, 3, 4 and 5 mg/L of ammonia concentrations were added continuously in seawater during ozonation.

Bouland et al. (2004) mentioned that ammonia has a delaying effect on the formation of the bromate ions, since the ammonia reacts with the hypobromite ions to form bromamines. According to Berne et al. (2004), if ammonia is continuously present in the seawater it will react with free bromine. Therefore, a bromide regeneration cycle will occur and bromate formation is blocked as long as ammonia still present in seawater during ozonation as mentioned by Berne et al. (2004).

Hofmann (2000) also mentioned that ammonia effectiveness may also be influenced by the chemical properties of bromamines. These species are inherently unstable, and during their decay bromide is released back into the bromate formation pathway. The nitrogen, in turn, is released as nitrogen gas or nitrate, neither of which inhibits bromate formation. Thus, as bromamines decay the available ammonia decreases while bromide remains in the system. Once the ammonia is gone, bromate formation can resume provided that there is still ozone in the water.

Bromate (BrO_3^-) is an undesirable by-product formed during ozonation of bromide containing waters. This compound has been declared a potential carcinogen (Kurokawa et al., 1990).

Bromate and other brominated compounds are toxic to fish and humans and can be produced by O_3 in the presence of bromide in sea water (Amy et al., 1994; Health Canada, 1999; Hofmann, 2000). Richardson et al. (1981) studied the effects of bromate on striped bass (*Morone saxatilis*) and observed a 24-h LC_{50} of 697 mg/L of BrO_3^- concentration based on embryo hatching rates. In contrast, the newly hatched larvae were markedly more sensitive to bromated and the 96-h LC_{50} value was 31 mg/L of BrO_3^- concentration. The early life stages of fish (newly hatched larvae) appear to be more susceptible to the effects of bromate than are the subsequent pro-larval or juvenile life stages. According to Hutchinson et al. (1997) that the fish embryos are relatively insensitive to bromate, presumably due to the protective of the chorion (commonly termed the "egg membrane"). In term of marine phytoplankton species (*Glenodinium halli, Isochrysis galbana, Skeletonema costatum* and *Thalassiosira pseudonana*), Erikson and Freeman (1978) reported that the species showed median effect (lethal) of the concentration of bromate was >13.6 mg/L. Crecelius (1979) and Stewart et al. (1979) observed that lethal concentration of bromate on larval stage of pacific oyster (*Crassostrea gigas*) was 30 mg/L and that on eastern oyster (*Crassostrea virginica*) was 0.05 – 0.1 mg/L.

Ozone is a strong oxidizing agent and has been used in water treatment for disinfection and decomposition of organic matter. During ozone treatment of fresh water, ammonia is converted to nitrate but the rate of this reaction is very slow and cannot be expected to remove ammonia effectively (Singer and Zilli, 1975; Haag et al., 1984). Furthermore, the nitrate concentration resulting from oxidation of ammonia by ozone would reach toxic levels beyond the tolerable limit for supporting aquatic life (Kobayashi et al., 1993; Lin and Wu, 1996). Therefore, ozone treatment of fresh water cannot be considered as a suitable method for nitrogen removal. In seawater, however, oxidation of ammonia by ozone would be different from that in fresh water due to the presence of chloride and bromide ions (Tanaka and Matsumura, 2002). During ozone treatment of water containing bromide, ammonia can be converted to nitrogen gas, during this process ammonia converted to nitrogen gas either directly by ozone or by the oxidized bromide (Kobayashi et al., 1993; Yang et al., 1997).

4.2. Nitrite oxidation by ozonation

Ozone was significantly ($p < 0.05$) oxidized nitrite during ozonation. In this experiment, average nitrite reduction rate by 0.1 mg/L of ozonation was at the rate of $y = -0.0008x + 0.1002$. According to Yang et al. (1999) during ozonation nitrite oxidized into nitrate and oxygen and the reaction is as follow: $NO_2^- + O_3 \rightarrow NO_3^- + O_2$.

Nitrite is highly toxic to aquatic animals and convert to nitrate by nitrifying bacteria (Lawson, 1995). Although nitrite is converted to nitrate quickly by ozone and nitrifying bacteria in a properly balanced biofilter, it is a problem in recirculating system because it is being created on a constant basis, so the fish are continually exposed to certain concentrations (Timmons and Ebeling, 2007).

Nitrite (NO_2-N) is the ionized form of nitrous acid (HNO_2), and it can be lethal as NH_3-N. Nitrite levels in fish ponds typically ranges from 0.5 to 5 mg/L (Boyd, 1982). Nitrite is toxic because it affects the blood hemoglobin's ability to carry oxygen. When nitrite enters the bloodstream, it oxidizes the iron in the hemoglobin molecule from the ferrous state to the ferric state. The resulting product is called methemoglobin, which has a characteristic brown color (Timmons and Ebeling, 2007). A similar condition is thought to occur with the hemocyanin in crustaceans (Colt and Armstrong, 1981; Romaire 1985). The amount of nitrite that moves into bloodstream of fish is influenced greatly by concentration of chloride in the water. High nitrite levels in aquaculture systems with low chloride levels can cause reduced feeding activities, poor feed conversions, lowered resistance to diseases and mortality (Lawson, 1995).

4.3. Nitrate oxidation by ozonation

Average reduction rate of nitrate by 0.1 mg/L ozonation in this experiment was at the rate of $y = -0.0068x + 1.9846$. Nitrate was significantly ($p < 0.05$) oxidized by 0.1 ppm of ozone concentration.

Nitrate is ultimate product of the nitrification process and can be accumulate continuously in the recirculating system. Nitrogenous matter in the recirculating system is usually ammonia, resulting from urea and solids excreted by fish. The urea is degraded in the water into ammonia and CO_2. Other sources of nitrate are the oxidation of nitrite due the presence of residual ozone as well as by nitrifying bacteria (Tango and Gagnon, 2003). Rahmadi (2010) mentioned the reduction of nitrate during ozonation in seawater maybe due to direct reaction with ozone or due to reaction with other ions that were created by ozonation.

Nitrate is usually nontoxic to aquatic animals except at very high concentrations. Nitrate toxicity may be a problem only in recirculating systems due to constant water reuse but it can be control by daily water exchanges. Nitrate is the least toxic of the inorganic nitrogen compounds. The effects of nitrite on aquatic animals are similar with nitrite and having to do with osmoregulation and oxygen transport but the concentrations at which fish are affected are much higher (Lawson, 1995). The 96-hour LC_{50} of NO_3-N to many fish and invertebrates lies between 1,000 and 3,000 mg/L (Wickins, 1976; Colt and Tchobanoglous, 1976).

4.4. Dissolved oxygen change during ozonation

During ozonation dissolved oxygen in the seawater was increased from 7.87 to 9.40 mg/L for 1 hour and reached 14.37 mg/L within 6 hours. DO concentration was stabilized at 14.60 mg/L from 11 hours to 24 hours. Ozone has seen widely used in aquaculture because it has a rapid reaction rate, produces few harmful reaction by-products in freshwater and oxygen are produced as an end-product of reaction (Timmons and Ebeling, 2007). Hofmann and Andrew (2007) mentioned that oxygen can be produced during bromide oxidation by ozone ($O_3 + Br^- \rightarrow O_2 + OBr^-$) or monobromamine oxidation by ozone ($3O_3 + NH_2Br \rightarrow 2H^+ + NO_3^- + Br^- + 3O_2$).

Dissolved oxygen and temperature control the metabolism of fish and invertebrates. Together, these two environmental variables are the dominant determinants of every fish environmental (Lawson, 1995).

Although the atmosphere contains nearly 21% of oxygen gas, oxygen only slightly soluble in the water. Thus, water contains only small amounts of dissolved oxygen available for fish respiration, but with ozonation oxygen concentration in the water can be enhanced.

4.5. pH change during ozonation

Seawater is buffered by the bicarbonate-borate system and has a relatively stable pH at 8.0 to 8.5. The optimum pH for the growth and health of most aquatic animals is in the range of 6.5 to 9.0. Exposure to extreme pH can be stressful or lethal to them (Timmons and Ebeling, 2007).

In this experiment, pH level was decreased from 8.20 to 7.81 within 6 hours. This reduction of pH level was indicated due to decrement of hydroxyl radicals in bromide cycle to formed bromate during ozonation in seawater. Hydroxyl radicals were reacted with free bromine (HOBr/ BrO^-) and produce hypobromite radicals (BrO^o), and then BrO^o oxidized by ozone to formed bromate (BrO_3^-). Hydroxyl radicals related with pH level in the water. If hydroxyl radicals are decrease, pH level also will decrease. Lin and Wu (1996) also mentioned that the pH of water containing NH_4^+ or NO_2^- will decreased during ozonation primarily because of conversion of NH_4^+ or NO_2^- to NO_3^- which is acid.

V. CONCLUSION

Ammonia was significantly (p < 0.05) suppressed bromate formation in seawater during ozonation. The linear relationship was found between ammonia concentration and the suppression time of bromate formation, bromate was not formed for 6 minutes when 0.5 mg/L ammonia was treated. When 1, 2, 3, 4, and 5 mg/L of ammonia were treated, bromate formation was suppressed for 15, 30, 45, 60 and 75 minutes, respectively. Therefore, ammonia concentrations and the time for suppress bromate in seawater during ozonation was expressed as the equation of $y = 15.205x – 0.7808$ (r^2=0.99). No bromate was formed when 1, 2, 3, 4 and 5 mg/L of ammonia were added continuously with the intervals of 15, 30, 45, 60 and 75 minutes, respectively.

Nitrite and nitrate was significantly ($p < 0.05$) oxidized by 0.1 mg/L of ozone concentration. Average reduction rate of nitrite was $y = -0.0008x + 0.1002$ and that in nitrate was $y = -0.0068x + 1.9846$, respectively.

During ozonation in seawater, dissolved oxygen was increased from 7.87 to 14.37 mg/L within 6 hours, and DO was stabilized at 14.60 mg/L from 11 hours to 24 hours. During ozonation pH was decreased from 8.20 to 7.98 within 3 hours and after 6 hours pH was decreased to 7.81.

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Finally, I would like to dedicate this thesis to my parents and my brother for their love and patience.

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