



# บันทึกข้อความ

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เรื่อง ขออนุมัติค่าตอบแทนการตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

เรียน รองคณบดีฝ่ายวิจัยและวิชาการ ผ่านหัวหน้าภาควิชาวิศวกรรมเคมี

อ้างถึงประกาศฉบับที่ 40/2550 ประกาศ ณ วันที่ 22 ตุลาคม 2550 คณะวิศวกรรมศาสตร์ เรื่อง “หลักเกณฑ์การจ่ายค่าตอบแทนการตีพิมพ์ผลงานวารสารวิชาการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยอุบลราชธานี” ตามความทราบแล้วนั้น

เนื่องด้วยดิฉัน นางสาวสุนา สิริพัฒนานกุล อาจารย์ประจำภาควิชาวิศวกรรมเคมี ได้ตีพิมพ์บทความวิชาการ เรื่อง “Mineralization and biodegradability enhancement of natural organic matter by ozone-VUV in comparison with ozone, VUV, ozone-UV, and UV: Effects of pH and ozone dose” ในวารสารระดับนานาชาติ Water Research Vol. 44 (2010) 3531-3543 โดยมีสัดส่วนการทำงานคิดเป็นร้อยละ 20 ดังนั้นดิฉันจึงใคร่ขออนุมัติค่าตอบแทนการตีพิมพ์ผลงานดังกล่าว

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(ดร.สุนา สิริพัฒนานกุล)

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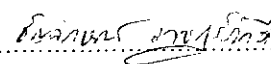
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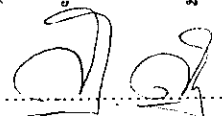
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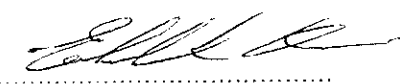
Thunyalux Ratpukdi, Sumana Siripattanakul, and Eakalak Khan. Mineralization and biodegradability enhancement of natural organic matter by ozone–VUV in comparison with ozone, VUV, ozone–UV, and UV: Effects of pH and ozone dose. Water Research Volume 44, Issue 11, 2010, Pages 3531-3543.

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ลงชื่อ.....  
(Prof. Dr. Eakalak Khan)



# Mineralization and biodegradability enhancement of natural organic matter by ozone–VUV in comparison with ozone, VUV, ozone–UV, and UV: Effects of pH and ozone dose

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## ABSTRACT

The increase in mineralization and biodegradability of natural organic matter (NOM) by ozone–vacuum ultraviolet (VUV) in comparison with ozone, VUV, ozone–ultraviolet (UV), and UV were investigated. The effects of operating parameters including pH and ozone dose were evaluated. Results showed that the mineralization rate of dissolved organic carbon (DOC) provided by the processes tested was in the following order: ozone–VUV > VUV > ozone–UV > ozone > UV. Among three pH studied (7, 9, and 11), pH 7 provided the highest DOC mineralization rate and biodegradability increase. A synergistic effect was observed when combining ozone with UV or VUV at pH 7 and 9 but not at pH 11. The oxidized NOM samples were separated into six fractions based on polarity (hydrophobic/hydrophilic) and charge (acid/neutral/base) to reveal NOM characteristic changes. Ozone–VUV was effective in mineralizing hydrophobic neutral and acid fractions. The hydrophilic neutral fraction was a major NOM fraction after oxidation (39–87%) and was contributed to by the biodegradable DOC produced during oxidation. High performance size exclusion chromatography results revealed that the combination of UV or VUV with ozone was more effective in the decomposition of high molecular weight compounds than ozone alone.

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## 1. Introduction

Removal of natural organic matter (NOM) is one of the main goals in drinking water treatment. This is because NOM can cause color, taste and odor, and bacterial regrowth in the water distribution system. In addition, NOM can form carcinogenic byproducts such as trihalomethane (THMs) and haloacetic acids (HAAs) upon reacting with chlorine. NOM is a complex mixture of organic compounds and bulk organic carbon parameters, including total and dissolved organic carbon, do not provide any details on the chemical

characteristics of NOM. NOM fractionation into different subgroups of compounds based on polarity (hydrophobic/hydrophilic) and charge (acid/neutral/base) is required to understand the effect of treatment processes on complex NOM.

Ozonation followed by biological filtration has been shown to effectively remove NOM from water. Ozone and/or hydroxyl radicals (OH<sup>•</sup>) generated from the decomposition of ozone degrade recalcitrant organic compounds to smaller molecules, which are more hydrophilic and biodegradable. Bacteria in the biological filter utilize the oxidized organic compounds

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as a substrate resulting in the effluent that is more biostable and has less potential to form THMs or HAAs.

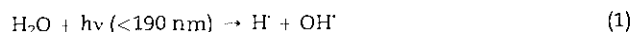
Although ozonation of water generates  $\text{OH}^\bullet$  which is a highly reactive and nonselective oxidant, more  $\text{OH}^\bullet$  can be generated through the combinations of oxidant and catalyst or different oxidants in the same reactor. The most common combinations are ozone–ultraviolet (UV), hydrogen peroxide ( $\text{H}_2\text{O}_2$ )–UV and ozone– $\text{H}_2\text{O}_2$  (Gottschalk et al., 2000). Among these processes, ozone–UV has the highest  $\text{OH}^\bullet$  yield per mass of oxidants (Gottschalk et al., 2000). The  $\text{OH}^\bullet$  production can be from different pathways (Fig. 1).

During the past decade, ozone–UV has received attention in the drinking water and wastewater fields. Numerous studies found that the ozone–UV process was more effective for the destruction of synthetic organic compounds than ozone alone (Amat et al., 2005; Beltrán et al., 1995; Chang et al., 2007; Garoma and Gurol, 2004; Ku et al., 2006). However, research investigating the application of ozone–UV for NOM removal in drinking water has been limited. Previous studies focused on the mineralization of NOM and reduction of THM and HAA formation potential of NOM (Chin and Bérubé, 2005; Glaze et al., 1982; Kusakabe et al., 1990), as well as its biodegradability after oxidation (Li et al., 2006).

There has been only one study that investigated the removal of NOM fractions of biologically treated municipal wastewater by ozone–UV process (Gong et al., 2008). Four NOM fractions, hydrophobic acid, non-acid hydrophobic, transphilic and hydrophilic, were examined. Results showed that ozone–UV process was more efficient at removing dissolved organic carbon (DOC) than ozone alone (90% versus 36%). All four NOM fractions were oxidized simultaneously by ozone–UV while ozone oxidized hydrophobic fractions first followed by transphilic and hydrophilic fractions.

In all of the previous studies on NOM removal by ozone–UV, UV lamps emitting a wavelength of 254 nm were used. At this wavelength, the molar absorption coefficient of ozone ( $3300 \text{ M}^{-1} \text{ cm}^{-1}$ ) is the highest resulting in the maximum rate of ozone photolysis (Legrini et al., 1993). However,  $\text{H}_2\text{O}_2$ , formed in situ during ozone photolysis, has a relatively low molar absorption coefficient ( $18.6 \text{ M}^{-1} \text{ cm}^{-1}$ ) at this wavelength. As a consequence, the production of  $\text{OH}^\bullet$  is not maximized.

Vacuum UV (VUV) is an alternative approach that may result in greater  $\text{OH}^\bullet$  generation. The VUV light source emits the wavelengths of 185 nm and 254 nm simultaneously. At the UV wavelength of 185 nm,  $\text{OH}^\bullet$  is generated from homolysis of water (Equation (1)) (Gonzalez et al., 2004).



Recently, there have been several studies on the application of VUV for NOM removal (Buchanan et al., 2004, 2005, 2008; Dobrović et al., 2007). It has been reported that VUV

mineralizes and increases the biodegradability of NOM to a greater extent than regular UV light, which emits only the wavelength of 254 nm (Buchanan et al., 2005). Based on NOM fractionation results, VUV significantly transformed hydrophobic fractions into lower molecular weight hydrophilic charged and hydrophilic neutral fractions. Echigo et al. (1996) reported that ozone–VUV (185 + 254 nm) performed best for the decomposition of 1 mg/L organophosphoric acid triesters compared to ozone, VUV, and ozone– $\text{H}_2\text{O}_2$  systems.

To the best of our knowledge, the application of ozone and VUV in combination for NOM removal has never been investigated. Ozone–VUV has potential for more effective NOM removal than ozone–UV. This is because VUV can provide additional production of  $\text{OH}^\bullet$  through direct water homolysis and from the reaction with  $\text{H}_2\text{O}_2$  (Gonzalez et al., 2004). In addition, VUV has lower electrical energy per order ( $E_{\text{EO}}$ ) for NOM removal than UV (Thomson et al., 2002). With the costs of UV and VUV lamps being comparable (Universal Light Source Inc., 2009), the application of ozone–VUV becomes more attractive. However, there are several factors that need to be understood in order to operate this process effectively.

This research investigated the use of ozone–VUV for mineralizing NOM and increasing its biodegradability. Two operating parameters of the process including ozone dosage and pH were the variables studied. The performances of the process were compared with those of ozone, VUV, ozone–UV, and UV. The effects of all five processes on different NOM fractions were evaluated. Fractionation of oxidized NOM remaining after the biodegradable DOC (BDOC) test was performed. High performance size exclusion chromatography (HPSEC) was used to examine the molecular weight distribution of NOM subjected to these processes.

## 2. Materials and method

### 2.1. Water sample

Water samples used in this study were collected from the Moorhead Water Treatment Plant, Moorhead, MN, USA after coagulation and softening by ferric sulfate and lime/soda ash. Approximately 20 L of the water sample were filtered through a 1  $\mu\text{m}$  pore-size glass fiber filter (Type A/E, Pall Life Science, Port Washington, NY, USA) for each run of experiment. The characteristics of the samples are shown in Table 1.

### 2.2. Experimental setup

Fig. 2 shows a schematic diagram of an ozone–VUV experimental system. The setup of an ozone–UV system was the same except that VUV lamps were replaced with UV lamps. The stainless steel reactor had a diameter of 30 cm and a height of 25 cm, and was filled with 16 L of the filtered water sample. Mixing (>60 rpm) was provided by a magnetic stirring system. The reactor was equipped with 4 ozone glass diffusers and 4 VUV lamps (model GPH383T5/VH/HO, Universal Light Source Inc., San Francisco, CA, USA). The lamps have a power input of 30 W per lamp. The 4 UV lamps (GPH383T5/L/HO) emitting only a 254 nm wavelength were also acquired from the same source. Ozone was generated from high purity oxygen using an ozone

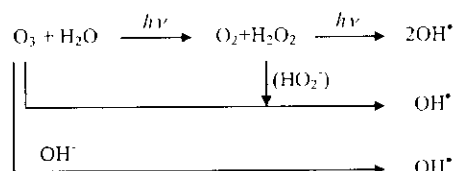


Fig. 1 –  $\text{OH}^\bullet$  generation pathway in ozone–UV process.

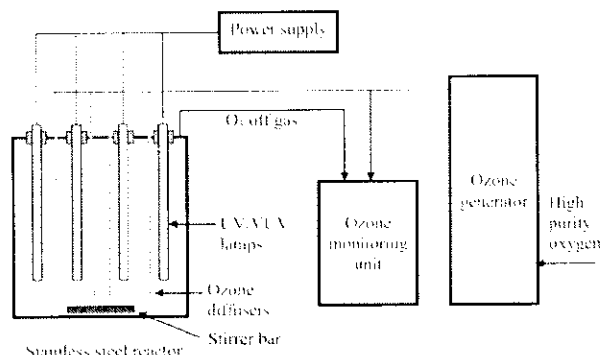
**Table 1** – Characteristics of coagulated and softened water samples from the Moorhead Water Treatment Plant, MN, USA ( $n = 5$  for dissolved oxygen and  $n = 54$  for the other parameters).

Parameters	Average $\pm$ standard deviation	Range
DOC (mg/L)	$4.18 \pm 0.60$	3.43–5.48
BDOC (mg/L)	$0.57 \pm 0.36$	0.21–1.62
UV absorbance at 254 nm ( $\text{cm}^{-1}$ )	$0.043 \pm 0.004$	0.037–0.054
Specific UV absorbance ( $\text{L/mg C m}$ )	$1.04 \pm 0.18$	0.75–1.45
Dissolved oxygen (mg/L)	$8.91 \pm 0.08$	8.83–9.04
Alkalinity (mg/L as $\text{CaCO}_3$ )	$70.05 \pm 12.35$	42–94
Hardness (mg/L as $\text{CaCO}_3$ )	$89.73 \pm 6.83$	76–110
pH	$11.21 \pm 0.25$	10.63–11.67
Turbidity (NTU)	$0.10 \pm 0.02$	0.07–0.13

generator (T-816 Ozonator, Ozone Engineering Inc., El Sobrante, CA, USA). The ozone gas concentration was controlled at approximately 3.5 mg/L by setting the power output of the generator at 58 V. The ozone dosage was adjusted by changing the gas flow rate. The ozone feed gas and off gas concentrations were monitored by an ozone gas monitoring system (PCI LC-400, PCI Ozone and Control System Inc., West Caldwell, NJ, USA). UV and VUV experiments were performed in the same manner except no ozone gas was fed to the reactor. Ozonation alone experiments were conducted in the same reactor with UV or VUV lamps off.

### 2.3. Experimental design and procedure

For the ozone and ozone–VUV systems, experiments were conducted by varying ozone dosage (1, 2 and 4 mg  $\text{O}_3/\text{mg DOC}$ ) and initial pH (7, 9 and 11). Ozone–UV experiments followed the same design except that only two ozone dosages of 1 and 4 mg  $\text{O}_3/\text{mg DOC}$  were applied. The power of VUV and UV in the ozone–VUV and ozone–UV experiments was 120 W. For the UV and VUV systems, the same three pH values were studied while the VUV power was varied at 30, 60, 120 W and only one UV power of 120 W was tested. The ozone dosages used were within a typical range for mineralization and biodegradability increase of NOM in drinking water (Carlson and Amy, 1997; Cipparone et al., 1997; Yavich et al., 2004). The pH values



**Fig. 2** – An experimental setup.

studied covered a normal range of pH of water entering the ozonation systems. Sulfuric acid and sodium hydroxide were used to adjust the pH of the coagulated and softened water to 7 and 9. After the pH adjustment, the alkalinity was  $8.08 \pm 2.23$  and  $29.38 \pm 5.04$  mg/L as  $\text{CaCO}_3$  at pH 7 and 9. Note that the pH adjustment was not required for pH 11 because it was approximately the pH of the coagulated and softened water.

The reactor was operated in a semi batch mode in which ozone was continuously introduced to 16 L of the water in the reactor during the course of experiment. To achieve the VUV power of 30, 60 and 120 W, 1, 2, and 4 VUV lamps were turned on, respectively. For each experimental condition, the same water sample (48 L) was used by dividing it into three portions for triplicate experiments. Three hundred fifty milliliters were taken by siphoning through Tygon® tubing SE-200 at the reaction times of 0, 15, 30, 45, and 60 min for DOC, UV absorbance at 254 nm ( $\text{UV}_{254}$ ), residual ozone, and BDOC measurements. In addition, at the end of the run (60 min), two portions of 1 L samples were collected. One portion was used for NOM fractionation while the other underwent BDOC incubation and NOM fractionation, successively. The NOM in coagulated and softened water samples before oxidation (used in the experiments) and after subjected to the BDOC incubation was also fractionated. A water sample of 40 mL was collected at 60 min for HPSEC analysis only for the following experiments at pH 7: ozone–VUV (4 mg  $\text{O}_3/\text{mg C}$  and 120 W), ozone–UV (4 mg  $\text{O}_3/\text{mg C}$  and 120 W), ozone (1 and 4 mg  $\text{O}_3/\text{mg C}$ ), and VUV (120 W). The HPSEC analysis was performed on one of the coagulated and softened water samples as well.

Hydroxyl radical was measured for the following experimental conditions: ozone–UV (4 mg  $\text{O}_3/\text{mg C}$ ) and ozone–VUV (4 mg  $\text{O}_3/\text{mg C}$ ) at pH 7. Hydroxyl radical was measured indirectly based on the oxidation kinetics of *p*-chlorobenzoic acid (pCBA, Sigma–Aldrich, Milwaukee, WI, USA) spiked in the reactor at 400  $\mu\text{g/L}$  (Rosenfeldt and Linden, 2007). Samples (2 mL) were taken for pCBA analysis at the same time intervals as for DOC measurement. pCBA was used as a probe compound for  $\text{OH}^\cdot$  measurement because of its relatively low reactivity with ozone ( $0.15 \text{ L}/(\text{mol s})$ ) and high reactivity with  $\text{OH}^\cdot$  ( $5 \times 10^9 \text{ L}/(\text{mol s})$ ). The  $\text{OH}^\cdot$  exposure ( $\text{OH}^\cdot$  concentration  $\times$  time) was determined according the following equation:

$$\int_0^t [\text{OH}^\cdot] dt = \frac{(k_{\text{obs}} - k_d)t}{k_{\text{OH}^\cdot \text{pCBA}}} \quad (2)$$

where  $t$  is the reaction time (s),  $k_{\text{obs}}$  is an observed pseudo first order removal rate of pCBA ( $\text{s}^{-1}$ ),  $k_d$  is a pseudo first order rate constant of pCBA removal by direct photolysis ( $\text{s}^{-1}$ ), and  $k_{\text{OH}^\cdot \text{pCBA}}$  is a second order reaction rate constant of pCBA with  $\text{OH}^\cdot$  ( $5 \times 10^9 \text{ L}/(\text{mol s})$ ). In the ozone–VUV experiments, pCBA could be degraded by not only  $\text{OH}^\cdot$  but also VUV through direct photolysis. To account for the effect of direct photolysis,  $\text{OH}^\cdot$  must be scavenged during the ozone–VUV experiments. This was achieved by adding *t*-butanol (5 mmol/L) into the reactor at the beginning of the experiments (Kutschera et al., 2009).

### 2.4. Analyses

Dissolved organic carbon was analyzed according to Standard Methods (APHA et al., 1998) using an ultraviolet/persulfate

oxidation total organic carbon (TOC) analyzer (Phoenix 8000, Tekmar Dohrmann, OH, USA). The DOC of each sample, which was filtered through a 0.45  $\mu\text{m}$  hydrophilic polyethersulfone membrane filter (prewashed by 200 mL of deionized water) (Pall Life Science), was measured twice. The TOC analyzer was calibrated according to the instrument manual.  $\text{UV}_{254}$  was determined using a spectrophotometer (Genesys™ 10 UV–Vis, Thermo Spectronic, NY, USA). Specific ultraviolet absorbance (SUVA), an indicator of relative unsaturated carbon amount, was determined by dividing  $\text{UV}_{254}$  by DOC.

Ozone residual concentration was analyzed using an indigo colorimetric method following APHA et al. (1998). The concentration of pCBA was measured using a high performance liquid chromatography (HPLC) system (System Gold® 126, Beckman Coulter Inc., Fullerton, CA, USA) with a LUNA 5  $\mu\text{m}$ , 150  $\times$  3.00 mm, C18 column (Phenomenex, Torrance, CA, USA). The mobile phase was acetonitrile:water (50:50). The water was added with formic acid (0.66 mL/L). The HPLC system was operated at a flow rate of 0.65 mL/min with an injection volume of 50  $\mu\text{L}$ . NOM was fractionated into six fractions including hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophilic acid (HPHA), hydrophilic neutral (HPIN) and hydrophilic base (HPIB) using a series of solid phase extraction cartridges. The details of the fractionation technique are described elsewhere (Ratpukdi et al., 2009). Although the experiments were triplicated, the fractionation of water sample was performed only once since the procedure is time consuming and labor intensive.

The molecular weight distribution of the samples was determined by HPSEC. The HPSEC setup was an HPLC with a UV detector (Shimadzu, Tokyo, Japan) and a size exclusion column (Inertsil WP 300 Diol silica column, 5  $\mu\text{m}$ , 300 Å, 250  $\times$  7.6 mm ID, GL Sciences, Tokyo, Japan). A mobile phase, which was a sodium chloride solution of 0.1 M (pH of 6.8), delivered the samples (or standard solutions) through the system at a flow rate of 1 mL/min for 20 min. Benzoic acid (molecular weight of 122.1 Da) and sodium polystyrene sulfonate (molecular weight of 4300, 6800, 17,000, and 32,000 Da) were used as standard solutions. The function "Autofit Peak III Deconvolution" in a program, Systat PeakFit 4.12, was used to resolve the aggregate peaks into a number of Gaussian peaks for quantitative analysis (Sarathy and Mohseni, 2007). The HPSEC chromatograms were divided into five fractions as follows: <350 Da, 350–700 Da, 700–1050 Da, 1050–1400 Da, and >1400 Da. The amount of each fraction was determined by summing the areas under the peaks within the corresponding range. The molecular weight range of NOM in the water sample in this study was smaller than the molecular weight range of NOM reported for raw water (500–50,000 Da) (Chow et al., 2008) because the water sample had been coagulated and softened.

The BDOC test was performed according to a batch procedure by Khan et al. (1999). The pH of sample was adjusted to  $7.0 \pm 0.2$  by 1 N of  $\text{H}_2\text{SO}_4$  before being filtered through a 0.45  $\mu\text{m}$  hydrophilic polyethersulfone membrane filter (prewashed by 200 mL of deionized water) (Pall Life Science). The DOC concentration of the filtered sample was measured. After that, the sample was transferred into a 300 mL biochemical oxygen demand bottle and inoculated

with 1 mL of mixed liquor suspended solids (MLSS) from the Moorhead Wastewater Treatment Plant, Moorhead, MN, USA. Then, it was incubated at 20 °C for 5 days. After the incubation, the sample was then filtered through a 0.45  $\mu\text{m}$  hydrophilic polyethersulfone membrane filter (prewashed by 200 mL of deionized water) again and analyzed for DOC. A blank sample, which is deionized water inoculated with MLSS, was included. The BDOC concentration was based on the difference in DOC reduction in the sample and the blank during the incubation. For 1 L NOM fractionation samples, BDOC was determined in a similar manner as described above except that 3.3 mL of MLSS seed was used.

A two tailed t-test was performed to determine whether the levels of DOC,  $\text{UV}_{254}$  and biodegradability (BDOC/DOC) under different conditions were significantly different. A probability ( $p$ ) value of less than 0.05 was adopted as a criterion to justify that the data were significantly different. The PHStat Program of the Microsoft Excel version 12.0 was used for statistical analysis.

### 3. Results and discussion

#### 3.1. Removal of DOC

The DOC concentrations at different times have been normalized by the initial DOC. These DOC ratios are shown in Fig. 3. The error bar indicates the standard deviation of experimental error. The DOC removal tended to be linear with time and agreed well with a zero order model ( $r^2$  presented in Table 2). A similar trend was also observed by Gong et al. (2008) who investigated the oxidation of NOM in secondary effluent wastewater by ozone and ozone–UV. They found that the reduction rate of DOC was linear with time during the first 100 and 60 min for ozone and ozone–UV processes, respectively. Table 2 summarizes the DOC removal kinetic rates. The UV wavelength (UV versus VUV), ozone dosage, and pH were found to have significant effects on DOC mineralization rate and efficiency (Table 2 and Fig. 3).

An increase in the ozone dosage resulted in increases in DOC mineralization (removal) and its rate. In the ozone–VUV system, the DOC mineralization rates  $\pm$  95% confidence interval at ozone dosages of 1, 2, and 4 mg  $\text{O}_3/\text{mg C}$  (VUV 120 W) at pH 7 were  $0.0068 \pm 0.0002$ ,  $0.0079 \pm 0.0004$ ,  $0.0120 \pm 0.0005$  mg/(L min), respectively. There was a slight but statistically significant improvement in the rate when the ozone dosage was increased from 1 to 2 mg  $\text{O}_3/\text{mg C}$  ( $p = 0.0004$ ) while the rate of DOC mineralization increased substantially when ozone dosage was doubled from 2 to 4 mg  $\text{O}_3/\text{mg C}$  ( $p = 3.73 \times 10^{-6}$ ). In the ozone–UV process, the ozone dosage also had a positive relationship with the DOC mineralization rate. However, the effect of ozone dosage was less than that observed in the ozone–VUV process. The DOC mineralization rate increased about 1.5 fold between the ozone dosages of 1 and 4 mg  $\text{O}_3/\text{mg C}$  (pH 7).

Increasing ozone dosage provided more available molecular ozone and  $\text{OH}^\cdot$  (from ozone photolysis) for DOC mineralization. For example, ozone residual concentration in the ozone–VUV process (pH 7) with 1 and 4 mg  $\text{O}_3/\text{mg C}$  (pH 7) ranged 0.008–0.01 mg  $\text{O}_3/\text{L}$  and 0.11–0.20 mg  $\text{O}_3/\text{L}$ ,

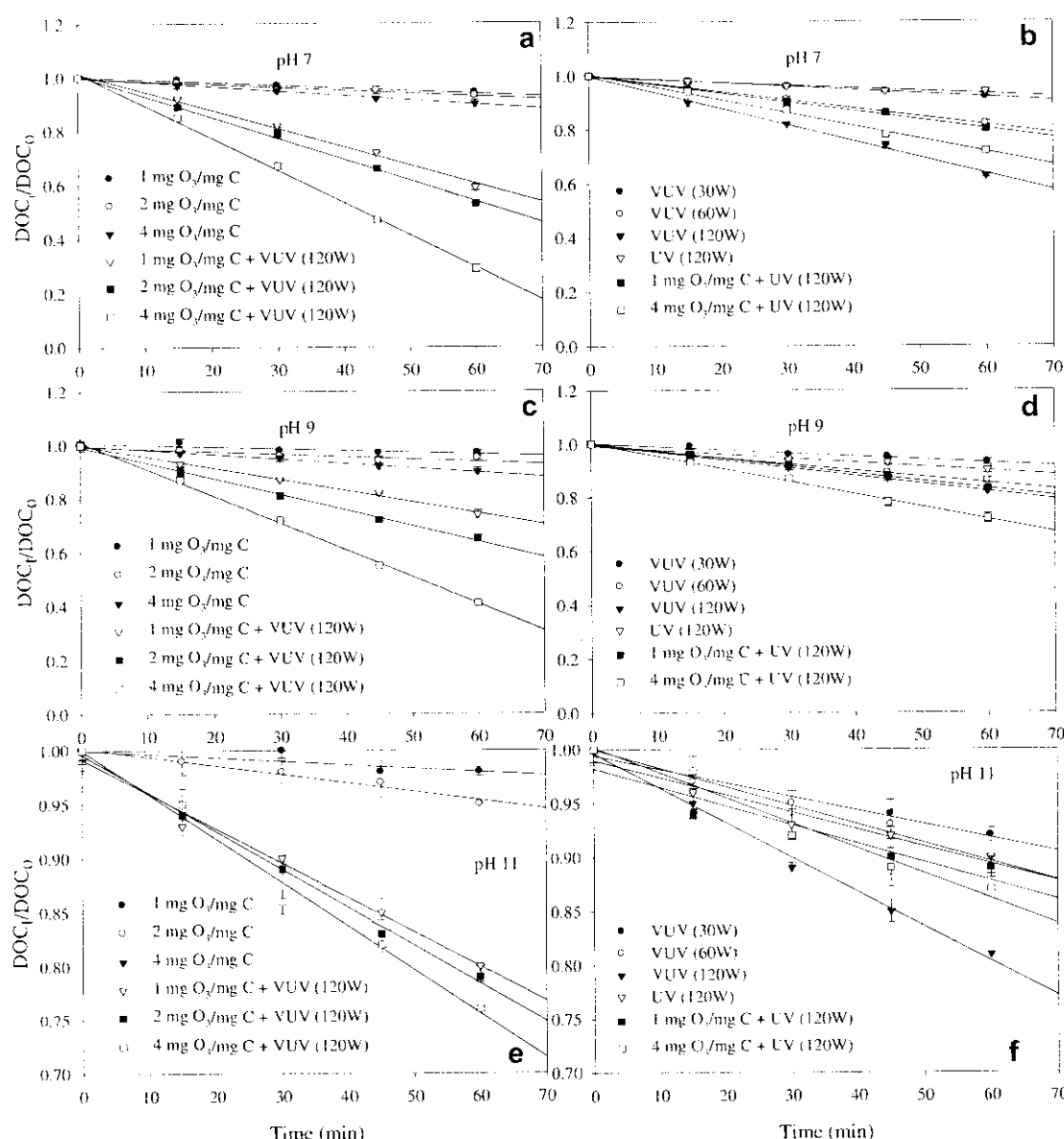


Fig. 3 – DOC at different times ( $DOC_t$ ) normalized by initial DOC ( $DOC_0$ ) provided by  $O_3$ , UV, VUV,  $O_3$  + UV,  $O_3$  + VUV at pH 7 (a and b), 9 (c and d), and 11 (e and f).

respectively. The  $OH^\cdot$  exposure at the same conditions was  $9.2 \times 10^{-12}$  mol min/L and  $1.16 \times 10^{-11}$  mol min/L, respectively. In addition, the better DOC mineralization performance at the higher ozone dosages might be due to how the ozone was applied to the system. The higher ozone dosages were attained by increasing the gas flow rate which facilitated more ozone gas transfer to the water. At pH 7, the ozone mass transfer rates of the system with only ozone at the ozone dosages of 1, 2, and 4 mg  $O_3$ /mg C were  $0.54 \pm 0.06$  mg/min,  $0.66 \pm 0.05$  mg/min, and  $1.38 \pm 0.08$  mg/min. A similar pattern was also observed at pH 9. However, at pH 11 there was little improvement in the DOC mineralization rate at the higher ozone dosages. The effect of ozone dosages was significant for ozonation alone at all three pH values ( $p \leq 0.025$ ), with the exception of between 1 and 2 mg  $O_3$ /mg C at pH 7 ( $p = 0.196$ ).

These results suggested that there could be an inhibitory effect on ozone–VUV and ozone–UV oxidation at pH 11.

When comparing among the treatment systems at the same pH, ozone dosage, and UV/VUV power, the DOC mineralization rate was in the following order: ozone–VUV > VUV > ozone–UV > ozone > UV. There was an exception at pH 9; the DOC mineralization rate of 4 mg  $O_3$ /mg C with UV was better than that of VUV. This could be due to different organic constituents in the water samples. The DOC of coagulated and softened water was high (5.45 mg/L) for the VUV experiment at pH 9 due to snow melting, while it was low (3.45 mg/L) for the ozone–UV experiment at pH 9. Note that the DOC range of coagulated and softened water used in this study was 3.43–5.48 mg/L (Table 1). At pH 7 and 11, even at 1 mg  $O_3$ /mg C dose with VUV (120 W), the DOC removal and its

**Table 2 – Summary of DOC removal and its rate constant, SUVA reduction, and BDOC/DOC ratio.**

Experimental conditions		DOC removal rate (mg/L min) ( $r^2$ )	DOC removal at 60 min (%)	SUVA reduction at 60 min (%)	BDOC/DOC	
$O_3$ (mg $O_3$ /mg C), VUV or UV (W)	pH				Initial	At 60 min
$O_3$ (1)	7	0.0010 (0.9610)	5.51	48.18	0.10	0.18
$O_3$ (2)	7	0.0012 (0.9601)	7.10	53.08	0.13	0.26
$O_3$ (4)	7	0.0017 (0.9942)	10.06	58.30	0.15	0.27
$O_3$ (1) + VUV (120)	7	0.0068 (0.9941)	40.75	61.64	0.11	0.48
$O_3$ (2) + VUV (120)	7	0.0079 (0.9969)	47.41	64.03	0.16	0.62
$O_3$ (4) + VUV (120)	7	0.0120 (0.9981)	71.21	64.38	0.09	0.68
VUV (30)	7	0.0013 (0.9962)	8.09	40.42	0.11	0.20
VUV (60)	7	0.0030 (0.9991)	18.11	56.17	0.15	0.37
VUV (120)	7	0.0061 (0.9978)	37.01	57.09	0.10	0.42
UV (120)	7	0.0012 (0.9488)	6.45	34.04	0.14	0.25
$O_3$ (1) + UV (120)	7	0.0032 (0.9991)	19.59	70.26	0.07	0.43
$O_3$ (4) + UV (120)	7	0.0049 (0.9941)	28.35	74.36	0.09	0.40
$O_3$ (1)	9	0.0007 (0.7630)	3.35	43.57	0.27	0.33
$O_3$ (2)	9	0.0009 (0.8363)	4.81	51.52	0.08	0.22
$O_3$ (4)	9	0.0017 (0.9991)	10.31	57.12	0.09	0.20
$O_3$ (1) + VUV (120)	9	0.0042 (0.9964)	25.80	71.12	0.30	0.46
$O_3$ (2) + VUV (120)	9	0.0060 (0.9985)	35.59	67.31	0.08	0.42
$O_3$ (4) + VUV (120)	9	0.0099 (0.9979)	58.58	67.38	0.13	0.64
VUV (30)	9	0.0012 (0.9860)	7.48	43.38	0.10	0.19
VUV (60)	9	0.0024 (0.9893)	14.42	52.70	0.11	0.26
VUV (120)	9	0.0029 (0.9965)	18.05	67.26	0.29	0.38
UV (120)	9	0.0016 (0.9670)	10.28	45.51	0.16	0.27
$O_3$ (1) + UV (120)	9	0.0028 (0.9968)	16.97	76.44	0.11	0.35
$O_3$ (4) + UV (120)	9	0.0047 (0.9970)	27.73	70.56	0.15	0.49
$O_3$ (1)	11	0.0004 (0.7956)	2.45	30.91	0.08	0.11
$O_3$ (2)	11	0.0007 (0.8849)	5.22	37.66	0.07	0.16
$O_3$ (4)	11	0.0016 (0.9938)	9.74	47.38	0.10	0.24
$O_3$ (1) + VUV (120)	11	0.0032 (0.9881)	19.85	74.41	0.08	0.39
$O_3$ (2) + VUV (120)	11	0.0035 (0.9958)	21.09	71.20	0.10	0.44
$O_3$ (4) + VUV (120)	11	0.0040 (0.9864)	23.74	80.33	0.08	0.41
VUV (30)	11	0.0012 (0.9373)	7.84	34.90	0.07	0.20
VUV (60)	11	0.0018 (0.9923)	10.83	47.84	0.07	0.19
VUV (120)	11	0.0031 (0.9912)	18.89	59.86	0.07	0.24
UV (120)	11	0.0016 (0.9531)	9.94	43.39	0.14	0.34
$O_3$ (1) + UV (120)	11	0.0018 (0.8998)	11.37	68.66	0.20	0.43
$O_3$ (4) + UV (120)	11	0.0023 (0.9579)	12.71	73.56	0.14	0.44

rate were significantly higher than those of 4 mg  $O_3$ /mg C alone, VUV (120 W), and 4 mg  $O_3$ /mg C with UV ( $p \leq 0.0014$ ). The DOC removal rate and efficiency of VUV (120 W) were better than those of 4 mg  $O_3$ /mg C with UV ( $p = 7 \times 10^{-6}$ ).

The ozone–VUV system provided an approximately two fold greater mineralization rate and efficiency when compared to the ozone–UV system. This result was expected since in the ozone–VUV system, the VUV generated more  $OH^\cdot$  through direct water homolysis and reaction with  $H_2O_2$  (produced from ozone photolysis) (Garoma and Gurol, 2004; Gonzalez et al., 2004). The exposure of hydroxyl radicals of ozone–VUV and ozone–UV ( $O_3 = 4$  mg  $O_3$ /mg C) at pH 7 was  $1.16 \times 10^{-11}$  mol min/L and  $3.98 \times 10^{-12}$  mol min/L, respectively. A synergistic effect was observed when combining ozone with UV and VUV at pH 7 and 9 but not at pH 11. For example, at pH 7 ( $O_3 = 4$  mg  $O_3$ /mg C and VUV = 120 W), the DOC removal for ozone, VUV, and ozone–VUV was 10.0%, 37.0%, and 71.2% while at pH 11 they were 9.7%, 18.9%, and 23.7%, respectively. The summation of the DOC removal at pH 11 of ozone alone and VUV alone was more than ozone–VUV system (28.6% versus 23.7%).

As shown in Fig. 3 and Table 2, pH was found to have a substantial effect on DOC mineralization kinetics. The DOC removal rate increased as pH decreased. Beltrán et al. (1995) reported a similar observation that the oxidation rate decreased as pH increased from 7 to 12 in an ozone–UV experiment for fluorene removal. Increasing pH results in more  $OH^\cdot$  which accelerates the decomposition of ozone to  $OH^\cdot$ . However, increasing pH also reduces the amount of ozone available for direct photolysis with VUV to form  $H_2O_2$ , which is also a precursor for  $OH^\cdot$  production. In addition, at high pH the dissociation of  $OH^\cdot$  to oxygen anion radical ( $O^\cdot$ ) takes place (Equation (3)) resulting in  $OH^\cdot$  reduction. An alternative explanation is that at high pH the NOM molecules containing acid functional groups are in the deprotonated (anionic) form. Quici et al. (2008) observed the reduction of removal rate of citric acid (mostly in the tri- and tetra-anion forms) by VUV at pH 11. The radical  $O^\cdot$  is less reactive and more selective than  $OH^\cdot$  and its reaction with anionic molecules decreased because of coulombic repulsion. The effect of hydroxyl radical scavenging by carbonate/bicarbonate species at different pH can also be used to explain the effect of pH on



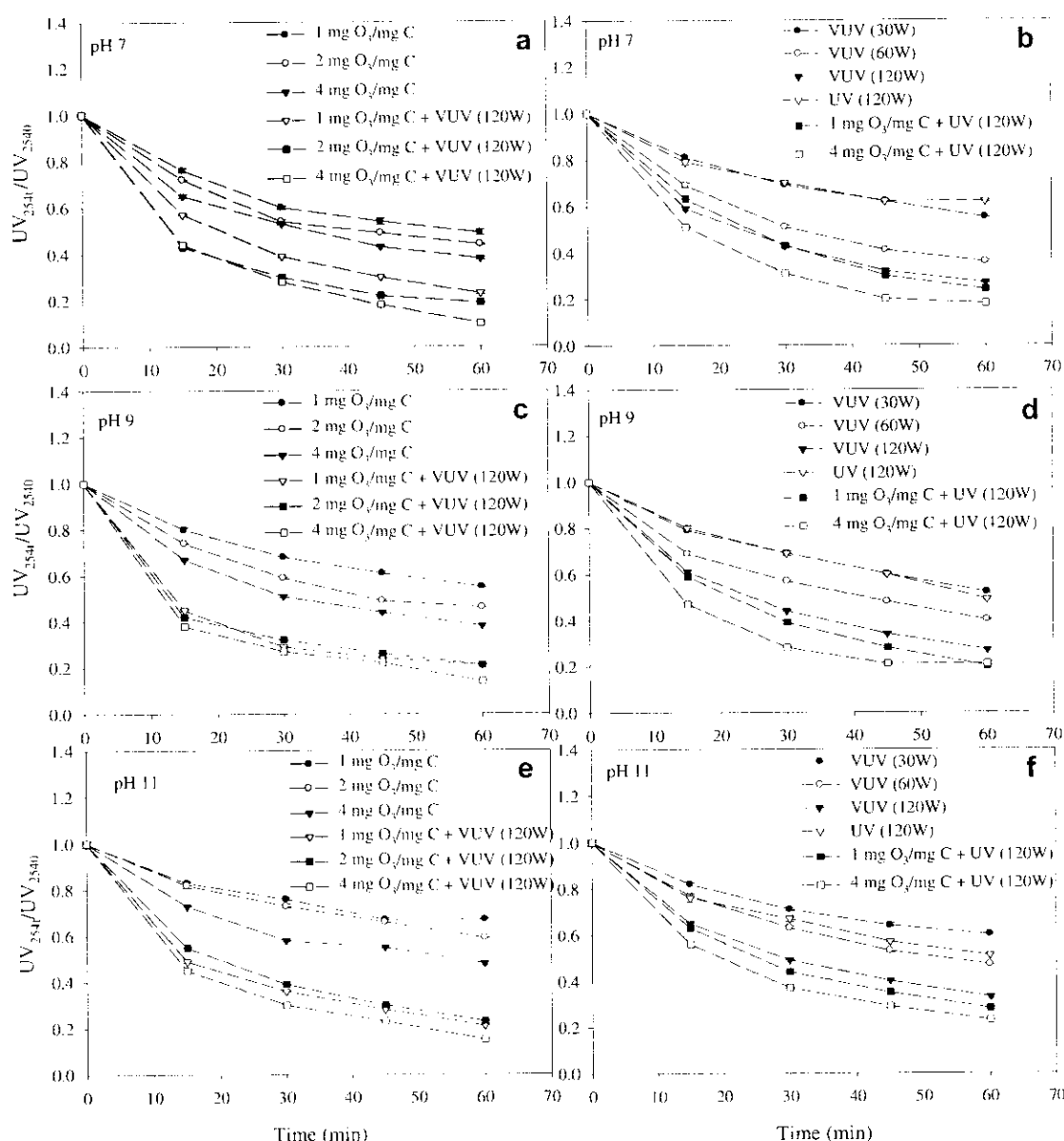


Fig. 4 – UV<sub>254</sub> at different times (UV<sub>254t</sub>) normalized by initial UV<sub>254</sub> (UV<sub>2540</sub>) provided by O<sub>3</sub>, UV, VUV, O<sub>3</sub> + UV, O<sub>3</sub> + VUV at pH 7 (a and b), 9 (c and d), and 11 (e and f).

NOM mineralization. Carbonate is more effective in scavenging hydroxyl radicals compared to bicarbonate. At higher pH, carbonate concentration increases resulting in less hydroxyl radicals available for reaction with NOM.



### 3.2. UV<sub>254</sub> and SUVA changes

UV<sub>254</sub> and SUVA are commonly used as the indicators of a relative amount of unsaturated and/or aromatic carbon of NOM. The average SUVA of the coagulated and softened water samples was 1.04 (L/mg C m) indicating that they contained mostly non humic substances (Edzwald and Tobiason, 1999).

UV<sub>254</sub> at different times normalized by initial UV<sub>254</sub>, and SUVA reduction at 60 min are presented in Fig. 4 and Table 2, respectively. For all experimental conditions, a rapid decrease of UV<sub>254</sub> was observed during the first 15 min indicating that the unsaturated and/or aromatic carbon molecules were preferentially oxidized. After that, the reduction of UV<sub>254</sub> started to decline and level off at 30 or 45 min for some conditions. The leveling off of UV<sub>254</sub> indicated no further reduction of unsaturated or aromatic organic molecules. Higher UV<sub>254</sub> reduction compared to DOC removal at the end of the experiment suggested incomplete mineralization of organic molecules degraded from unsaturated and/or aromatic organics. The reduction of UV<sub>254</sub> was made up of the decay of rapid reacting constituents and slow reacting

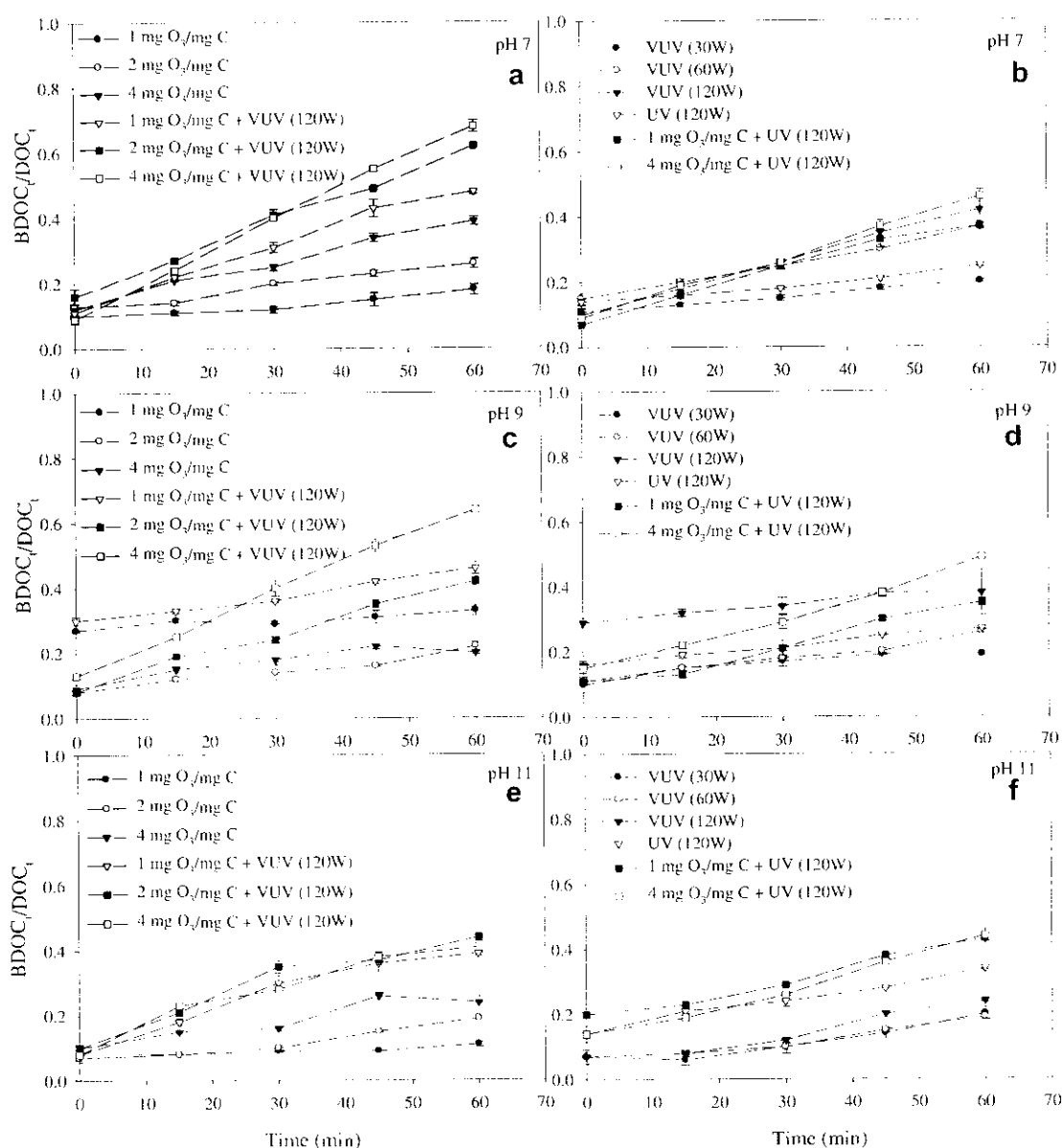


Fig. 5 – Biodegradability at different times (BDOC at different times or BDOC<sub>t</sub> divided by DOC<sub>t</sub>) provided by O<sub>3</sub>, UV, VUV, O<sub>3</sub> + UV, O<sub>3</sub> + VUV at pH 7 (a and b), 9 (c and d), and 11 (e and f).

constituents, respectively. Similar trends were also observed for NOM removal by VUV (Buchanan et al., 2005), and ozone–UV and ozone alone (Gong et al., 2008).

An increase in the ozone dosage led to more UV<sub>254</sub> reduction for ozone, ozone–UV, and ozone–VUV processes. For example, at pH 7, the ozone–VUV system provided UV<sub>254</sub> reduction of 77%, 81%, and 90% at the ozone dosages of 1, 2, and 4 mg O<sub>3</sub>/mg C, respectively. These efficiencies were statistically different ( $p \leq 3.4 \times 10^{-6}$ ). By comparing among the oxidation processes at the same pH, ozone dosage and UV/VUV power, the UV<sub>254</sub> reduction was in the following order: ozone–VUV > ozone–UV > VUV > ozone > UV. The order was different from that for the DOC removal; VUV mineralized DOC more efficiently than ozone–UV. The superiority of ozone–UV

over VUV in UV<sub>254</sub> reduction could be because of the direct reaction of ozone through the electrophilic substitution reaction with unsaturated and/or aromatic bonds (Beltrán, 2004). At the same pH, ozone of 1 mg O<sub>3</sub>/mg C + VUV (120 W) and ozone of 4 mg O<sub>3</sub>/mg C + UV had comparable UV<sub>254</sub> reduction ( $p < 0.831$ ). It was observed that SUVA reduction by ozone–UV was higher than by ozone–VUV (Table 2). For the ozone–UV process, the degradation of unsaturated and/or aromatic molecules to smaller organic molecules dominated the mineralization since a higher reduction of UV<sub>254</sub> (80%) compared to DOC mineralization (<29%) was observed. The pH had less effect on the UV<sub>254</sub> reduction compared to DOC mineralization. For the same system, UV<sub>254</sub> reduction was comparable at pH 7 and 9 but was 5–10% lower at pH 11.

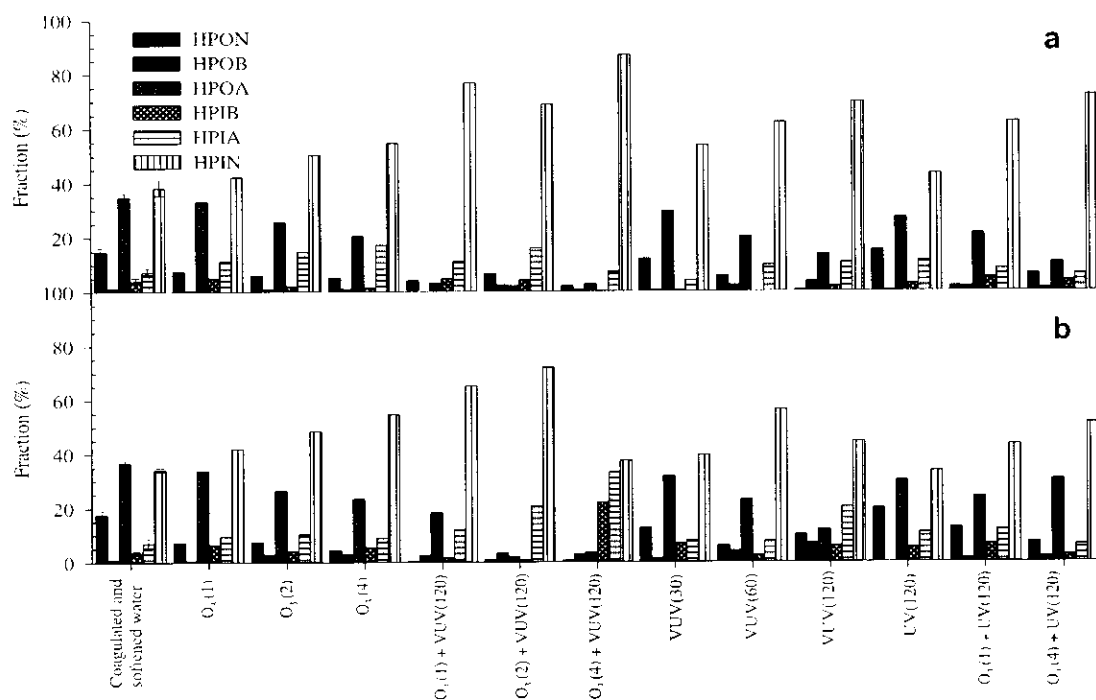


Fig. 6 – (a) NOM fractions of coagulated and softened water before and after  $O_3$ , UV, VUV,  $O_3$  + UV,  $O_3$  + VUV at pH 7 and (b) NOM fractions of unoxidized and oxidized coagulated and softened water after BDOC test.  $O_3$  (mg  $O_3$ /mg C) and VUV or UV (W).

### 3.3. Biodegradability change

The ratio of BDOC and DOC (BDOC/DOC) describes the fraction of biodegradable organic portion relative to the total organic content (biodegradability). Fig. 5 shows a plot between BDOC/

DOC versus time for different experiments. For untreated samples, BDOC/DOC ranged from 0.07 to 0.30 (Table 2). As shown in Fig. 5, BDOC/DOC increased with time. The BDOC/DOC after 60 min of oxidation ranged from 0.11 to 0.68. The additions of UV and VUV to the ozonation process generated

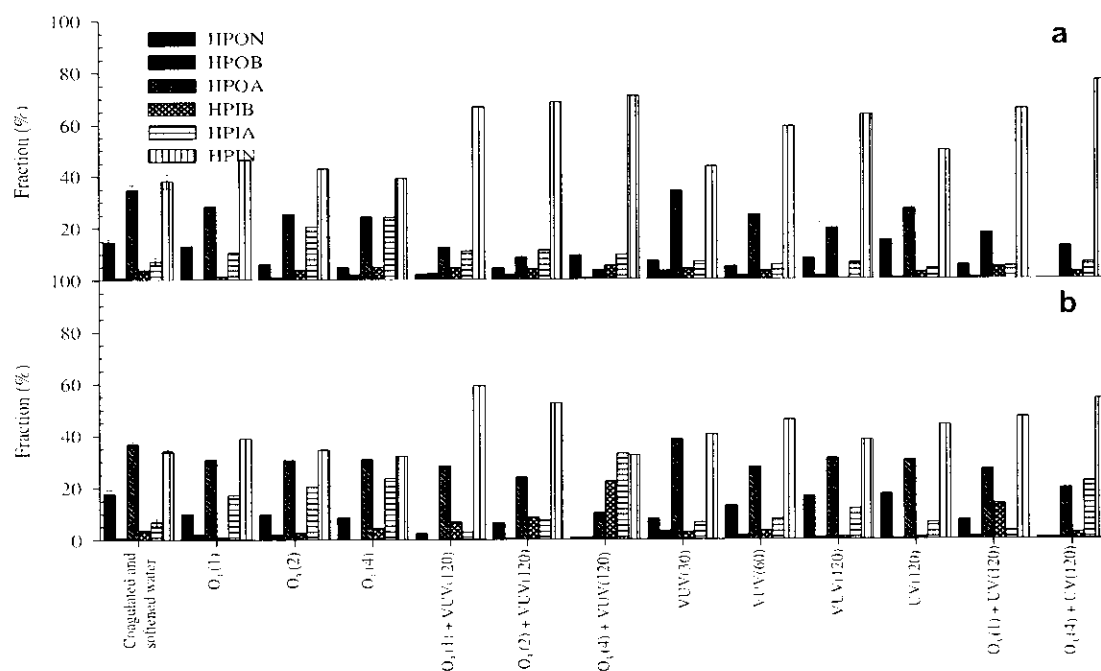


Fig. 7 – (a) NOM fractions of coagulated and softened water before and after  $O_3$ , UV, VUV,  $O_3$  + UV,  $O_3$  + VUV at pH 9 and (b) NOM fractions of unoxidized and oxidized coagulated and softened water after BDOC test.  $O_3$  (mg  $O_3$ /mg C) and VUV or UV (W).

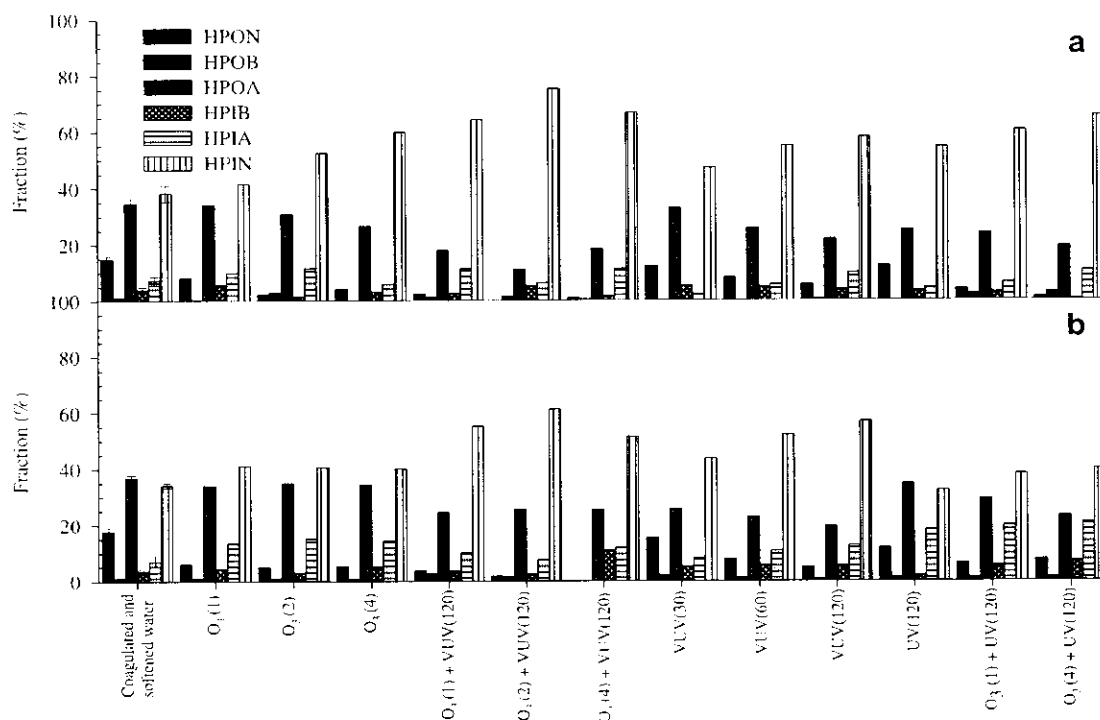


Fig. 8 – (a) NOM fractions of coagulated and softened water before and after  $O_3$ , UV, VUV,  $O_3$  + UV,  $O_3$  + VUV at pH 11 and (b) NOM fractions of unoxidized and oxidized coagulated and softened water after BDOC test.  $O_3$  (mg  $O_3$ /mg C) and VUV or UV (W).

more BDOC formation than ozone alone. The ozone–VUV system provided higher BDOC/DOC and a faster rate of BDOC/DOC increase compared to the ozone–UV system. This was due to more mineralization of DOC in the ozone–VUV system since the BDOC levels generated by both systems were not significantly different. For example, at pH 7 and ozone dosage of 4 mg  $O_3$ /mg C, BDOC and DOC at 60 min were  $0.70 \pm 0.04$  mg/L and  $1.03 \pm 0.02$  mg/L for the ozone–VUV system compared to  $1.03 \pm 0.07$  mg/L and  $2.56 \pm 0.03$  mg/L for the ozone–UV system.

Among the processes studied, the biodegradability increase was in the following order: ozone–VUV > ozone–UV > VUV >

ozone > UV. The ozone–VUV at 1 mg  $O_3$ /mg C provided comparable biodegradability to ozone–UV at 4 mg  $O_3$ /mg C ( $p > 0.183$ ). This indicates that the same biodegradability can be achieved with less ozone dosage if it is supplemented with VUV instead of UV. The rankings of treatment processes studied for  $UV_{254}$  reduction and biodegradability increase were in the same order. The decomposition of unsaturated and/or aromatic organics likely contributed to the formation of biodegradable compounds.

For the effect of pH, BDOC/DOC values were comparable at pH 7 and 9 for the same ozone dose and VUV/UV power ( $p > 0.062$ ). However, lower BDOC/DOC values were observed at pH 11. This could be due to less mineralization of DOC by the ozone–VUV and ozone–UV systems at pH 11. Under some conditions, BDOC/DOC reached a plateau at 45 min. The plateau suggested that BDOC decreased at the same percentage as DOC, or BDOC and DOC remained relatively constant. It was noticed that high BDOC/DOC (>60%) at 60 min was achieved by ozone–VUV at pH 7 and 9. If the oxidized water was followed by biofiltration, a substantial amount of DOC (as high as 60%) would be eliminated through the removal of BDOC. BDOC at 5 days is associated with rapid BDOC (Khan et al., 1999; Volk et al., 1994) and is a good surrogate of BDOC that would be removed by biofiltration.

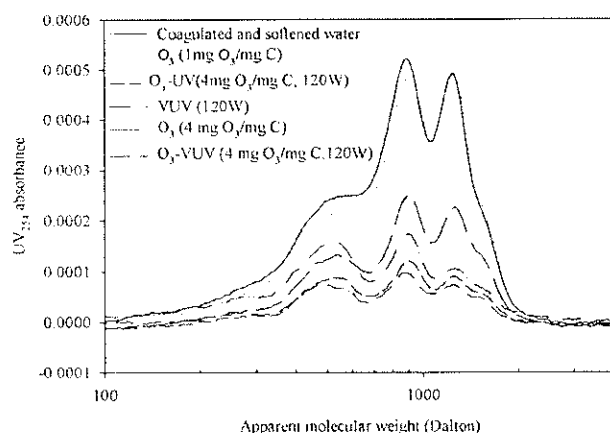


Fig. 9 – HPSEC chromatograms of water samples before and after treated by ozone, ozone–UV, ozone–VUV, and VUV at pH 7.

### 3.4. Fractions of NOM before and after oxidation, and after BDOC test

Fractions of NOM in coagulated and softened water before and after the oxidation, and NOM in coagulated and softened

**Table 3 – Molecular weight distribution of NOM before and after oxidation (pH 7).**

Samples	Molecular weight distribution (%) [change of the area count compared to coagulated and softened water, %]				
	<350 Da	350–700 Da	700–1050 Da	1050–1400 Da	>1400 Da
Coagulated and softened water	3.6	16.0	33.5	31.7	15.1
O <sub>3</sub> (1 mg O <sub>3</sub> /mg C)	2.2 [45.2]	15.0 [13.7]	33.8 [7.4]	33.6 [2.7]	15.5 [5.7]
O <sub>3</sub> (4 mg O <sub>3</sub> /mg C)	1.1 [93.4]	23.7 [68.5]	31.9 [79.8]	24.7 [83.5]	18.5 [74.0]
+ UV (120 W)					
VUV (120 W)	7.4 [29.7]	23.6 [49.1]	30.8 [68.3]	20.3 [77.9]	17.8 [59.4]
O <sub>3</sub> (4 mg O <sub>3</sub> /mg C)	1.3 [83.7]	17.5 [48.5]	31.1 [56.5]	28.1 [58.5]	22.0 [31.7]
O <sub>3</sub> (4 mg O <sub>3</sub> /mg C)	2.4 [88.5]	22.1 [75.5]	31.6 [83.3]	21.5 [88.0]	22.4 [73.7]
+ VUV (120 W)					

water and oxidized NOM after the BDOC test are shown in Figs. 6–8 (for initial pH 7, 9, and 11 used in the oxidation, respectively). These NOM fractionation results provided insight into the treatability of different groups of organic compounds in NOM by oxidation and biodegradation. The information is useful for evaluating the effectiveness of the processes for the removal of NOM fractions that are problematic such as those with potential to form carcinogenic disinfection byproducts.

NOM in coagulated and softened water consisted of HPON of  $14.8 \pm 2.3\%$ , HPOB of  $1.0 \pm 0.4\%$ , HPOA of  $34.8 \pm 3.5\%$ , HPIB of  $3.9 \pm 1.7\%$ , HPIA of  $7.3 \pm 2.6\%$ , and HPIN of  $38.3 \pm 5.1\%$ . The percentage ratio between hydrophobic and hydrophilic was approximately 50:50. As shown in Figs. 6a, 7a, and 8a, the oxidation processes not only mineralized NOM but also changed the NOM characteristic to be more hydrophilic. For the ozone and ozone–UV systems, increasing ozone dosage caused reductions in HPON and HPOA fractions and increases in HPIA and HPIN fractions. For the ozone system at pH 7, HPOA fraction decreased to 33%, 26%, and 21%, while HPIN fraction increased to 42%, 49%, and 54% at the ozone dosages of 1, 2, 4 mg O<sub>3</sub>/mg C, respectively. With the addition of UV (pH 7), ozone had transformed NOM to be more hydrophilic. For the ozone–UV system (1 and 4 mg O<sub>3</sub>/mg C, UV = 120 W), HPOA fraction was reduced to 21% and 11% while HPIN fraction was increased to 62% and 72%, respectively. This could be due to more generation of OH<sup>•</sup> which reacted less selectively to NOM fractions. Increasing VUV power provided similar effects (more HPOA reduction and more HPIN formation) as increasing ozone dosage.

The combination of ozone and VUV caused a substantial change in NOM characteristic. The majority of NOM was transformed into HPIN fraction (>64%). Particularly after being treated with the ozone dosage of 4 mg O<sub>3</sub>/mg C and VUV of 120 W at pH 7, HPIN fraction increased to 87% leaving the other five fractions only 13%. The high percentage of HPIN fraction suggested the formation of short chain aliphatic of aldehydes and ketones which are the major components of HPIN fraction (Swietlik et al., 2004). Liu et al. (2008) reported increases in formaldehyde and acetone levels as well as HPIN fraction of NOM treated by UV at a wavelength of 365 nm (UVA)–TiO<sub>2</sub> and UVA TiO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub> processes. The effect of pH in the oxidation processes showed a similar pattern in terms of the characteristic of NOM fractions. At the lower pH, the processes tended to yield more hydrophilic fractions. This could be due to higher reduction of UV<sub>254</sub> (unsaturated and/or aromatic carbon) as pH decreased.

Biological removal of oxidized NOM is presented in Figs. 6b, 7b, and 8b for pH 7, 9, and 11, respectively. These figures show the composition of remaining NOM after the BDOC test, which is a surrogate indicator of how much NOM would be removed by biofiltration. In the coagulated and softened water, BDOC was 0.57 mg/L or 14% of DOC. The oxidation changed the NOM structure to smaller molecules, more hydrophilic, and more biodegradable. The HPIA and HPIN fractions accumulated during the oxidation contributed to the majority of BDOC pool. These compounds are aldehydes, ketones, and short chain carboxylic acids, which are common byproducts of ozonated and/or UV treated water (Swietlik et al., 2004; Thomson et al., 2002). Reduction in the percentage of HPIN fraction after the BDOC test indicated relatively high biodegradability of the fraction. This effect was more remarkable for the ozone–VUV system at the ozone dosage of 4 mg O<sub>3</sub>/mg C, and pH 7 and 9; the percentage of HPIN decreased from 87% to 38% and 71%–32%, respectively. Although HPIN and HPIA are the major portions of BDOC, they still remained the main fractions of NOM after biodegradation (the BDOC test) under all experimental conditions. Buchanan et al. (2008) reported a similar finding that HPIN was a dominant NOM fraction after VUV irradiation and biological activated carbon filtration.

### 3.5. Effect of oxidation processes on NOM molecular weight distribution

HPSEC chromatograms of the coagulated and softened sample and selected samples after 60 min treatment by ozone, ozone–UV, ozone–VUV, and VUV at pH 7 are shown in Fig. 9. The percent distribution of NOM in different molecular weight ranges is presented in Table 3. The number in the bracket refers to percent change of area under the chromatogram of oxidized samples relative to the area under the chromatogram of the coagulated and softened sample. It should be noted that the molecular weight distributions of the samples covered only chromophoric NOM molecules which absorb UV at a wavelength of 254 nm associated with the HPLC unit and UV detector used to acquire the HPSEC chromatogram. Therefore the reduction of the area does not guarantee the mineralization of NOM.

The coagulated and softened sample mostly consisted of molecules ranging from 100 to 2000 Da with two major peaks at around 900 Da and 1200 Da, a large shoulder peak at 500 Da, and a small shoulder peak at 1500 Da. The range of molecular

weight of 700–1400 Da accounted for 67% of the sample (Table 3). It was clear that the oxidation processes degraded high molecular weight compounds to lower ones as the percent NOM distribution in the range of 1050–1400 Da decreased while that in the range of 350–700 Da increased (Table 3). The combination of UV or VUV with ozone was found to be effective in reducing all molecular weight ranges (more than 69–93% change of the area). Ozone alone was able to oxidize large molecular weight fractions but less effective compared to ozone–UV and ozone–VUV because of less OH<sup>•</sup> production. Ozone was effective in oxidizing molecules with lower molecular weights (<350 Da). OH<sup>•</sup> might be responsible for oxidizing NOM constituents with higher molecular weights. Westerhoff et al. (1999) observed a positive correlation between the molecular weight and aromaticity of NOM and the reaction rate constant between OH<sup>•</sup> and NOM. It was explained that higher molecular weight compounds tend to be more aromatic and may have larger numbers of reaction sites.

It is interesting that the VUV process had the least reduction in the <350 Da fraction (only 29.7%) while it preferentially oxidized high molecular weight fractions (49.1–77.9% change of the area count relative to the unoxidized sample). Similar results were observed in other advanced oxidation processes such as TiO<sub>2</sub> photocatalysis (Liu et al., 2008) and UV–H<sub>2</sub>O<sub>2</sub> (Sarathy and Mohseni, 2007). This could be due to the depolymerization of larger molecules to smaller molecules (Thomson et al., 2004). The decomposition of compounds with higher molecular weights agreed with more biodegradable fraction and less UV<sub>254</sub> and SUVA in the samples after the oxidation.

#### 4. Conclusions

The findings of this research show that the ozone–VUV process has potential for the effective removal of NOM. The ozone–VUV process demonstrated the best performance for DOC mineralization, UV<sub>254</sub> reduction, and biodegradability (BDOC/DOC) increase compared to the ozone, VUV, ozone–UV, and UV processes. The synergistic effect in the ozone–VUV process makes the technology more attractive to the water treatment industry. The biodegradability increase by the ozone–VUV process indicates the benefit of NOM removal in subsequent biological filters. A study of the process with a biological filter is recommended to determine how the system affects the biostability of water as well as the reduction in the formation of disinfection byproducts such as THMs and HAAs. The kinetic modeling of DOC mineralization and biodegradability increase by the ozone–VUV process should be developed. Also the effect of the process on the formation of bromate (carcinogenic ozonation byproduct) in bromide containing water should be investigated.

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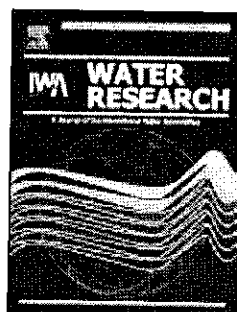
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