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# Impact of Water Quality on the Formation of Bromate and Formaldehyde during Water Ozonation

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## 요 약

본 연구는 humic acid 및 bromide를 함유한 상수 원수에 오존 처리를 수행함에 있어 수질 특성 및 공정조건에 따른 bromate 및 formaldehyde의 생성을 고찰하였다. 회분식 실험장치를 이용하여 오존의 주입농도, DOC 농도, bromide 농도, pH, 알칼리도 및 반응 시간을 변화시키면서 오존 처리시 생성되는 대표적인 부산물인 bromate 및 formaldehyde의 거동을 파악하였다. 본 연구에서 검토된 영향 인자 중 수중의 pH조건은 bromate 및 formaldehyde의 생성에 가장 중요한 인자로 나타났다. DOC(dissolved organic carbon) 농도가 증가할수록 bromate 생성은 감소하였고 formaldehyde의 생성은 증가하였다. 오존처리를 통해 UV254는 효율적으로 감소되었고, UV254의 감소율 및 오존 농도는 선형 관계를 나타냈다.

**Keywords:** ozonation, BDOC (biodegradable organic carbon), bromate, formaldehyde, UV254 (UV absorbance at 254 nm), water quality

## I. Introduction

Conventional water treatment systems exhibit technological and economic limitations treating various pollution sources in raw water caused by rapid urbanization and industrialization. Needs and expectations of people for superior tap water are increasing day by day. Established conventional water treatment focuses mostly on removing suspended matters, which includes turbidity and pathogenic microorganisms.[1] However, it is difficult to remove various pollutants such as humic acid, synthetic detergent and ammonia nitrogen.[2-5] Therefore, advanced or complementary water treatment such as ozonation and biological activated carbon, is adopted in need.[6-8]

It is known well that ozone has strong oxidizing power and can be used for diverse purposes such as the suppression of THMs formation, improvement of coagulation and filtration, removal of taste and odor, oxidation of organic matter and elimination of algae.[8-10] The research on ozonation with humic acid was initially performed to solve the problem related to the suppression of THMs formation by chlorination. Ozonation is used to convert persistent organics to biodegradable matters rather than to reduce organics.

Ozonation generates by-products such as aldehydes and bromate. Aldehydes are classified as biodegradable organic matter (BOM) and potentially carcinogenic. The main aldehydes in water are formaldehyde, acetaldehyde, glyoxal and methylglyoxal. Schalekamp confirmed the existence of aldehydes in ozonated water at mg/*l* level through Switzerland's water treatment.[11] The formation of aldehydes increased with increasing ozone dosage up to 5 mg/*l* but decreased above that dosage.

Bromate, which is known as a carcinogen, is reported to be a by-product formed during ozonation. Bromide exists in raw water because of ocean penetration, geological reasons and the inflow of industrial wastewater.[12-16] The existence of organic matter appears to contribute the formation of bromate. Ozekin *et al.* reported that approximately

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65% of bromate formed was originated by radical reaction when the water does not contain natural organic matter (NOM) and that of 100% was found by radical reaction in water containing NOM.[14]

Ozonation is often applied together with biological treatment.[17,18] This treatment is used to oxidize the chlorination by-products such as THMs, and remove the BOM (biodegradable organic matter) that forms by the succeeding biological process. It has been reported that biologically activated carbon (BAC) has a low bromate removal efficiency.[17]

This research was performed to evaluate the formation of bromate and formaldehyde on water quality characteristics such as the level of DOC, bromide, ozone dosage, pH, alkalinity during ozonation and the variation in BDOC that can influence microbial growth in water distribution systems. Other goal of this research is to examine the condition for minimizing the formed disinfection by-products (DBPs) during ozonation, and to come up with suitable control strategies. In addition, an empirical bromate formation model was developed based on this experimental study.

## II. Materials and Method

A batch reactor was used to evaluate the DBPs formation during ozonation with bromide in the presence of humic acid. The ozone contactor has an inside diameter of 15 cm and a height of 150 cm, and its total capacity is 3 *l*. Ozone was produced by a Triple O System (Model 1994) ozonator. Ozone stock solution was prepared by bubbling ozone gas through DOC- free water. The level of ozone, DOC concentration, pH, alkalinity and bromide concentration were varied in order to measure their influence on the formation of bromate and formaldehydes and to evaluate on the variation of BDOC and the removal of UV254 materials during ozonation.

Ozone residuals were measured using the Indigo colorimetric method by standard method 4500-$O_3$ B.[19] The reaction container was filled with solutions including bromide and humic acid. The pH and alkalinity were controlled by analytical grade 0.05 N $NaHCO_3$, 0.01 M $KH_2PO_4$ and 0.04% NaOH before injection of an ozone stock solution. When the ozone stock solution was added, the reactor was immediately mixed by a magnetic stirrer. Samples were collected while the reaction time was reached and subsequently quenched by the addition of 0.1 M $Na_2SO_4$.

Humic acid was purchased from Aldrich Chemical. The following process is needed to make a humic acid stock solution. One gram of humic acid was dissolved in NaOH solution, and then ultra pure distilled water was put into the solution and stirred for 24 hr. The BDOC concentration was measured by assessing the difference between the initial DOC and the minimum DOC after cultivation.[20] $UV_{254}$ was determined by using a UV visible spectrophotometer with a 10 mm cell at 254 nm.

Bromide was added as analytical grade sodium bromide. A Dionex ion chromatograph (DX-500) was used to determine the bromide and bromate concentrations. DOC concentration was analyzed using a Shimadzu TOC-5000 analyzer as an NPOC (non-purge able organic carbon) mode. Alkalinity was measured according to standard method 2320. The concentrations of formaldehydes were determined by a high-performance liquid chromatography (HPLC) on a C-18 column. Injection volume was 20 m*l* and absorbance was detected at 360 nm. The solution was filtered through a Sep-pak DNPH silica cartridge, and then the filtrate was reacted with 2,4-DNPH (dinitrophenylhydrazine) before analysis by HPLC.

## III. Results and Discussion

### 1. Effects of Variation in UV254

Fig. 1(a) depicts the variation of UV254 on the levels of DOC and bromide. The level of DOC was adjusted between 0.5 and 3 mg/*l* and that of bromide were between 0 mg/*l* and 0.8 mg/*l*. The removal efficiency of UV254 absorbance materials was 67, 71, 52, 42 and 34% compared to values of initial UV254 for humic acid of 0.5, 1, 2, 2.5 and 3 mg/*l* after ozonation when bromide was not added. The highest removal efficiency of UV254 at DOC 1 mg/*l* was 73.6, 70.8, 72.1, 73.2, 72.3 and 71.7% for bromide 0, 0.08, 0.14, 0.33, 0.5 and 0.08 mg/*l*, respectively. This result suggests that the existence of bromide did not contribute to the decrease in UV254.

The value of UV254 was monitored during

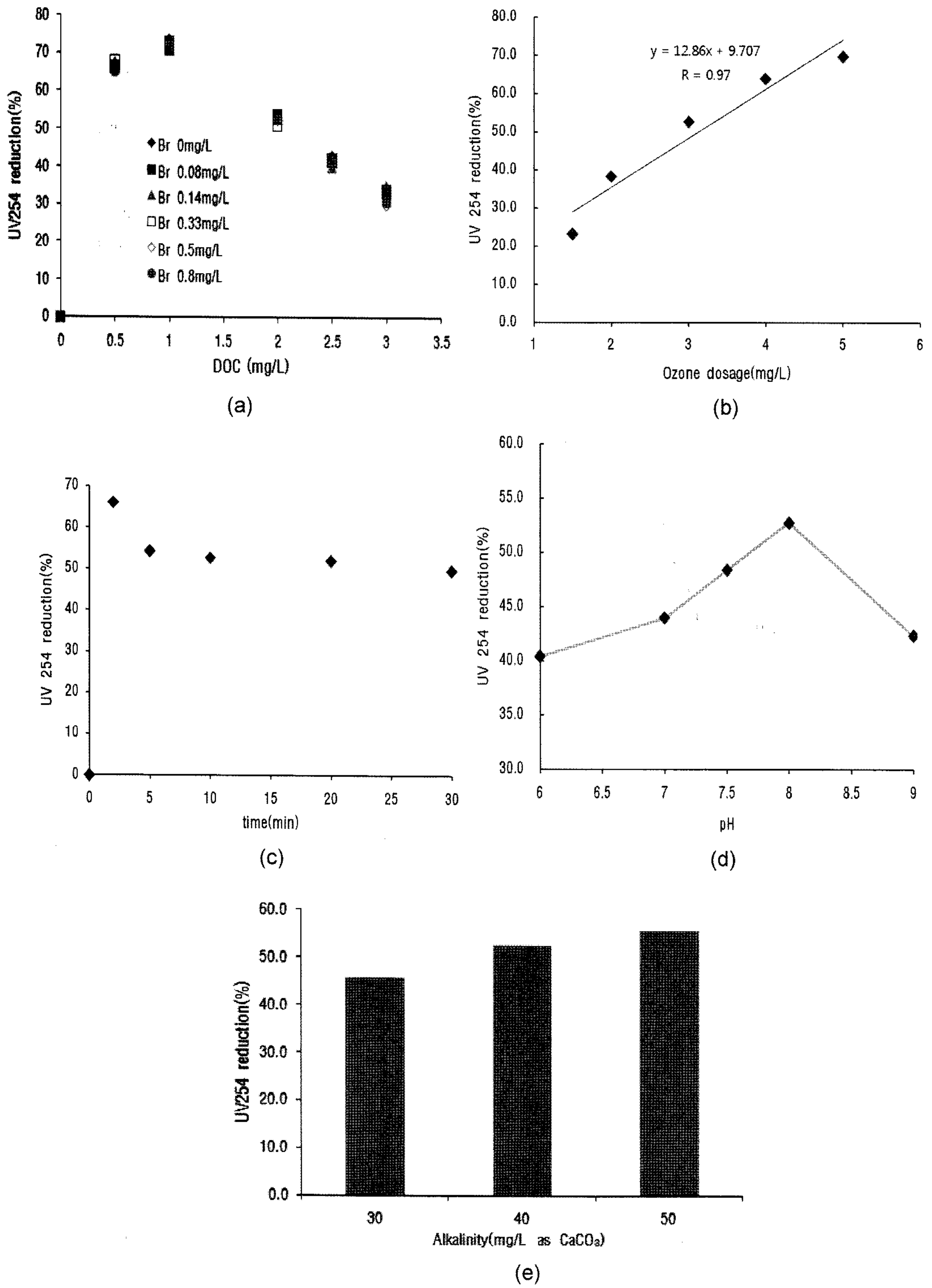


**Fig. 1.** The variation of UV254 on different water factors during ozonation : Influence of DOC (a), ozone dosage (b), contact time (c), pH (d) and alkalinity (e).

10 min of ozonation with humic acid (2 mg/*l*) and bromide (0.14 mg/*l*), as shown in Fig. 1(b). The percentage of UV254 reduction showed a linear relationship with ozone dosage. The removal rates of UV254 were 23.1, 38.4, 52.7, 64.0 and 69.7% for 1.5, 2, 3, 4 and 5 mg/*l* of ozone, respectively.

The variation of UV254 during ozonation was observed to determine the optimum reaction time for UV254 reduction. The highest UV254 reduction rate was 66.2% at 2 min, and it decreased between 5 min and 30 min of contact time (Fig. 1(c)). This result was similar to Choi *et al.*'s report.[21)]

The decrease in UV254 measured at different pH is shown in Fig. 1(d). The reduction rate of UV254 increased with increasing pH between pH 6 and pH 8, and after reaching the highest reduction point at pH 8, it declined until pH 9. Ozone decomposition increased with increasing OH radicals at pH 9. The reduction rate of UV254 increased with increasing alkalinity (Fig. 1(e)). Rechhow *et al.* reported that the ozonation efficiency was increased by enhancing the half-life of ozone decomposition with some level of alkalinity.[22)]

**2. Effect of Variation in BDOC**

This experiment was performed to understand the variation of BDOC formation on water influencing factors after ozonation. The bromide and humic acid concentration were adjusted in the range between 0-0.8 and 0-3 mg/*l*, to observe the effect of BDOC formation on the concentration of organic and bromide in this experiment (Fig. 2(a)). The level of BDOC increases with increasing DOC concentration, however, the amount of BDOC formed did not increase at over 1 mg/*l* of DOC. Approximately three times as much as BDOC formed at a DOC concentration of 3 mg/*l* as formed under no DOC condition at the a bromide range between 0 and 0.9 mg/*l*. However, the formation behavior of BDOC was not consistent with the bromide concentration. It appears that the bromide concentration might not contribute to the formation of BDOC.

Fig. 2(b) shows the variation in BDOC according to ozone dosage concentration. The formation of BDOC increased with increasing ozone dosage between 1.5 and 5 mg of ozone. The level of BDOC increased at higher concentrations of injection ozone. It seemed that biodegradability rapidly increases in the range of 0-2 mg $O_3$/mg C at a given concentration ratio of ozone and carbon in ozonated water, and BDOC react gently with ozone over 2 mg $O_3$/mg C. It appears that ozone dosage has a linear relationship with BDOC formed, *BDOC (mg/l)=0.189 ozone(mg/l)-0.103* (r=0.97).

The BDOC variation with time while 3 mg/*l* of ozone was injected is depicted in Fig. 2(c). The increase of BDOC occurred mostly before 5 min. The ratio of BDOC at 10 min to that at 30 min was over 0.91. It was thought that 5-10 min should be adequate contact time during ozonation to improve biodegradability.

The variation of BDOC on pH condition is shown in Fig. 2(d). The ratio of BDOC formed to initial BDOC at pH 6, 7, 7.5, 8 and 9 was 2.21, 2.71, 3.32, 2.95 and 2.52, respectively. This result shows that the level of BDOC was highest at pH 7.5. In other words, the optimum pH condition is 7.5 while ozone is applied for the conversion of biodegradable low molecular matter. The least BDOC was found at pH 6.0.

The impact of alkalinity on the formation of BDOC is presented in Fig. 2(e). The level of BDOC increased as alkalinity increased. The values of BDOC at 30, 40, 50 mg/*l* as $CaCO_3$ were 2.61, 2.95 and 3.23 times higher than the initial value. It appeared that the existence of some level of alkalinity could contribute to the enhancement of biodegradability during ozonation.

**3. Effect of Bromate Formation**

These experiments were performed to evaluate the variations of bromate formation during ozonation on water influential factors (Fig. 3). The level of bromate was observed at different dosage of bromide between 0.08 and 0.8 mg/*l*, and at DOC levels between 0.5 and 3 mg/*l*, while 3 mg/*l* of ozone was applied at pH 8 (Fig. 3(a)). The formation of bromate increased with increases in the bromide concentration and decreased with increasing concentration of DOC. It appears that ozone react preferentially with humic acid in the presence of both bromide and humic acid. The level of bromate while the DOC level was over 2 mg/*l* and the level of bromide under 0.08 mg/*l*, which are likely typical values in raw water, was detected to be under 25

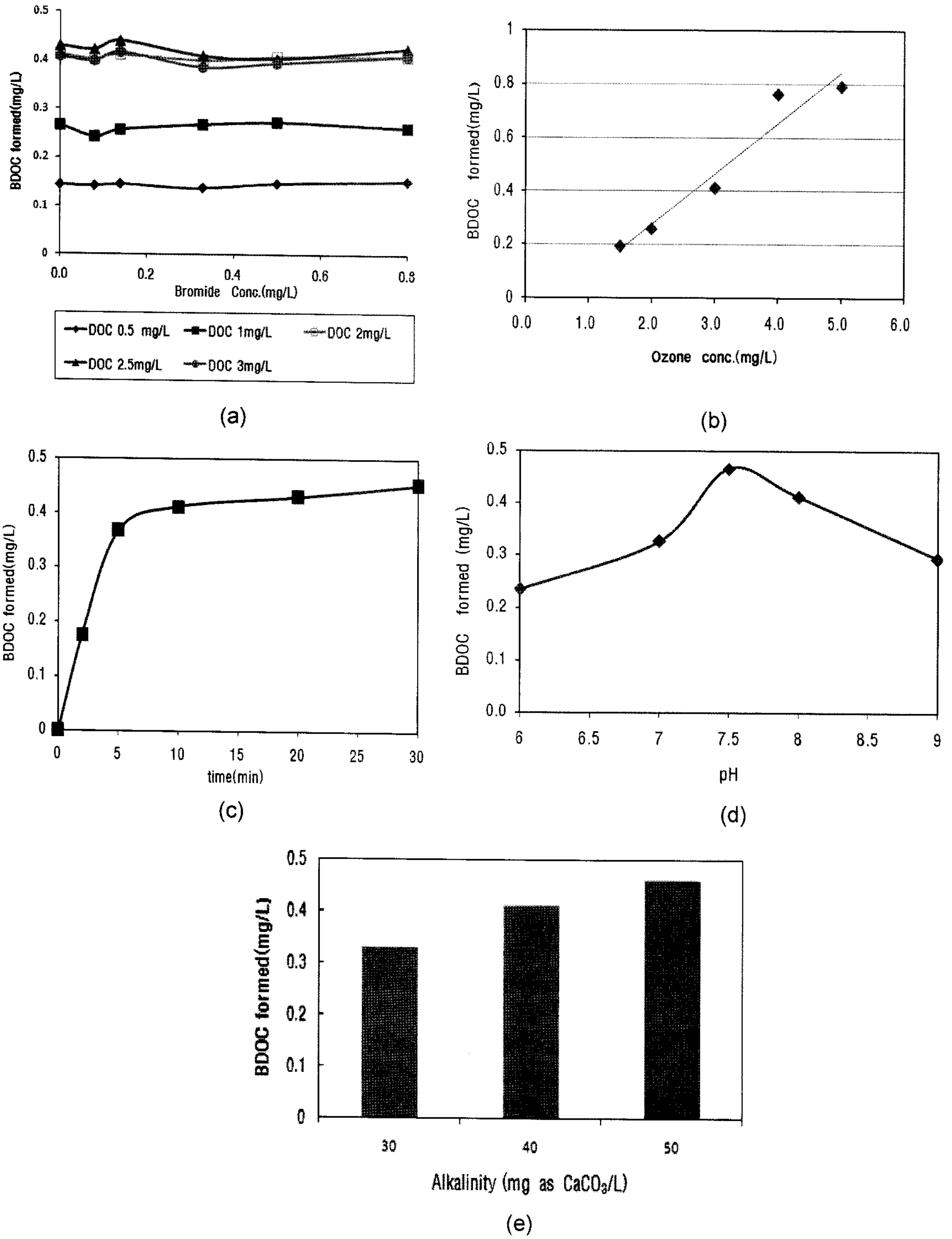


**Fig. 2.** The variation of BDOC formation on different water factors during ozonation : Influence of DOC (a), ozone dosage (b), contact time (c), pH (d) and alkalinity (e).

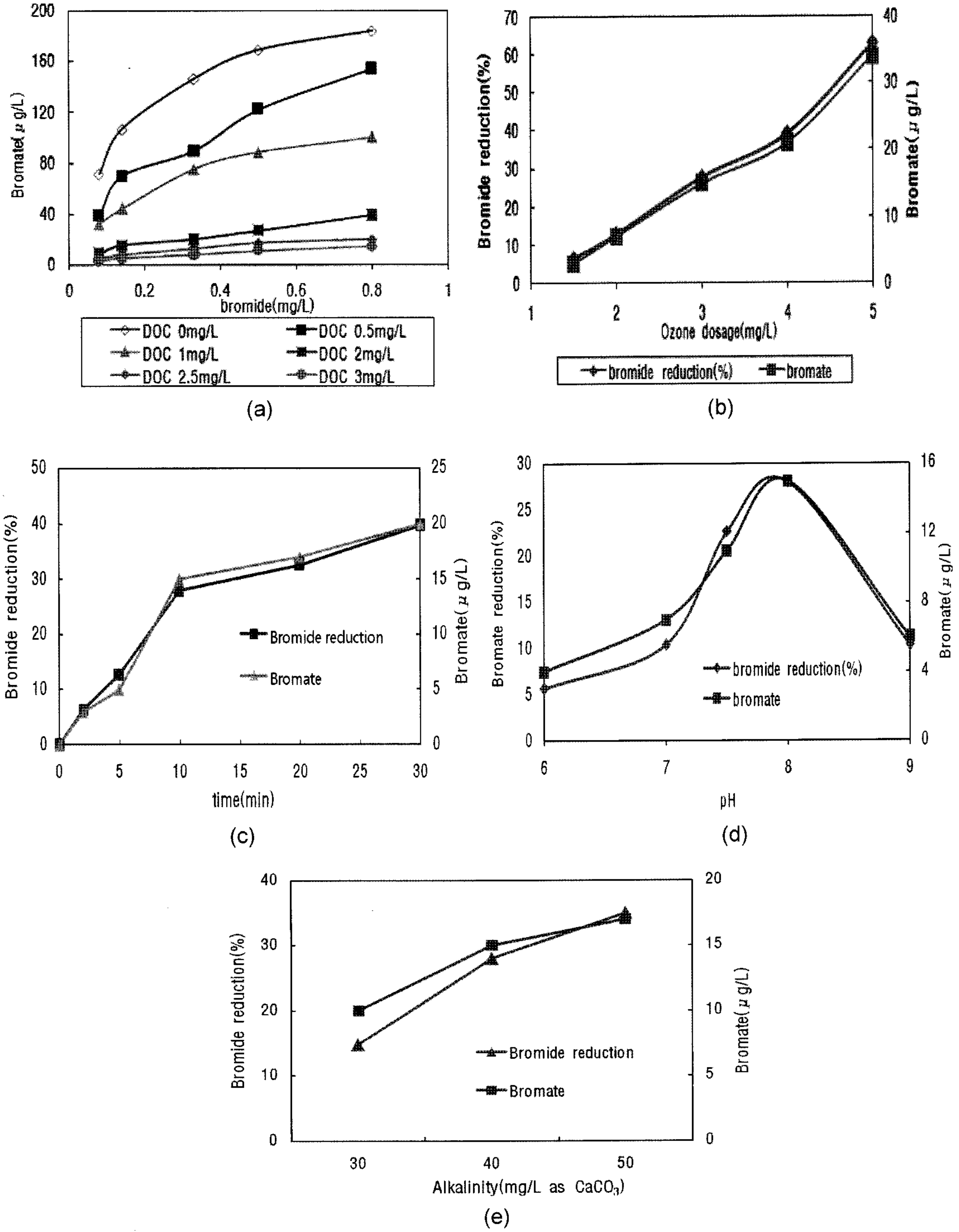


**Fig. 3.** The variation of bromate formation and bromide reduction on different water factors during ozonation : Influence of DOC (a), ozone dosage (b), contact time(c), pH (d) and alkalinity (e).

μg/*l* which is the WHO's recommendation level.

The effect of ozone concenration on the formation of bromate and reduction of bromide during 10 min of ozonation is depicted in Fig. 3(b). The concentrations of DOC and bromide were adjusted to 2 and 0.14 mg/*l*, respectively. The reduction rate of bromide was 6.4, 12.9, 28.1, 39.3 and 62.9% for 1.5, 2, 3, 4 and 5 mg $O_3$/*l*, respectively, during 10 min. The level of bromate was 3, 7, 15, 21 and 34 μg/*l* for 1.5, 2, 3, 4 and, 5 mg $O_3$/*l*, respectively, which show that bromate formation increased with increasing ozone dosages. The bromate formed was 28 μg/*l*, which exceeds WHO's recommendation level, while ozone was applied at 3 mg/*l* in the condition of this experiment.

The level of bromide fell rapidly for 10 min, and then decreased gently until 30 min of ozonation (Fig. 3(c)). Seventy percent of the bromide was reduced in 10 min compared to that at 30 min while ozone, humic acid and bromide were applied at 3, 2 and 0.14 mg/*l* at pH 8. The ratio of bromate formed at 10 min to that at 30 min was 0.75.

The formation of bromate and reduction of bromide on pH condition were observed during ozonation with 3 mg $O_3$/*l* under the condition of 0.14 mg/*l* of bromide and 2 mg/*l* of DOC (Fig. 3(d)). The reduction rate of bromide was highest at pH 8. The lowest concentration of bromate formed was 4 μg/*l* at pH 6. This was because bromine, which is a mediate-product while bromide was oxidized by ozonation under pH 6, has low-reactivity with ozone and bromide ion almost exists as a type of HOBr. The formation of bromate decreased with declining pH between pH 6 and 8. 6 μg/*l* of bromate was formed at pH 9.

The variations of bromide and bromate levels as a function of alkalinity during ozonation are shown in Fig. 2(e). The experimental condition was controlled as follows: The level of bromide of 0.14mg/*l*, DOC of 2 mg/*l* and ozone of 3 mg/*l* was applied for 10 min contact time. The rate of bromide reduction and bromate formation increased while the level of alkalinity was enhanced.

Based on these results, an empirical model that shows the effects of initial bromide concentration, pH, alkalinity, ozone dosage, time and, organic concentration on bromate concentration is presented as follows:

$$[BrO_3^-] = 10^{-5.06}[DOC]^{-0.82}[Br^-]^{1.01}[pH]^{4.05}[alkalinity]^{0.69}[ozone]^{1.89}[time]^{0.56} \quad (1)$$

Where,

$BrO_3^-$ : bromate concentration (μg/*l*), $3 \le [BrO_3^-]$

$Br^-$ : bromide concentration (mg/*l*), $0.01 \le [Br^-] \le 0.8$

DOC : DOC concentration (mg/*l*), $0.5 \le DOC \le 3.0$

pH : $6.0 \le pH \le 8$

Alkalinity: (mg/*l* as $CaCO_3$), $30 \le alkalinity \le 50$

Ozone : ozone dose (mg/*l*), $1.5 \le O_3 \le 5.0$

time : reaction time (min), $2 \le t \le 30$

A multiple linear regression shows that increasing bromide, pH, alkalinity and ozone concentration increase bromate formation, but that increasing DOC decreases bromate formation. The effect of the variables, from strongest to weakest, is pH, ozone concentration, DOC and alkalinity. Especially, pH is the most important variable affecting bromate formation.

### 4. Effect of Formaldehydes Formation

The formaldehyde formed was evaluated with the influence of DOC 0.5-3 mg/*l* and bromide between 0.08 and 0.8 mg/*l* during 10 min of ozonation. Ozone was applied at 3 mg/*l*. The formaldehyde formed was 0, 7.4, 19.4, 37.3, 48.7 and 63.5 μg/*l* while humic acid was applied at levels of 0.5, 1, 2, 2.5 and 3 mg/*l* without bromide addition (Fig. 4(a)). The formaldehyde concentration increased with increasing levels of DOC, but showed no distinct correction with the bromide level.

The variation of the formation of formaldehyde on ozone concentration is shown in Fig. 4(b). The formaldehyde detected was between 10.3 and 55.2 μg/*l* when 1.5-5 mg/*l* of ozone was applied. The level of formaldehyde formed increased with increasing ozone level under 4 mg/*l*. The highest bromate value at 4 mg/*l* was 55.2 μg/*l* and it decreased to 28.7 μg/*l* at an ozone level of 5 mg/*l*.

The highest formaldehyde concentration was shown at 10 min of contact time but the curve of formaldehyde as shown in Fig. 4(c) was fluctuated unsteadily with regard to time. This result is consistent with the report of Choi *et al.* (1998), who said the formaldehyde level did not shown con-

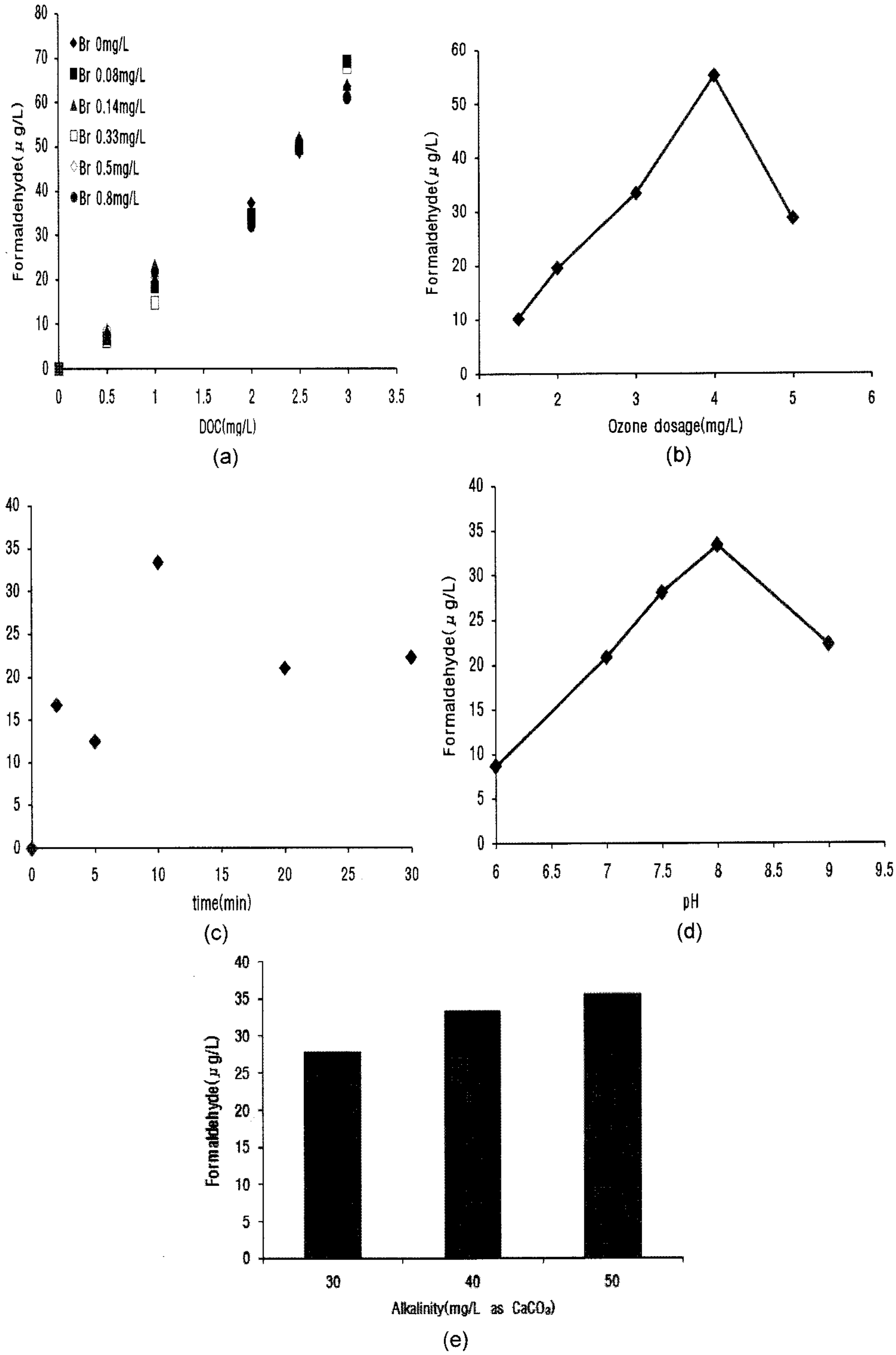


**Fig. 4.** The variation of formaldehyde formation on different water factors during ozonation : Influence of DOC (a), ozone dosage (b), contact time (c), pH (d) and alkalinity (e).

sistency with time.

The impact of pH on the formation of formaldehyde formation was evaluated at 2 mg/*l* of DOC during ozonation (Fig. 4(d)). The level of formaldehyde increased with increasing pH between pH 6 and pH 8, and decreased above pH 8. The highest level of formaldehyde shown was 33.4 μg/*l* at pH 8, and the lowest was 8.7 μg/*l* at pH 6.

Variation in the formaldehyde level was observed at alkalinity levels between 30 mg/*l* and 50 mg/*l* during ozonation (Fig. 4(e)). Formaldehyde formation increased when the alkalinity level increased. The highest value, shown at 50 mg/*l* as $CaCO_3$ was 35.6 μg/*l*.

## IV. Conclusions

This research was to evaluate the influences of water variables on the formation of bromate and formaldehyde and the variation in biodegradability during ozonation. The variables selected included humic acid, ozone dosage, pH, alkalinity and bromide concentration. The following key findings were obtained from the experiment results.

The results of batch experiments showed that the order of these variables in terms of the strength of their effect on bromate formation was pH, ozone dose, bromide level, DOC concentration and alkalinity. pH has the strongest effect on bromate formation. Sufficient reaction time was not a key variable affecting bromate formation during ozonation. Bromate concentration increased mostly in 10 min but it still increased up to 30 min of contact time.

The data showed that the formation of formaldehyde increased with increasing DOC level. As the pH of ozonation lowered, less formaldehyde was formed under pH 8. Bromide concentration did no affect the formation of formaldehyde during ozonation. No correlation was found between formaldehyde formation and contact time.

The reduction rate of UV254 was observed to increase with increasing ozone dosage. BDOC formation was favored at high pH, DOC and ozone dose. Ozone dose shows a proportional relationship with BDOC. However, the bromide concentration did not impact biodegradability or UV254.

This research suggests an empirical prediction model of bromate formation under various water conditions. The model showed the variablility of bromate formation in their variables and these independent variables also contributed to the behavior of BDOC during ozonation. pH control strategies can be used to minimize bromate formation while ozone is applied in water treatment. However, the future modeling based on pilot and full scale conditions should be required to establish the detail DBPs control strategies at water utility because these results may be reflect a batch reactor spcific. In addition, water utilities are needed to keep the balance between DBPs formation and the oxidation (or disinfection) requirements on different water quility while they introduce an ozonation system and plan to assess suitable strategies.

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