Characteristic Study of Assimilable Organic Carbon (AOC) Formation Potential in Drinking Water

[1]JI HOON KIM*, [1]YOUNG JU KIM, [1]DAE SUNG LEE AND [2]TAHIR IMRAN QURESHI
[1]*Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, South Korea.*
[2]*Department of Chemical Engineering, NFC-Institute of Engineering and Technological Training, Multan, Pakistan.*

(Received on 24th October 2009, accepted in revised form 23rd January 2010)

Summary: Characteristic study of assimilable organic carbon formation potential (AOCFP) at different reaction conditions of ozonation using model raw water containing humic substances and natural source drinking water was conducted. At low ozone dosage, assimilable organic carbon (AOC) concentration tended to increase. Maximum AOC concentration was determined when the residual ozone started to be measured. Therefore, ozone dosage required at maximum AOC concentration was found suitable to measure AOCFP in sample water. No significant relationship between dissolved organic carbon and respective ozone dosages was established. Variations in pH conditions found to have great influence on the development of AOC in sample water. Highest AOC concentration was estimated at pH 8 and a significant reduction in AOC concentration was observed as the system moved towards higher basic conditions, i.e., from pH 8 to pH 9.

Introduction

Bacterial regrowth potential in drinking water has been acknowledged as leading cause in deteriorating water quality due to corrosion in pipes, change in water color, generation of bad taste and odour and increased turbidity as well. Heterotrophic bacteria in water are adhered on the surface of the pipes in distribution system and develop in the form of microorganism film. Over the time, proliferation and detachment of bacterial film in water distribution system continues making water quality low. Unfortunately, some bacteria in biofilm are not eliminated even by high chlorine residual [1]. Moreover, pathogenic bacteria such as *Klebsiella spp.* and *Enterobacter spp.* in biofilm offer more resistance to free chlorine in comparison to single bacteria in water [2]. This is because the pathogen is apt to form biofilm more easily than single bacteria. Bacterial regrowth should be controlled to secure drinking water quality.

Bacterial regrowth formation potential can be measured as the amount of AOC that helps regrowth of bacteria in distribution system [3]. VanDer Kooij [4] recommended that AOC should be less than 10 μg/L to limit growth of heterotrophic plate counts (HPCs) bacteria in unchlorinated water. Concentration of AOC, however, seems difficult to control by conventional drinking water treatment techniques [5-8]. Currently, ozonation has been applied extensively in water treatment because it can effectively kill harmful microorganisms and minimize production of insignificant concentration of trihalomethanes (THMs) and chlorinated disinfection by-products (DBPs) [9-10].

Ozonation can be performed by direct ozone reactions or through radical chain mechanism as the indirect ozone reaction depends on reaction conditions such as pH. The ozone consumption rate in the presence of aquatic humic substances could depend on pH values and the existence of radical scavengers [11-13]. Hydroxide ions catalyze decomposition of ozone to yield highly reactive and non-selective hydroxyl radicals, which have higher oxidation potential than ozone. When water containing natural organic matter (NOM), such as humic substances, is ozonized, the NOM is transformed into biodegradable carbons as DBPs [14-15]. The produced biodegradable carbons mean an increase in AOC concentration and biofilm forming potential. Organic matter changed into AOC by oxidation of ozone could not completely be removed despite water treatment operations such as filtration, coagulation/sedimentation. In present study, those organic matters were named as AOC precursors. Therefore, evaluation of both AOC and AOC precursors should be considered. It is also required to reappraise variation in AOC concentration by

*To whom all correspondence should be addressed.

oxidation of ozone. The difference between AOC precursors and AOC before ozonation should be distinguished. However, it seems difficult to identify all kinds of AOC precursors. Therefore, present study confirmed when all AOC precursors would change into AOC by finding maximum concentration of AOC through ozonation under different conditions.

Objectives of this study were to find out optimum conditions to measure assimilable organic carbon forming potential. Water samples of model raw water containing humic substances and source drinking water were investigated. AOC concentrations with varying ozone dosage for respective water samples were measured. Also relationship between AOC and other factors such as residual ozone, dissolved organic carbon (DOC), UV absorbance at 260 nm (E260), trihalomethane formation potential (THMFP) were examined. Especially, variation of AOC with respect to pH for source drinking water was addressed.

Results and Discussion

Ozonation of Model Raw Water (MRW)

Samples of model raw water were dosed at different ozone concentration (1.0 – 20 mg O_3/L-water). Fig. 1 shows concentration of AOC (P17, NOX) at respective ozone dosage. Initial AOC concentration in the sample water was about 50 µg/L. AOC concentration increased as ozone dosage increased up to 4 mg/L and then rapidly decreased. Maximum AOC concentration observed at 4 mg/L of ozone dosage was 85.5 µg/L. It is about 1.7 times higher than the initial concentration. At this dosage, AOC-NOX concentration was 50.6 µg/L, 2.5 times higher than the initial concentration. AOC concentration was primarily increased due to AOC-NOX concentration than AOC-P17. Moreover, AOC-NOX showed wider fluctuation than AOC-P17. At low ozone dosage, humic substances in the model raw water might be transformed into biodegradable substances expressed mainly as AOC-NOX. In other words, some AOC precursors could be changed into AOC. On the other hand, high ozone dosage may hinder AOC precursors to be changed into AOC subsequently AOC concentration decreased sharply. Therefore, suitable ozone dosage to measure AOCFP was determined as 4 mg/L.

Increase of AOC at lower dosage of ozone was also discussed by Miltner *et al.*, [16]. While working on the control of AOC through ozonation they revealed that the rise in AOC of ozonated source water might be due to the result of minor increase in AOC-P17 and AOC-NOX, to the point at which the ratio of O_3/TOC is two. On the other hand, decrease in AOC at high dosage of ozone could be explained on two reasons. Firstly, the large dosages of ozone may react with organic matter in source water to form some inhibitors that further suppress the growth of AOC. Secondly, more biodegradable organic matter may have been transformed into CO_2 when more ozone was applied.

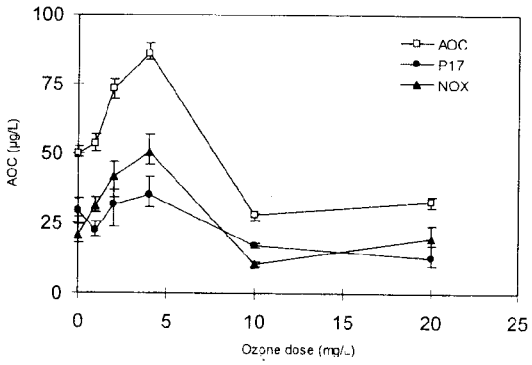


Fig. 1: Profile of MRW-AOC concentration with respect to ozone dosage.

Residual ozone in sample water indicates that no more organic substances can be decomposed by ozonation. Variations in residual ozone concentration for model raw water are presented in Fig. 2. Residual ozone of 0.7 mg/L began to be detected at 4 mg/L of ozone dosage. Ozone dosages of 10 and 20 mg/L led to the residual ozone of 4.7 and 15.3 mg/L, respectively. After the threshold of ozone dosage of about 4 mg/L, the residual ozone increased with dosage. The ozone concentration 4 mg/L consumed to oxidize organic matter in model raw water corresponds to the suitable ozone dosage to measure AOCFP.

Variations in concentration of DOC and E260 (UV absorbance at 260 nm) in model raw water with respect to ozone dosage are shown in Fig. 3 (a & b). Their initial concentrations were 5.2 mg/L and 0.3 (L/mole.cm), respectively. DOC concentration did not show any significant change with ozone dosage. Average DOC concentration after ozonation was recorded at 5.5 mg/L. Unlike DOC, E260 decreased rapidly even at a low dosage of ozone of 1 to 2 mg/L. E260 remained more or less same at 5 to 10 mg/L of

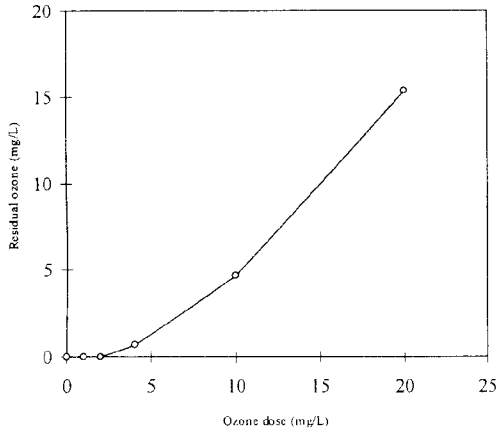


Fig. 2: Profile of MRW residual ozone with respect to ozone dosage.

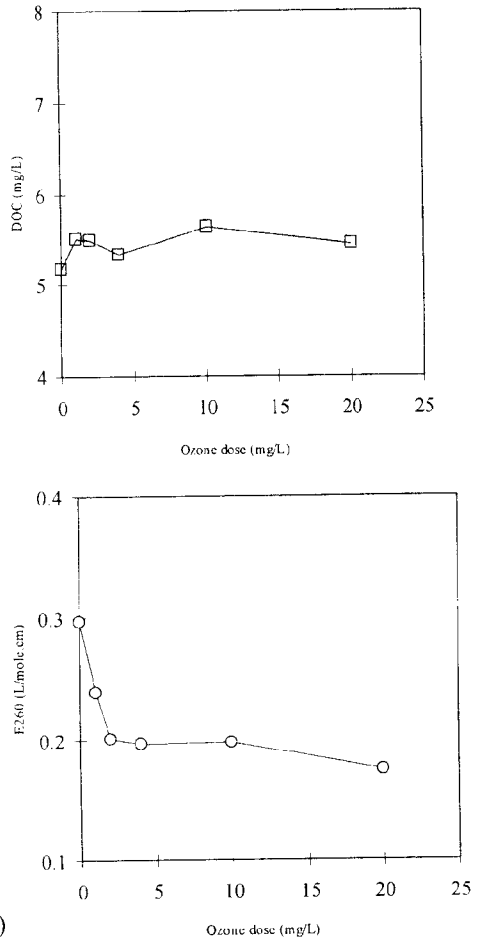


Fig. 3: Profile of DOC and E260 concentration in MRW with respect to ozone dosage.

ozone dosage and decreased again at 20 mg/L of ozone dosage. This phenomenon suggested that the unsaturated compounds measured at UV 260 nm did not increase by ozonation. Fig. 3 (a & b) did not determine any significant relationship between AOC and DOC or E260.

In model raw water sample, THMFP with respect to ozone dosage was also measured (Fig. 4). Before ozonation, sample was chlorinated at a dose of chlorine 2 mg/L and THMFP was tested at 0 mg/L ozone dose. THMFP decreased rapidly from 35 μg/L to 15 μg/L at ozone dosage of 2 mg/L. However, no reduction in THMFP was observed at ozone dosage between 4 to 10 mg/L. At the rate of ozone dosage of 20 mg/L, THMFP decreased to about 6 μg/L, i.e., 83 % reduction of THMFP in water sample. Application of free chlorine as pre-oxidant and to provide a disinfection residual could increase AOC concentration. However, it could also effectively control microbial growth in the drinking water supply system. Gagnon *et. al.*, [17.] investigated that if free chlorine residuals are below a critical amount C_{crit}, then the level of biodegradable organic matter significantly affect distribution system microbial growth. At residual level greater than C_{crit}, biodegradable organic matter did not promote bacterial growth.

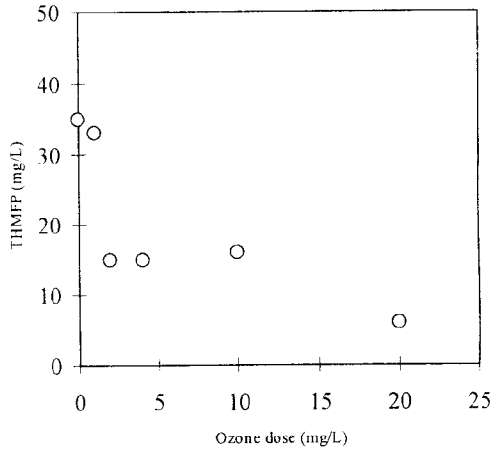


Fig. 4: Profile of THMFP in MRW with respect to ozone dosage at chlorine dose 2 mg/L.

Ozonation of Source Drinking Water (SDW)

Source drinking water samples were taken from a water treatment facility located at the dam and were ozonide at varying ozone dosage. Samples of

SDW showed similar trends with that of MRW while ozonating. However, the maximum AOC of about 59 µg/L in SDW was observed at 3 mg/L ozone dosage. While the maximum AOC of MRW was observed at 4 mg/L ozone dosage. The maximum AOC was about 0.5 times of the initial concentration of 39 µg/L. It was concluded that relatively lower ozone dosage was required in SDW to ascertain AOCFP since initial concentration of AOC in SDW was lower than the initial concentration of AOC in MRW. Fig. 5 showed that concentration of AOC-NOX was higher than that of AOC-P17 at higher rate of ozone dosage. Unlike MRW, the trends of AOC-P17 in SDW were not in agreement with that of AOC-NOX or AOC. Maximum concentration of AOC-NOX and AOC-P17 were observed at different rate of ozone dosage. For AOC-P17, maximum concentration was observed at 2 mg/L ozone dosage and no sharp peak of AOC-P17 was observed. After 6 mg/L of ozone dosage, both AOC-NOX and AOC-P17 were nearly at steady state condition. However, the concentration of AOC-NOX after 6 mg/L of ozone was found higher than its initial concentration while concentration of AOC-P17 after 6 mg/L of ozone dosage was found lower than its initial concentration. This might be due to more active role of AOC-NOX than AOC-P17 in AOC formation potential.

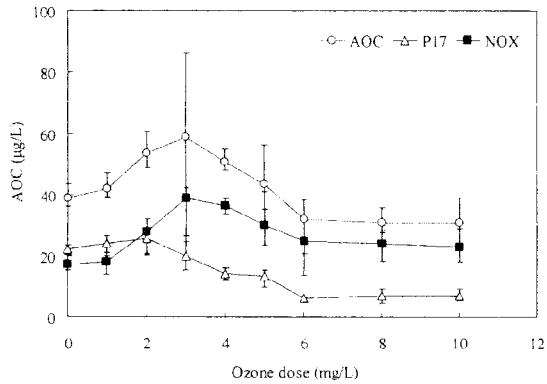


Fig. 5: Profile of SDW-AOC with respect to ozone dosage.

The similar phenomenon of increased AOC-NOX activity was observed by Lai *et. al.*, [18] while working on the effect of ozonation and filtration on AOC value of water from eutrophic lake. They revealed that most of the organic matter was effectively removed by treatment processes that included coagulation, sedimentation and filtration. Therefore, post ozonation reacted markedly with organic matter in the treated water to generated more carboxylic organic substrate that was easily used by NOX strain leading to increased AOC-NOX activity in the sample mixture.

Variations in residual ozone concentration with respect to ozone dosages were also measured for SDW (Fig. 6). Residual ozone of about 0.1 mg/L was detected at 3 mg/L of ozone dosage. As expected, residual ozone increased with ozone dosage above 3 mg/L. It became steady at 8 to 10 mg/L of ozone dosage. In similar manner like MRW, maximum AOC in SDW was detected at the ozone dosage (3 mg/L) at which the residual ozone began to be observed.

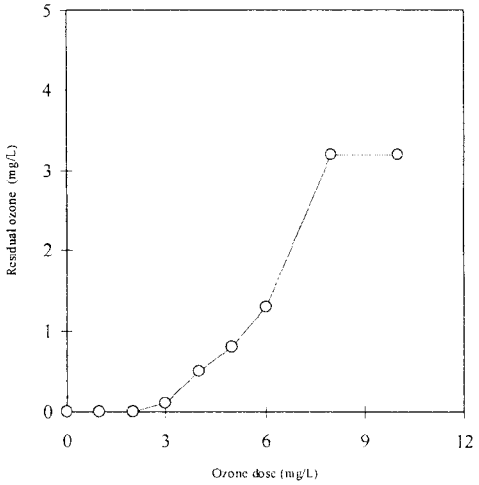
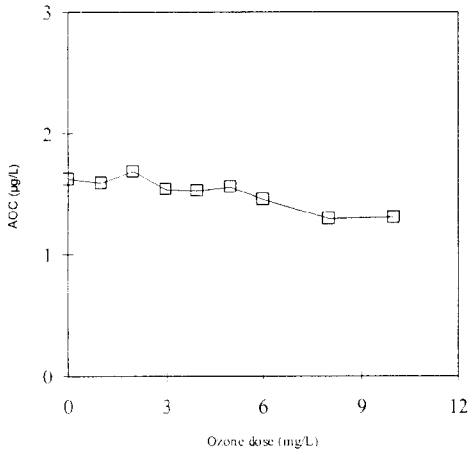
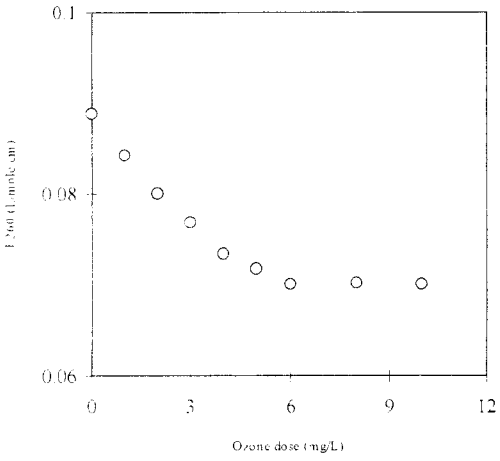


Fig. 6: Profile of SDW-residual ozone with ozone dosage.

Changes in DOC and E260 with respect to ozone dosage in SDW were also measured. Concentration of DOC and E260 were found 1.63 mg/L and 0.09 (L/mole.cm), respectively (Fig. 7 a & b). And these values were very low than the values of MRW. DOC decreased gradually with ozone dosage. Average DOC was estimated at 1.5 mg/L. E260 also decreased gradually at a lower dosage of ozone but stabilized at above 6 mg/L of ozone dosage. The reduced amount of E260 in SDW was much less than the amount reduced in MRW samples. This might be due to less amount of DOC in SDW than in MRW. From the data, no relationship between AOC and DOC or E260 could be determined for SDW.



(a)



(b)

Fig. 7: Profile of DOC and E260 in SDW with respect to ozone dosage.

Ozonation of SDW was also carried out under varying conditions of pH (pH 6 ~ pH 9) in order to assess the AOC concentration with respect to the amount of hydroxyl radicals generated by self-decomposition of ozone (Fig. 8). It was confirmed that AOC concentration increased at 3 mg/L ozone dosage in the former results at pH 7. Therefore, 3 mg/L ozone dosage was employed for this test. AOC increased with the increase of pH and maximum concentration of AOC was observed at pH 8. However, as the pH increased from 8, AOC rapidly started decreasing. Therefore, pH would have considerable influence on the concentration of AOC related to the organic substances decomposed by OH radicals, the intermediate of the self-decomposition of ozone in basic solution (indirect reaction of ozone at pH > 8).

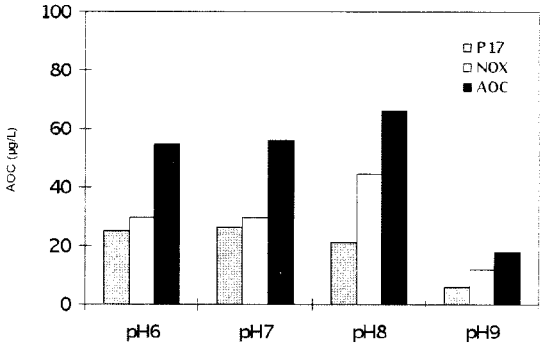


Fig. 8: Profile of AOC with respect to pH values at ozone dosage 3 mg/L.

At high pH value, *i.e.*, until pH 8, amount of AOC increases. This might be due to that efficiency of UV/O_3 system increased at higher pH. High pH refers to the presence of high concentration of OH- ions that may lead to hydroxyl radical formation through an indirect route. H_2O^- is the conjugated base of H_2O_2, which at pH ~ 8 will predominantly convert to H_2O_2, which is a source of hydroxyl radicals. Increased amount of OH-radical in reaction mixture might lead to the formation of more AOC. On the other hand, decrease of AOC concentration at pH above 8 is might be due to functioning of scavenging effects of H_2O_2 that reduces amount of OH-radicals in the solution with ultimate reduction in AOC concentration in the sample mixture [19].

Experimental

Water Samples

Present study employed two types of water samples: model raw water and source drinking water. Model raw water was prepared using humic acid (Sigma-Aldrich Chemical Company, USA). 1.0 g of humic acid dried at 100 °C for 4 hours was dissolved in 100 mL of 0.1 N NaOH and stirred for 24 hours. It was diluted by 1000 times by using distilled water. The diluted water sample was filtered through 0.45 μm filter paper and pH of the sample was adjusted at 7.0. Another water sample named SDW was taken from a water treatment facility located in Furushizawa Dam, Japan. pH of this sample was also adjusted at 7.0. Three liter of each water sample was used for a series of experiment.

Ozonation Procedure

Ozonation experiment was carried out with a bench-scale ozonation system which consisted of an

ozone generator (ISHIMORI Company, Inc., Japan), and a 5 L ozone reactor column (10 cm in diameter, 90 cm in height). Ozone produced from lab-grade oxygen was fed into ozone contact column through a porous glass frit at the bottom of the column. Schematic diagram of ozonation was shown in Fig. 9. Water samples of 3 L volume were continuously dosed with ozone gas at a flow rate of 0.6 L/min. Although 1~2 mg/L of ozone dosage is adopted for drinking water treatment, higher concentration of ozone, however, was considered to find out optimum conditions to measure AOCFP. Ozone concentration at gas inlet and outlet was measured by a portable gas detection kit (GASTEC, Inc., Japan). Residual ozone in water sample was analyzed by standard method [20].

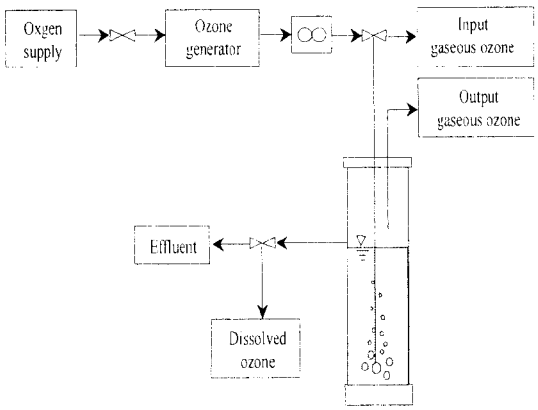


Fig. 9: Schematic diagram of ozonation.

AOC Determination

AOC determination is based on the measurement of the maximum extent of growth of a selected pure bacterial culture in representative water samples in which indigenous bacteria have been killed or inactivated by heat treatment [21-22]. Colony counts are used for determining bacterial densities. Analytical method developed by VanDer Kooij (1990) was adopted in the present study. The method employs *Pseudomonas fluorescens* strain P17 and *Spirillum species* strain NOX. These two microorganisms prefer different groups of compounds. P17 has a great nutritional versatility, and may grow on a variety of carbohydrates, aromatic acids and amino acids. It can also grow on carboxylic acids, with the exception of formic, glyoxylic and oxalic acids as typical by-products of ozonation. Therefore, the growth of strain P17 was used for the determination of the concentration of aromatic and amino acids etc. In case of NOX, it cannot utilize carbohydrates, alcohols, or aromatic acids but a wide range of carboxylic acids. Strain NOX can also utilize a few amino acids; however, this organism cannot assimilate amino acids when growing on mixtures of compounds. Therefore, the growth of strain NOX was used for the determination of the concentration of carboxylic acids in water. All glassware was thoroughly cleaned and rendered organic carbon-free by combustion at 550 °C for 1.0 h. Samples were incubated at 15 ± 0.5 °C and the number of colony was measured with the plate count technique after 72 ± 3 h incubation at 28 ± 1 °C on R2A agar. The total AOC in microorganisms per liter of equivalent acetate-carbon is the sum of AOC-P17 and AOC-NOX. In the present study, the yield coefficient of P17 and NOX were measured as 4.1×10^7 μg acetate-C/L and 1.2×10^7 μg acetate-C/L, respectively.

Conclusions

Ozone dosage for maximum AOC concentration was equal to that at which residual ozone began to be detected regardless of the water samples taken in this experiment. Such ozone dosage could be considered as threshold for the estimation of AOCFP. After threshold of ozone dosage, AOC concentration decreased with an increase in ozone dosage while residual ozone increased. Ozone required for oxidation of organic matter in sample water was fixed while biodegradability of organic matter depended on ozone dosage that caused variations in AOC concentration. Increase of oxidant to decompose organic matter could not ensure increase of biodegradability. Therefore, it could be suggested that the threshold of ozone dosage was one of the suitable conditions to measure AOCFP. Unlike AOC concentration, THMFP showed a tendency to decrease rapidly at low ozone dosage. Since humic substances were the representative organic substances responsible for increasing AOC concentration in this experiment, results of this study could be employed on samples of other drinking water sources. Increase in AOC concentration was mainly depended on AOC-NOX at pH 8. However, AOC concentration decreased rapidly at pH >9. Variations in AOC concentration were very sensitive to ozone dosage in basic conditions. Overall, pH 8 seemed to be one of the most suitable values to measure AOCFP.

Acknowledgement

This work was financially supported by Korean Ministry of Environment (MOE) under ET Human Resource Development Project.

References

1. Y. P. Tsai, T. Y. Pai and J. M. Qiu, *Journal of Biotechnology*, **111**, 155 (2004).
2. J. H. Lars and E. Harry, *Water Research*, **35**, 1106 (2001).
3. M. K. Aleksandra and V. D. Dick, *Water Research*, **38**, 3971 (2004).
4. D. VanDer Kooij, in: G. A. Mcfeter (Ed.), Drinking water Microbiology, Springer-Verlag, New York (1990).
5. C. E. Isabel and A. R. Andrew, *Journal of Membrane Science*, **175**, 1 (2000).
6. C. Colin and K. Ocelie, *Water Research*, **34**, 2629 (2000).
7. W. Liu, H. Wu, Z. Wang, S. L. Ong, J. Y. Hu and W. J. Ng, *Water Research*, **36**, 891 (2002).
8. D. VanDer Kooij, H. R. Veenendaal, C. Baars-Lorist, D. W. VanDer Klift and Y. C. Drost, *Water Research*, **29**, 1655 (1995).
9. I. C. Escobar and A. A. Randall, *Water Research*, **35**, 4444 (2001).
10. J. L. Markku, T. M. Ilkka, V. Terttu and J. M. Pertti, *Water Research*, **36**, 3681 (2002).
11. A. Y. Alex, K. H. Lee, K. C. Chen, P. Lars and J. M. Susan, *Water Research*, **38**, 2839 (2004).
12. M. J. Lehtonen, I. T. Miettinen, T. Vartainen and P. J. Martikainen, *Water Research*, **36**, 3681 (2002).
13. E. Orlandini, J. C. Kruithof, J. P. VandDer Hoek, M. A. Siebel and J. C. Schippers, *J. Water SRT-Aqua*, **46**, 49 (1998).
14. H. C. Kim and M. J. Yu, *Water Research*, **39**, 4779 (2005).
15. P. Monika, H. Koen and V. K. Chris, *Water Research*, **39**, 2259 (2005).
16. R. J. Miltner, S. Summer, J. Wang, J. Swertfeger and E. W. Rice, In the Proceedings of the Water Quality Technology Conference, *American Water Works Association*, Denver CO (1992).
17. G. A. Gagnon, P. M. Kuck, G. S. Irwin and P. J. Ollos, In the Proceedings of Protecting Water Quality in the Distribution System, *American Water Works Association*, Denver CO (1998).
18. W. L. Lai, H. H. Yeh and I. C. Tseng, *Ozone: Science and Engineering*, **28**, 35 (2006).
19. Y. J. Kim, J. S. Ho, J. H. Kim, M. S. Khan and T. I. Qureshi, *Journal of the Chemical Society of Pakistan*, **30**, 365 (2008).
20. APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, Washington DC (1998).
21. F. Jorge, R. Ferran and L. Franciso, *Water Research*, **28**, 1463 (1994).
22. Z. Weidong and A. D. Francis, *Water Research*, **36**, 1469 (2002).