

UV/H₂O₂ Treatment of Drinking Water: Impacts on NOM Characteristics

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ABSTRACT

The impact of ultraviolet/hydrogen peroxide (UV/H₂O₂) advanced oxidation process (AOP) on natural organic matter (NOM) was evaluated. Operating conditions were selected based on those feasible for commercial drinking water applications. Results showed that at fluences less than or equal to 2000 mJ/cm² and initial H₂O₂ concentrations less than or equal to 15 mg/L NOM was not completely mineralized. Yet, UV/H₂O₂ partially oxidized NOM leading to the breakdown of aromatic structures. UV/H₂O₂ preferentially reacted with high molecular weight species leading the formation of lower molecular weight species. Formed low molecular compounds included aldehydes, which increased by up to 7 times from the concentration present in untreated water.

Key words: UV/H₂O₂; natural organic matter; advanced oxidation; drinking water treatment

INTRODUCTION

Ultraviolet (UV) based advanced oxidation processes (AOPs) are increasingly being considered as effective alternatives for the removal of organic compounds in water and wastewater. In drinking water, the ultraviolet/hydrogen peroxide (UV/H₂O₂) AOP has already been applied commercially for the removal of organic micro-pollutants (Sarathy and Mohseni, 2006) and the number of drinking water applications has been steadily increasing since the dawn of the 21st century. UV/H₂O₂ has been demonstrated to be an effective technology for treating organic micro-pollutants, such as pesticides and taste and odour compounds, and carrying out primary disinfection.

One of the key parameters affecting the performance of UV/H₂O₂ AOP is the presence of natural organic matter (NOM) in source water. NOM scavenges hydroxyl radicals necessary for contaminant degradation, absorbs UV that would otherwise be available for photolysis of H₂O₂, and may undergo changes in structure that could possibly affect the water's biological regrowth potential (BRP) and NOM's potential to form chlorination disinfection by-products (DBPs). Raw surface waters can contain substantial NOM that serves as a precursor to the DBPs (Oliver and Lawrence, 1979). The main DBPs identified in drinking water have been trihalomethanes (THMs) and haloacetic acids (HAAs), which are documented to adversely impact human health (Richardson, 1998).

While much research has focused on developing applications for UV/H₂O₂, little attempt has been made to evaluate the impact of UV/H₂O₂ on NOM. Specifically, the

results of hydroxyl radical ([•]OH) reaction with NOM have not garnered much attention. This is of particular importance since NOM plays a critical role in the treatment and distribution of drinking water, contributing to BRP and the formation of DBPs. Past studies have demonstrated that substantial reduction of DBP formation potential (DBP-FP) could be achieved using UV/H₂O₂ (Wang et al., 2000; Kleiser and Frimmel, 2000; Liu et al., 2002; Thomson et al., 2004b; Toor and Mohseni, 2007). But, all these studies mainly focussed on strong advanced oxidation conditions made possible by very long UV exposures (i.e. fluence) and/or high H₂O₂ concentration. Under such conditions NOM is mineralised leading to a reduction in the concentration of NOM. Such operating parameters are not economically feasible when scaled up. Little attempt has been made to evaluate the UV/H₂O₂ impact on NOM under conditions representing large-scale applications, which are not likely to exceed an operating fluence of 2000 mJ/cm² and a H₂O₂ concentration of 20 mg/L.

EXPERIMENTAL

Source Water

Water used in all experiments was obtained from the Capilano Reservoir, serving the Greater Vancouver Region, British Columbia, Canada. The damming of the Capilano River, which is fed by fall and winter rain runoff and the spring snowmelt, forms the reservoir. Given the low total organic carbon (TOC) and absorbance of 254 nm UV (A₂₅₄) (Table I) Capilano water (CW) is a surface water of very high quality and presently undergoes no coagulation/

flocculation or filtration prior to chlorine disinfection. However, high turbidity events do occur during which time the reservoir's supply is shutdown until turbidity levels return to normal (Table I).

Table I. Physical and chemical parameters for water originating from Capilano Reservoir during 2005. (source: the Greater Vancouver Water District Quality Control Annual Report, 2005)

Parameter	Average	Range
Alkalinity as CaCO ₃ (mg/L)	2.7	2.1-3.6
Dissolved organic carbon (mg/L)	2.0	1.6-2.7
Total organic carbon (mg/L)	2.0	1.5-2.9
Hardness as CaCO ₃ (mg/L)	4.10	3.36-4.85
pH	6.5	6.2-6.9
Turbidity (NTU)	1	0.32-5.9
A ₂₅₄ (cm ⁻¹)	0.081	0.055-0.108

UV/H₂O₂ Treatment

A collimated beam apparatus, consisting of low pressure UV lamp (Trojan Technologies, London, ON) positioned 28 cm above a circular stirred reactor chamber was employed for the batch UV/ H₂O₂ studies. The reactor chamber was 3.2 cm in diameter and the water pathlength was 4.66 cm. Samples were irradiated for calculated durations to achieve five different delivered fluences from 0 to 1400 mJ/cm². H₂O₂ (30%, Fisher Scientific) was added initially to the reactor chamber at the concentrations of 0, 5, 10, 15, and 20 mg/L. Each treatment condition was carried out in duplicate. The entire water sample volume (200 mL) was used for the various analyses described below. H₂O₂ containing samples were quenched of H₂O₂ using 0.2 mg/L bovine liver catalase (Aldrich Canada) prior to A₂₅₄, TOC, and high performance size exclusion chromatography (HPSEC) measurements and prior to chlorination.

Analytical Methods

Incident UV irradiance of 254 nm light, across the surface of the water (E_{surface}), was determined by iodide/iodate actinometry (Rahn, 1997) where potassium iodide (Reagent A.C.S., Fisher Scientific) irradiated by UV led to the formation of triiodide. Potassium iodate (Certified A.C.S., Fisher Scientific) acted as an electron scavenger while sodium borate (Laboratory grade, Fisher Scientific) buffered the reaction at a pH of 9.25 (Rahn, 1997). A radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) served as a reference. The fluence rate (E_{avg}) was used to calculate the delivered fluence. E_{avg} was defined as the product of E_{surface}, the reflection factor (RF) equal to 0.975 (Bolton and Linden, 2003), and the water factor (WF) and the divergence factor (DF). WF and DF are based on the water absorbance, path length, and the distance between the lamp and water surface

(equations given by Bolton and Linden, 2003).

$$[1] E_{avg} = E_{surface} \cdot E_{surface} \cdot WF \cdot DF$$

H₂O₂ concentration was measured by reaction with iodide catalyzed by molybdate (Klassen et al., 1994). TOC was measured using a combustion catalytic oxidation/nondispersive infrared sensor TOC analyzer (Shimadzu TOC-VCPH). Absorbance measurements were determined using a UV-Vis spectrophotometer (Shimadzu UV-Mini 1240) with a cell pathlength of 1 cm.

HPSEC was employed to determine the apparent molecular weight (AMW) distribution of NOM in untreated and treated waters. Following the method described by Pelekani et al. (1999), a Waters 1535 Binary HPLC Pump fitted with a Waters Protein-Pak™ 125 Å column and a Waters 2487 Dual λ Absorbance Detector, set to detection at 260 nm, served as the instrument for HPSEC analysis. The carrier solvent consisted of 0.02 M phosphate buffer (Laboratory grade, Fisher Scientific), at pH 6.8, adjusted with sodium chloride (Certified A.C.S., Fisher Scientific) to 0.1 M ionic strength and the column flowrate was 0.7 mL/min. AMW was correlated to retention time by calibration with polysulfonate standards (7 kDa PSS7K, 4 kDa PSS4K, 2 kDa PSS2K, American Polymer Standards Corporation) and acetone (Certified A.C.S., Fisher Scientific) at a concentration of 1 g/L. HPSEC data were imported into PeakFit which was used for resolution of all



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HPSEC chromatograms. The resolved peaks were placed into AMW fractions based on their retention times and then quantified.

Results and Discussion

CW was treated by UV/ H₂O₂ at fluences of 0, 500, 1000, 1500, and 2000 mJ/cm² and initial H₂O₂ concentrations close to 0, 5, and 15 mg/L. In the absence of UV, that is only H₂O₂, the concentration and structure of NOM was not significantly altered (data not shown). Thus, H₂O₂ itself has a minimal impact on the oxidation of NOM. Similarly, in the absence of H₂O₂, that is only UV irradiation, NOM did not breakdown by direct photolysis, up to a fluence of 2000 mJ/cm² (data not shown). Research conclusively reports that any significant impact of 254 nm UV on NOM begins to be observed at very high fluences (>4,000 mJ/cm²), which are unfeasible for commercial applications due to energy demand (Thomson et al., 2002a; Thomson et al. 2002b; Parkinson et al., 2003; Buchanan et al., 2004; Thomson et al. 2004a; Thomson et al. 2004b; Buchanan et al., 2005; Buchanan et al., 2006).

Under advanced oxidation conditions, that is a combination of UV and H₂O₂, significant oxidation of NOM was observed. However, this oxidation was not complete since there was no observed decrease in TOC, the concentration of NOM (Figure 1). But, partial oxidation did occur as a reduction in A₂₅₄ was observed, indicating degradation of aromatic species (Figure 2). Aromatic species were further removed as both fluence and initial H₂O₂ concentration increased. As fluence is increased, •OH continue to be generated so aromatic species are degraded further as a result of increased exposure to •OH. As initial H₂O₂ concentration is increased, the steady-state •OH concentration increases (Sharpless and Linden, 2003) so aromatic species are further degraded as a result of increased concentration of •OH.

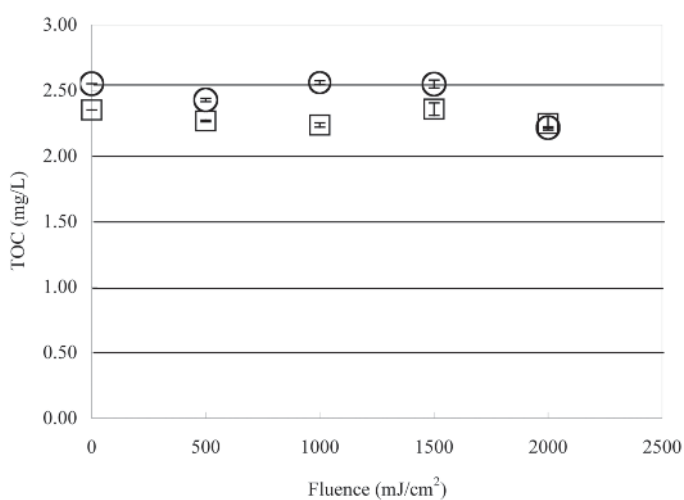


Figure 1. The impact of fluence and initial H₂O₂ concentrations of 15 (O) and 5 (□) mg/L on TOC. Points represent the average of two samples, each measured three times. Error bars represent the standard deviation between the average measurements for two samples.

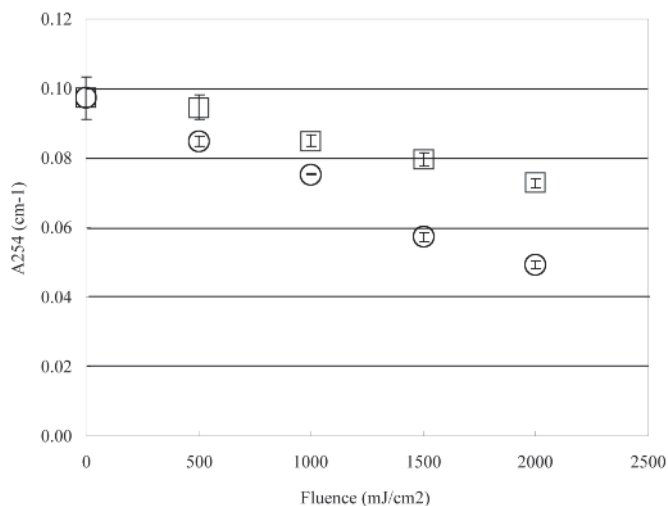


Figure 2. The impact of fluence and initial H₂O₂ concentrations of 15 (O) and 5 (□) mg/L on A₂₅₄. Points represent the average of two samples, each measured three times. Error bars represent the standard deviation between the average measurements for two samples.

The lack of complete oxidation but clear fragmentation of aromatic species suggests that larger NOM was fragmented into smaller species during the UV/H₂O₂ conditions applied. HPSEC was employed to observe the change in AMW distribution of aromatic species. Figure 3 represents the change in AMW of CW treated over a range of fluences at an initial H₂O₂ concentration of 5 mg/L. As the fluence is increased, there is a significant reduction in the highest AMW fraction, >1450 Da, up to a 57% reduction at a fluence of 2000 mJ/cm². The next two largest fractions, 1200-1450 Da and 950-1200 Da, also undergo significant reductions but are lower than the reduction seen in the >1450 Da. Moreover, the 950-1200 Da fraction is reduced less than the 1200-1450 Da fraction. This suggests that, although •OH is reactively non-specific, the reaction rate constant between •OH and chromophoric NOM is dependent on molecular weight (i.e. size). Therefore, larger molecular weight species react more rapidly with •OH resulting in a greater reduction in these species.

While the larger AMW fractions underwent significant reductions, this was accompanied by the formation of smaller AMW fractions (Figure 3). The 750-950 Da, 550-750 Da, and the <550 Da all increased in concentration after UV/H₂O₂ treatment. Furthermore, the reduction in higher AMW fractions and concomitant formation of smaller AMW fractions led to a shift in molecular size distribution from one with a majority of large species to a more even molecular size distribution.

HPSEC provided the change in molecular weight distribution of aromatic species since the UV detector only detects 254 nm absorbing species. To determine if the observed increase in low AMW fractions was in fact

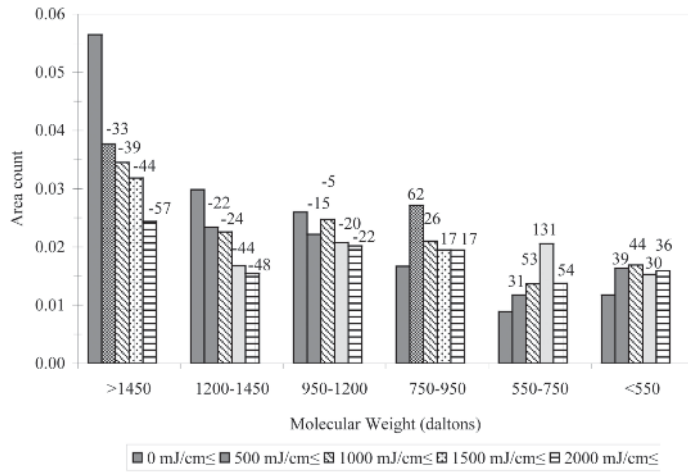


Figure 3. Change in AMW fractions during the UV/H₂O₂ treatment of CW over a range of fluences and an initial H₂O₂ concentration of 5 mg/L. Bars represent the average of two samples, each measured once. Data labels indicate percent change.

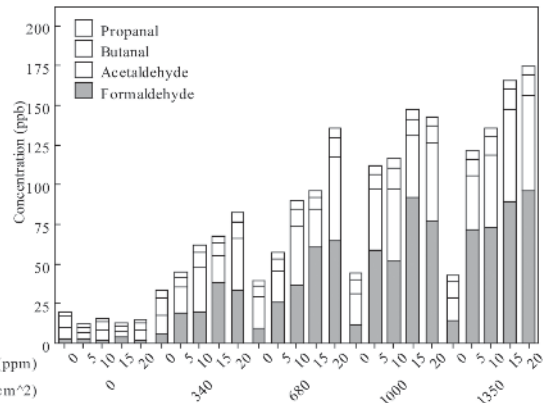


Figure 4. Change in concentration of aldehydes during the UV/H₂O₂ treatment of CW over a range of fluences and initial H₂O₂ concentrations. Bars represent the average of two samples, each measured twice.

increasing the concentration of low molecular weight compounds, the change in concentration of aldehydes, during UV/H₂O₂ treatment, was observed (Figure 4). Samples were analysed for 10 different aldehydes but only the 4 smallest aldehydes, formaldehyde, acetaldehyde,

butanal, and propanal, were detected. In CW, the concentration of all four aldehydes is below 25 ppb. Exposure to H₂O₂ alone did not change the concentration of aldehydes. In the absence of H₂O₂, that is only UV irradiation, there was an observed increase in the total

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concentration of aldehydes up to about 45 ppb at a fluence of 1350 mJ/cm². Under advanced oxidation conditions, the concentration of aldehydes increased dramatically. At an initial H₂O₂ concentration of 20 mg/L and a fluence of 1350 mJ/cm², the concentration of aldehydes reached close to 175 ppb. Additionally, it was clearly observed that an increase in either initial H₂O₂ concentration or fluence was accompanied by a greater formation of aldehydes. Note that, the increase in aldehydes is mainly due to an increase in formaldehyde and acetaldehyde, with propanal and butanal contributing less so.

CONCLUSIONS

This study investigated the impact of UV/H₂O₂ advanced oxidation on NOM present in untreated surface water. UV fluences and initial H₂O₂ concentrations applied were based on those feasible for commercial drinking water applications. Under such conditions:

- Complete oxidation, or mineralisation, of NOM did not take place as indicated by no observed change in TOC.
- NOM underwent significant partial oxidation as indicated by a reduction in aromatic species.
- •OH preferentially reacted with high AMW species leading to the formation of lower AMW species.

- The increase in low AMW species was supported by an observed increase in aldehydes.

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