

A Case Study of Characterization of AOC Formation

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Abstract

The variation of assimilable organic carbon(AOC) concentration at each condition of ozonation was investigated using a model water and drinking water resource. AOC concentration of model raw water and drinking water resource tended to increase at low ozone dose. The maximum AOC concentration was detected when the residual ozone begin to be measured. Also, the AOC concentration increase at pH 8 compared to both pH 6 and 7 while that for pH 9 decreased rapidly. The removal characteristics of trihalomethane formation potential(THMFP) by ozonation was also investigated. Unlike the trend of AOC, the THMFP concentration never increased by ozonation but decreased even at low ozone dosage. From these results, the ozone dosage would be effective to simultaneously decrease both AOC and THMFP.

Key Words : AOC, Ozonation, Humic substance, THMFP

1. Introduction

The bacterial regrowth in drinking water distribution system has been recognized as a potential water quality problem such as deterioration of water quality, corrosion of pipes, bad tastes and odors. The bacteria adhered on the surface of pipe lines repeat the proliferation and the detachment while forming biofilms on the surface. Bacteria survived in the biofilms would exfoliate from the surface of pipes after regrowth. Some bacteria in biofilms would not be eliminated by high chlorine residual during disinfection(Christian, 2000; Jun, 2005; Escobar, 2001). Therefore, bacterial regrowth should be controlled to keep the safety of drinking water. The bacterial regrowth formation potential can be measured as assimilable organic carbon(AOC),

because the bacterial regrowth is associated with AOC(Tsai, 2004; Liu, 2002). The concentration of the AOC, however, is difficult to be controlled by conventional treatment for drinking water(Winn, Article in press). Currently, the ozonation has been applied on water treatment extensively since it could effectively kill harmful microorganisms and minimize the production of insignificant concentration of trihalomethanes (THMs) or other chlorinated disinfection by-products (DBPs)(Dick, 1995; Markku, 2002). When the water containing natural organic matter (NOM) such as humic substances is ozonized, the DBPs could be produced. Since the NOM is transferred into biodegradable carbons, the DBPs increase the concentration of the AOC helping regrowth of bacteria in the distribution system(Lars, 2001; Lsabel, 2000; Colin, 2000). It was known that ozonation might cause the increase of biofilm formation potential. It can be considered that the increase of AOC concentration by ozonation would mean: (1) the existence of AOC precursors, (2) the

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oxidation changed AOC precursors into AOC, (3) in adequate AOC precursors by treatments as such filtration and coagulation/sedimentation before oxidation. If the existence of AOC precursor is taken into consideration, it is necessary to separate not only AOC but also AOC precursors and re-evaluate the variation of AOC concentration by oxidation. The present study is aimed to assess the variation of AOC concentration by ozonation using the model raw water and drinking water resource. We also assessed the relationship between the AOC concentration and the other factors such as DOC, E260 and THMFP.

2. Materials and Methods

2.1. Model raw water

The model raw water was prepared using humic acid (Aldrich chemical company, Inc., USA). The 1 g of humic acid dried at 100°C for 4 hours was poured with 100 mL 0.1N NaOH. After stirring for 24 hours, it was diluted 1000 times with distilled water. Later, the model raw water was filtered with 0.45 µm glass fiber filters. Finally, the pH was adjusted between 7 and 8. Three liter of the model raw water was used for AOC measurement and ozonation.

2.2. Ozonation procedure

The ozonation test was carried out with ozonation system at a bench scale, which consisted of an ozone generator (ISHIMORI company, Inc., Japan), ozone reactor column (900 mm height and 100 mm in diameter) of 5 L volume. Ozone produced from pure grade oxygen was fed into the ozone contact column through a porous glass frit at the bottom of the column. Ozone gas was supplied with several ozone dosage continuously into the 3 L sample water at a flow rate of 0.6 L/min at 20±0.5°C as shown in Table 1. Since 1~2 mg/L ozone dosage is mostly employed in real water treatment system, we used ozone of higher concentration to find out the optimum

condition to measure AOCFP. The ozone concentration in the gas inlet and outlet was measured by portable gas detection kit (GASTEC, Inc., Japan). The residual ozone in the model raw water was analyzed based on the standard method for the examination of water and wastewater (Standard Methods, 20th edn).

2.3. AOC determination

The analytical method developed by van der Kooij (Tsai, 2004; Liu, 2002) was adopted in the present study. The method employe *Pseudomonas fluorescens* strain P17 and *Spirillum species* strain NOX. These two microorganisms prefer different groups of compounds. The growth of strain P17 was used to determine the concentration of aromatic and amino acids ect. In case of NOX, it was used to determine the concentration of carboxylic acids in water (Tsai, 2004; Liu, 2002). The samples were incubated at 15 ± 0.5°C and the number of colony forming units (CFU) was measured in 9 petri-dishes for each sample water after 7, 9 and 11 days. The colonies were measured with the plate count technique after 72 ± 3h incubation at 28 ± 1°C on R2A agar.

Table 1. The Conditions of the Ozonation

ITEM	Sample Water (L)	Dose (mg-O ₃ /L-air)	Reaction time (min)
Run-1			2.5
Run-2			5
Run-3			7.5
Run-4			10
Run-5	3	2	12.5
Run-6			15
Run-7			20
Run-8			25
Run-8			50

3. Results and Discussion

The ozone concentration in the model raw water decreased owing to the oxidation of organic

substances in the sample water. The residual ozone began to be detected when ozone dose was 4 mg/L. At this ozone dose condition, the residual ozone concentration was 0.7 mg/L. The residual ozone of 4.7 and 15.3 mg/L was detected when ozone dosage was increased to 10 and 20 mg/L, respectively. Based on the consumed ozone at Run 3, 4 and 5, the concentration of ozone consumed to oxidize the model raw water was considered to be about 4 mg/L. The concentration of AOC as the sum of concentrations of both AOC-P17 and AOC-NOX was measured to be 50 $\mu\text{g/L}$ in the model raw water before ozonation. The AOC concentration after ozonation tended to increase until ozone dose reached to 4 mg/L and decrease with ozone dose when it was higher than 4 mg/L as shown in Fig. 1. The AOC concentration increases a little with 1 mg/L ozone dose. In case of ozone dosage of 2 and 4 mg/L, the AOC concentration increases sharply up to 73 and 86 $\mu\text{g/L}$, respectively. The maximum AOC concentration was especially obtained when the ozone dosage was 4 mg/L. The AOC-NOX concentration at this ozone dosage was 50.6 $\mu\text{g/L}$ which was 2.5 times as high as that in the model raw water. The figure shows that the variance of AOC concentration is affected more

by AOC-NOX than by AOC-P17. The AOC-NOX shows higher variation than AOC-P17. When the ozone was dosed up to 10 and 20 mg/L, both AOC-P17 and AOC-NOX decrease rapidly and the concentration of AOC at these ozone dosages was lower than that of the model raw water. It was considered that the humic acids are converted into biodegradable substances such as AOC-NOX at low ozone dosage and it is totally decomposed by subsequent high ozone dosage. We confirmed that the suitable ozone dose to measure the AOCFP was about 4 mg/L and this condition could be known by the time when residual ozone began to be detected.

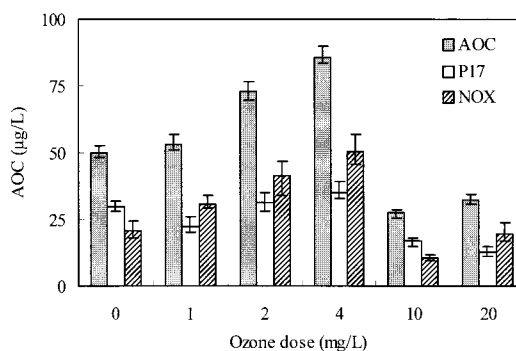


Fig. 1. The variation of AOC concentration by ozonation.

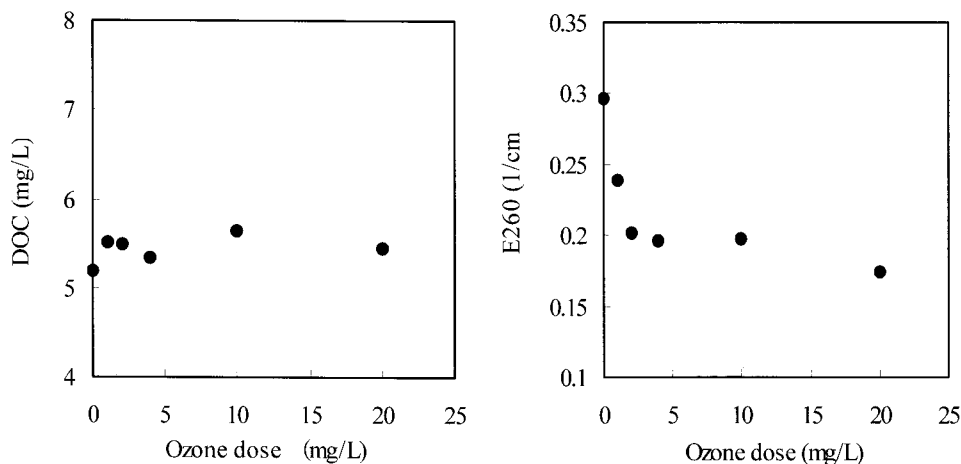


Fig. 2. The variation of DOC and E260 after ozonation.

Before ozonation, the concentration of DOC and UV absorbance at 260 nm (E260) of the model raw water was 5.2 mg/L and 0.3(1/cm) respectively. The variance of DOC and E260 with ozone dose are shown in Fig. 2. The concentration of DOC did not change with ozone dosage. The average concentration after ozonation was about 5.5 mg/L. In contrast with DOC, E260 decreased rapidly at even low ozone dosage rates of 1 and 2 mg/L. This phenomena suggested that the low molecular substances which could not be detected with UV260 increase by ozonation. In spite of little change of E260 at 5 and 10 mg/l ozone dose, E260 decreased at the ozone dosage of 20 mg/L. From these results, it was found that the variations of DOC concentration and E260 after ozonation dose not have significant relationships with AOC variation. On the other hand, the THMFP concentration after ozonation has a tendency to decrease as shown in Fig. 3. Especially when ozone dose was 2 mg/L, the THMFP decreased rapidly from 35 $\mu\text{g/L}$ to 15 $\mu\text{g/L}$. When the ozone dosage was 4 and 10 mg/L, however, there is no reduction of THMFP concentration. Moreover, at 20 mg/L ozone dose, the THMFP concentration decreases to about 6 $\mu\text{g/L}$ which means 83% reduction of THMFP in model raw water. Also to assess the AOC in drinking water resource, we performed

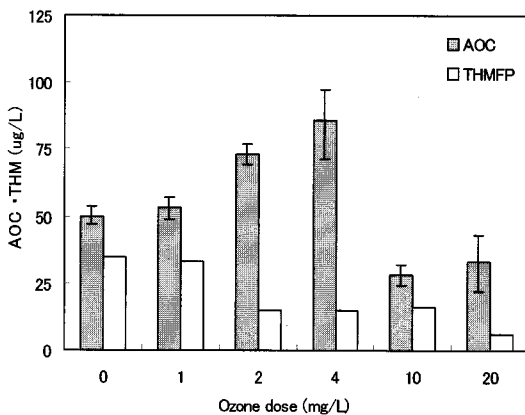


Fig. 3. The variations of AOC, THMFP after ozonation.

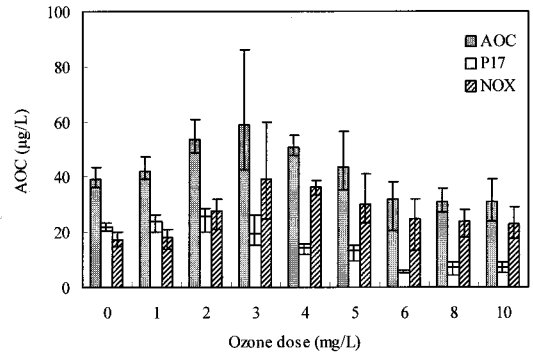


Fig. 4. The variation of AOC concentration at each ozone dose.

ozonation under different ozone dose. The ozone dose changed to 8 steps from 0 to 10 mg/L. The results are shown in Fig.4. The AOC concentration of raw water was about 40 $\mu\text{g/L}$. The concentration of AOC-P17 was higher compared to the AOC-NOX concentration. However, the ratio of AOC components changed with ozone dose increasing. From the 2 mg/L ozone dosage, the AOC-NOX concentration was higher than the AOC-P17 concentration in all ozone dosages.

Although the AOC-NOX and AOC-P17 concentration increased when the ozone dosage was 1 and 2 mg/L, the concentration of AOC-P17 began to decrease when the ozone dose was 3 mg/L. However, the maximum AOC concentration was analyzed at this ozone dosage. Later on AOC concentration decreased with ozone dose increasing. The AOC-NOX concentration also decreased with the AOC-P17 decreasing. From 6 mg/L ozone dose, the AOC concentration was almost unchanged. That concentration of AOC decreased rather than the raw water that was not ozonated. Although the AOC-P17 concentration decreased more compared to the concentration of raw water, the AOC-NOX concentration was higher than the concentration of raw water. The residual ozone was not detected at the 1 and 2 mg/L ozone dose. At 3 mg/L of ozone dosage, the residual ozone began to be detected, and was about 0.1 mg/L. The residual ozone

began to have increased gradually after 3 mg/L of ozone dosage, and when the ozone dose was 8 and 10 mg/L, the residual ozone concentration was about 3.2 mg/L, respectively. The same result with the variation of AOC concentration where the model raw water included the humic substances, it can be said that the AOC concentration by ozonation is related to the residual ozone concentration. Although the AOC concentration increased at the low ozone dosage when the residual ozone began to be detected, the AOC concentration decreased with increase of residual ozone. The variance of DOC and UV absorbance at 260 nm(E260) with ozone dose increasing are shown in Fig.5. The concentration of DOC and E260 of the raw water before ozonation was 1.63 mg/L and 0.09(1/cm), respectively. The concentration of DOC decreased just a little when the ozone dose was 8, 10 mg/L. However, at that ozone dosage, the reduction of DOC was only 0.3 mg/L compared with the raw water. The average concentration after ozonation was about 1.5 mg/L.

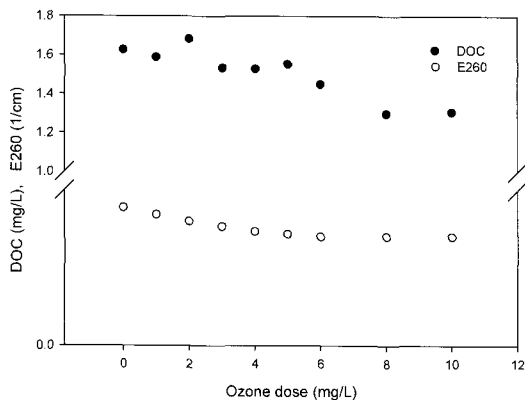


Fig.5. The variation of DOC and E260 after ozonation.

In case of E260, it also decreased gradually at even low ozone dosage rates. However, from 6mg/L of ozone dosage, E260 did not change. This result suggested that the low molecular substances which could not be detected by UV260, increase by ozonation

and it means that unsaturated compounds increased. It was also found that the variations of DOC concentration and E260 after ozonation dose not have significant relationships with the variation of AOC concentration. We also carried out ozonation while changing pH (from 6 to 9) in raw water in order to assess AOC concentration according to an amount of hydroxyl radicals ($\cdot\text{OH}$) generated by self-decomposition of ozone. From the former experiment under pH 7, it was confirmed that the AOC concentration rapidly increased when the 2 or 3 mg/L of ozone was dozed. The amounts of ozone were therefore employed in this experiment. The AOC concentration according to pH is presented in Fig. 6. The residual ozone was detected at 3 mg/L, same as the result of the previous experiment. The AOC concentration according to pH varies in the same way regardless of the amount of ozone dosage. The AOC concentration for 3 mg/L was higher than that for 2 mg/L with the exception of pH 9. The AOC concentration would not change for the raw water from pH 6 to pH 7. The AOC concentration by the direct reaction of ozone in an acid solution could be estimated by an amount of ozone dosage regardless of pH. On the other hand, the AOC concentration is sensitive to pH in the alkali solution. The AOC concentration for pH 8 than pH 7 increased while that for pH 9 decreased rapidly. Namely,

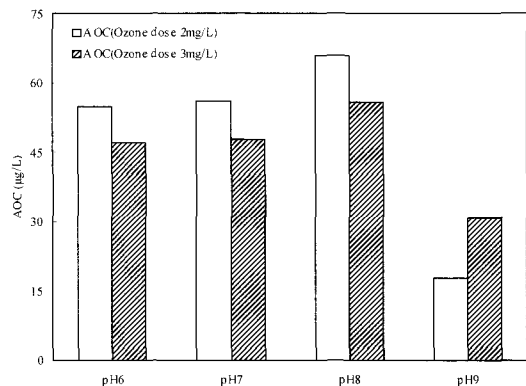


Fig. 6. The variation of AOC concentration at each pH.

the maximum AOC concentration was detected at pH 8. Therefore, the pH would have considerable influence on the variation of AOC concentration related to the organic substances decomposed by OH radicals, the intermediate of the self-decomposition of ozone in the alkali solution. Although the more organic substance could be decomposed, the AOC concentration would not increase when OH radicals increased with higher pH.

4. Conclusions

We performed a series of experiments in which the model raw water containing humic substances was ozonized with different ozone dosage to estimate AOCFP. And the removal characteristics of AOC and THMFP by ozonation were investigated. AOC concentration increased with ozone dosage until residual ozone is detected. The maximum AOC concentration was obtained at 4mg/L ozone dose, which was the condition that the residual ozone began to be detected. Thus, the time when residual ozone begin to be detected could be considered as the suitable condition to measure AOCFP. It was also found that the increase of AOC concentration by ozonation was mainly due to the AOC-NOX generated as by-products of ozonation. And there was no significant relationship between the AOC and DOC or E260. Unlike the AOC concentration, the THMFP concentration had a tendency to decrease rapidly at low ozone dose (1, 2 mg/L). Since AOC decreased with subsequent high ozone dosage, over ozonation will be effective to reduce simultaneously the AOC and the THMFP. Since the humic substances are the representative organic substances to increase concentration of AOC, the results of this study could be expanded into general raw water samples from water source. From these results, the residual ozone concentration will be a useful factor to determine a suitable condition to measure the

AOCFP and to control simultaneously both AOC and THMFP.

Acknowledgements

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