



# Transformation of humic acid and halogenated byproduct formation in UV-chlorine processes



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## ARTICLE INFO

### Article history:

Received 1 March 2016

Received in revised form

20 June 2016

Accepted 24 June 2016

Available online 26 June 2016

### Keywords:

UV-chlorine

Hydroxyl radical

Chlorine radical

Humic acid

Disinfection byproducts

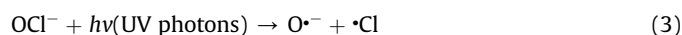
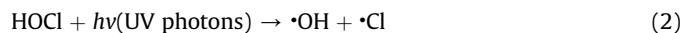
## ABSTRACT

The synergistic effect of ultraviolet light (UV) and chlorine on the structural transformation of Humic Acid (HA) and formation of chloro-disinfection byproducts (DBPs) in water were investigated, with chlorination as a reference. The transformation and mineralization of HA were enhanced upon co-exposure to UV and chlorine. Electron spin resonance (ESR) studies revealed that hydroxyl radical ( $\cdot\text{OH}$ ) and chlorine radical ( $\cdot\text{Cl}$ ) were predominant active species in a pH range from 4 to 7, while  $\cdot\text{Cl}$  dominated at pH 2 and pH higher than 7. The impact of different radicals on the transformation of HA was investigated by UV<sub>254</sub>, fluorescence and TOC measurements.  $\cdot\text{OH}$  were found to be responsible for the removal of chromophoric groups and mineralization of HA, while  $\cdot\text{Cl}$  mainly reacted with HA and intermediates from HA degradation. Due to the competitive and synergistic reaction of  $\cdot\text{OH}$  and  $\cdot\text{Cl}$  with HA, higher removal of HA and lower formation of chloro-DBPs appeared in UV-chlorine than chlorination, thus the combined UV-chlorine processes should be a promising method for water purification.

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## 1. Introduction

Ultraviolet (UV) irradiation is a promising alternative as a primary disinfectant that does not produce disinfection byproducts (DBPs) (Liberti et al., 2002; Li and Blatchley, 2009; Weng et al., 2012). It is usually used together with chlorine to achieve multiple-barrier disinfection and maintain residual protection. With addition of chlorine before or during UV disinfection, co-exposure to both chlorine and UV light could lead to different changes in natural organic matter (NOM) and formation of DBPs. According to previous works, the following processes are involved under different pH conditions during the photochemical reactions of chlorine in water (Buxton and Subhani, 1971; Oliver and Carey, 1977; Nowell and Hoigne, 1992):



Different forms of free chlorine under UV irradiation in aqueous solution would generate different reactive radicals, and induce a series of radical-type chain reactions. NOM is ubiquitous in natural water and acts as the major precursor for DBPs in drinking water (Kim and Yu, 2007; Tian et al., 2013). Upon UV and chlorine co-exposure, NOM may be attacked simultaneously by free chlorine species and different radicals (such as  $\cdot\text{OH}$  and  $\cdot\text{Cl}$ ). Thus, the DBPs formed may greatly differ from those from chlorination alone. However, information on DBPs generation during combined UV and chlorine treatment is scarce, as most studies have focused on sequential exposure to UV and free chlorine/chloramine (Lyon et al., 2012). Some researchers found no significant increase in DBPs in sequential exposure to UV and free chlorine (Zhao et al.,

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2011), while other findings indicated that some DBPs such as chloroform (TCM), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and cyanogen chloride (DCAN) showed statistically significant enhancements (Liu et al., 2006; Wang et al., 2015b). Above results were predominantly attributed to the impact of UV irradiation on the DBPs precursors, in which NOM was degraded into smaller molecules (Liu et al., 2012a), increasing the reactivity with chlorine. The UV and chlorine co-exposure process involved chlorine atom ( $\bullet\text{Cl}$ ),  $\bullet\text{OH}$  and its conjugate base  $\text{O}^{\bullet-}$  with high free radical concentration (Watts and Linden, 2007; Jin et al., 2011; Chan et al., 2012), which is fundamentally different from the reactive species in sequential exposure.

Humic acid (HA), a major component of NOM, is ubiquitous in drinking water. The contamination of HA not only affects the odor, color and taste of water, but also prevents the adsorption of target substances, and forms complexes with heavy metals and micro-pollutants (Li and Korshin, 2002; Ates et al., 2007). Importantly, in the presence of chlorine radicals with strong oxidizing abilities, HA has been found to be an important precursor for the formation of DBPs (Kim and Yu, 2007; Philippe et al., 2010). Upon UV and chlorine co-exposure, the interactions between HA molecules and radicals further complicate the reactions. However, the transformation of HA and the formation of DBPs have not been verified during co-exposure to UV and chlorine. On the other hand, the role of  $\bullet\text{Cl}$  has usually been ignored due to the highly nonselective oxidation of  $\bullet\text{OH}$  for the destruction of contaminants. In general,  $\bullet\text{Cl}$  is strong but selective (Wang et al., 2015b), and can be quickly scavenged ( $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) by chloride ( $\text{Cl}^-$ ) in free chlorine solutions to form  $\text{Cl}_2^{\bullet-}$ , which however has negligible reactivity with NOM (Nagarajan and Fessenden, 1985; Buxton et al., 2000). The role of  $\bullet\text{Cl}$  in forming organic DBPs might therefore depend on its competitive reactivity with NOM compared to chloride. Unfortunately, no reaction rate with NOM has been reported. As a hypothetical example, it is assumed that  $\bullet\text{Cl}$  reacts with NOM at the same rate as with benzene ( $1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) (Fang et al., 2014), suggesting that the role of  $\bullet\text{Cl}$  in organic DBPs formation would be non-negligible. Therefore, it is of great importance for practical water treatment to better understand the processes of HA degradation by co-exposure to UV irradiation and chlorine.

In this study, the influence of UV irradiation and chlorine on the structural transformation of HA molecules as well as the formation of DBPs were systematically investigated. By investigating the role of different radicals on the removal of HA molecules under different pH conditions, it was found that  $\bullet\text{OH}$  radicals were the dominant reactive species for the mineralization reaction, while chlorine radicals ( $\bullet\text{Cl}$ ) played an important role in the destruction of molecular structures. Due to the efficient removal of HA, unprecedented suppression of the formation of intermediate products was also achieved in the condition of co-exposure. Our research not only provides fundamental understanding on the roles of radicals in the structural transformation of HA in UV-chlorine processes, but also has broad applicability for optimizing water treatment by reducing DBPs formation.

## 2. Materials and methods

### 2.1. Materials and reagents

Solutions were prepared from reagent-grade chemicals and ultrapure water (18.2 M $\Omega$ /cm) supplied by a NANO pure system (Milli-Q). Sodium hypochlorite (NaOCl) solution (about 5% available chlorine), sodium hydroxide (NaOH), potassium phosphate ( $\text{KH}_2\text{PO}_4$ ), disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ), and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) were at analytical grade or better. *N,N*-Diethyl-*p*-phenylenediamine sulfate (DPD) was purchased from

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HA obtained from Sigma Aldrich (St. Louis, MO, USA) was dissolved in ultrapure water and filtered through an ultrafiltration membrane (Millipore 10,000 Da) to prepare a stock NOM solution. Standards for DBPs analysis: TCM and halogenated volatiles as a mixture of DBPs including DCAN, trichloroacetonitrile (TCAN), chloral hydrate (CH), chloropicrin (CP), 1,1-dichloropropanone (DCP) and 1,1,1-trichloro-2-propanone (TCP) were purchased from AccuStandard (USA). Two species of haloacetic acids (HAAs), DCAA and TCAA, were purchased from Biomart Ltd. (China).

### 2.2. UV reactor

A UV reactor consisting of a stainless steel tube (i.d. = 3.2 cm) with a volume of 100 mL was used. A LP-Hg UV lamp (TUV 16W T5 4P-SE, Philips, Netherlands) with quartz sleeve (i.d. = 2.2 cm) was fixed in the center of the reactor. The UV intensity was measured using an ultraviolet radiometer at the value of 3.06 mW/cm<sup>2</sup>.

### 2.3. Experimental procedures

Chlorination experiments were carried out in a 100 mL batch reactor equipped with a stir bar to ensure homogeneous reaction, which was controlled at  $25 \pm 1$  °C. Experiments were initiated by adding calculated aliquots of concentrated chlorine solution to the reactor containing HA (dissolved organic carbon DOC = 3.5 mg/L), with chlorine dosage of 20 mg/L in all cases. Solution pH was adjusted with small volumes of 0.01, 0.1, or 1 M  $\text{H}_2\text{SO}_4$  and NaOH (for pH 2, 7, 12) and buffered solution using 10 mM phosphate solutions (for pH 6–8).

UV irradiation alone was carried out without chlorine in UV reactor. For the co-exposure of UV and chlorine, it was carried out in the presence of chlorine with UV irradiation. Chlorine solution was added into a 100 mL HA solution with the initial concentration of DOC at 3.5 mg/L in all cases. Then, solution pH was adjusted under vigorous stirring. After 30 s, the solution was rapidly poured into the UV reactor.

At given time intervals during all processes, 2 mL of solution was rapidly transferred into an plastic centrifuge tube containing 10 mM  $\text{Na}_2\text{S}_2\text{O}_3$  (molar ratio of  $\text{Na}_2\text{S}_2\text{O}_3/\text{HOCl} = 1$ ) to quench the reaction and stored for analysis of the concentration of HA using UV/Vis absorbance analysis, fluorescence spectroscopy and gel filtration chromatography (GPC). Additionally, 1 mL of solution was taken for analysis of the concentration of chlorine residual. After the reaction, DOC of the HA solution was measured using  $\text{TOC-V}_{\text{CPH}}$  in all cases. At least two replications of each experiment were carried out.

### 2.4. Analytical methods

A total organic carbon analyzer  $\text{TOC-V}_{\text{CPH}}$  (Shimadzu Co., Japan) was used to measure DOC. The concentration of residual chlorine was standardized by the *N,N*-Diethyl-*p*-phenylenediamine spectrophotometry method (DPD). The UV/Vis absorbance was measured in a U-3010 spectrophotometer (Hitachi High-Technologies Co., Japan) in the range from 200 nm to 800 nm. The specific UV absorbance at 254 nm was used to evaluate the degradation of HA. Fluorescence spectroscopic (FS) analysis was carried out using a fluorescence spectrometer (F-4600, Hitachi High-Technologies Co., Japan) in steady state mode with L-geometry. Fluorescence spectra were recorded with the excitation wavelengths in the range of 200–400 nm and the emission wavelengths in the range of 290–550 nm. GPC used a PL-GPC 50 system (Agilent Co., USA) equipped with a photodiode array UV/Vis detector (SPD-M10A). A TSK-GEL column (G3000PWxl,

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