Natural organic matter removal by enhanced photo-oxidation using low pressure mercury vapour lamps

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Abstract High efficiency, low pressure mercury vapour lamps producing radiation at the wavelengths of 254 plus 185 nm and 254 nm only, were used to investigate the H2O2 enhanced photo-oxidation of natural organic matter (NOM). NOM is a problem in drinking water for a number of reasons: aesthetics; it provides an energy source for the growth of microorganisms in the distribution system; and reacts with chlorine to produce potentially harmful disinfection by-products. One promising oxidant for the removal of NOM from drinking water is the hydroxyl radical. The aim of this work was to investigate the kinetics, mechanisms, and feasibility of treatment of a highly coloured natural water by H2O2 enhanced UV (254 nm alone or with 185 nm). Kinetic models were applied to the data as a tool to understand the mechanisms and give a basis for process scale-up. Electrical energy per order criteria were used to determine the most efficient process. Irradiation by 254 plus 185 nm was found to be more efficient than 254 nm alone for low H2O2 doses, although at higher doses the performance of the two systems became similar. Size exclusion chromatography revealed three distinct fragmentation patterns for the different processes.

Keywords Advanced oxidation process (AOP); drinking water; hydrogen peroxide (H2O2); natural organic matter (NOM); ultraviolet (UV) photooxidation

Introduction

Natural organic matter (NOM) in drinking water is a direct problem due to colour and taste. Indirectly, NOM is a problem because it reacts with the most commonly used disinfectant, chlorine, to form disinfection by-products. In addition, NOM acts as a food source for bacterial regrowth in potable water distribution systems, and reduces the efficiency of many water treatment operations, such as particle removal, and trace organics removal by oxidation or adsorption (Gottschalk et al., 2000). A number of conventional processes exist for the removal of NOM from drinking water, but these generally concentrate the NOM creating a disposal problem. Ozone/biological activated carbon is widely used to control disinfection by product precursors and increase biological stability. The UV/H2O2 advanced oxidation process is being investigated as an alternative to ozone for removal of organic micropollutants (e.g. pesticides) and pathogenic microorganisms (e.g. Cryptosporidium), and avoid formation of bromate (Kruithof and Kamp, 2000).

The use of UV alone at 254 nm, the main wavelength produced by low pressure mercury vapour lamps, is generally not considered to be an energy efficient process for the removal of organics from water because of the high doses required (Legrini et al., 1993). The simplified photo-oxidation reaction scheme is (Legrini et al., 1993):

\[
\begin{align*}
C & \rightarrow C^* \\
C^* + O_2 & \rightarrow C^*O_2^{-} \\
R^* + O_2 & \rightarrow RO_2^* \rightarrow \text{fragmentation}
\end{align*}
\]
The first step involves a chromophoric (“colour bearing”) organic molecule absorbing light energy, promoting it to a higher energy (excited) state. This excited state may react with a reactive species (oxygen shown) creating a rapidly reacting species and a carbon radical cation. In the presence of oxygen, organic radicals rapidly form organic peroxy radicals which react further to yield carbonyl compounds, carboxylic acids, and inorganic carbon.

A possible way to reduce the energy consumption would be to increase hydroxyl radical (•OH) concentration. Vacuum ultraviolet light (185 nm) is able to photolyse water:

\[
\text{H}_2\text{O} \rightarrow \text{H} \cdot + \text{HO} \bullet \quad (2)
\]

Alternatively, hydrogen peroxide undergoes photolysis to provide another source of hydroxyl radicals (Von Sonntag et al., 1993):

\[
\text{H}_2\text{O}_2 \rightarrow 2\text{HO} \bullet \quad (3)
\]

The hydroxyl radical is a powerful oxidant that reacts by electrophilic addition or hydrogen abstraction (shown) to form an organic radical (Von Sonntag et al., 1993):

\[
\text{HO} \bullet + \text{RH} \rightarrow \text{R} \bullet + \text{H}_2\text{O} \quad (4)
\]

followed by formation of an organo-peroxyl radical and its fragmentation.

A number of studies have investigated the use of UV/H₂O₂ (Parkinson et al., 2000; Wang et al., 2000) for DOC removal from drinking water. The use of vacuum ultraviolet (185 nm) to further enhance this process appears not to have been studied to date.

Materials and methods

The water used in this study was collected from the East Moorabool System, Victoria, in January 2001 during a period of drought, from Upper Stony Creek Reservoir. The water characteristics are listed in Table 1.

All water was filtered through pre-washed 0.45 µm hydrophilic membranes (Durapore PVDF) before irradiation. An annular UV reactor with a working volume of 0.9 L and path-length 1.9 cm was used in this study. Two lamps with identical physical dimensions were used: one lamp with output primarily at 254 nm referred to hereafter as the “N-lamp” (Australian Ultra Violet Services G36T15NU) and the “H-lamp” with output at 254 and 185 nm (Australian Ultra Violet Services G36T15HU). The total absorbed light intensity, as determined by H₂O₂ actinometry (Beltrán et al., 1995), for the N-lamp was 1.2 × 10⁻⁵ einstein L⁻¹ s⁻¹ or 5.6 W L⁻¹ for an input electrical power of 39 W. The intensity of 185 nm radiation emitted by the H-lamp was measured using methanol actinometry (Heit et al., 1998) as 2.0 × 10⁻⁶ einsteins L⁻¹ s⁻¹ or 1.3 W L⁻¹. The power draw of the H-lamp was quoted by the vendor as 46 W. During all experiments the air or nitrogen circulating past the lamp was maintained at 28 ± 1°C and the water sample at 23 ± 1°C by a peltier-cooled water stream. The samples were mixed and aerated by humidified air during irradiation. The H-lamp was also used to generate ozone in air pumped through an empty reactor.

Table 1 Water characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg C/L)</td>
<td>11.4</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Alkalinity to pH 3.7</td>
<td>45</td>
</tr>
<tr>
<td>(mg CaCO₃/L)</td>
<td>Potentiometric titration</td>
</tr>
<tr>
<td>SUVA (m⁻¹.L.mgC⁻¹)</td>
<td>4.1</td>
</tr>
<tr>
<td>Iron (mg Fe.L⁻¹)</td>
<td>1.1</td>
</tr>
</tbody>
</table>

TiO₂ photocatalytic method

A₉₅₄/DOC/pathlength
sparged into the sample. The transferred ozone doses were measured iodometrically. The progress of the reaction was monitored by dissolved organic carbon (DOC) concentration (AnaTOC Series 2 Analyser) and absorbance at 254 nm (A$_{254}$) (Unicam UV/Vis Spectrophotometer Model UV2). Hydrogen peroxide concentration was determined using the method of Bader et al. (1988). Molecular size distribution was determined using high performance size exclusion chromatography (HPSEC) with UV detection, so only chromophoric molecules were detected (Pelekani et al., 1999).

**Results and discussion**

**The effect of UV radiation alone on DOC concentration and A$_{254}$**

The radiation from the two different lamps resulted in very different kinetics for the reduction of absorbance (A$_{254}$) and DOC concentration. The H-lamp was approximately five times more effective than the N-lamp for reducing the DOC concentration and A$_{254}$.

For both lamps the kinetics of A$_{254}$ loss followed parallel first order rate laws, indicating that the NOM was composed of a mixture of different chromophores that reacted at different rates. The chromophores were divided into three groups: refractory, slow reacting, and quick reacting, and the cumulative result of adding the individual groups can be seen (Figure 1, H-lamp). A similar, but more rigorous, model based on the Lambert–Beer Law has been applied to sunlight irradiated systems (Andrews et al., 2000), but in the present study simpler first-order kinetics were applied to allow comparison with the enhanced photo-oxidation results. Different proportions of A$_{254}$ fitted into the fast and slow reactant categories (Table 2). For the N-lamp system, the bulk of the A$_{254}$ reacted slowly and a small fraction had to be assigned to the fast reacting category to model the fast initial drop in A$_{254}$. For the H-lamp the situation appeared to be different, with the bulk of the chromophoric material reacting quickly, with smaller amounts of slowly-reactive material present. Refractory material was included in the model to account for non photolabile compounds (including inorganics).

The DOC removal kinetics for the H-lamp fitted pseudo first-order rate laws which indicated that DOC concentration drove its own removal, possibly by reaction with an oxidant that was available at a constant concentration (Figure 1). There was a delay of approximately 10 minutes before mineralisation became noticeable; it appears that the oxidant was reacting with the quick reacting chromophores during this period. The DOC concentration continued to decrease long after the bulk of the A$_{254}$ had been removed, suggesting that chromophoric material was either not required in this process, or only required to initiate the reaction. In contrast, the removal of DOC for the N-lamp followed zero order kinetics which showed DOC concentration was not driving the DOC removal reaction.

**Figure 1** The effect of photolysis alone on the DOC concentration and A$_{254}$. Experimental data shown as symbols and model predictions as lines. The chart for the H-lamp also shows the model predictions for the refractory, slow- and quick-reacting chromophores.
Kinetics of UV/H₂O₂ oxidation of NOM

In the presence of H₂O₂, the NOM breakdown process can be divided into three parts: concurrent rapid chromophore reaction and H₂O₂ photolysis, followed by DOC mineralisation (Figure 2).

The H₂O₂ concentration as a function of irradiation time was modelled using the numerical solution of the photochemical rate equation developed from the Lambert–Beer Law (Leifer, 1988; Beltrán et al., 1995) with the screening effect of the NOM at any time estimated using the A₂₅₄ kinetic models:

\[
\frac{d[H_2O_2]}{dt} = \Phi \left( \frac{\varepsilon[H_2O_2]}{\varepsilon[H_2O_2] + \alpha(t)} \right) I_0 \left[ 1 - \exp \left[ -2.303L(\varepsilon[H_2O_2] + \alpha(t)) \right] \right]
\]

where \([H_2O_2] = H_2O_2\) concentration (M), \(\Phi = \) overall quantum yield (1.0 M. einstein⁻¹; Liao and Gurol, 1995), \(I_0 = 254\) nm intensity (einstein L⁻¹ s⁻¹) (the H-lamp intensity was not measured, and for modeling purposes was assumed greater than the N-lamp intensity by the ratio of lamp electrical powers), \(L = \) path length in reactor (cm), \(\varepsilon = H_2O_2\) molar absorptivity (19 M⁻¹.cm⁻¹; Crittenden et al., 1999), \(\alpha(t) = \) attenuation coefficient of the medium at time \(t\) equal to absorbance in a 1 cm cell \((A_{254})\) (cm⁻¹). The experimental data was estimated well \((R^2\) ranged from 0.972–0.998), using an overall quantum yield of unity (Figure 2).

Liao and Gurol (1995) found that even though the primary quantum yield of H₂O₂ photolysis is 0.5 (i.e. \(H_2O_2 + hv \rightarrow 2\cdotOH\)), the overall quantum yield of hydrogen peroxide photolysis was still unity (i.e. \(H_2O_2 + hv 0.5\ O_2+H_2O\)), even in the presence of high concentrations of carbonate radical scavengers, and surmised that the carbonate radicals were equivalent chain reaction propagators to the hydroxyl radicals they had consumed. If peroxide was modelled as the only chromophore in the system the H₂O₂ concentration predicted was much lower than measured, which showed that screening by other chromophores (mainly NOM) was important. Lastly, after 90 minutes of irradiation, the hydrogen peroxide residuals were noticeably higher in the H-lamp irradiated system (0.8 cf. 0.3 mg H₂O₂ L⁻¹) which may have been due to recombination of hydroxyl or superoxide/peroxyl radicals formed as a result of water photolysis at 185 nm.

For the N-lamp, the onset of mineralisation was delayed whilst the quick reacting chromophores were eliminated (Figure 2). The delays are related to the half-lives of these chromophores: 10, 5 and 3 minutes for 10.5, 21 and 58 mg H₂O₂ L⁻¹, respectively (from \(k_1\) rate constants, Table 2). It appears that before NOM mineralisation becomes noticeable the large chromophores need to be at least partially broken down. Removal of these

### Table 2 Model constants

<table>
<thead>
<tr>
<th>Lamp</th>
<th>Initial H₂O₂ dose mg L⁻¹</th>
<th>(A_0(0)) quick</th>
<th>(A_0(0)) slow</th>
<th>(A_{254}(0)) refractory</th>
<th>(k_1)</th>
<th>(k_2)</th>
<th>(R^2)</th>
<th>(k^1)</th>
<th>DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0</td>
<td>0.023</td>
<td>-0.362</td>
<td>0.353</td>
<td>-0.005</td>
<td>0.05</td>
<td>0.997</td>
<td>-0.004</td>
<td>0.956</td>
</tr>
<tr>
<td>N</td>
<td>10.5</td>
<td>0.184</td>
<td>-0.067</td>
<td>0.202</td>
<td>-0.014</td>
<td>0.05</td>
<td>0.999</td>
<td>-0.010</td>
<td>0.978</td>
</tr>
<tr>
<td>N</td>
<td>24</td>
<td>0.173</td>
<td>-0.151</td>
<td>0.219</td>
<td>-0.035</td>
<td>0.05</td>
<td>0.999</td>
<td>-0.022</td>
<td>0.991</td>
</tr>
<tr>
<td>N</td>
<td>58</td>
<td>0.243</td>
<td>-0.230</td>
<td>0.138</td>
<td>-0.036</td>
<td>0.05</td>
<td>0.996</td>
<td>-0.057</td>
<td>0.904</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>0.096</td>
<td>-0.071</td>
<td>0.290</td>
<td>-0.019</td>
<td>0.05</td>
<td>0.999</td>
<td>-0.011</td>
<td>0.979</td>
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<tr>
<td>H</td>
<td>10.8</td>
<td>0.170</td>
<td>-0.092</td>
<td>0.215</td>
<td>-0.023</td>
<td>0.05</td>
<td>0.999</td>
<td>-0.015</td>
<td>0.971</td>
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<tr>
<td>H</td>
<td>26</td>
<td>0.240</td>
<td>-0.127</td>
<td>0.152</td>
<td>-0.024</td>
<td>0.05</td>
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<td>0.994</td>
</tr>
<tr>
<td>H</td>
<td>53</td>
<td>0.248</td>
<td>-0.176</td>
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<td>-0.031</td>
<td>0.05</td>
<td>0.998</td>
<td>-0.036</td>
<td>0.973</td>
</tr>
</tbody>
</table>

1 Data fitted pseudo first-order kinetics and units are min⁻¹, except for the N-lamp without hydrogen peroxide which was zero order and units are mgC L⁻¹ min⁻¹.
2 Correlation coefficients are for applicable data range only (i.e. excluding the dashed line portion, see Figure 2). For the complete data set they may be less than indicated.
chromophores, and their inherent attenuating effect, will lead to an increase in hydrogen peroxide photolysis and hence accelerate the oxidation process. There was no noticeable delay for H$_2$O$_2$/H-lamp irradiated systems, this may be due to higher instantaneous *OH concentrations caused by photolysis of water by irradiation at 185 nm.

The initial H$_2$O$_2$ dose influenced the final DOC concentration achieved, indicating the stoichiometric nature of the reactions (Figure 2). The DOC data approximately fit the pseudo first-order kinetic models in all cases, indicating that DOC was mineralised by reaction with an oxidant in steady state concentration. For a steady state *OH concentration to occur a balance of radical creation reactions (photolysis) and consumption reactions (reaction with H$_2$O$_2$, scavengers (carbonate species), radical–radical reactions, and humics) must exist (Crittenden et al., 1999). For lower doses and extended durations the model breaks down (indicated by dashed lines in Figure 2), probably because the H$_2$O$_2$ concentration was depleted and hence *OH concentration declined. The pseudo first-order rate constants of

**Figure 2** The effect of irradiation on A$_{254}$, DOC and H$_2$O$_2$ concentrations using the N- and H-lamps with differing initial H$_2$O$_2$ doses. Symbols show experimental data. Lines show kinetic models.
NOM mineralisation increase linearly with increasing initial hydrogen peroxide dose (Table 2) with 

$$-k = 0.0009 \times [\text{H}_2\text{O}_2] + 0.0016, \quad R^2 = 0.992, \quad N = 3, \quad \text{for the N-lamp and}$$

$$-k = 0.0005 \times [\text{H}_2\text{O}_2] + 0.107, \quad R^2 = 0.996, \quad N = 4, \quad \text{for the H-lamp ([H}_2\text{O}_2]\text{ concentration in mg L}^{-1}$$

and \(k\) in min\(^{-1}\)). This suggests that not only did a steady state \(\cdot\text{OH}\) concentration exist in the reactor, but it was also in proportion to the initial \(\text{H}_2\text{O}_2\) concentration. Wang et al. (2000) reported the first-order rate constants for humic removal (5 mgC L\(^{-1}\)) increased with initial \(\text{H}_2\text{O}_2\) dose, and reached a maximum at 100 mg\(\text{H}_2\text{O}_2\) L\(^{-1}\), due to \(\text{H}_2\text{O}_2\) inhibitory effects. In the present work the maximum hydrogen peroxide dose (50 mg\(\text{H}_2\text{O}_2\) L\(^{-1}\)) used was insufficient to inhibit the rate of mineralisation of the natural water NOM (11 mgC L\(^{-1}\)). The mineralisation rate constants were calculated from the time when a decrease in DOC was detected, and as mentioned previously the onset of mineralisation was appreciably delayed in the N-lamp/\(\text{H}_2\text{O}_2\) system, this explains why its rate constant responds twice as quickly to increasing initial hydrogen peroxide dose, when compared to the H-lamp/\(\text{H}_2\text{O}_2\) case where DOC mineralisation commenced immediately.

Parallel first order kinetics were applied to the absorbance (A\(_{254}\)) data with excellent correlation (Table 2), and these models were invaluable for modelling the hydrogen peroxide photolysis. The rate constants of the quick reacting chromophores became increasingly negative with increasing hydrogen peroxide dose (Table 2). Also, the quantity of chromophoric material in the quick reacting category increased with peroxide dose and appeared to plateau at around \(A_1(0) = 0.25\). The initial rate of reaction of fast reacting chromophores [i.e. the product \(k_1 \times A_1(0)\)] was linearly related to the initial peroxide dose [for N-lamp: \(k_1 A_1(0) = 0.0008 \times [\text{H}_2\text{O}_2] + 0.006, \quad N = 4, \quad R^2 = 0.991; \quad \text{H-lamp:} \quad k_1 A_1(0) = 0.0007 \times [\text{H}_2\text{O}_2] + 0.0085, \quad N = 4, \quad R^2 = 0.973, \quad k_1 A_1(0)\) in mins\(^{-1}\) and [\(\text{H}_2\text{O}_2\) in mg\(\text{H}_2\text{O}_2\) L\(^{-1}\)]. The slope relationship suggested a steady-state oxidant concentration was present in proportion to the initial hydrogen peroxide concentration, and the high intercept value showing direct photolysis was important too. Whilst the physical meaning of these categories is still unclear, there is evidence that these quick reacting chromophores represent the larger molecular weight compounds (Figure 4).

Our hypothesis that a steady state hydroxyl radical concentration was present in the reactor in proportion to the initial hydrogen peroxide dose was tested by performing a mass balance on hydroxyl radical (De Laat et al., 1994):

$$\frac{d[\cdot\text{OH}]}{dt} = \frac{d[\text{H}_2\text{O}_2]}{dt}_{\text{photolysis}} - k_{\text{DOC}}[\cdot\text{OH}][\text{DOC}] - k_{\text{H}_2\text{O}_2}[\cdot\text{OH}][\text{H}_2\text{O}_2] - \sum k_i[S_i][\cdot\text{OH}]$$

where \([\cdot\text{OH}] = \text{hydroxyl radical concentration at time} \ t \ (\text{M}), \frac{d[\text{H}_2\text{O}_2]}{dt} = \text{the rate of photolysis of hydrogen peroxide (equation given previously)}, \ k_{\text{DOC}} = \text{the rate of reaction of hydroxyl radicals and DOC} \ (2.3 \times 10^4 \ (\text{mgC/L})^{-1} \ s^{-1}), \ Brezonik \text{ and Fulkerson-Brekken, 1998), [DOC] = the concentration of NOM (mgC/L)}, \ k_{\text{H}_2\text{O}_2} = \text{the rate of reaction of hydroxyl radicals and H}_2\text{O}_2 \ (2.7 \times 10^7 \ M^{-1} \ s^{-1}, \ De Laat et al., 1994), [\text{H}_2\text{O}_2] = \text{hydrogen peroxide concentration at time} \ t \ (\text{M}), \ k_i = \text{the rate of reaction of hydroxyl radicals and scavenger} \ (M^{-1} \ s^{-1}), \ [S_i] = \text{concentration of scavenger species} \ i \ (\text{M}). \) This shows that for a steady-state hydroxyl radical concentration to be present (i.e. rate of accumulation of hydroxyl radical equal to zero), formation of hydroxyl radical from hydrogen peroxide photolysis must be in balance with loss in NOM mineralisation reactions, \(\text{H}_2\text{O}_2\) reaction, and reaction with scavengers. For the alkalinity and pH conditions of the water studied scavenging by carbonate species and ionisation of hydrogen peroxide are negligible. If hydroxyl radical concentration was in steady state then a plot of hydrogen peroxide photolysis rate versus rate constants of hydroxyl radical consumption determined using the experimental data for various times should be a line of constant slope equal to \([\cdot\text{OH}]_{\text{ss}}\). This was found to be true and the hydroxyl radical concentration increased with initial hydrogen...
peroxide dose (Figure 3). The steady-state hydroxyl radical concentrations indicated for samples without hydrogen peroxide addition were estimated by dividing the rate constant measured by $k_{DOC}$. For lower hydrogen peroxide doses the line intersects the x-axis indicating that hydrogen peroxide was depleted before NOM mineralisation was complete.

The effect of the processes on molecular size distribution

Three different trends are evident from the size exclusion chromatograms: photolysis at 254 nm preferentially removed large chromophores with some evidence of concomitant formation of smaller molecules; ozone was not size specific in its action; UV/H$_2$O$_2$ treatment and irradiation by 254 plus 185 nm photolysis preferentially removed larger molecules except in the initial stages (Figures 4 and 5).

Electrical energy per order criteria

The main operating cost of advanced oxidation processes is the electrical power required to run the lamps. One comparative measure of the efficiency of advanced oxidation processes is the electrical energy required to reduce the target compound concentration by an order of magnitude in a cubic metre of solution, or $E_{EO}$ (Bolton et al., 2001). For the process combinations studied, the lowest $E_{EO}$ for DOC removal results from the highest doses used (approx. 50 mg H$_2$O$_2$ L$^{-1}$). If the target parameter was A$_{254}$ (i.e. removal of conjugated double bonds from NOM prior to a biological treatment), then 20 mg H$_2$O$_2$ L$^{-1}$ appears optimum (Figure 6). For comparison, the $E_{EO}$ of a 2:1 ozone:organic carbon dose
(experimentally generated by UV, but calculated assuming a corona discharge energy efficiency of 30 kWh kgO<sub>3</sub>–1) for A<sub>254</sub> removal was 0.5 kWh kL–3, clearly superior to UV/H<sub>2</sub>O<sub>2</sub> for A<sub>254</sub> removal, but it is important to note that for this ozone dose the DOC concentration remained unchanged. At higher doses, there is a diminishing $E_{EO}$ return, because $E_{EO}$ is inversely proportional to the reaction rate constant, hence the hyperbolic shape of the curve. The main advantage of the H-lamp appears to be the powerful nature of photolysis alone, it performs with an efficiency similar to that of the N-lamp with 10 mg H<sub>2</sub>O<sub>2</sub> L<sup>–1</sup>. At H<sub>2</sub>O<sub>2</sub> doses greater than 15 mg L<sup>–1</sup> the two lamps behave essentially the same, it appears the benefit of in situ generation of hydroxyl radical from water photolysis at 185 nm was lost when high H<sub>2</sub>O<sub>2</sub> doses were used.

**Conclusions**

UV/H<sub>2</sub>O<sub>2</sub> treatment was investigated for the removal of NOM from a natural water using two lamps generating 254 nm alone (N-lamp) and with 185 nm radiation (H-lamp). For photolysis alone the H-lamp outperformed the N-lamp for both A<sub>254</sub> and DOC removal due to in situ formation of •OH. At doses of more than 15 mg H<sub>2</sub>O<sub>2</sub> L<sup>–1</sup> the performance of the lamps became similar, especially when considered on the basis of electrical input energy. For the conditions studied, substantial DOC removal required H<sub>2</sub>O<sub>2</sub> doses of 5 mg H<sub>2</sub>O<sub>2</sub> per mg C.

The process appeared to proceed in a stepwise fashion: simultaneous chromophoric NOM removal and H<sub>2</sub>O<sub>2</sub> photolysis, followed by NOM mineralisation. The kinetics of chromophore removal were modelled by parallel first order kinetic equations with excellent correlation. H<sub>2</sub>O<sub>2</sub> photolysis was successfully modelled using the photochemical rate equation based on the Lambert–Beer law. After the lag period, during which the chromophores were reacting, pseudo first-order kinetic equations applied to the DOC concentration data in H<sub>2</sub>O<sub>2</sub>/N-lamp and H-lamp alone treatments. Similar kinetic equations could be applied to the H<sub>2</sub>O<sub>2</sub>/H-lamp system without the lag period, implying reaction with
a steady state hydroxyl radical concentration. The mineralisation rate constants were found to be proportional to the initial hydrogen peroxide dose, implying the steady state hydroxyl radical concentration was proportional to the initial peroxide dose. Photolysis, hydroxyl radical and ozone appear to react with different molecular size specificity with the NOM chromophores: ozone was non-specific, UV (254 nm) preferentially removed larger molecules, whilst all other processes showed weaker preferential removal of larger molecules.

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References