



Influence of chloride on the 185 nm advanced oxidation process

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HIGHLIGHTS

- Chloride is a major absorber of 185 nm photons at environmentally relevant concentrations.
- Under 185 nm irradiation, absorption by chloride produces the chlorine atom radical (Cl•).
- Like the hydroxyl radical (OH•), Cl• may react with solutes at near diffusion limited rates.
- 185 nm treatment efficiency depends on relative reactivities of OH• and Cl•.

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ABSTRACT

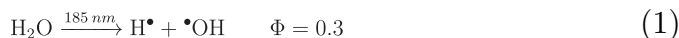
The use of 185 nm radiation from a conventional low pressure mercury lamp generates the hydroxyl radical (•OH) from the photolysis of water and offers an advanced oxidation process (AOP) for water treatment that does not require chemical addition. However, the influence of the water matrix on the process differs substantially from that of other ultraviolet and ozone based processes. In particular chloride (Cl⁻), and not water, absorbs the majority of 185 nm photons when [Cl⁻] > 20 mg L⁻¹ and generates the chlorine atom radical (Cl•) as a reactive species. Evidence suggests that when Cl⁻ is present, Cl• and •OH both contribute to contaminant degradation to varying extents. Using nonselective (carbamazepine) and selective (nitrobenzene) radical probes, as well as nonselective (t-butanol), and selective (acetone and acetate) radical scavengers, the influence of Cl⁻, and therefore 185 nm AOP treatment efficiency, is observed to strongly depend on four independent second-order radical rate constants. Furthermore, ionic strength effects support the assumption that Cl• is in equilibrium with the relatively nonreactive dichlorine radical anion (Cl₂•⁻).

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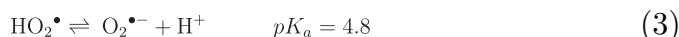
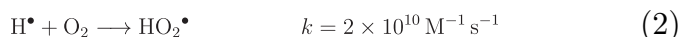
1. Introduction

UV-based advanced oxidation processes (AOPs) may be used to augment drinking water treatment when sources are impaired by trace contaminants refractory to conventional treatment (Howe et al., 2012). Among the most feasible AOPs, UV photolysis of H₂O₂ (UV-H₂O₂) provides a small footprint, absence of a waste stream, lack of undesirable by-products such as bromate, and simultaneous disinfection. However, the on-site storage of H₂O₂, its addition upstream of UV reactors, and its removal downstream, introduce increased process complexity and cost. In addition to the dominant emission line of the conventional low pressure mercury lamp at 254 nm, a second weaker emission at 185 nm is present (Phillips, 1983). The 185 nm wavelength occurs at the start of the

broad absorption band of the first excited state of water (Okabe, 1978), with an absorption coefficient of 1.8 cm⁻¹ (Weeks et al., 1963), and resulting in the photolysis of water to generate •OH with a quantum yield of 0.3 Getoff and Schenck, 1968:



In the presence of dissolved oxygen, H• is scavenged at diffusion limited rates (Buxton et al., 1988), to produce the relatively nonreactive acid-base pair HO₂•/O₂•⁻ (Bielski et al., 1985):



Most organic solutes are attacked by •OH with reaction rate constants typically on the order of 10⁸ M⁻¹s⁻¹ (Buxton et al., 1988;

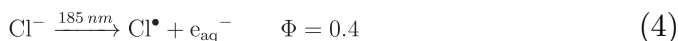
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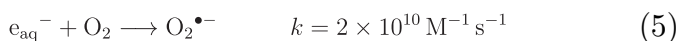
Westerhoff et al., 1999). The relatively longer lifetime of $\bullet\text{OH}$ relative to $\text{H}\bullet$ results in oxidative conditions and thus an AOP that does not require chemical addition.

The high absorbance of water at 185 nm imposes substantial geometrical constraints on reactor design. Knowledge of the relevant reactive species, their reactions and associated rate constants are critical components for the design of efficient 185 nm reactors. Yet, understanding of the impact of the water matrix on the 185 nm AOP is currently limited and the influence of major solutes has not been adequately reported in the literature (Zoschke et al., 2014).

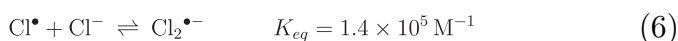
Several inorganic anions, chloride in particular, are known to strongly absorb 185 nm photons due to charge-transfer-to-solvent (CTS) absorption bands (Fox et al., 1978; Fox, 1970; Barrett et al., 1965; Hayon and McGarvey, 1967; Jortner et al., 1964). The molar absorption coefficient for chloride at 185 nm (ϵ_{185}) has been reported as $3800 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$ by Dainton and Fowles (1965) and $\sim 3500 \text{ M}^{-1} \text{ cm}^{-1}$ by Weeks et al. (1963). These values are in agreement with our measurement of $3540 \pm 150 \text{ M}^{-1} \text{ cm}^{-1}$, using a new method described elsewhere (Furatian, 2017). Such a value implies that a greater fraction of 185 nm photons are absorbed by Cl^- than by water above approximately 20 Mg L^{-1} , well within the range of many natural waters (Wetzel, 2001; Drever, 1988). Radiation chemistry literature reports a 185 nm quantum yield for the ejection of an electron and generation of $\text{Cl}\bullet$ of approximately 0.4, (Jortner et al., 1964, Dainton and Fowles, 1965) comparable to the photolysis of water:



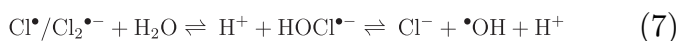
As with $\text{H}\bullet$, the solvated electron is efficiently scavenged by dissolved oxygen (Buxton et al., 1988):



The $\text{Cl}\bullet$ reacts with chloride to produce the relatively nonreactive dichlorine radical anion $\text{Cl}_2^{\bullet -}$ (Hasegawa and Neta, 1978). A reverse reaction forms the equilibrium:



in which $\text{Cl}_2^{\bullet -}$ is heavily favoured. (Buxton et al., 1998) Both $\text{Cl}\bullet$ and $\text{Cl}_2^{\bullet -}$ react with water via the postulated equilibria terminating in formation of $\bullet\text{OH}$:



At neutral pH with $[\text{Cl}^-] < 0.1 \text{ M}$, the overall equilibrium given by (7) is reported to lie far to the right (Buxton et al., 1998). Yet, in the presence of dissolved organic matter (DOM), $\bullet\text{OH}$ will be consumed at near diffusion limited rates and no equilibrium is expected.

Despite this, $\text{Cl}\bullet$ may nevertheless contribute significantly to contaminant degradation. As with $\bullet\text{OH}$, reaction rates between $\text{Cl}\bullet$ and many organic molecules approach the diffusion limit. Reported reaction rate constants for $\text{Cl}\bullet$ are limited, yet indicate similarities between $\bullet\text{OH}$ and $\text{Cl}\bullet$ for small organic molecules (Buxton et al., 2000). In addition to differences in relative reactivities with target contaminants, variations in the reactivities of $\bullet\text{OH}$ and $\text{Cl}\bullet$ with background organic matter must be considered in assessing treatment efficiency.

This work presents evidence for the role of $\text{Cl}\bullet$ in the 185 nm regime as a first step in understanding the influence of major inorganic solutes in natural waters on the 185 nm AOP. Additionally, techniques used here may prove useful to those studying other

AOPs, such as the UV photolysis of chlorine (UV- Cl_2).

2. Experimental section

Experiments consisted of a series of batch irradiations of assembled solutions of known composition spiked with a probe compound. Under steady-state conditions, degradation of the probe compound C follows pseudo-first order kinetics with an experimentally observed rate constant k' (i.e. $\ln([C_t]/[C_0]) = -k't$). Observed changes in k' correlate to changes in solution composition.

2.1. Apparatus

UV irradiations using conventional low pressure mercury lamps (Light Sources Inc, USA) were conducted using two types of quasi-collimated beam apparatus (Bolton and Linden, 2003). For experiments using only 254 nm radiation, a 42 W lamp was used with a quartz envelope doped with titanium to block 185 nm. For experiments using both 185 and 254 nm, a second apparatus was equipped with a 10 W lamp not doped with titanium and thus transparent to both wavelengths. Furthermore, the optical path was purged with ultrapure nitrogen gas to prevent ozone formation. Samples exposed to 254 nm alone were placed in open vessels with small stir bars and a liquid depth of approximately 2.0 cm. Samples exposed to both 185 and 254 nm were sealed in cylindrical fused silica cells of 1.0 cm path length (Starna, UK) with miniature teflon coated stir bars. Please refer to Supplementary Materials for diagram of the 185 nm apparatus.

2.2. Probe compounds selection and characterization

Since typically molar absorption coefficients (ϵ) are less than $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and quantum yields (Φ) are less than unity (Wayne, 1988), direct photolysis at 185 nm is generally negligible for contaminants in aqueous systems at concentrations of $1 \mu\text{g L}^{-1}$ or less. Thus, the two main degradation processes for trace contaminants include direct photolysis at 254 nm and oxidation by $\bullet\text{OH}$ generated by 185 nm photolysis of water. In order to study the effects of 185 nm alone, a simple method involves selecting a probe compound for which direct photolysis at 254 nm is negligible. In solutions of low absorbance ($A_\lambda \ll 1$), the rate constant of direct photolysis at 254 nm (k'_d) is proportional to the product of molar absorption coefficient (ϵ_{254}) and photolysis quantum yield (Φ_{254}) (Bolton and Stefan, 2002). Experimentally determined values ϵ_{254} and Φ_{254} were determined to be $6759 \pm 190 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.00067 ± 0.00002 for carbamazepine (CBZ), $6240 \pm 130 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.007 ± 0.001 for nitrobenzene (NB), and $3410 \pm 75 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.011 ± 0.003 for *para*-chlorobenzoic acid (pCBA). Values obtained are in agreement with those reported elsewhere for CBZ (Vogna et al., 2004; Pereira et al., 2007) and NB (Rodriguez et al., 2000), though no values of Φ_{254} for pCBA were found in the literature. CBZ best satisfies the above condition for a convenient probe with negligible photolysis at 254 nm. While pCBA has often been used as a probe compound in AOP studies, the use of CBZ eliminates the need to correct for direct photolysis at 254 nm at higher fluence values. Furthermore, CBZ exhibits superior chromatography by HPLC, providing wider dynamic range and a lower limit of quantitation. The second-order $\bullet\text{OH}$ rate constant for CBZ was determined experimentally as $6.8 \pm 0.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by competitive kinetics with pCBA as the reference with rate constant $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Neta et al., 1968), in agreement with values reported elsewhere (Pereira et al., 2007; Huber et al., 2003). NB as a probe has the useful property of being relatively nonreactive to $\text{Cl}\bullet$ based on structure-reactivity arguments and evidence from gas-

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