Comparative OH radical oxidation using UV-Cl$_2$ and UV-H$_2$O$_2$ processes

Michael J. Watts, Erik J. Rosenfeldt and Karl G. Linden

ABSTRACT

Hydroxyl radicals ($^\bullet$OH) are a direct photolysis product of both aqueous free chlorine and hydrogen peroxide under UV irradiation. The photooxidation rates of an OH-radical probe compound, nitrobenzene, were compared in aqueous solutions of free chlorine, and H$_2$O$_2$, exposed to monochromatic UV irradiation (254 nm). Acidic ($<$ pH 6) free chlorine solutions had the highest observed rates of nitrobenzene decay. In deionized water, with initial oxidant concentrations $<$ 0.15 mM, the first order nitrobenzene decay rates increased in the following order of treatments: UV-Cl$_2$(pH 7) $<$ UV-H$_2$O$_2$ $<$ UV-Cl$_2$ (pH 6) $<$ UV-Cl$_2$ (pH 5). However, water quality had a significant impact; background photon and radical scavengers led to reduced rates of nitrobenzene decay in natural waters. Analysis of the necessary energy input required to achieve 90% nitrobenzene degradation showed UV-Cl$_2$ at pH 5 to be the most efficient oxidation process whereas at neutral pH, process efficiency was a function of the initial concentration of the oxidant; at 0.05 or 0.06 mM initial oxidant, UV-Cl$_2$ was the most efficient oxidation process, while at $>$0.15 mM initial oxidant, UV-H$_2$O$_2$ was most efficient.

Key words | advanced oxidation process, fluence rate, free chlorine, hydrogen peroxide, nitrobenzene, ultraviolet

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INTRODUCTION

Increased detection of anthropogenic organic contaminants in water has driven investigations of advanced oxidation processes (AOPs) for water treatment. AOPs utilize the highly reactive $^\bullet$OH to oxidize organics in water. Several photo-sensitized AOPs, including UV-TiO$_2$, UV-H$_2$O$_2$, photo-Fenton, and UV-O$_3$ have been utilized for aqueous hydroxyl radical formation. The fundamental photochemistry of the UV-H$_2$O$_2$ AOP has been previously reported (Glaze *et al.* 1987; Legrini *et al.* 1993; Liao & Gurol 1995), and UV-AOP has been incorporated for oxidation of unwanted organic chemicals at several full-scale potable water treatment operations (Kruithof *et al.* 2002; Cotton & Collins 2006). However, UV-H$_2$O$_2$ AOP often requires significantly higher UV fluences than when UV is used for disinfection purposes. As an example, four-log$_{10}$ inactivation credit for rotavirus can require monochromatic UV fluences up to 50 mJ cm^{-2}

(Hijnen *et al.* 2006), while using UV-H$_2$O$_2$ to oxidize 70% of the taste and odor causing compounds, geosmin and methylisoborneol (MIB), requires fluence values on the order of 1000 mJ cm^{-2} with polychromatic UV (Rosenfeldt *et al.* 2005). Therefore the goal of AOP research and design continues to be to maximize the release of powerful free radicals while minimizing the energy demand.

UV disinfection is a function of photon absorption by target pathogens, and UV water treatment processes are typically placed following treatment processes which result in removal of particulates, dissolved organic matter (DOM) and other UV light absorbers from a natural water. These transmittance enhancing processes include coagulation, filtration, and preoxidation with either chlorine or ozone (Cushing *et al.* 2001; Ormeci *et al.* 2005). Adding free chlorine as a pre-oxidant or as a disinfectant prior to a

filtration step can lead to the presence of free chlorine in a post-filtration UV reactor. UV light absorption (between 200 and 350 nm) by free chlorine species, OCl^- and $HOCl$, can produce aqueous free radicals (Buxton & Subhani 1972; Molina *et al.* 1980; Nowell & Hoigne 1992*a*; Nowell & Hoigne 1992*b*; Thomsen *et al.* 2001; Watts & Linden 2007), and lead to advanced oxidation conditions. Recent work, intended to illuminate the fundamental photochemistry of common chlorine oxidants ($HOCl$, OCl^-, NH_2Cl), found that free chlorine has a quantum yield (ϕ, mol Es^{-1}) greater than 1.0 in aqueous solutions irradiated with low pressure Hg germicidal UV lamps (LP), implying the presence of radical chemistry (Feng *et al.* 2007; Watts & Linden 2007).

This work examines the efficiency of UV in combination with free chlorine species for oxidizing a target organic compound, nitrobenzene (NB), and comparing the oxidation efficiency to that of UV-H₂O₂. NB is an ideal model organic contaminant for this comparison due to its fast second-order rate of reaction with $^\bullet OH$ ($k_{OH,NB} = 3.9 \times 10^9$ $M^{-1} s^{-1}$) (Buxton *et al.* 1988), its resistance to chlorine and H₂O₂ oxidation (Nowell & Hoigne 1992*b*), and its negligible rate of direct photolysis in competition kinetic experiments utilizing UV-254 nm (Shemer *et al.* 2006). Nitrobenzene was listed on the 2nd USEPA Contaminant Candidate List (USEPA 2005) and has been detected in European and North American surface waters at concentrations as high as 67 µg L^{-1} (Davies 2003).

In this study, rates of oxidation of NB by both UV-Cl₂ and UV-H₂O₂ processes are compared, accounting for pH effects, and water quality effects. Additionally, byproduct formation is qualitatively examined to assess similarities or differences in the process chemistries. The predominant products of $^\bullet OH$-induced NB oxidation are known to be 4-nitrophenol (4NP), 3-nitrophenol (3NP), and 2-nitrophenol (2NP) (Rodriguez *et al.* 2003). Finally, the total energy input required to achieve 1-log of NB oxidation per volume of post-sand-filtration water is compared for each of the examined AOPs.

METHODS

Materials

NB (Fluka, >99%) was purchased from Sigma-Aldrich; EDTA, HPLC-grade water, and H₂O₂ (30%) from Fisher Chemical; n,n-diethyl-p-phenylenediamine DPD (>97%) from Aldrich; HPLC-grade acetonitrile (ACN) from Mallinckrodt and Baker. Free chlorine stock solutions were prepared using household NaOCl (Clorox®, 5.7% free available chlorine). NaOCl solutions were stored away from sunlight. Impurities due to decomposition and manufacturing were not accounted for; constituents of liquid bleach, other than NaOCl and NaOH, can include chlorate, chloride, and transition metal ions (Gordon *et al.* 1997). Chloride ion can be a significant scavenger of $^\bullet OH$, with a reaction rate of $4.3 \times 10^9 M^{-1} s^{-1}$ (Laat *et al.* 2004). All chemicals were used as purchased and solutions were prepared in deionized, lab-grade water.

UV irradiation

The quasi-collimated beam apparatus contained 4 low pressure Hg germicidal UV lamps (General Electric #G15T8) with predominantly 254 nm emissions. The total radiant energy of 254 nm emitted by the UV source over a given exposure time is the UV dose, or fluence (H', mJ cm^{-2}). Calculating the UV fluence applied to an aqueous solution required a measurement of the UV irradiance (mW cm^{-2}) incident to the surface. A radiometer (IL 1700, SED 240/W, International Light, Peabody, MA), with a UV detector calibrated to 254 nm, was used to measure the incident irradiance. Average UV fluence applied to the entire solution volume was calculated by multiplying the incident irradiance by factors accounting for the divergence of the collimated beam, reflection at the water surface (Reflection Factor = 0.975), variation in the irradiance over the surface of the solution, and photon absorption with depth in the water column (Water Factor varied with concentration of oxidants and water quality), as in Bolton & Linden (2003). UV exposures were performed in dishes (70 × 50 Pyrex ®) containing 100 ml of continuously stirred bulk solution (solution depth = 2.83 cm and area:volume = 0.35 cm²/cm³), and remained open to the atmosphere during UV exposure.

Analysis

Chlorine residual concentrations were analyzed according to the DPD colorimetric method using a Cary UV-VIS spectrophotometer to measure sample absorbance at

515 nm (Eaton *et al.* 1995). Calibration curves for this analysis method were developed using $KMnO_4$ solutions. All free chlorine concentrations were measured as mg L^{-1} Cl_2. Aqueous H_2O_2 concentrations were determined according to the previously published "I_3^- method" (Klassen *et al.* 1994). Oxidant concentrations were converted from measured mg/L values to mM units (as Cl_2 or as H_2O_2) in order to accurately compare oxidant levels on a molar basis (1 mg/L as Cl_2 = 0.014 mM HOCl or OCl^-, 1 mg/L H_2O_2 = 0.029 mM H_2O_2). Aqueous concentrations of NB were determined using a Varian Prostar HPLC, equipped with a photodiode array detector. A sample injection volume of 100 μL was passed through a reverse phase C-18, 7.5 × 150 mm, column with a 50:50 ACN:H_2O mobile phase (isocratic).

RESULTS AND DISCUSSION

Nitrobenzene oxidation and oxidant photolysis in lab-grade water

To compare the NB oxidation rates in UV-irradiated solutions of H_2O_2 and HOCl/OCl^-, deionized water was spiked with NB ($[NB]_0 = 5$ μM) and oxidant ($[Oxidant]_0 \leq 0.35$ mM) and exposed to LP UV (duplicate exposures for each set of conditions). After free chlorine addition, dilute phosphoric acid was added to adjust the pH and subsequently the percentage of HOCl in solution (100% HOCl when solution pH ≤ 5.2 at 20° C). A comparison of NB oxidation and oxidant photolysis during UV + 0.11 mM free chlorine (pH 5, 6, 7) and UV + 0.11 mM H_2O_2 (pH 7) is shown in Figure 1.

Several differences between the UV-Cl_2 and UV-H_2O_2 processes are illustrated in Figure 1. At equimolar oxidant concentration, NB degradation rates were faster in 100% HOCl solutions exposed to LP UV. However, pH-adjustment had significant impact on NB degradation rates in the UV-Cl_2 system, while having no affect on the UV/H_2O_2 system (data not shown in Figure 1). Additionally, as observed in Figure 1b, Cl_2 degraded well with UV fluence, while H_2O_2 is not significantly degraded over an applied UV fluence of 500 mJ cm^{-2}. Both free chlorine species (HOCl and OCl^-) display similar molar absorption coefficients at 254 nm
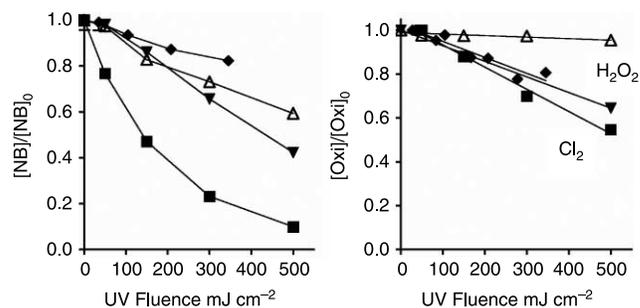

Figure 1 | The fraction remaining of [NB] (left) and Oxidant ([Oxi]) (right) in UV-irradiated deionized water solutions of 5 μM NB and 0.11 mM Cl_2 (pH 5 ■, pH 6 ▼, and pH 7 ◆), or 5 μM NB and 0.11 mM H_2O_2 (pH 7 △), with increasing UV fluence (mJ cm^{-2}). (0.11 mM = 7.7 mg/L as Cl_2 & 3.74 mg/L as H_2O_2) .

($\varepsilon_{254,HOCl} = 54$ $M^{-1}cm^{-1}$ & $\varepsilon_{254,OCl-} = 48$ $M^{-1}cm^{-1}$; Watts & Linden 2007) and absorb approximately double the energy at 254 nm than H_2O_2 ($\varepsilon = 0.19$ M^{-1} cm^{-1}, Crittenden *et al.* 1999). However, the absorption characteristics of the oxidants do not fully explain the discrepancy in photolysis observed in Figure 1(b).

Another interesting observation from Figure 1 is that the free chlorine species photolyzed at approximately the same rate regardless of pH, despite the wide variation in resulting NB oxidation rates with pH. This data would seem to indicate that even though the free chlorine species are photolyzing at the same rate regardless of pH, the resulting formation of OH radical is significantly impacted by speciation of the free chlorine oxidant species. Previous studies have indicated that more free radicals are formed from HOCl photolysis as compared to photolysis of OCl^- (Nowell & Crosby 1986). Additionally, studies have indicated that the quantum yield of hydroxyl and chlorine radicals from HOCl photolysis is 1.4 mol Es^{-1} (Watts & Linden 2007), whereas that of OCl^- to hydroxyl and chlorine radicals is only 0.28 mol Es^{-1} (Buxton & Subhani 1972).

### Nitrobenzene oxidation with variable initial oxidant concentration

For UV-H_2O_2 processes utilizing low initial oxidant concentrations (< 20 mg/L H_2O_2) and LP UV, oxidation rates increase linearly with increased oxidant (Sharpless & Linden 2003). Figure 2 illustrates that this trend is the case for the relationships between the pseudo first-order fluence-based rate constants of NB photodegradation, k'_{NB}, and the
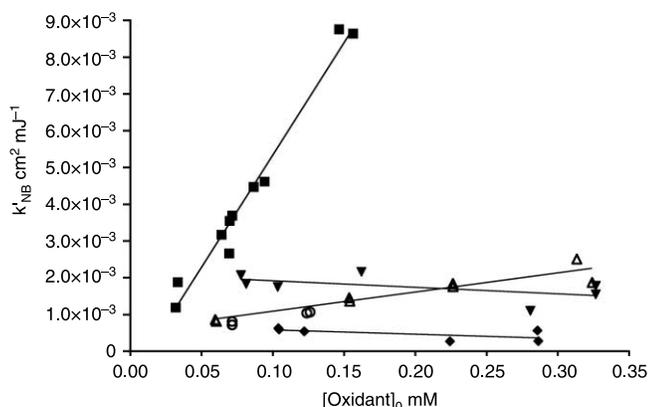
Figure 2 | Pseudo-first-order fluence-based rate constants, k' (cm² mJ⁻¹), for NB photodegradation in deionized water containing free chlorine at pH 5 (■), pH 6 (▼), or pH 7 (◆); in deionized water containing hydrogen peroxide at pH 5 (△), or pH 7 (○).

initial dose of pure HOCl (pH 5) and H₂O₂, for the concentration range tested.

Figure 2 highlights a second explanation for the reduction in k'$_{NB}$ with increased pH for the UV/Cl₂ systems, relating to the radical scavenging potential of the utilized oxidant. The only competition with our target oxidation species (nitrobenzene) for free radicals in lab-grade water comes from the added oxidant in solution, and in that regard, OCl⁻ is a much more efficient •OH competitor than HOCl. The second-order reaction rate constants with OH radical for OCl⁻ is 8.0×10^9 M⁻¹ s⁻¹ while for HOCl is only 8.5×10^4 M⁻¹ s⁻¹. This discrepancy is major, and significantly impacts oxidation of nitrobenzene in solutions containing only a small amount of OCl⁻.
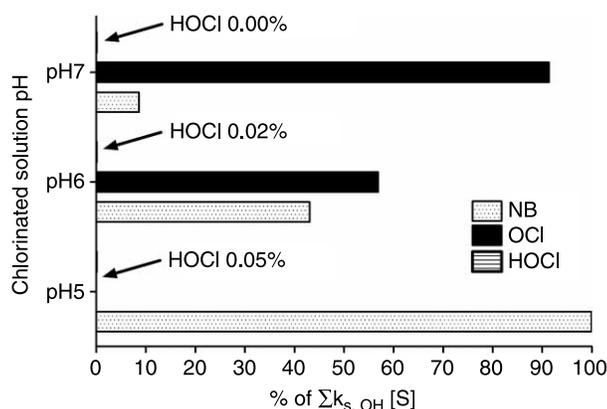
Figure 3 | The fraction of available-OH• consumed by scavengers in solutions at varying pH initially consisting of 5 μM NB and 0.11 mM Cl₂.

Figure 3 displays this effect, indicating the relative percentage of •OH which reacts with nitrobenzene, HOCl, and OCl⁻. A small fraction of free chlorine as OCl⁻ (3% at pH 6) significantly reduces the amount of •OH available for oxidation of NB, thus reducing k'$_{NB}$ significantly.

Another interesting observation in Figure 2 is how an increase in oxidant increases nitrobenzene oxidation for the UV/Cl₂ process at pH 5, but not at pH 6 and pH 7. To explain these results, we can examine the pseudo-first order rate constants of nitrobenzene oxidation (k'$_{NB}$) in more detail. For the UV/H₂O₂ AOP, it has been shown that the pseudo-first order rate constant of degradation can be reasonably estimated with the steady-state •OH concentration ([OH]$_{ss}$) assumption, k'$_{NB}$ = $k_{OH,NB}$[OH]$_{ss}$ (Glaze *et al.* 1995). Assuming the kinetics of the UV/HOCl AOP can be estimated with the same relationship, consideration of [OH]$_{ss}$ as a function of initial oxidant can explain pH effects on the chlorine oxidation trends observed in Figures 1 and 2. Equation A describes [OH]$_{ss}$ for the pH 5 case, where HOCl is the predominant chlorine species.

$$[OH]_{ss} = \frac{\frac{I_o(254)(1-e^{-2.303a(254)b})}{2.303b}\frac{\varepsilon_{Cl_2}(254)}{a(254)}[Cl_2]_T\Phi_{OHform}}{\sum k_{OH,Cl_2}[Cl_2]_T + k_{OH,NB}[NB]} \quad (A)$$

$I_o(254)$ is the intensity of UV radiation incident to the surface of the sample at 254 nm (Es cm⁻² s⁻¹), a(254) is the UV absorbance of the sample at 254 nm (cm⁻¹), $\varepsilon_{Cl2}(254)$ is the molar extinction coefficient of the free chlorine species at 254 nm (~50 M⁻¹cm⁻¹ for HOCl and OCl⁻), [Cl₂]$_T$ = total concentration of free chlorine (mixture of HOCl and OCl⁻), Φ_{OHform} is the quantum yield of OH radical formation due to photolysis of free chlorine species at 254 nm, and $\sum k_{OH,Cl_2}[Cl_2]_T$ is the sum of hydroxyl radical scavenging factors for the chlorine oxidant species ($\sum k_{OH,Cl_2}[Cl_2]_T = k_{OH,HOCl}[HOCl] + k_{OH,OCl^-}[OCl^-]$). In the pH 5 case, there is no OCl⁻ so the only oxidant scavenger is HOCl. Because HOCl reacts very slowly with •OH, $k_{OH,NB}$[NB] $>> \sum k_{OH,Cl_2}[Cl_2]_T$ (Figure 3), Equation A reduces to:

$$[OH]_{ss} = \frac{\frac{I_o(254)(1-e^{-2.303a(254)b})}{2.303b}\frac{\varepsilon_{Cl_2}(254)}{a(254)}[Cl_2]_T\Phi_{OHform}}{k_{OH,NB}[NB]} \quad (B)$$

Inspection of Equation B shows that an increase in [Cl₂]$_T$ will lead to a linear increase in [OH]$_{ss}$, and an increase in

k'_{NB}. However, the derivation is slightly different for the case where OCl^- dominates oxidation (pH 6 and pH 7). Since OCl^- displays such a fast rate constant with $^\bullet OH$, even a small amount of the dissociated free chlorine species present in solution results in $\sum k_{OH,Cl_2}[Cl_2]_T \gg k_{OH,NB}[NB]$ (Figure 3), so Equation A reduces to:

$$[OH]_{ss} = \frac{\frac{I_o(254)(1-e^{-2.303a(254)b})}{2.303b}\frac{\varepsilon_{Cl_2}(254)}{a(254)}[Cl_2]_T \Phi_{OHform}}{\sum k_{OH,Cl_2}[Cl_2]_T} \qquad (C)$$

Equation C simplifies further such that the free chlorine concentrations in the numerator and denominator cancel, indicating that $[OH]_{ss}$ is independent of initial oxidant concentration.

Products of UV-Cl₂ and UV-H₂O₂ NB oxidation in lab-grade water

Isomers of nitrophenol (4-, 3-, and 2-NP) are the predominant products of the reaction between $^\bullet OH$ and NB (Rodriguez *et al.* 2003). To qualitatively compare chemistry following photooxidation of NB in free chlorine and H₂O₂ solutions, HPLC analysis was used to track the formation of

4-, 3-, and 2-NP. Figure 4 presents HPLC chromatograms from samples taken from a HOCl solution (pH 5.1) and H₂O₂ solution (pH 7), using the same isocratic 50:50 ACN:H₂O elution.

The applied LP-UV fluence for each solution was 150 mJ cm⁻². To achieve the same level of NB oxidation ([NB]/[NB]₀ = 0.6), the chlorine solution was spiked to 0.07 mM as Cl₂ while the hydrogen peroxide solution was spiked to 0.5 mM. It is apparent from the chromatograms that the chemistry differs in the two treated solutions; 4-, 3-, and 2-NP are responsible for the three major peaks in the UV-H₂O₂ chromatogram, while several other peaks are detected in the UV-Cl₂ chromatogram. Detector responses to 3NP were similar in both samples, while 2NP and 4NP were present at reduced levels in the chlorinated solution. Of the unknown products detected, one of the most polar compounds had an identical retention time to an elution of a dilute standard of parachloronitrophenol (2-chloro-4-nitrophenol). Isomers of chloronitrobenzene (1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, and 1-chloro-4-nitrobenzene) were also analyzed but did not have retention times which matched the unknown products. Further exploration into the possible
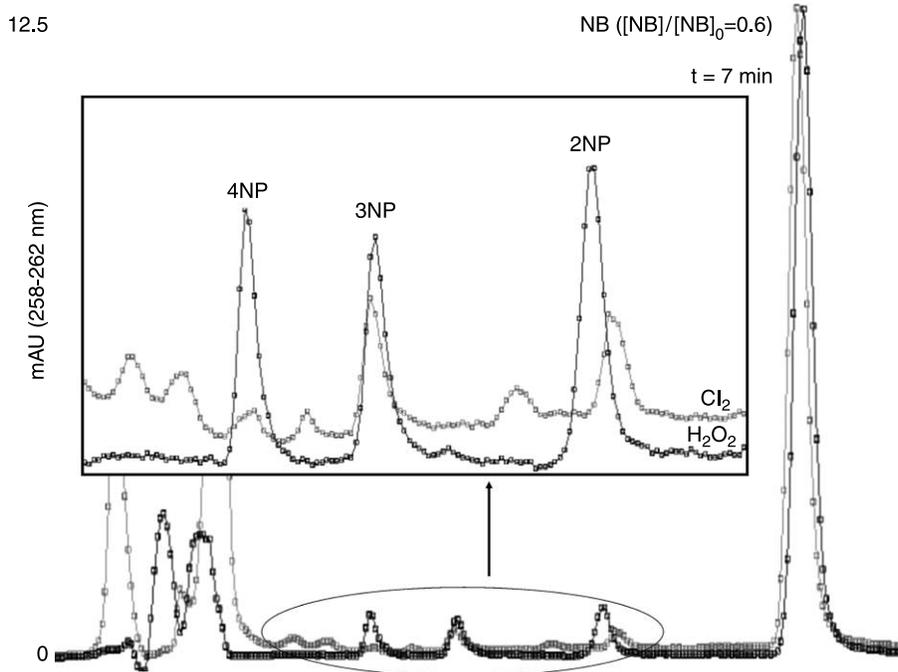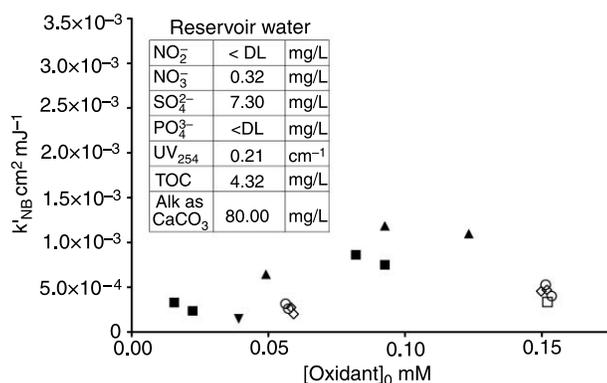

Figure 4 | HPLC Chromatograms (photodiode array detector; 260 nm) of samples taken from UV irradiated deionized water solutions of 5 μM NB and 5 mg L⁻¹ free chlorine (pH 5, *background*) or 17 mg L⁻¹ hydrogen peroxide, *foreground*); UV fluence: 150 mJ cm⁻² (LP UV). Inset: 8 × -Zoom.

halogenated products formed was outside the scope of the reported work and would benefit from analysis of the total organic halides present in waters of varying quality, after varying levels of UV-Cl$_2$ oxidation. Further exploration with mass spectroscopy would also help elucidate the radical chemistry of aqueous UV-Cl$_2$-treated solutions for oxidizing an aromatic organic compound.
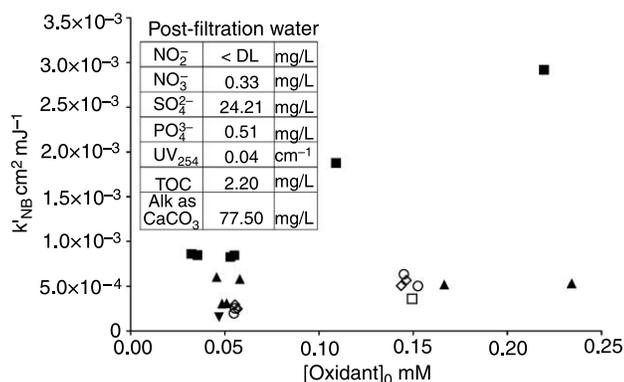
Effect of natural waters

Figures 5 and 6 report data for the observed k'$_{NB}$ in solutions of reservoir water and post-sand-filtration water (Williams Water Treatment Plant, Durham, NC) containing free chlorine or H$_2$O$_2$ at pH 5, 7, or 9.5.

As was expected, photodegradation of 5 μM NB was retarded in both waters, due to the presence of many known photon and •OH scavengers in natural waters, including NOM, HCO$_3^-$, CO$_3^{-2}$, and NO$_2^-$/NO$_3^-$ (shown in inset table). NB oxidation rates were slowed more significantly in the reservoir water as compared to the post-sand filtration waters for two reasons. First, because of greater background UV absorbance at 254 nm (0.21 cm^{-1} for reservoir and 0.04 cm^{-1} for post-sand filtrate), the photo-formation rate of •OH was slowed. Additionally, the concentration of •OH scavengers is greater in the reservoir water, indicating that less of the •OH formed was available for NB oxidation.

The experiments in natural water further elucidated the effect of pH on the UV/Cl$_2$ system. At pH 7, where the OCl$^-$ accounts for 24% of the available free chlorine, neither water quality nor oxidant concentration significantly impacted NB oxidation. In all pH 7 waters (DI, reservoir, and post-sand-filtration), k'$_{NB}$ ranged from 0.5 × 10^{-3} to 1.0 × 10^{-3} (cm^2 mJ^{-1}), with no discernable pattern in the variation. This gives further evidence to the lab-grade water observation that OCl$^-$ scavenges a vast majority of the •OH available for oxidation at pH 7. When an analysis similar to that used in Figure 2 is performed on the reservoir and post-sand-filtration waters, OCl$^-$ consumes 61% and 72% of the •OH produced at pH 7 (compared to 91% in the DI water case). These percentages are apparently enough such that the rate of NB oxidation at pH 7 does not change significantly, even with the addition of more oxidant or the presence of scavengers.

Figure 5 | k'$_{NB}$ observed in solutions of reservoir water containing free chlorine at pH 5 (■), pH 7 (▲), or pH 9.5 (▼); reservoir water containing H₂O₂ at pH 5 (○), pH 7 (◇), or pH 9.5 (□).

Figure 6 | k'$_{NB}$ observed in solutions of rapid-sand filtration water containing free chlorine at pH 5 (■), pH 7 (▲), or pH 9.5 (▼); reservoir water containing H₂O₂ at pH 5 (○), pH 7 (◇), or pH 9.5 (□).

Cost comparison of UV-Cl$_2$ and UV-H$_2$O$_2$

Previous research into the efficiency of AOP processes has used measures of the energy required to achieve a predetermined level of treatment, or a steady-state concentration of •OH, as a basis for comparison (Bolton & Stefan 2002; Rosenfeldt *et al.* 2006). Rosenfeldt *et al.* (2006) converted an applied UV fluence in a bench-scale UV reactor to the theoretical required UV energy to achieve a desired level of oxidation in a UV reactor, using Equation D.

$$U_{lamp(254)} = \frac{\frac{E'_{a(254)}t}{RF \times WF} \times \frac{A}{V} \times \frac{1h}{3600s} \times \frac{1kW}{1 \times 10^6 mW}}{\eta_{UV}} \quad (D)$$
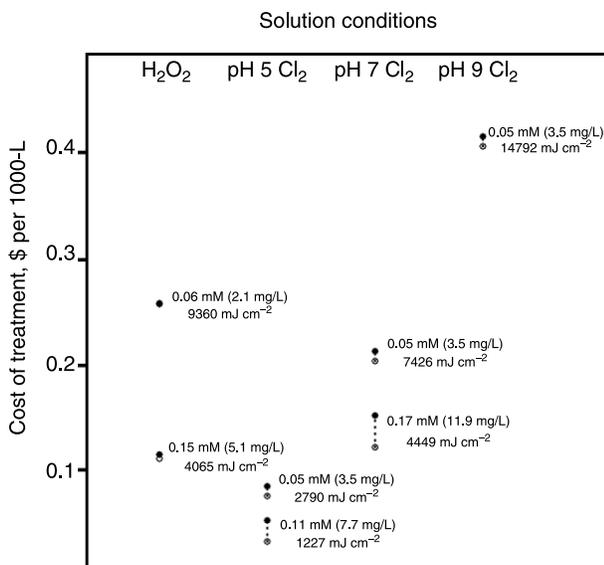
In Equation D, $U_{lamp(254)}$ is the LP UV energy requirement for a given fluence (kW h 1000 L^{-1}), $E'_{a(254)}$ is the 254 nm average

fluence rate in the reactor (mW cm^{-2}), RF is the reflection factor (for photons across the air/quartz/water interface), WF is the water factor accounting for light attenuation across the depth of a water column, A/V is the ratio of the surface area of the water, incident to the emitted photons, to the volume of the bulk solution (cm^2 L^{-1}), and η_{UV} is the LP UV lamp efficiency according to the USEPA (30%) (USEPA 2006). Conversion of the calculated UV lamp energy (U$_{lamp(254)}$) to an equivalent cost (in US\$) per 1000 litres of treated water was accomplished using an average cost per kWh of electrical energy (0.074 US\$ kWh^{-1} (Moody 2003)). The cost of the required chemical oxidant (C$_{oxidant}$ in US\$ per 1000-L^{-1}) was calculated by multiplying the cost per kg of oxidant (2.60 US\$ kg^{-1} as Cl$_2$ and 0.68 US\$ kg^{-1} of H$_2$O$_2$ (USEPA 1999) by the concentration of oxidant. The total cost, C$_{total}$ (US\$ 1000 L^{-1}), is calculated with Equation E.

$$C_{total} = C_{lamp(254)} + C_{oxidant} \qquad (E)$$

Figure 7 shows the calculated energy demands of UV-Cl$_2$ and UV-H$_2$O$_2$ treatments of 5μM NB in post-sand-filtration waters to achieve a 1-log reduction in NB.

Data from sampled post-sand-filtration water was used for this analysis due to the likely placement of UV reactors after mixed-media filtration, in a hypothetical advanced water treatment retro-fit. The efficiency of the UV-Cl$_2$ advanced oxidation process in acidic solutions (pH 5) relative to UV-H$_2$O$_2$ and UV-Cl$_2$ at all other pHs is evident. However, comparisons between the energy demand of UV-H$_2$O$_2$ and UV-Cl$_2$ in solutions of varying pH do not account for the costs associated with pH adjustment. Degrading 90% of the initial 5μM of NB with UV-Cl$_2$ (100% HOCl) cost ~3 times less than with UV-H$_2$O$_2$ at equimolar initial oxidant levels (0.05 mM), but deliberate acidification of treated water prior to a UV-Cl$_2$ process would incur additional costs depending upon the volume treated. For all cases, C$_{oxidant}$ was dwarfed by C$_{lamp}$ (calculated UV fluences ranged from 1227 for Cl$_2$-pH 5 to 14792 mJ cm^{-2} for Cl$_2$-pH 9), indicating that AOP-cost optimization is primarily a function of reducing the UV fluence required for 1-log NB oxidation (or improving the efficiency of photon delivery, η_{UV}). Increasing initial hydrogen peroxide from 0.06 mM to 0.15 mM greatly reduced the UV fluence required to achieve 1-log NB oxidation, thereby reducing U$_{total}$ by half, despite nearly tripling the oxidant concentration.

CONCLUSIONS

Under neutral to acidic conditions in the presence of free chlorine, the use of UV irradiation will create oxidative conditions capable of degrading chemical pollutants in water. In lab-grade chlorinated water, an applied UV fluence of 100 mJ cm^{-2} led to a 5% reduction in free chlorine. At pH 5, the formed $^{\bullet}$OH from this 5% reduction was observed to oxidize ~40% of the initial spiked-nitrobenzene concentration (5 μM); at neutral pH, ~8% NB oxidation was observed at this fluence. Nitrobenzene photodegradation was fastest in acidic solutions (pH 5) of free chlorine irradiated with LP UV. However, water quality and free chlorine speciation (dictated by solution pH) had a major impact on the observed k'$_{NB}$. In pH 5 solutions of chlorinated lab-grade water, nitrobenzene was determined (based on the theoretical sum of $^{\bullet}$OH-scavenging) to be the principal sink for $^{\bullet}$OH, while increasing the solution pH from 5 to 6 or 7 resulted in OCl$^-$ as the primary $^{\bullet}$OH scavenger. At pH 7, OCl$^-$ scavenging was so great, that the

Figure 7 | The cost (US\$ 1000L^{-1}) required for 1-log NB oxidation in post-sand-filtration water treated with UV-Cl$_2$ and UV-H$_2$O$_2$; initial oxidant concentrations in mM with initial oxidant concentrations in mg/L (in parentheses). Total cost (●) and the cost due to UV delivery (○) are presented along with oxidant costs (- - - -).

rate of NB oxidation did not change significantly regardless of oxidant concentration or water quality. Oxidation of NB by UV/-Cl$_2$ (low pH) and UV/-H_2O_2 was slowed in natural waters due to the presence of natural $^\bullet$OH scavenging species. For the UV-H_2O_2 process, only initial oxidant concentration (increased [H_2O_2]$_0$ led to increased k'$_{NB}$) and the concentration of background $^\bullet$OH-scavengers had any effect on observed k'$_{NB}$. Discrepancies in the HPLC chromatograms of the UV-Cl$_2$ and UV-H_2O_2 oxidation of NB indicate differences in radical chemistry between the two oxidation processes. While previous work has hypothesized that hydroxyl radical is the primary radical formed from the photolysis of free chlorine (Nowell & Hoigne 1992a), the HPLC results suggest the action of other radicals. Additionally, UV-Cl$_2$ (pH 5) was found to be less energy intensive than UV-H_2O_2 for degrading 90% of NB$_o$ in post-sand-filtration water, but at neutral pH with increased oxidant level, UV-H_2O_2 was the more cost efficient AOP. The reported cost comparison did not account for additional costs associated with pH adjustment.

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