The effects of ultraviolet/H$_2$O$_2$ advanced oxidation on the content and characteristics of groundwater natural organic matter


ABSTRACT

This work investigates the effects of ultraviolet (UV)/H$_2$O$_2$ advanced oxidation on the content and characteristics of natural organic matter (NOM) originating from two different groundwaters (3.03–9.69 mg/L total organic carbon (TOC), 2.71–4.31 Lmg$^{-1}$m$^{-1}$/C$_0$1m$^{-1}$ specific ultraviolet absorbance (SUVA)). Application of UV irradiation resulted in a minor reduction in the total content of NOM. Using UV/H$_2$O$_2$ advanced oxidation led to a significant reduction of the aromatic character of NOM (SUVA was reduced by up to 80%) and an increase in the hydrophilic character of the residual NOM, with the optimal UV/H$_2$O$_2$ treatment conditions depending on the water type. In addition, fluctuations in trihalomethane formation potential (THMFP) were observed depending on the UV/H$_2$O$_2$ process conditions, with a maximal reduction of about 40% achieved for both waters.

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INTRODUCTION

Natural organic matter (NOM) presents a complex mixture of source-dependent organic compounds with different molecular sizes and properties. Aquatic NOM consists of hydrophobic compounds rich in aromatic carbon, phenolic structures and conjugated double bonds, and hydrophilic compounds with a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids (Martin-Mousset et al. 1997; Goslan et al. 2002; Matilainen et al. 2010). NOM present in drinking water sources plays an important role during treatment. NOM contributes to taste and odour, acts as a carrier of metals and harmful chemicals and produces biologically unstable water (Lamsal et al. 2011; Lin & Wang 2011; Joseph et al. 2012).

NOM is considered to be the major precursor of disinfection by-products (DBPs), most commonly the trihalomethanes (THMs) and haloacetic acids (HAAAs) (Krasner et al. 2006; Wei et al. 2010). The main DBP precursor is generally considered to be the hydrophobic high molecular weight fraction of NOM (Hua & Reckhow 2007; Bond et al. 2009; Liu et al. 2010), but the hydrophilic and low molecular mass fractions of NOM also have a significant role in DBP formation (Hua & Reckhow 2007; Bond et al. 2009). Moreover, bromine and iodine have been established to be more reactive with hydrophilic and low molecular mass NOM in the formation of THM and HAA (Liang & Singer 2003; Hua & Reckhow 2007; Chiang et al. 2009; Molnar et al. 2013).

Advanced oxidation processes have attracted significant interest in drinking water treatment due to the generation of hydroxyl radicals (·OH) which can oxidize NOM and specific DBP precursors. One such advanced oxidation process, the UV/H$_2$O$_2$ process, involves generation of ·OH through UV photolysis of H$_2$O$_2$ and is widely applicable due to the use of UV in disinfection (Lin & Wang 2011; Metz et al. 2011; Bazri et al. 2012). The ·OH act as a strong oxidant and transform NOM. Previous studies reported that UV/H$_2$O$_2$ treatment led to a reduction in NOM aromaticity (Kleiser & Frimmel 2000; Goslan et al. 2006; Toor &
Mohseni 2007; Sarathy & Mohseni 2010; Black & Bérubé 2014; Sindelar et al. 2014), shifts to smaller molecular size NOM (Sarathy & Mohseni 2009) and the creation of more biodegradable compounds (Toor & Mohseni 2007; Sarathy & Mohseni 2009; Bazri et al. 2012). Under strong advanced oxidation conditions (i.e. long irradiation time and/or high H2O2 concentrations) NOM becomes mineralized, indicated by a decrease in the total organic carbon (TOC) content (Kleiser & Frimmel 2000; Wang et al. 2005; Sarathy & Mohseni 2007).

Many studies have also shown that the UV/H2O2 process impacts the specific precursors of DBPs. Changes in NOM structural characteristics caused by the UV/H2O2 process can lead to the reduction of THM formation potential (THMFP) (Toor & Mohseni 2007; Sarathy & Mohseni 2010; Lamsal et al. 2011) and may shift speciation of DBPs to more brominated compounds (Buchanan et al. 2006). Dotson et al. (2010), Metz et al. (2011) and Lin & Wang (2011) have pointed out that THMFP during the UV/H2O2 process could even increase. The differing behaviours of NOM in water is related to the different process conditions such as UV fluence and H2O2 dose, as well NOM content and characteristics. Other water parameters, such as alkalinity (mostly carbonated species) could be in competition with NOM in the scavenging of OH radicals (Matilainen & Sillanpää 2010; Bazri et al. 2012).

In their review paper, Matilainen & Sillanpää (2010) also suggest that the combination of high UV fluence and high peroxide concentration is required to generate OH high enough to significantly reduce NOM content and disinfection by-product formation potential (DBPFP).

This research investigates the effects of UV/H2O2 advanced oxidation on the amount and character of NOM from two different types of groundwater. The effect of UV/H2O2 on changes in NOM reactivity towards THM formation was also investigated.

**EXPERIMENT AND METHODS**

**Samples and reagents**

The laboratory investigation used two groundwaters from Vojvodina, Republic of Serbia which differ in the content and characteristics of their NOM. Standards for THM (chloroform, CF; bromodichloromethane, BDCM; dibromo-chloromethane, DBCM; and bromoform, BF) analysis and internal standard fluorobenzene were purchased from Supelco in concentrations of 2,000 μg/mL. All solvents were obtained from J.T. Baker for organic residue analysis; 30% w/w reagent grade H2O2 was purchased from POCH S.A. All other chemicals were analytical grade and were used without further purification.

**UV/H2O2 treatment**

UV/H2O2 experiments were carried out using a photochemical reactor of stainless steel (internal diameter 63 mm; length 365 mm; volume 0.7 L) equipped with a 253.7 nm wavelength UV low pressure mercury lamp (Philips TUV 16 W). The UV lamp was placed in the centre of the reactor and was covered with a quartz reaction vessel. A diagram of the reactor is given in Figure 1.

The design of the reactor is such that it may be used in batch or flow modes, as presented in Figure 1. For the UV/H2O2 experiments, raw water was spiked with H2O2 solution to obtain 10 and 30 mg/L in water, and the applied UV dose or fluence was in the range 300–9,000 mJ/cm² in batch mode. Similarly, control UV photolysis was carried out with no H2O2 addition. The range of applied UV...
doses is comparable with that described in the literature (Goslan et al. 2006; Toor & Mohseni 2007; Sarathy & Mohseni 2010; Sindelar et al. 2014), and was used to investigate the influence of a wide range of UV doses combined with H2O2 on the NOM characteristics and reactivities of different groundwaters. After treatment, the water samples were analyzed for TOC content, UV254 absorbance and THMFP while specific ultraviolet absorbance (SUVA) values were calculated.

**Analytical methods**

Water samples were analyzed for TOC content by Elementar LiquiTOCII, with oxidation by platinum catalysed combustion at 850 °C.

UV254 absorbance measurements were performed in accordance with *Standard Methods* (APHA 2012) on a CINTRA 1010, GBC Scientific Equipment spectrophotometer at a wavelength of 254 nm, with a 1 cm quartz cell, and the SUVA (L mg⁻¹m⁻¹) was calculated:

\[
SUVA = \frac{UV_{254} \times 100}{TOC}
\]

THMFP was determined according to *Standard Methods* (APHA 2012). At the end of the 7-day reaction period, the samples were dechlorinated, and THMs were analyzed.

**RESULTS AND DISCUSSION**

**Raw groundwater characteristics**

Table 1 shows the characteristics of the raw groundwaters. The waters differ in the character and content of NOM. Water A has a higher NOM content (9.69 ± 0.48 mg/L TOC) than water B (3.03 ± 0.34 mg/L TOC). The UV

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of measurement</th>
<th>Water A</th>
<th>Water B</th>
<th>No. of measurements (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.01 ± 0.10</td>
<td>7.81 ± 0.10</td>
<td>10</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg CaCO₃/L</td>
<td>1415 ± 189</td>
<td>731 ± 98</td>
<td>10</td>
</tr>
<tr>
<td>Bromide</td>
<td>μg/L</td>
<td>374 ± 32</td>
<td>98.6 ± 9.7</td>
<td>5</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>9.69 ± 0.48</td>
<td>3.03 ± 0.34</td>
<td>5</td>
</tr>
<tr>
<td>UV254</td>
<td>cm⁻¹</td>
<td>0.418 ± 0.03</td>
<td>0.082 ± 0.02</td>
<td>5</td>
</tr>
<tr>
<td>SUVA</td>
<td>L mg⁻¹m⁻¹</td>
<td>4.31 ± 0.11</td>
<td>2.71 ± 0.09</td>
<td>5</td>
</tr>
<tr>
<td>THMFP</td>
<td>μg/L</td>
<td>455 ± 22</td>
<td>20.8 ± 5.4</td>
<td>3</td>
</tr>
<tr>
<td>CFFP</td>
<td></td>
<td>242 ± 43</td>
<td>15.4 ± 4.6</td>
<td></td>
</tr>
<tr>
<td>BDCMFPI</td>
<td></td>
<td>148 ± 30</td>
<td>3.40 ± 2.09</td>
<td></td>
</tr>
<tr>
<td>DBCMFPI</td>
<td></td>
<td>61.1 ± 17.2</td>
<td>1.60 ± 0.59</td>
<td></td>
</tr>
<tr>
<td>BRFP</td>
<td></td>
<td>4.44 ± 1.71</td>
<td>0.450 ± 0.291</td>
<td></td>
</tr>
</tbody>
</table>

SD (standard deviation) based on n (number of measurements).
absorbance at 254 nm and the specific UV absorbance indicate that the NOM from water A is mainly hydrophobic in nature \(0.418 \pm 0.03 \text{ cm}^{-1} \text{ UV}_{254}; 4.31 \pm 0.11 \text{ Lmg}^{-1} \text{m}^{-1} \text{ SUVA}\) whereas water B contains a mixture of hydrophobic and hydrophilic NOM fractions \(0.082 \pm 0.02 \text{ UV}_{254}; 2.71 \pm 0.09 \text{ Lmg}^{-1} \text{m}^{-1} \text{ SUVA}\).

The investigated waters also have high alkalinity and bromide ion concentrations, which could affect the efficacy of the applied oxidation treatment and the distribution of chlorinated and brominated DBPs. Thus, the high level of NOM and bromide in water A resulted in high reactivity towards THMFP \(455 \pm 22 \mu g/L\) with a high proportion of brominated THMs observed \(47\% \) of the total THMFP). In contrast, the lower amounts of NOM and bromide in water B led to the significantly lower THMFP \(20.8 \pm 5.4 \mu g/L\), with CF being the most abundant THM, contributing \(74\% \) of the total THMs formed.

**Effects of UV/H\(_2\)O\(_2\) advanced oxidation treatment on NOM content and character**

Figure 2 illustrates the changes observed in TOC content in waters after UV photolysis and UV/H\(_2\)O\(_2\) advanced oxidation. The application of UV irradiation alone resulted in a minor reduction in the total content of NOM, where in water A, TOC removal was insignificant (maximum \(3\%\)), whereas for water B with the lower NOM content, removal efficacy was slightly higher (up to \(9\% \) TOC reduction). UV photolysis resulted in slightly better efficacy for UV\(_{254}\) and SUVA reduction, removing up to \(17\% \) for water A and \(22\% \) for water B (Figure 3). These results are in agreement with previous research stating that UV treatment on its own has a minor impact upon UV\(_{254}\) and almost no impact on the removal of TOC (Toor & Mohseni 2007; Lamsal et al. 2011; Bazri et al. 2012).

The control experiments with UV treatment alone were carried out in order to assess the effectiveness of UV/H\(_2\)O\(_2\) advanced oxidation for NOM removal. The effects of UV/H\(_2\)O\(_2\) treatment, with two different H\(_2\)O\(_2\) doses (10 and 30 mg/L), on TOC, UV\(_{254}\) and SUVA values, are also presented in Figures 2 and 3.

The results given indicate that applying UV/H\(_2\)O\(_2\) improves the degree of TOC removal for both waters compared to photolysis alone. The required dose of oxidation agent H\(_2\)O\(_2\) for optimal NOM removal varies depending on the water and has higher impact on TOC reduction than the applied UV dose in the UV/H\(_2\)O\(_2\) process. Thus, the most effective TOC reduction for water A was achieved using 10 mg H\(_2\)O\(_2\)/L (up to \(12\%\)) while for water B there

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**Figure 2** | The effect of UV photolysis and UV/H\(_2\)O\(_2\) advanced oxidation on the TOC content.
were no significant differences in the efficacy depending on the oxidant dose (up to 29%) (Figure 2).

The UV/H\textsubscript{2}O\textsubscript{2} advanced oxidation treatment improves NOM oxidation, which is particularly apparent from the UV\textsubscript{254} and SUVA values which indicate the loss of aromatic NOM and increasing hydrophilic NOM (Figure 3). The maximum oxidation of NOM into smaller molecules (reduction of about 78–85% UV\textsubscript{254} and 76–80% SUVA) in water type B required a lower initial H\textsubscript{2}O\textsubscript{2} dose (10 mg/L) and lower UV dose (6,000 mJ/cm\textsuperscript{2}) than water type A (30 mg/L and 9,000 mJ/cm\textsuperscript{2}). It was expected that the more hydrophobic NOM in water A would be easier to oxidize than the NOM in water B. However, the high TOC and alkalinity in water A contributed more to the peroxide consumption. The carbonate and bicarbonate ions present in water A could also react with the \(\cdot\text{OH}\) available for NOM oxidation, resulting in the need for a greater amount of oxidant as well as UV dose for maximal process efficacy for water A.

Other authors also indicate that alkalinity competes with NOM by scavenging OH radicals (Gottschalk et al. 2000; Tuhkanen 2005; Matilainen & Sillanpää 2010; Bazri et al. 2012). The oxidation of NOM and a decrease in hydrophobicity after the UV/H\textsubscript{2}O\textsubscript{2} treatment can be noted according to the residual SUVA values which drop to 1.01 Lmg\textsuperscript{-1}m\textsuperscript{-1} for water A and even to 0.53 Lmg\textsuperscript{-1}m\textsuperscript{-1} for water B, indicating the dominantly hydrophilic character of residual NOM. Sarathy & Mohseni (2007) also found that using UV/H\textsubscript{2}O\textsubscript{2}, partial oxidation of NOM occurs resulting in a reduction of aromaticity and increasing the smaller molecular weight fractions.

Lamsal et al. (2011) reported a similar effectiveness of the UV process (using 1,140 mJ/cm\textsuperscript{2} and 25 mg/L H\textsubscript{2}O\textsubscript{2}) for
NOM reduction (11–60% UV$_{254}^{−}$ and 3–23% TOC). Studies by Goslan et al. (2006) and Sindelar et al. (2014) which investigated water with higher NOM content applied greater UV doses (22 J/cm$^2$, 2.0 mM H$_2$O$_2$ and 26.1 J/cm$^2$, 100 mg H$_2$O$_2$/L) to achieve maximum UV$_{245}^{−}$ reductions of up to 94 and 97% respectively. These differences and the results given above indicate that apart from the TOC and alkalinity, NOM characteristics are very significant for advanced oxidation efficiency.

The effects of UV/H$_2$O$_2$ advanced oxidation treatment on the THMFP

The THMFPs of the raw and UV/H$_2$O$_2$ treated waters are shown in Figure 4. Fluctuations and even increasing THMFP were observed for both waters, depending on the process conditions. A reduction in THMFP was achieved only using 300 and 1,500 mJ/cm$^2$ during UV/H$_2$O$_2$ process and the maximal removal was very similar for both waters (37–43%). In addition, for both H$_2$O$_2$ doses and waters, using UV fluence higher than 1,500 mJ/cm$^2$ led to the THMFP increasing, reaching a maximum by applying 4,500 mJ/cm$^2$, and then gradually decreasing again. It was determined that using 4,500 mJ/cm$^2$ of the UV/H$_2$O$_2$ process, THMFP rose to 738 µg/L in water A and 77.0 µg/L in water B, which is 1.6 and 3.7 times more than the raw water, respectively. The greater relative increase in THMFP in water B could be explained by the higher reactivity of its NOM, which is more hydrophilic in nature than the NOM originating from water A. CF was the major THM species formed by the chlorination of UV/H$_2$O$_2$-treated water, followed by BDCM, DBCM and BR. For water A,
using a lower H$_2$O$_2$ dose, the proportion of brominated THM precursors was similar to the raw water and was 48–52% of the total. Increasing the oxidant dose to 30 mg H$_2$O$_2$/L increased the share of brominated THMs in the treated water up to 70% due to the increasing hydrophilicity of the residual NOM. The increase in brominated THMs formed by chlorination of UV/H$_2$O$_2$-treated water is probably a consequence of the greater affinity of bromine towards the hydrophilic NOM fraction rather than that of the hydrophobic NOM fraction, as shown by Liang & Singer (2005) and Chiang et al. (2009). For water B, the proportion of brominated THM precursors also rises after UV/H$_2$O$_2$ treatment, but CF remains the most abundant THM species.

The results show that even though SUVA is a relatively good indicator for DBP formation, it cannot be assumed that structural changes in NOM during advanced oxidation, based on the SUVA, are in good correlation with THMFP under all treatment conditions. Other researchers have also concluded that chemical alteration by UV/H$_2$O$_2$ has the potential to cause the formation of new DBP precursors (Dotson et al. 2010; Lin & Wang 2011; Metz et al. 2011). Thus, Dotson et al. (2010) reported that whilst using 1,000 mJ/cm$^2$ and 10 mg H$_2$O$_2$/L, the THM yield increased. Toor & Mohseni (2007) also observed a slight increase in THMFP using 0–1,000 mJ/cm$^2$ combined with 4 mg H$_2$O$_2$/L. Conversely, Lamsal et al. (2011) found that THMFP can be effectively reduced using UV/H$_2$O$_2$ advanced oxidation (1,140 mJ/cm$^2$, 23 mg H$_2$O$_2$/L). Sarathy & Mohseni (2010) found that coupling UV/H$_2$O$_2$ with pre-treatment for removal of hydrophobic NOM could improve NOM mineralization and THMFP reduction. The results given here and in the literature indicate that in addition to the H$_2$O$_2$ dose and UV dose, the raw water quality and NOM character are very important parameters for the formation of radicals and effective reduction of THM precursors.

CONCLUSION

Using UV/H$_2$O$_2$ advanced oxidation, NOM undergoes structural changes which are indicated by a significant reduction in SUVA, and the residual NOM is of mainly hydrophilic character. Apart from the amount of NOM and its character, other raw water quality parameters also impact the efficacy of the UV/H$_2$O$_2$ process for NOM removal. Thus water A with a higher content of mainly hydrophobic NOM and a higher alkalinity required a greater H$_2$O$_2$ dose for optimal UV$_{254}$ and SUVA reduction than water B. In addition, significant reductions in SUVA were not followed by corresponding reductions in THMFP under all investigated UV/H$_2$O$_2$ process conditions. Residual hydrophilic NOM in treated water can have even higher reactivity towards chlorine than in raw water, producing higher amounts of brominated THMs. Formation of the more toxic brominated THMs was also favoured over CF formation in chlorinated samples with higher initial concentrations of bromide. Maximal THMFP removal of about 40% was achieved in both waters applying 300–1,500 mJ/cm$^2$ of UV/H$_2$O$_2$ treatment.

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